Metal-Orga nic Frameworks as Basic Catalysts for Liquid Phase Reactions

Metallorganische Gerüstverbindungen als basische Katalysatoren für Flüssigphasen-Reaktionen

Der Technischen Fakultät
der Friedrich-Alexander-Universität Erlangen-Nürnberg

zur Erlangung des Doktorgrades Dr.-Ing.

vorgelegt von

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Als Dissertation genehmigt

von der Technischen Fakultät

der Friedrich-Alexander-Universität Erlangen-Nürnberg

Tag der mündlichen Prüfung: 11.04.2017

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Aus Gründen der wissenschaftlichen Priorität wurden einige Ergebnisse der vorliegenden Dissertation bereits in der Fachliteratur veröffentlicht:


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1 Motivation and Scope

Many organic syntheses of complex molecules used as drugs or fine chemicals, involve carbanion species as important intermediates in at least one step of the reaction mechanism. For the creation of such a carbanion usually a base, either in stoichiometric amounts or acting as a catalyst, is needed to abstract a proton of a C-H bond [1]. In most state of the art procedures used in industry, basic catalysts are applied homogeneously dissolved in the liquid phase which comes along with the well-known problems of separating the catalyst from the product stream. Typical homogenous basic catalysts are metal hydroxides and alkoxides or organic amines such as NaOH, KOH, NaOEt and dialkylaminopyridines [2,3].

While the development of porous solid acids was one of the main research fields in industrial chemistry in the 20th century, the investigation of basic materials has experienced much less attention [4]. As solid acidic catalysts, mostly zeolites and related materials are used due to their high thermal and chemical stability, high porosity with defined pore sizes in the micropore range and the ease of preparation of these materials in their acidic form [5]. While acid sites are present in such aluminosilicate materials by nature due to the replacement of Si$^{4+}$ by Al$^{3+}$ and charge compensation by H$^+$ in the tetrahedral SiO$_2$ framework, basic centers can only be generated by the exchange of surface bound protons with alkali or alkaline-earth cations. Predominantly cesium is used for the generation of strong basic sites in the pore system of a zeolite [1]. Alternative solid materials that have been studied as basic catalysts are metal oxides like MgO and hydrotalcite in the parent form or as Al-Mg mixed metal oxide after calcination. In addition, the functionalization of silica materials with amine-containing organic moieties has been studied [6] as well as the nitridation of microporous aluminosilicates and aluminophosphates with ammonia [7].

Typical methods for the characterization of the amount and strength of the basic sites of such catalysts are temperature programmed desorption (TPD) of acidic adsorbates like carbon dioxide and the observation of the interaction of CO$_2$ and other probe molecules like pyrrole by infrared spectroscopy [4]. Another way for the evaluation of the activity of basic catalysts is the comparison of their performance in test reactions.
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However, the comparison of results from different literature sources is difficult due to large differences in the reaction conditions (solvent used, temperature, educt concentrations, catalyst amount etc.).

Typical industrially relevant base-catalyzed reactions are the isomerization of alkenes and alkynes by double bond migration, nucleophilic ring opening of epoxides, transesterification reactions and C-C bond formations by condensation reactions of carbonyl groups as in the aldol or the Knoevenagel condensation. The latter is frequently used as a test reaction to demonstrate the activity of newly developed basic catalysts.

In recent years, the use of metal-organic frameworks (MOFs) as catalytically active solids has been regarded as very promising due to the potential of designing the pore size and the chemical properties of the internal surface and the potential of bridging the pore size gap between zeolites and mesoporous materials [8]. Especially MOFs with covalently bound amino groups have been discussed as potential basic catalysts for condensation reactions of carbonyl groups [9,10].

The scope of this work is the identification, preparation and characterization of suitable NH$_2$-containing MOFs, the optimization of the synthesis procedures and the evaluation of their eligibility as solid basic catalysts in comparison to conventional basic solids in the Knoevenagel condensation of benzaldehyde with malononitrile and ethyl cyanoacetate, respectively. Therefore, appropriate reaction conditions have to be identified in order to exclude any unwanted promoting influence and assure accurate and reliable analysis of the reaction mixtures. For the investigation of different influences, the catalytic activities of isostructural MOFs with different pore sizes and geometries, and isostructural MOFs based on different metals will be compared as well as isostructural MOFs with and without amino groups.

In addition, the influence of the utilization of ionic liquids, containing the desired linker as the anion, on the structure and properties of the synthesized metal-organic framework will be studied employing the Al-MIL-53 structure as an example.
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2.1 Metal-organic frameworks (MOFs)

2.1.1 Definition, classification and properties

Metal-organic frameworks (MOFs) are a fascinating class of crystalline materials, which provide unique properties that are investigated for many types of industrially or environmentally relevant applications [11]. According to the latest recommendations of the IUPAC Inorganic Chemistry Division [12], MOFs are regarded as a sub class of coordination networks. A coordination network is defined as “a coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions” [12]. In the special case of a metal-organic framework this extension has to be realized with organic ligands and the resulting network must “contain potential voids”. In the same recommendation the use of the common term “hybrid organic-inorganic material”, which is frequently used to describe the nature of MOFs, is explicitly discouraged since the term “hybrid material” is of common use in the fields of ceramization and sol-gel processing. The term “metal-organic framework” was established in 1995 by Yaghi and Li in their description of a crystalline material with the composition Cu(4,4’-bpy)$_{1.5}$NO$_3$(H$_2$O)$_{1.5}$ [13].

Over the last two decades, MOF related research has found attention in many scientific disciplines, not only in inorganic, physical and materials chemistry dealing with the synthesis, characterization and properties of the crystalline compounds themselves, but also in rather unrelated research like biomedicine [14,15]. The overall output of publications that report on the synthesis or utilization of MOFs has been, and still is, consistently rising as demonstrated by the number hits resulted for the search for “metal-organic framework” in the web-based scientific database “web of science” (Figure 2.1).
Figure 2.1: Illustration of the evolution of scientific publications concerning metal-organic frameworks. The numbers for each year are the number of results found in Web of Science employing the search topic “metal-organic framework”.

The networks of MOFs are constructed from metal nodes and multivalent organic linker molecules. As nodes, simple isolated metal ions are known as well as rather complicated so called secondary building units (SBU) which contain several metal ions and additional ligands, most commonly oxides and/or hydroxides [16–19]. An excellent overview of potential SBUs with different geometries and numbers of extension points is given in the review by Tranchemontagne et al. [20]. As linkers, mostly multidentate ligands with strongly coordinating groups such as pyridyls, imidazolates or carboxylates are employed, to name the most prominent ones.

According to Kitagawa et al., porous coordination compounds (also known as porous coordination polymers, PCPs), and MOFs in particular, can be classified in the three categories 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> generation [21]. Since, as Kitagawa mentions, “nature dislikes vacuums”, it is not possible to synthesize materials with vacant spaces. As a result, the pores of as-synthesized materials are always filled with guest or template molecules. In the case of MOFs, this will mostly be solvent molecules and / or unreacted linkers or molecular metal complexes. The key parameter for the classification of a MOF as belonging to one of the three generations is the effect of the removal of those guest molecules on the structure of the material (Figure 2.2). 1<sup>st</sup> generation compounds are described as materials with potentially microporous
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Frameworks which irreversibly collapse upon removal of the guest molecules. As a consequence, the formation of empty voids is impossible for this category. In contrast, the framework topology of 2\textsuperscript{nd} generation compounds remains unchanged upon guest molecule removal due to the rigidity and robustness of the networks. As a result 2\textsuperscript{nd} generation MOFs exhibit permanent porosity in their activated form and are, hence, of particular interest for any application oriented research. 3\textsuperscript{rd} generation compounds possess flexible frameworks which allows the dynamic alternation of the network. This change of the crystal structure and thereby the geometry of the pores can be reversibly triggered by external stimuli including temperature, light, electric fields or guest molecules. The most prominent example for a 3\textsuperscript{rd} generation porous coordination polymer is MIL-53 which will be discussed in detail in chapter 2.4.4. The pore geometries formed by metal-organic frameworks can be of different dimensionality from 0D individual cavities via 1D channels and 2D layers to open 3D interconnected channel systems.

Figure 2.2: Schematic illustration of the behavior of 1st, 2nd and 3rd generation PCPs upon guest molecule removal.
A paradigmatic example for the construction of a MOF with a distinct network geometry is the synthesis of the prototypical MOF-5, which was presented by Yaghi et al. in 1999 [17]. The MOF-5 network is based on an oxo-centered tetrameric zinc SBU in which the metal centers are bridged by carboxylate groups (Figure 2.3). This motif has previously been known from a number of discrete zinc carboxylates [22]. The six points of extension in all three dimensions provided by the carboxylates are utilized by the employment of terephthalate anions as organic linkers to build a cubic 3D network with the Zn₄O SBUs at the corners as shown in figure 2.3.

This framework does not collapse upon removal of solvent molecules from the pores and hence possesses a remarkable porosity in the activated form with a specific BET area of 2320 m² g⁻¹ and a pore volume of 1.04 cm³ g⁻¹. This means that 80 % of the crystal volume are empty voids which have been proven to be accessible for guest molecules such as chloroform or cyclohexane. Hence, MOF-5 is a perfect example for a 2nd generation MOF with a 3D pore system of intersecting channels.

Based on the same SBU and network topology, the principle of reticular chemistry was introduced by the group of Yaghi in 2002 [23,24]. By using a series of linear
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dicarboxylate linkers of different lengths and/or carrying different functional groups they succeeded to synthesize a series of 16 isoreticular MOFs (IRMOF-1 to 16). The largest one, IRMOF-16 (Zn₄O(TPDC)₃; TPDC = terphenyl-4,4’”-dicarboxylate) shows the same topology, but the edge length of the unit cell is twice as long compared to the smallest IRMOF, Zn₄O(fumarate)₃. This results in an enlargement of the unit cell volume by a factor of eight. It is also noted that the expansion of the dimensions of such a highly symmetric system leads to interpenetration of several networks of the same type which causes a reduction of the accessible pore volume and a higher density of the resulting solid. The degree of interpenetration can be controlled by adjustment of the synthesis conditions.

This straightforward strategy of expanding the framework of MOFs by the use of extended organic linkers led to the development of materials with unprecedented properties. Two remarkable examples are NU-110 and IRMOF-74-XI. NU-110 (Cu₃(BHEHPI); BHEHPI = 5,5’,5”-((((benzene-1,3,5-triyltris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))-tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))triisophthalate) is the largest of a series of isoreticular MOFs based on hexatopic linkers and possesses the highest specific BET area reported for a MOF of 7140 m² g⁻¹ [25]. IRMOF-74-XI is based on the topology of MOF-74, also known as CPO-27 but with an extended linker constructed as a linear chain of eleven phenylene units. This material provides channel-like pores with a diameter of 9.8 nm [26] which is the largest open aperture reported for a MOF to date.

Other groundbreaking examples for materials which have inspired scientists around the globe to enter the field of metal-organic framework compounds are HKUST-1[27], MIL-53 [18,19,28], ZIF-8 [16], MIL-101 [29] and UiO-66 [30] (Figure 2.4).
Figure 2.4: Characteristic structural units of a) HKUST-1, b) UiO-66, c) MIL-53(ht), d) ZIF-8 and e) MIL-101.
2.1.2 Syntheses of MOFs

a) Solvothermal conditions

In the classical solvothermal approach (when water is used as the solvent denoted as hydrothermal) the reaction takes place at high temperatures and pressures which enhances the solubility and mobility of the reactants, especially of large organic linker molecules [11]. In solvothermal syntheses, the metal component is usually employed as a mononuclear inorganic salt, which makes it hard to control the reaction and to influence the formed structure. Therefore, methods for influencing the geometry of the nodes of the network have been developed.

i) Modulated synthesis

In this approach, a monodentate ligand with the same coordinating group as the final linker (in most cases a monocarboxylic acid like formic, acetic or benzoic acid) is added as a modulator to the synthesis mixture to allow the secondary building units to form in-situ as soluble complexes which are subsequently connected by the multidentate linkers via a ligand exchange to form the rigid network of the MOF (Figure 2.5) [31–33].

ii) Controlled SBU synthesis

In the controlled SBU approach, preformed metal clusters with the same geometry as the SBU of the desired MOF but with the respective monodentate ligands are employed as node precursors. These ligands are exchanged by the organic linkers during the crystallization process to form the desired network structure (Figure 2.5). This strategy led to the successful synthesis of MIL-88 and MIL-89 [34,35], UiO-66 [36] or MOF-5 derivatives with zinc, beryllium and cobalt [37], just to name a few.
In addition to the classical hydro- or solvothermal synthesis strategy, which was inspired by the chemistry of zeolites and other inorganic materials, many sophisticated variations have been developed recently [38].

Replacement of the parent polydentate carboxylic acids by the corresponding methyl esters [39], sodium salts [40] or purely organic imidazolium salts as demonstrated in this work [41] has also been shown to have tremendous influence on the success of the synthesis approach, the required synthesis temperature and the properties of the resulting MOFs.

b) Microwave and ultrasonic methods

As an alternative to conventional electrical heating, microwave-assisted MOF syntheses are meanwhile well established [42]. This strategy typically leads to the formation of nano sized crystals in a fraction of the reaction time, compared to conventional heating, as recently demonstrated for the case of Cr-MIL-101 and UiO-66 [43,44]. This is explained by the rapid and very homogeneous heating of the
reaction mixture by direct interaction of the solvent with the microwave radiation while conventional electric heating usually causes the formation of different temperature zones within the reaction vessel. Therefore, dissolution of the starting materials is faster in the warmer regions, while nucleation of the crystalline materials preferably begins in the cooler region, which promotes the growth of larger crystallites.

In so called sonochemical syntheses, ultrasound is utilized as energy source for the efficient and environmentally friendly production of MOFs. The ultrasonic treatment causes an alternating pattern of pressures in the liquid phase due to the powerful sonic waves, leading to cavitation processes. Thereby hot spots with extreme temperatures and pressures evolve for the very short time span of a few microseconds that can force the chemical reactions to occur [11].

c) Electrochemical method

The electrochemical synthesis of MOFs has been pioneered by BASF researchers [45] and optimized for the example of HKUST-1 by Hartmann et al. [46]. In this strategy, the framework metal is not applied in the form of soluble salts, but the metal ions are directly dissolved from a metal anode in an electrolyte filled electrochemical cell. Thereby the influence of counter-anions from the metal salt on the structure and the purity of the synthesized compound can be efficiently excluded.

d) Ionothermal method

The ionothermal method is a special case of the solvothermal approach and utilizes the unique properties of ionic liquids as solvents [47]. The macroscopic properties of the ionic liquids, predominantly their extremely low volatility and high thermal stability, drastically facilitate the synthesis procedure since no pressure vessels are needed even for high temperature syntheses [11]. As even more beneficial for the synthesis of metal-organic frameworks the chemical properties of ionic liquids are discussed. The high solubility of both, inorganic metal salts and organic molecules enhances the availability of the reactants during the synthesis an allows a significant reduction of the reaction temperature compared to hydrothermal conditions [48]. Furthermore it
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has been shown that ionic liquids, especially those based on rather hydrophilic anions, can act as templates that can alter the structure and the pore geometry of the resulting porous coordination polymers. In some cases, the ionothermal method even gives access to MOF structures that have not been synthesized before in classical solvents as reported by Martins et al. for a series of zinc imidazolate frameworks [49].

e) Mechanochemical method

Solvent free MOF syntheses have been achieved in mechanochemical procedures where strong mechanical forces, as present for example in an oscillating ball mill, are utilized to influence physical changes and chemical reactions [50]. The addition of a minimum amount of liquid (water or other solvents) can drastically accelerate the mechanochemical reaction by enhancing precursor mobility [11].

2.1.3 Functionalization of metal-organic frameworks

For chemical functionalization of the internal surface of a metal-organic framework, mainly three strategies are employed:

a) Direct synthesis from functional linkers

In many cases synthesis conditions can be varied to successfully prepare functional derivatives of known MOFs employing functionalized linker variants. Most frequently terephthalate based MOFs such as MOF-5, UiO-66, MIL-53 and MIL-101 have been modified by the utilization of terephthalic acid derivatives, substituted with -NH₂, -NO₂, alkyl, or halide groups in the 2-position. In some cases (e.g., CAU-1), a functionalized linker is even mandatory for the synthesis of the particular structure and attempts to replace it by the unfunctionalized derivative fail. Some recent and prominent examples are discussed in detail in chapter 2.4.
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b) Post-synthetic grafting of bifunctional molecules by coordination to open metal sites

Modification of the properties of a MOF by exchanging non structure-building ligands of the SBUs was already reported as early as 1999 in the original description of HKUST-1 [27], where the coordinatively unsaturated sites of the copper centers have been modified by the coordination of pyridine. Another prominent example is Cr-MIL-101 with ethylene diamine coordinated to the accessible chromium centers [51], introducing free primary amino moieties as basic functional groups. The same concept has been used to introduce chiral molecules like (S)-N-(pyridin-3-yl)pyrrolidine-2-carboxamide and (S)-N-(pyridin-4-yl)pyrrolidine-2-carboxamide [52]. This technique of incorporation of additional functionality offers the opportunity to introduce groups which would decompose under synthesis conditions or prevent the formation of the desired network. However, the resulting materials must be expected to suffer significant leaching of functional groups at least in liquid phase applications.

c) Covalent post-synthetic modification of a functional linker

For most post-synthetic approaches, anchor points of the organic linkers are used to create covalent bonds with a reactive agent. Very often amino groups in stable MOFs with accessible voids like IRMOF-3 (MOF-5-NH$_2$), UiO-66-NH$_2$ or Al-MIL-53-NH$_2$ are modified by reaction with anhydrides [53,54], isocyanates [55] or aldehydes [56].

Since a complete overview of the potential of functionalization and modification of metal-organic frameworks is beyond the scope of this work, the reader is referred to extensive reviews dealing with this field of MOF chemistry [57,58].

2.2 Applications of metal-organic frameworks

The high tunability of MOFs in order to tailor-make their properties as described in the previous paragraphs has originated research activities in various fields of applications which provide a large potential for the use of this class of materials in
different areas of the chemical industry [59,60]. The most impactful topics discussed in this context are gas storage, separation and the use of MOFs as solid catalysts in heterogeneously catalyzed reactions [61–68]. In addition, MOFs can be utilized as chemical sensors [69] and as sorbents for heat transformation for example by the cyclic ad- and desorption of water [70,71]. Recent approaches even investigate the mechanical properties of metal-organic frameworks caused by their structural flexibility which gives rise to a potential for their use in shock absorbers [72].

2.2.1 Metal-organic frameworks as solid catalysts

In addition to the topics presented above, the utilization of MOFs as solid catalysts in heterogeneously catalyzed reactions is one of the most interesting fields of application and has been intensely reviewed in the last decade [8,9,61,62,73,74]. Metal-organic framework catalysts are classified by the nature of their active sites. In general, a major distinction is made between MOFs which are used as supports for highly dispersed catalyst particles and others that shelter reactive groups or atoms at a certain position of the framework.

a) Encapsulated guests as active species:

In the case of encapsulation of active species such as metal nanoparticles (MNPs) polyoxometallates (POMs) or large organometallic complexes in the pores of the frameworks, mainly the geometrical properties of the supporting MOF, i.e. pore and window diameters are utilized. In addition, the basic chemical properties and the resulting electronic environment of the inner surface of some MOFs is believed to be beneficial for the stability and activity of the guest particles due to optimized electronic interaction with the surface [61].

Deposition of rhodium [75] or palladium [76] on Cr-MIL-101 has resulted in the formation of highly active catalysts for the hydroformylation of alkenes and the selective hydrogenation of 2,3,5-trimethylbenzoquinone to 2,3,5-trimethylhydroquinone, respectively. The same MOF has been used for the
immobilization of vanadium, leading to an active catalyst for the oxidation of sulfides to sulfoxides and sulfones [77]. The beneficial effect of structural properties of such systems has been shown by Sun et al. who compared the activities of gold-loaded Cr-MIL-53 and Cr-MIL-101 in the oxidation of cyclohexane to cyclohexanone and cyclohexanol [78]. Both catalysts show higher activities than Au-MNPs deposited on other substrates and Au/Cr-MIL-101 shows a higher selectivity compared to Au/Cr-MIL-53 due to the defined size of the gold particles in the pores. A positive influence of amino-functionalization was reported by Huang et al. for the Suzuki-Miyaura cross-coupling reaction catalyzed by Pd nanoparticles supported by Al-MIL-53-NH\textsubscript{2} [79]. The presence of the amino groups results in a stabilization of the MNPs and prevents agglomeration. Hence, a lower activity is observed for unfunctionalized Pd/Al-MIL-53.

Due to the mesoporous cavities present in the MIL-101 framework (see chapter 2.4.1), MOFs with this topology have been used for the encapsulation of catalytically active polyoxometallates (POMs). Such composites have been successfully applied as catalysts for the dehydration of methanol to dimethyl ether and longer chain hydrocarbons [80], or the dehydration of fructose and glucose to 5-hydroxymethylfurfural [81]. Large organometallic molecules such as metalloporphyrins have also been encapsulated in the pores of metal-organic frameworks and the resulting materials have been found to be active catalysts. A Mn-porphyrin entrapped in the pores of an Indium 4,5-imidazoledicarboxylate was successfully tested as catalyst for the oxidation of cyclohexane with tert-butyl hydroperoxide and Cu- and Mn-porphyrins supported on the copper based pcu-MOF were employed for the oxidation of 3,5-di-\textit{tert}-butylcatechol with H\textsubscript{2}O\textsubscript{2}, respectively [82,83].

b) Framework metals as active species:

The most obvious approach of using MOFs as solid catalysts is the utilization of the framework metal ions as catalytically active species due to their similarity to soluble metal complexes used as homogenous catalysts. There are many examples following this concept based on MOFs which possess open metal sites or so called coordinatively unsaturated sites (CUS) after activation by thermal removal of
coordinating solvent molecules. The unsaturated copper centers present in activated HKUST-1 (see chapter 2.4.6) have been demonstrated to be catalytically active sites for various reactions such as the chemical reduction of p-nitrophenol in the presence of sodium tetrahydroborate [84] or the acid catalyzed aza-Michael reaction of benzylamine with ethyl acrylate [85]. Cr-MIL-101 and Fe-MIL-101 have been found to catalyze oxidation reactions of cyclohexene, limonene, alpha-pinene, cyclopentene or cyclohexane [86–89]. Several derivatives of CPO-27 with Co, Mg, Mn, Ni and Zn as metal centers have been compared as catalysts in cyanosilylation and oxidation reactions. It was found, that all derivatives catalyze the cyanosilylation of aldehydes with trimethylsilylcyanide while the oxidation of styrene with tert-butylhydroperoxide is only promoted by the cobalt and manganese variants of CPO-27 [90].

c) Functional linkers as active species:

The third important strategy is the utilization of functional groups bound to the organic linkers, either prior to synthesis or introduced via post-synthetic modification (cf. chapter 2.1.3). The post-synthetic modification allows the generation of specialized organocatalysts or even the complexation of secondary transition metals by chelating ligands. Most frequently, acidic and basic moieties are incorporated into the framework by use of terephthalic acid derivatives functionalized with sulfonic acid groups and primary amines. Recently a new sulfonic acid functionalized zirconium terephthalate MOF has been proven to be an active and recyclable catalyst for the esterification of acetic acid with n-butanol, while Cr-MIL-101-SO$_3$H deactivates in a non-recyclable way under the same conditions [91].

A number of studies have been reported in recent years in which amine-functionalized MOFs are utilized as basic solid catalysts. As a versatile test reaction for the evaluation of the activity of those basic catalysts the Knoevenagel condensation is meanwhile well established. A detailed insight in this reaction and representative examples for well performing catalysts are given in the following chapter.
2.3 The Knoevenagel condensation

The Knoevenagel condensation is the reaction of a carbonyl compound, most commonly an aldehyde, with an active methylene group. The activity of the methylene compound is determined by the strength of the electron withdrawing substituents. The three most common methylene compounds which are also studied in this work show an increasing acidity in the order of diethyl malonate \((pK_a = 16.4) <\) ethyl cyanoacetate \((pK_a = 13.1) <\) malononitrile \((pK_a = 11.1)\) [92]. Due to the different acidities of the reactants, this reaction is a versatile tool for the comparison of the base strength of different catalysts. However, it has to be taken into account that also other factors like the employed solvent, the reaction conditions and the presence of additional supporting active sites have a significant influence on the reaction rate. In the case of microporous solid catalysts, the different dimensions of the malonic acid derivatives have an additional influence on the diffusion rates of the educt and the resulting product molecules and, thus, the activity and the selectivity of the catalyst.

The Knoevenagel condensation is catalyzed by a variety of basic catalysts. Typically, this reaction is homogeneously catalyzed by molecular amines like piperidine. The underlying solely base-catalyzed mechanism is based on the deprotonation of the acidic methylene group of the basic amine followed by a nucleophilic attack by the resulting carbanion on the carbonyl carbon atom. Subsequent elimination of one molecule of water releases the final condensation product (Scheme 2.1).

![Scheme 2.1: Proposed mechanism for the Knoevenagel condensation of benzaldehyde and an active methylene compound homogeneously catalyzed by an amine.](image)

For heterogeneous catalysts, more complicated mechanisms involving additional acidic centers have been proposed. For silica gel that has been functionalized by
immobilization of amino groups, Angeletti et al. proposed the following bifunctional mechanism (Scheme 2.2) [93]. In the first step the methylene component, in this case malononitrile, is deprotonated by the basic amine. The nucleophilic attack of the resulting carbanion on the carbonyl group of benzaldehyde is facilitated by the formation of a hydrogen bond between the carbonyl oxygen and an acidic silanol group in direct proximity of the basic center. In the following step the elimination of water from the alcoholic intermediate is again induced by the formation of a hydrogen bond between the silanol group and the OH-moiety and the eliminated water is adsorbed on the hydrophilic catalyst surface. A similar importance of the role of neighbored silanol groups has been reported for ammonia-treated FSM-16 catalysts that show the highest reaction rates in the Knoevenagel condensation when a large number of NH$_2$- and OH-groups are in direct proximity [94].
Proposed mechanism for the Knoevenagel condensation of benzaldehyde and malononitrile catalyzed by amine-functionalized silica involving both, basic amino and acidic silanol groups as active centers (adapted from [93]).

Similar conclusions have been drawn by Ernst and coworkers after evaluation of the catalytic activity of various nitridated aluminosilicate and aluminophosphate materials in the Knoevenagel condensation [7]. In all cases, the treatment of the catalysts with ammonia at elevated temperatures results in a significant rise in activity. The
comparison of zeolites with different Si/Al ratios showed that nitridated NaY and DAY catalysts reach full conversion after 5 and 2 hours, respectively, while aluminum-rich nitridated NaX shows a yield of benzylidene malononitrile of only 52% after 24 hours. This drastically reduced activity is assigned to a rapid deactivation of the very hydrophilic surface of this compound [95].

For aluminum phosphate-type catalysts, Climent et al proposed a mechanism for the Knoevenagel condensation of benzaldehyde with ester-type methylene compounds that suggests the incorporation of Broensted-acidic P-OH functionalities at the surface in two different stages (Scheme 2.3) [96]. As discussed for Si-OH-groups above, the aldehyde compound is activated by the formation of a hydrogen bond to a surface OH-group. In addition, a neighboring OH-group forms another hydrogen bond to the carbonyl oxygen of the ester group of the methylene component which leads to the stabilization of the carbanion species in the form of an enolate intermediate that can now attack the activated aldehyde carbon.

Scheme 2.3: Proposed mechanism for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate catalyzed by an aluminophosphate catalyst (adapted from [96].
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Due to the large variety of reaction conditions chosen by different researches for the Knoevenagel condensation as a test reaction, a direct comparison of catalytic activities of catalysts from different sources is in most cases not possible. However, a comparison of metal-organic framework catalysts to silica based materials has been attempted by Hwang et al. In their study they compared Cr-MIL-101 in the parent form and different derivatives that have been functionalized by grafting of nitrogen-containing reagents to the coordinatively unsaturated sites of the framework (cf. chapter 2.4.1) to unfunctionalized and amine-functionalized samples of SBA-15 [51]. As a test reaction, the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate (1 mmol each) in 25 mL of cyclohexane at 80 °C with 20 mg of catalyst was employed. The MOF-based catalysts exhibit higher activities than the SBA-15 derivatives with even higher selectivity (Table 2.1), which is explained by the superior accessibility of the 3D pore system and the high density of active sites. For both classes of catalysts it has been confirmed that the amino groups can be regarded as the predominantly active sites.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion / %</th>
<th>Selectivity / %</th>
<th>TOF / h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-MIL-101</td>
<td>31.5</td>
<td>99.4</td>
<td>-</td>
</tr>
<tr>
<td>ED-Cr-MIL-101</td>
<td>97.7</td>
<td>99.1</td>
<td>328</td>
</tr>
<tr>
<td>APS-Cr-MIL-101</td>
<td>96.3</td>
<td>99.3</td>
<td>168</td>
</tr>
<tr>
<td>SBA-15</td>
<td>2.6</td>
<td>93.0</td>
<td>-</td>
</tr>
<tr>
<td>APS-SBA-15</td>
<td>74.8</td>
<td>93.5</td>
<td>32</td>
</tr>
</tbody>
</table>

ED = ethylene diamine; APS = aminopropyltrialkoxysilane; TOFs related to molar amount of nitrogen.

In 2009, Gascon et al. reported the use of amino-functionalized MOFs, namely IRMOF-3 and Al-MIL-53-NH₂ as solid catalysts for the base-catalyzed Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate [10]. It was found that the
activity of the IRMOF-3 catalysts strongly depends on the solvent used. While polar solvents like DMSO, ethanol or DMF have a positive influence on the reaction rate, only negligible yields were detected when the reaction was carried out in non-polar and aprotic toluene. In the case of Al-MIL-53-NH₂ almost no product yield was detected under the same reaction conditions, which is explained by the strong adsorption of educt and product molecules in the narrow pores of this MOF. Although the recyclability of the IRMOF-3 catalyst was proven by reusing it several times, it should be noted that in many cases of Gascon’s study a very high initial activity is followed by a comparably low reaction rate. Thus, the given initial turnover frequencies are not useful for a valid comparison. This indicates that the performance of the catalyst decreases rapidly under reaction conditions, which might be caused by partial hydrolysis of the MOF by the water formed as a byproduct in the Knoevenagel condensation. A high moisture sensitivity of Zn₄O based MOFs has been discussed in the literature before [97]. It is also clearly shown by removal of the MOF from the hot reaction mixture, that no active species are leached form the solid catalyst and the soluble analogue aniline shows a drastically reduced activity compared to the aromatic amino groups incorporated in the metal-organic framework. The authors furthermore report that the Knoevenagel condensation is in this case initiated by the formation of a surface bound imine species resulting from the condensation of benzaldehyde with an amino group (Scheme 2.4).

**Scheme 2.4: Proposed mechanism of the Knoevenagel condensation incorcoration a surface bound imine intermediate (X = electron withdrawing group).**

Further investigations of IRMOF-3 as a basic catalyst in the Knoevenagel condensation by Llabrés i Xamena et al. and a comparison of its activity to the unfunctionalized analogue MOF-5, which also shows a significant catalytic activity depending on the amount of defect sites, demonstrated that the amino groups are
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not the only catalytically active species in this type of catalyst [98]. It was hence concluded that IRMOF-3 acts as an unintentional bifunctional catalyst which utilizes the basic amino groups and acidic Zn-OH species or coordinatively unsaturated sites at the zinc centers, formed by partial hydrolysis of the MOF, in a bifunctional mechanism, similar to the one proposed for aluminophosphate catalysts (cf. chapter 2.3.)

Parallel to the work described in this thesis, Serra-Crespo et al. reported the use of Al-MIL-101-NH₂ as basic catalyst in the same reaction [99]. They reported that this amine-functionalized MOF is able to promote the Knoevenagel condensation even when toluene is used as solvent.

Similar results were recently published by Yang et al. for the use of the zirconium MOFs UiO-66-NH₂ and UiO-66 as catalysts in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate [92]. They also report that the use of hydrophobic solvents like toluene, tetrahydrofuran and ethyl acetate gives only minor conversions of benzaldehyde, viz. 1 to 3 % after two hours at 40 °C while under the same conditions conversions of 92 and 95 % are reached in DMF and DMSO, respectively. It was found, that UiO-66-NH₂ shows a significantly higher catalytic activity than UiO-66, which accelerates the reaction although no basic amines are present in the framework. However, the soluble linker analogue dimethyl 2-aminoterephthalate only shows a negligible catalytic activity. The authors conclude from their results that the acid-base catalyzed Knoevenagel condensation proceeds via the formation of an imine intermediate as shown in Scheme 2.4 whose formation is facilitated by the interaction of the aldehyde oxygen with Lewis-acidic zirconium centers (Scheme 2.5).

![Scheme 2.5: Proposed activation of the aldehyde by Lewis-acidic metal centers in direct proximity to the amino group.](image-url)
In order to explain the catalytic activity of unfunctionalized carboxylate-based MOFs in this reaction, Panchenko et al. proposed a mechanism based on the simultaneous activation of the aldehyde and the methylene group by the M-O bond which acts as a Lewis-acid-base pair [100]. According to this mechanism (Scheme 2.6), the carbonyl group of the aldehyde is activated by coordinating to the Lewis-acidic metal center, while the methylene group is deprotonated by the neighboring anionic oxygen forming a carbanion intermediate. In the same work, the UiO-66-NH$_2$-catalyzed Knoevenagel condensation of benzaldehyde and diethyl malonate is reported as a solvent-free reaction at 100 °C. However, it has to be noted that in this study only the conversion of benzaldehyde is determined, while the product yield is not measured.

Scheme 2.6: Proposed mechanism for the Knoevenagel condensation of benzaldehyde and malononitrile catalyzed by a M-O acid-base pair.
2.4 Structures and properties of the MOFs employed in this study

For the exploration of MOFs as heterogeneous basic catalysts, they have to fulfill several requirements. In addition to a certain permanent porosity and accessible, non-coordinating amine moieties are crucial for this application. Moreover, a sufficient stability of the structures towards air and moisture is needed. Meanwhile a large variety of amino-functionalized MOFs has been reported [101]. The structural motifs of the NH₂-functionalized metal-organic frameworks employed in this work are discussed in this chapter.

2.4.1 MIL-101 (M₃OF(bdc)₃(H₂O)₂)

The first example for a MOF with the MIL-101 motif was published by the group of Férey in 2005 [29]. This material is described as a chromium(III) terephthalate, derived by the reaction of chromium(III)nitrate nonahydrate with terephthalic acid in the presence of hydrogen fluoride in equimolar amounts under hydrothermal conditions and autogenous pressure at 220 °C for eighth hours. This chromium(III)terephthalate was found to crystallize in the same extended MTN (Mobil Thirty-Nine) zeotype architecture as the trimesate based MIL-100. Due to the extension of the topology, the cubic unit cell of MIL-101 possesses a huge edge length of ~8.9 nm.

The nodes of this framework structure are built of trimeric μ₃-oxo centered chromium complexes. Each chromium ion has an octahedral coordination sphere with the axial positions being occupied by the central μ₃-oxide in the center of the triangle and two water molecules and one fluoride anion at the outward directing positions. The four equatorial positions of each octahedron are filled with carboxylate oxygen ligands. Each carboxylate group acts as a bridge between two metal centers. The final nodes of the MTN topology are formed by the connection of four of these trimeric SBU's via the terephthalate linker to form the so called supertetrahedra (Figure 2.6). These supertetrahedra have a free aperture of ~0.86 nm and give access to the micropores of the interconnected pore system. By corner sharing assembly of these tetrahedral
super units, two types of mesoporous cavities are embedded. The smaller one with an inner diameter of ~2.9 nm is delimited by 20 supertetrahedra and is exclusively accessible through pentagonal windows with a free aperture of 1.2 nm. The larger, which is built up from 28 of the supertetrahedra has an inner diameter of 3.4 nm and is, in addition to the pentagonal windows, connected to its neighboring cavities by even larger hexagonal openings with free dimensions of 1.47 x 1.6 nm (Figure 2.7). These cages are even large enough for direct imaging by transmission electron microscopy [102]. The overall ratio of the different cavities in the final structure is 17:2:1 (supertetrahedra:2.9 nm cages:3.4 nm cages). This very open structure gives rise for a very large porosity with a specific BET surface area of ca. 4100 m² g⁻¹ and a total pore volume close to 2.0 cm³ g⁻¹, which were, according to Férey et al. [29], the highest values reported at that time for all known crystalline and amorphous materials.

Figure 2.6: Trimeric secondary building unit (left) and two corner sharing supertetrahedra, formed by connection of the SBUs by terephthalate linkers (right) as observed in the MIL-101 structure.
Figure 2.7: Illustration of the two types of mesoporous cavities of the MIL-101 structure. While the smaller one possesses trigonal and pentagonal windows, the larger ones are connected to each other via additional hexagonal openings.

This complex structure, accommodating voids of different dimensions, causes a characteristically shaped nitrogen sorption isotherm which shows a stepwise uptake of gas molecules in three stages. The first step can be assigned to the filling of the microporous supertetrahedra along with the formation of the first layer of adsorbed molecules in the larger cavities. The following two steps are due to successive complete filling of the two types of mesoporous cages.

Surprisingly, this highly porous material shows a very good stability when exposed to air (several months) or different solvents, which gave rise to numerous attempts for modifications by employing alternative metal centers and/or functionalized linkers. Unfunctionalized derivatives are known with iron [103,104], titanium [105], and vanadium [106] as structure building metal centers. The direct synthesis of amino-
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Functionalized Fe-MIL-101-NH₂ from iron(III)chloride and 2-aminoterephthalic acid was achieved by Bauer et al. in a high throughput study [107]. The preparation of the Cr-MIL-101-NH₂ was first realized by Bernt et al. via post-synthetic nitration of parent Cr-MIL-101 and subsequent reduction of the nitro moieties [108]. Later, strategies for the direct synthesis of this compound were published [109] [110]. The existence of Al-MIL-101-NH₂ was first indicated by Ahnfeldt et al. [111]. In 2011 simultaneous to the development of an optimized procedure as part of this work [112,113], Serra-Crespo et al. published a solvothermal route for the synthesis of an Al-MIL-101-NH₂ derivative [99]. While the amino-functionalized V-MIL-101-NH₂ was synthesized under the same conditions as the parent V-MIL-101 [106], usually significant variations of the synthesis conditions (solvent used, temperature, concentrations etc.) have to be realized for the successful substitution of the metal and/or the linker. This is, in many cases, most probably due to the fact, that the MIL-101 phase is formed as a kinetic product, while the reaction under the same conditions ends with the thermodynamically more stable MIL-53 phase [114–116]. It must be noted that some of the MIL-101 derivatives reported in literature (V-MIL-101(-NH₂), Cr-MIL-101-NH₂ / -NO₂, Al-MIL-101-NH₂) exhibit, although their structural identity is proven by X-ray diffraction methods, comparably poor porosities that cannot solely be explained by the incorporation of functional groups at the framework struts.

2.4.2 CAU-1 (Al₄(OH)₂(OCH₃)₄(bdc-NH₂)₃)

The synthesis of CAU-1 was first reported by the group of N. Stock in 2009 [111] as the result of a sophisticated high throughput study of the system Al³⁺H₂bdc-NH₂/solvent. It is based on a unique SBU, which is built from eight octahedrally coordinated Al³⁺ ions. These metal centers are connected to each other alternatingly via corners and edges by sharing one hydroxide and two methoxide ligands, respectively, forming an eight-membered [Al₆(OH)₆(OCH₃)₆]¹²⁺ ring (Figure 2.8, left). Each of these wheel-shaped rings is connected via the linking 2-aminoterephthalate anions to twelve neighbors, thereby forming two types of cavities. The smaller one is of tetrahedral shape and has an inner diameter of ca. 0.5 nm, while the larger one has an octahedral geometry with an inner diameter of ca. 1.0 nm. Both cages are connected by and exclusively accessible through triangular windows with an open
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aperture of 0.3 to 0.4 nm (Figure 2.8, right). This rigid framework possesses high permanent porosity with a specific Langmuir surface area of approximately 1700 m$^2$ g$^{-1}$ and a micropore volume of 0.52 cm$^3$ g$^{-1}$.

![Crystal Structure of CAU-1](image)

Figure 2.8: Illustration of the crystal structure of CAU-1 showing the wheel-shaped eight-ring SBU (left) and the two different types of cages (right).

It is reported that this unusual structure is only formed when methanol is used as solvent and aluminum(III)chloride hexahydrate as the metal source in a 1:2 ratio to the linker 2-aminoterephtalate. All attempts to utilize aluminum(III)nitrate in the same synthesis leads to the formation of an Al-MIL-53-NH$_2$ type MOF while the utilization of aluminum(III)chloride hexahydrate as the metal source in different solvents leads to the formation of different phases such as Al-MIL-53-NH$_2$, Al-MIL-101-NH$_2$, CAU-1 and an unknown phase or mixtures of them. The fact that CAU-1 can only be successfully synthesized in methanol can be explained by the presence of bridging methoxide ligands in the SBU, which are mandatory for the formation of this structure.

Two years after the first report, Ahnfeldt and Stock showed that the induction as well as the crystallization time required for the synthesis of CAU-1 and the hydroxy-functionalized derivative CAU-1-(OH)$_2$ can be significantly reduced by using a microwave-based heating method instead of the conventional electric heating [117].
The UiO-66 structure is based on a hexameric zirconium building brick which was first reported as a SBU in this MOF by Cavka et al. in 2008 [30]. The six zirconium ions in this cluster form an octahedron whose triangular faces are alternatively capped by \( \mu_3\)-O and \( \mu_3\)-OH ligands. The edges of the polyhedra are bridged by the carboxylate groups of the terephthalic acid linkers, so that each of the \( \text{Zr}_6\text{O}_4\text{(OH)}_4 \) cores (Figure 2.9, left) is, similar to the structure of CAU-1, connected to twelve neighboring nodes, forming an extended cubic close packed (CCP) structure (Figure 2.9, right). This extended structure exhibits a permanent porosity with a Langmuir surface area of 1187 m\(^2\) g\(^{-1}\) and open apertures of the triangular windows of approximately 0.6 nm. This structure shows an exceptional thermal stability with a decomposition temperature of 540 °C, which can be assigned to the ability of the hexameric SBU to maintain its overall geometry upon dehydroxylation. At temperatures between 250 and 300 °C, two of the four hydroxy ligands are expelled as water together with the hydrogen of the two remaining \( \mu_3\)-hydroxides. This results in the formation of a \( \text{Zr}_6\text{O}_6 \) inner core with seven-coordinated zirconium centers. Since the zirconium ions stay on the corners of the octahedra during this process, the overall framework structure built by the terephthalate linkers remains virtually unchanged.

![Illustration](image.png)
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UiO-66 shows, in addition to the remarkable thermal stability, a very high chemical stability against solvents like water, DMF, benzene and acetone as well as a high mechanical resistance with the crystal structure remaining virtually unchanged after treatment at 10,000 kg cm$^{-2}$.

Wu et al. have shown that the porosity of UiO-66 is increased to values higher than the ones expected for the perfect framework by the incorporation of missing linker defect sites [118]. The addition of acetic acid as a modulator to the synthesis mixture leads thereby not only to the growth of larger crystals, but also to higher specific pore volumes of up to 0.65 cm$^3$ g$^{-1}$ instead of the 0.44 cm$^3$ g$^{-1}$ observed for the linker saturated material. Both effects, the dihydroxylation and the linker deficiency have also been studied and verified by theoretical approaches by Valenzano et al. [119].

The exceptional stability of the UiO-66 structure and the straightforward synthesis conditions have originated numerous research activities to investigate the optimization of the synthesis and the functionalization of the material. In 2010, Kandiah et al. succeeded in the synthesis of UiO-66 isostructural MOFs from -NH$_2$, -NO$_2$ and -Br tagged terephthalic acid derivatives by slight adjustment of the synthesis parameters [120].

A new procedure for the synthesis of -NH$_2$, (-NH$_2$)$_2$, -OH, (-OH)$_2$ and -NO$_2$ functionalized UiO-66 derivatives was published in 2013 by Katz et al [121]. In this approach hydrochloric acid is used as an additive that leads to higher porosities than the adaption of the synthesis protocol for unfunctionalized UiO-66. This is explained by the higher density of missing linker defects and the measured surface areas are comparable to those calculated for materials with only eight instead of twelve linkers per node. The role of the HCl is not fully understood but most probably it either leads to conditioning of the $N,N$-dimethylformamide by neutralization of basic impurities or to a preformation of the SBUs prior to linker binding.

For more detailed information about synthesis strategies and functionalization of UiO-66, including post-synthetic approaches, the reader is referred to a recent review that summarizes the evolution of zirconium(IV) based MOFs [122].
The first material with MIL-53 structure was described by the group of G. Férey in 2002 [18,28]. Cr-MIL-53 is derived from a hydrothermal reaction of equimolar amounts of chromium(III)nitrate nonahydrate, terephthalic acid and HF at 220 °C after three days. Since the fluoride is not present in the final material but mandatory for the successful synthesis of Cr-MIL-53, it can be regarded as a mineralizer. Two years later, an isostructural MOF based on aluminum was described by the same group [19]. The MIL-53 motif is based on a comparably simple SBU of $\text{MO}_4(\text{OH})_2$ octahedra which are connected to infinite chains by sharing the $\mu_2$-OH ligands in both axial positions of the octahedra. The four oxygen ligands in the equatorial positions are derived from the terephthalate linkers, which connect these chains in a rhombic arrangement to form a 3D framework with open one-dimensional diamond shaped channels (Figure 2.10). In the as-synthesized form, these channels are occupied by unreacted terephthalic acid molecules, leading to an essentially non-porous compound. The free terephthalic acid can be removed by calcination at 330 °C for three days to form the large pore high temperature form M-MIL-53-ht with pore dimensions of 0.85 x 0.85 nm and a specific BET surface area of ca. 1140 m$^2$ g$^{-1}$. Upon adsorption of water from ambient air, the rhombic channels contract perpendicular to the direction of the metal hydroxide chains, most probably due to hydrogen bonding between the adsorbed water and the $\mu_2$-OH groups. The resulting narrow pore or low temperature phase M-MIL-53-lt possesses pores of 0.23 x 1.36 nm which are, due to the occupancy by water, not accessible for guest molecules. This phase transformation is prominently known as “breathing effect” and is not observed for the vanadium analogue V-MIL-47, since here the vanadium is oxidized from V(III) to V(IV) and the bridging hydroxides are replaced by oxides during the calcination step in this case [123]. Interestingly, this effect can not only be triggered by the adsorption of water or other guest molecules such as carbon dioxide or alkanes [124], but also by a change of temperature [125].
An alternative activation procedure for Al-MIL-53 was proposed by Rallapalli et al. [126]. Here, the time and energy consuming calcination step is replaced by an adsorbate exchange step via extraction with \(N,N\)-dimethylformamide at 150 °C.

Figure 2.10: Illustration of the pore geometries of MIL-53-ht (top) and MIL-53-lt (bottom).
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followed by solvent exchange with methanol. The resulting material shows the same breathing effect as the calcined variant.

The properties of the Al-MIL-53 framework can be widely adjusted by the functionalization of the organic linker. Amongst others, derivatives with -NH₂ [127], -OH [128], -Cl, -Br, -CH₃, -NO₂ and (-OH)₂ [129] moieties have been reported.

Recently, the influence of different solvents on the properties of the resulting Al-MIL-53 material has been studied. Liu et al developed an ionothermal approach, where the ionic liquid 1-ethyl-3-methylimidazolium bromide ([EMIM]Br) was used as a recyclable solvent [48]. The Al-MIL-53 derivative shows an enhanced hydrophobicity and is, after thermal activation at 330 °C, present in a stable high-temperature form at ambient conditions. The influence of DMF on the breathing effect of Al-MIL-53 has been studied by Mounfield III and Walten [130]. They found, that the synthesis of Al-MIL-53 in DMF at 220 °C results in a material with a gradual, slight breathing behavior, while a sample synthesized in DMF at only 120 °C does not show a contraction of the structure at all and is stabilized in the ht-form. Fascinatingly, these Al-MIL-53 derivatives synthesized in DMF show a reduced stability against water. Another innovative route for the preparation of Al-MIL-53 was recently reported by Sánchez-Sánchez et al. [40]. In this approach the sodium salt of terephthalic acid is applied as the linker source, leading to a drastically enhanced availability of deprotonated terephthalate anions in the synthesis solution and thereby a reduction of the synthesis temperature. This approach yields nanocrystalline Al-MIL-53 even at room temperature with only negligible amounts of unreacted linker being present in the as-synthesized material.

Bayliss et al. developed a possibility for the preparation of Al-MIL-53 in a continuously operated reactor [131]. In their apparatus, the reaction takes place at 250 °C and at a very high pressure of 230 bar in a two bed system and the raw material is purified by extraction with supercritical ethanol.
In 2009, a new metal-organic framework based on the MIL-53 geometry was discovered in the group of Stefan Kaskel [132]. The new compound, denoted as DUT-5, has the same one dimensional chains of octahedrally coordinated Al\(^{3+}\) ions which are connected by \(\mu_2\)-OH groups at the axial positions while the equatorial positions are occupied by carboxylate oxygens. In contrast to MIL-53, where terephthalate is used as a linker between those chains, DUT-5 is formed from the extended 4,4′-biphenyl-1,1′-dicarboxylate, which results in an extended pore size of 1.11 nm for the infinite channel like pores (Figure 2.11) and a specific pore volume of 0.81 cm\(^3\) g\(^{-1}\) (S\(_{\text{BET}}\) (at p/p\(_0\) = 0.3) = 1613 m\(^2\) g\(^{-1}\)). Interestingly, other than the smaller Al-MIL-53, DUT-5 is only observed in the open pore form and a structural conversion by the adsorption of water has not been reported so far.

Figure 2.11: Pore system of DUT-5 built by connection of one-dimensional \([\text{Al(OH)}]_n\) chains via bpdc linkers.
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Very recently, while the experimental work of this study was already completed, the successful syntheses of several functionalized DUT-5 analogues, carrying -SO₂, -NH₂, -NO₂ [133], -C₂H and -N₃ [134] groups in the 2-position of the biphenyl linker, as well as strategies for further post-synthetic modifications have been reported.

2.4.6 HKUST-1 (Cu₃(btc)₂)

HKUST-1 or Cu₃btc₂ was first reported by Chui et al. in 1999 [27]. The structure is based on a dimeric Cu₂O₈ SBU, which is often denoted as “paddle wheel” (Figure 2.12). The coordinatively unsaturated sites (CUS) at the outer axial position of each copper ion are in the non-activated form capped by water or other solvent molecules. These SBUs are connected to each other via trimesate (benzene-1,3,5-tricarboxylate, btc) linkers to form face centered cubic crystals with a three-dimensional pore system of interconnected cuboctahedral pores with a diameter of 0.9 nm and smaller tetrahedral pores with a diameter of 0.5 nm which are accessible from the large pores through windows with a diameter of 0.35 nm (Figure 2.13). This leads to a permanent porosity with a specific BET surface area of up to 1800 m² g⁻¹.

Figure 2.12: Desolvated paddlewheel unit with the diatomic copper SBU and four trimesate linkers in the HKUST-1 structure.
While the first successful synthesis of HKUST-1 was achieved via a hydro-/solvothermal route, many variations have been developed meanwhile, including ambient pressure, electrochemical [46,84], room temperature [135] and even solvent-free mechanochemical [136] methods.

In 2012 Peikert et al. published an amino functionalized derivative of HKUST-1, HKUST-1-NH$_2$ (Cu$_3$(NH$_2$btc)$_2$, UHM-30 (University of Hamburg Materials)), which was synthesized from 2-amino-1,3,5-benzenetricarboxylic acid and explored in the context of adsorption and controlled release of nitrous oxide [137,138].

Figure 2.13: Illustration of the pore system of HKUST-1.
3 Experimental section

3.1 Instruments and methods

Nitrogen sorption isotherms have been measured using an ASAP 2000 / 2010 instrument with micropore option at -196 °C. Cold and warm free spaces of the filled sample tubes were determined by helium expansion prior to each measurement. All samples were degassed at 110 °C in fine vacuum for at least 12 h. Specific BET areas $A_{BET}$ were calculated in a pressure range, individually determined considering the consistency criteria proposed by Snurr et al [139] and the new recommendations of the UIPAC for the meaningful application of the BET method in the case of microporous solids [140]. If not described otherwise, total pore volumes were calculated at a relative pressure of $p/p_0 = 0.8$ to exclude the influence of interparticle condensation. Micropore volumes were, where applicable, calculated by the t-plot method.

For the measurement of hydrogen sorption isotherms, a Rubotherm IsoSORP magnetic suspension balance with automated gas dosing system was used.

Scanning electron micrographs (SEM) were recorded using a Carl Zeiss ULTRA 55 field emission scanning electron microscope.

Powder X-ray diffraction patterns were measured at a Panalytical X’Pert Pro instrument, equipped with a copper anode using Cu K$_{\alpha}$ radiation with a wavelength of 0.15418 nm and an auto sampler. For measurements in transmittance mode the samples were filled into glass capillaries under inert atmosphere and the capillaries were sealed by melting.

Fourier transform Infrared (FT-IR) spectra were recorded at a Jasco 4100 FT-IR spectrometer with a DLaTGS (i.e., deuterated and L-alanine-doped triglycine sulfate) detector with a resolution of 4 cm$^{-1}$. For standard analyses, a PIKE GladiATR attenuated total reflection (ATR) accessory with a single reflection diamond crystal was used. For recording spectra in diffuse reflectance infrared Fourier transform...
Experimental section

(DRIFT) mode, a Harrick Praying Mantis DRIFT accessory with high temperature reaction chamber equipped with 3 mm potassium bromide windows was used.

Nuclear magnetic resonance (NMR) spectra of purely organic samples were recorded in solution on a Jeol ECX 400 spectrometer at room temperature. $^1$H and $^{13}$C resonances were measured at frequencies of 400 MHz and 100.6 MHz, respectively. Chemical shifts are referenced against TMS.

NMR spectra of solid samples were recorded at an Agilent V500WB spectrometer ($^1$H frequency = 499.86 MHz) under magic angle spinning (MAS) conditions at room temperature using a 3.2 mm sample rotor. Detailed parameters of the measurements are given in table 3.1.

<table>
<thead>
<tr>
<th>Table 3.1: Parameters of solid state NMR measurements.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C ($^1$H-$^{13}$C CP)</td>
</tr>
<tr>
<td>(Al-MIL-101-NH$_2$)</td>
</tr>
<tr>
<td>resonance frequency</td>
</tr>
<tr>
<td>pw 90</td>
</tr>
<tr>
<td>rf-field strength</td>
</tr>
<tr>
<td>contact time</td>
</tr>
<tr>
<td>recycle delay</td>
</tr>
<tr>
<td>acquisition time</td>
</tr>
<tr>
<td>number of scans</td>
</tr>
<tr>
<td>Spinning speed</td>
</tr>
</tbody>
</table>

For elemental analyses, an EA Euro Vector EA 3000 instrument was used in CHNS configuration.
Experimental section

The compositions of the liquid phases of the catalytic test reactions were analyzed by gas chromatography using a Varian 3900 GC, equipped with a CP-Sil PONA CB (50 m, 0.21 mm, 0.6 μm) capillary column and an auto sampler.

3.2 Chemicals

All chemicals were used as purchased without further purification.

Table 3.2: Chemicals used in this study.

<table>
<thead>
<tr>
<th>Name / Abbreviation</th>
<th>Manufacturer / Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂bdC-NH₂</td>
<td>Sigma-Aldrich</td>
<td>99 %</td>
</tr>
<tr>
<td>DMF</td>
<td>Merck</td>
<td></td>
</tr>
<tr>
<td>AlCl₃ · 6 H₂O</td>
<td>Applichem</td>
<td>p. a.</td>
</tr>
<tr>
<td>ethanol (technical)</td>
<td>CSC Jäklechemie</td>
<td>96 %</td>
</tr>
<tr>
<td>FeCl₃ · 6 H₂O</td>
<td>Merck</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>terephthalic acid</td>
<td>Aldrich</td>
<td>98 %</td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>Aldrich</td>
<td>&gt; 99.5 %</td>
</tr>
<tr>
<td>methanol</td>
<td>VWR Chemicals / BDH - Prolabo</td>
<td>Normapur</td>
</tr>
<tr>
<td>Al(NO₃)₃ * 9 H₂O</td>
<td>Merck</td>
<td>&gt; 98.5 %</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>Merck</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>malononitrile</td>
<td>Merck</td>
<td>&gt; 98 %</td>
</tr>
<tr>
<td>piperidine</td>
<td>Merck</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>ethyl cyanoacetate</td>
<td>Merck</td>
<td>&gt; 98 %</td>
</tr>
<tr>
<td>H₂O</td>
<td>in house deionization</td>
<td></td>
</tr>
<tr>
<td>diethyl malonate</td>
<td>Merck</td>
<td>&gt; 98 %</td>
</tr>
</tbody>
</table>
3.3 Syntheses of metal-organic frameworks

3.3.1 Synthesis of Fe-MIL-101-NH$_2$

Fe-MIL-101-NH$_2$ was synthesized based on a published protocol [107]. In a 100 mL screw cap bottle, 2.70 g (10 mmol) of FeCl$_3$·6 H$_2$O were dissolved in 30 mL of DMF. To the clear solution, a solution of 900 mg (5 mmol) of 2-aminoterephthalic acid in 30 mL of DMF was added. The bottle was capped and the well-blended mixture heated to 110 °C in a preheated convection oven for 24 h. After cooling to room temperature, the dark brownish precipitate was separated from the mother liquor by
Experimental section

vacuum filtration. The filtration was immediately stopped when no liquid phase was left and the wet residue was quickly transferred to a cellulose extraction thimble and extracted in a 30 mL soxhlet apparatus with 100 mL of ethanol overnight. Thereafter, the wet and hot sediment containing thimble was transferred to a Schlenk tube and dried in vacuum first at room temperature and subsequently at 80 °C. The very fine, dark brown powder was then transferred to another Schlenk tube and stored under argon atmosphere.

3.3.2 Synthesis of Fe-MIL-101

Fe-MIL-101 was synthesized and activated following the same protocol as for Fe-MIL-101-NH₂, using 830 mg (5 mmol) of terephthalic acid instead of 2-aminoterephthalic acid.

3.3.3 Synthesis of CAU-1

In a typical synthesis, 2.33 g (9.6 mmol) of AlCl₃ · 6 H₂O and 0.58 g (3.2 mmol) of 2-aminoterephthalic acid were dissolved in 30 mL methanol. The mixture was split into three equal portions and filled into three 23 mL PTFE-lined stainless steel Parr autoclaves. The sealed autoclaves were placed in a preheated convection oven at 125 °C for 5 h. After cooling to room temperature, the bright yellow suspensions were separated by centrifugation. The solid fractions were combined, washed with methanol and purified by soxhlet extraction with 100 mL of methanol overnight. The yellow residue was dried at ambient conditions for three hours and at 90 °C for 24 h, respectively.

3.3.4 Synthesis of UiO-66-NH₂

In a 100 mL screw cap bottle, 117 mg (0.5 mmol) of dry ZrCl₄ were dissolved in 50 mL of DMF. After the addition of 92 mg (0.5 mmol) of 2-aminoterephthalic acid, the
bottle was capped and placed in a preheated convection oven at 120 °C for 24 h. After cooling to room temperature the yellowish precipitate was recovered by filtration, washed twice with DMF and twice with ethanol (20 mL each) and extracted with ethanol in a Soxhlet apparatus for 24 h. The solid material was first dried at ambient air for 1 h and subsequently at 90 °C overnight.

### 3.3.5 Synthesis of Al-MIL-53

The hydrothermal synthesis of conventional Al-MIL-53 was carried out following a published procedure [19]: 13 g (34.7 mmol) of aluminum(III)nitrate nonahydrate and 2.88 g (17.4 mmol) of terephthalic acid were suspended in 50 mL of deionized water in a PTFE-lined stainless steel autoclave with a total volume of 125 mL and heated to 220 °C in a preheated convection oven for 72 hours. After cooling to room temperature, the solid white solid was isolated by vacuum filtration, washed with deionized water and acetone and dried at ambient conditions overnight. The as-synthesized material was subsequently activated by heating to 330 °C with a ramp of 10 K min\(^{-1}\) in a muffle furnace and was kept at this temperature for another 72 hours before it was allowed to cool to room temperature again.

### 3.3.6 Synthesis of Al-MIL-53-NH\(_2\)

A sample of Al-MIL-53-NH\(_2\) was kindly provided by Martin Kriesten and Stefan Peil. Details on the synthesis procedure and characterization of the material are described in the Master Thesis of Stefan Peil, where the sample is denoted as “Probe 8”.

### 3.3.7 Batch synthesis of Al-MIL-101-NH\(_2\)-ba:

In a 100 mL screw cap glass bottle, 272 mg (1.5 mmol) of Hbdc-NH\(_2\) were dissolved in 60 mL of DMF. After complete dissolution, 724 mg (3 mmol) of AlCl\(_3\) \cdot 6 H\(_2\)O were added and the sealed bottle was instantly transferred to a preheated convection oven
with minimum agitation and heated to 110 °C for 24 hours. After cooling to room temperature, a thin white ring at the glass wall at about one third of the height of the liquid level could be observed in addition to a voluminous yellow precipitate. The complete solid was isolated by vacuum filtration or centrifugation, respectively, washed with DMF and ethanol and dried at ambient conditions. Subsequently, the raw material was purified by Soxhlet extraction with ca. 100 mL of ethanol overnight and activated by degassing at 100 °C in fine vacuum (p < 10⁻² mbar).

### 3.3.8 Batch synthesis of Al-MIL-101-NH₂-bb:

Al-MIL-101-NH₂-bb was synthesized analogous to the synthesis of Al-MIL-101-NH₂-ba, but instead of collecting the complete solid, only the suspended yellow precipitate from the bulk liquid phase was isolated by centrifugation.

### 3.3.9 Semi-batch synthesis of Al-MIL-101-NH₂-s:

In a typical synthesis of Al-MIL-101-NH₂-s, 272 mg (1.5 mmol) of 2-aminoterephthalic acid were dissolved in 60 mL of DMF in a 100 mL round bottom flask with a PTFE coated magnetic stirring bar and a plastic stopper. The solution was heated to 110 °C in an oil bath under vigorous stirring before 724 mg (3 mmol) of AlCl₃ · 6 H₂O were added in 7 equal portions with a time lag of 15 min between each two additions. After complete addition of all reactants, the mixture was kept at 110 °C for additional 3 h with, and 16 h without stirring. After cooling to room temperature the voluminous yellow precipitate was separated by either vacuum filtration or centrifugation, washed with DMF and EtOH and dried at r.t. for 3 h and subsequently at elevated temperature (90 to 110 °C) in a convection oven over night. The as-synthesized product was then purified by solvent exchange with 100 mL of ethanol in a 30 mL soxhlet apparatus and activated by heating at 110 °C in vacuum.
Experimental section

3.3.10 Synthesis of DUT-5-NH\(_2\) (Al-bp-MIL-53-NH\(_2\))

In a 100 mL screw cap bottle, 257.3 mg (1 mmol) of 2-amino-1,1'-biphenyl-4,4'-dicarboxylic acid and 525.2 mg (1.4 mmol) of Al(NO\(_3\))\(_3\) \cdot 9\,\text{H}_2\text{O} were dissolved in 30 mL of DMF. The sealed bottle was subsequently heated to 120 °C for 24 h. After cooling to room temperature, the orange powder was separated from the red mother liquor by centrifugation, washed twice with ethanol and dried at ambient conditions for three hours and thereafter at 90 °C for 24 h. Activation of the material was achieved by extraction with 100 mL ethanol in a soxhlet apparatus for three days and drying at 90 °C overnight.

3.3.11 Synthesis of is-MIL-53:

415 mg (1.5 mmol) of 1-ethyl-3-methylimidazolium hydrogen terephthalate ([EMIM]Hbdc) were suspended in 15 mL of DMF in a 25 mL screw-cap glass bottle. After stirring at room temperature of 1 h, 850 mg (2.25 mmol) of Al(NO\(_3\))\(_3\) \cdot 9\,\text{H}_2\text{O} were added and the mixture was stirred for additional 30 min at room temperature to allow for complete dissolution of all components. Thereafter, the stirring bar was removed and the capped bottle was placed in a preheated convection oven at 130 °C for 48 h. After cooling to room temperature, the voluminous white precipitate was separated by centrifugation and washed with 20 mL of DMF and twice with 20 mL of ethanol before drying at ambient conditions and subsequently at 130 °C for 24 h, respectively.
3.4 Organic Syntheses

3.4.1 Synthesis of benzylidenemalononitrile (BzMN)

Scheme 3.1: Reaction scheme of the piperidine-catalyzed Knoevenagel condensation of benzaldehyde and malononitrile to benzylidenemalononitrile.

30 mL of a methanol / water mixture (70 : 30 v/v) was submitted to a 100 mL round bottom flask and 10.2 mL (100 mmol) of benzaldehyde and 6.6 g (100 mmol) malononitrile were added. Upon the slow addition of 1 mL (10 mmol) of piperidine under vigorous stirring, an exothermic reaction accompanied by the formation of a voluminous white precipitate was observed. After cooling to room temperature, the precipitate was recovered by filtration and washed with cold (5 °C) methanol and subsequently recrystallized from methanol. The colorless needle-shaped crystals were isolated by decanting and washed with small portions of ice-cold methanol and dried in vacuo at room temperature for two days.
3.4.2 Synthesis of ethyl α-E-cyanocinnamate (EtCC)

Scheme 3.2: Reaction scheme of the piperidine-catalyzed Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ethyl α-E-cyanocinnamate.

30 mL of a ethanol / water mixture (70 : 30 v/v) was submitted to a 100 mL round bottom flask and 10.2 mL (100 mmol) of benzaldehyde and 10.7 mL (100 mmol) ethyl cyanoacetate were added. Upon the slow addition of 2 mL (20 mmol) of piperidine under vigorous stirring, an exothermic reaction and the formation of a voluminous white precipitate was observed. After cooling to room temperature, the precipitate was recovered by filtration and washed with cold (5 °C) ethanol and subsequently recrystallized from ethanol. The colorless needle-shaped crystals were isolated by decanting and washed with small portions of ice-cold ethanol and dried in vacuo at room temperature for two days.
Experimental section

3.4.3 Three-step synthesis of 2-amino-1,1’-biphenyl-4,4’-dicarboxylic acid

a) Synthesis of dimethyl 2-nitro-1,1’-biphenyl-4,4’-dicarboxylate

\[
\begin{align*}
\text{C}_{16}\text{H}_{14}\text{O}_4 & \quad \text{MW} = 270.28 \text{ g mol}^{-1} \\
\text{HNO}_3 \text{aq.} / \\
\text{H}_2\text{SO}_4 \text{aq.} & \quad \text{C}_{16}\text{H}_{13}\text{NO}_6 \\
& \quad 315.28 \text{ g mol}^{-1}
\end{align*}
\]

Scheme 3.3: Reaction scheme of the nitration of dimethyl 1,1’-biphenyl-4,4’-dicarboxylate to dimethyl 2-nitro-1,1’-biphenyl-4,4’-dicarboxylate.

The nitrating acid used in this step was prepared as follows: 5.59 g of 60 wt.-% nitric acid (equals 53.2 mmol of HNO\(_3\)) were diluted with concentrated sulfuric acid (96 wt.-%) to a total volume of 25 mL (c(HNO\(_3\)) = 2.13 mol L\(^{-1}\)).

In a 250 mL three neck round bottom flask, 10.00 g (37 mmol) of dimethyl 1,1’-biphenyl-4,4’-dicarboxylate were dissolved in 50 mL of conc. sulfuric acid (96 wt-%) and cooled to 5 °C with an ice cooled water bath. To this vigorously stirred solution, 17.35 mL of the previously prepared nitrating acid (37 mmol of HNO\(_3\)) were added drop-wise at a rate that allowed the temperature to be kept between 4 and 6 °C. After the addition was completed, stirring was continued for 15 minutes before the reaction mixture was added drop wise to approximately 250 mL of ice water, forming a white precipitate. This precipitate was isolated by filtration, thoroughly washed with deionized water and dissolved in 100 mL of ethyl acetate. The solution was washed three times with 50 mL of deionized water before the organic phase was dried with magnesium sulfate. After removal of the magnesium sulfate by filtration and solvent evaporation under reduced pressure, 9.4 g (29.8 mmol) of dimethyl 2-nitro-1,1’-biphenyl-4,4’-dicarboxylate were recovered (80.5 %). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta / \text{ppm} \ 8.56 (d; J = 1.6 \text{ Hz}; 1\text{H}), 8.30 (dd; J = 7.8, 1.6 \text{ Hz}; 1\text{H}), 8.12 (m; 2\text{H}), 7.55 (d; J = 8.2 \text{ Hz}; 1\text{H}), 7.41 (m; 2\text{H}), 4.00 (s; 3\text{H}), 3.95 (s; 3\text{H}).\)
Experimental section

b) Synthesis of dimethyl 2-amino-1,1'-biphenyl-4,4'-dicarboxylate

![Reaction scheme of the reduction of the nitro moiety of dimethyl 2-nitro-1,1'-biphenyl-4,4'-dicarboxylate to dimethyl 2-amino-1,1'-biphenyl-4,4'-dicarboxylate.]

Scheme 3.4: Reaction scheme of the reduction of the nitro moiety of dimethyl 2-nitro-1,1'-biphenyl-4,4'-dicarboxylate to dimethyl 2-amino-1,1'-biphenyl-4,4'-dicarboxylate.

3 g (9.5 mmol) of dimethyl 2-nitro-1,1'-biphenyl-4,4'-dicarboxylate were added to 120 mL of methanol in a 500 mL round bottom flask. To this mixture 6.7 g (56.5 mmol) of tin powder and 168 mL of 1 M aqueous HCl were added at room temperature. After addition of all components, the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux until a clear solution was obtained. The solution was allowed to cool to room temperature, poured into 500 mL of ice water and thereafter basified with a 6 M aqueous NaOH solution. The precipitate was isolated by filtration and dissolved in ethyl acetate. The organic solution was transferred into a separatory funnel, washed three times with water and dried over magnesium sulfate. After removal of the magnesium sulfate by filtration and solvent evaporation under reduced pressure, 1.8 g (6.3 mmol) of dimethyl 2-amino-1,1'-biphenyl-4,4'-dicarboxylate were obtained, corresponding to a yield of 66 %. $^1$H-NMR (400 MHz, CDCl$_3$) δ / ppm 8.13 (d; J = 7.8 Hz; 2H), 7.56 (d; J = 8.2 Hz; 2H), 7.48 (m; 2H), 7.18 (d; J = 7.8 Hz; 1H), 4.04 (br. S.; 2H), 3.95 (s; 3H), 3.92 (s; 3H).
c) Synthesis of 2-amino-1,1’-biphenyl-4,4’-dicarboxylic acid

\[ \begin{align*}
\text{O} & \quad \text{NH}_2 \\
\text{C}_{10} \text{H}_{15} \text{NO}_4 & \quad 285.30 \text{ g mol}^{-1} \\
\end{align*} \]

\[ \begin{align*}
\text{KOH aq.} & \quad \text{HO} \\
\text{O} & \quad \text{NH}_2 \\
\text{C}_{12} \text{H}_{11} \text{NO}_4 & \quad 257.25 \text{ g mol}^{-1} \\
\end{align*} \]

Scheme 3.5: Reaction scheme of the alkaline hydrolysis of the methyl esters of dimethyl 2-amino-1,1’-biphenyl-4,4’-dicarboxylate to 2-amino-1,1’-biphenyl-4,4’-dicarboxylic acid.

In a 50 mL round bottom flask, 1 g (3.5 mmol) of dimethyl 2-amino-1,1’-biphenyl-4,4’-dicarboxylate was suspended in 20 mL of a 1 M aqueous potassium hydroxide solution. The suspension was heated to reflux overnight, leading to complete dissolution. After cooling to room temperature, the solution was acidified with 1 M hydrochloric acid and chilled in a refrigerator at 4 °C for 5 h. Thereafter, the mixture was filtrated without warming and the solid residue was washed with cold 1 M hydrochloric acid and cold water (both 4 °C) and dried at ambient conditions and subsequently under reduced pressure. After drying, 875 mg (3.4 mmol, 97 %) of 2-amino-1,1’-biphenyl-4,4’-dicarboxylic acid were obtained. $^1$H-NMR (400 MHz, DMSO d-6) $\delta$ / ppm 7.98 (d; J = 8.2 Hz; 2H), 7.54 (d; J = 7.8 Hz; 2H), 7.38 (s; 1H), 7.18 (d; J = 8.0 Hz; 1H), 7.08 (d; J = 7.8 Hz; 1H), 5.17 (br. s.; 2H). $^{13}$C-NMR (100.6 MHz, DMSO d-6) $\delta$ / ppm 168.07, 167.67, 145.89, 143.92, 131.51, 130.76, 130.36 (2C), 129.96, 129.26 (2C), 128.93, 117.96, 116.83.

3.4.4 Synthesis of 1-ethyl-3-methylimidazolium hydrogen terephthalate ([EMIM]Hbdc)

1-ethyl-3-methylimidazolium hydrogen terephthalate ([EMIM]Hbdc) was provided by Johannes Schwegler from the group of Dr. Peter Schulz (chair of chemical reaction engineering at the Friedrich-Alexander-Universität Erlangen Nürnberg).
3.5 Catalytic test reactions

3.5.1 Batch experiments

The catalytic experiments were carried out in crimp cap vials with a total volume of 20 mL equipped with an elastomer septum. 70 mg of the solid catalyst as well as a magnetic stirring bar were filled into the vial before sealing it. The vial was evacuated and flushed with argon three times to ensure the absence of oxygen and hence prevent the oxidation of the aldehyde to the corresponding carboxylic acid, since this would lower the maximum yield and possibly lead to poisoning of the amino groups and destruction of the carboxylate based MOFs. Subsequently, 10 mL of toluene and 4 mmol of the respective malonic acid derivative were added using single use disposable syringes of the appropriate size, for high volumetric accuracy and thin needles with a diameter of only 0.6 mm for minimum violation of the septum. The vial was then placed in a preheated oil bath and stirred for 10 min at the reaction temperature. The subsequent addition of 4 mmol of benzaldehyde was regarded as starting point for the reaction. Two different elastomers, PTFE-coated butyl rubber and silicone, respectively, were tested as septum material. It clearly turned out, that the resistance of the PTFE-coated butyl rubber against solvent vapor at elevated temperatures is much higher compared to the silicone. Therefore, the butyl rubber septa were used for all further experiments. Nevertheless, the resistance of this material against solvents, especially toluene, is also limited. This leads to restrictions in the number of samples that can be taken from one run and the reaction time that can be monitored, because each puncture of the septum, especially with solvent filled needles, and long exposure time lead to a constantly increasing permeability of the rubber. This finally causes a significant evaporation of the solvent and, as a result, a higher concentration of the reactants and products and the calculation of higher apparent yields. Thus, usually not more than five samples were withdrawn for each run and a total reaction time of 48 hours was not exceeded.

In order to quench the reaction directly after withdrawing the sample, to protect the gaschromatographic equipment used for analysis and to ensure an accurate and reproducible quantification of the products, a sophisticated workup procedure was
Experimental section

applied. The samples (0.2 mL each) were directly added to a prepared mixture of 60 µL of \(n\)-decane as standard, 2.5 mL of ethyl acetate and 2 mL of a saturated aqueous sodium bicarbonate solution. The exact amount of each component was determined by weighing on a calibrated analysis balance. The quantification standard, \(n\)-decane, was added to each sample separately instead of direct addition to the reaction mixture to prevent any influence of the catalytic reaction by adsorption of \(n\)-decane on the porous catalyst. The biphasic mixture containing the sample, was then vigorously shaken to ensure complete extraction of metal salts and organic acids, which might harm the analytic equipment, to the aqueous phase. After allowing the phases to separate, the upper organic phase, containing the highly diluted products and no solid catalyst, was withdrawn using a glass Pasteur pipette and injected into a second pipette filled with a cotton wool stopper and a packing of anhydrous magnesium sulfate with a height of 2 cm. After this filtration over magnesium sulfate to minimize the water content and to remove even the finest catalyst particles, around one mL of the organic phase was collected in a 1.5 mL GC sample vial that was sealed with an unused septum equipped screw cap and used for gaschromatographic analysis. The major drawback of this workup procedure is the not negligible solubility of the educts in water. Hence, a reliable determination of the educt concentrations in the mother reaction mixture and the consequent calculation of the conversion is not possible. Instead, only the yields of the products, which exhibit a very poor solubility in water, were detected.

Calibration:

The applied gaschromatographic method has been calibrated for quantitative analyses of the desired products benzylidenemalononitrile, ethyl \(\alpha\)-E-cyanocinnamate and diethyl benzylidenemalonate, respectively. Therefore, samples with defined amounts of the product and the GC standard \(n\)-decane were prepared and analyzed. Afterwards, the ratio of the known molar amounts \(n_{\text{product}} : n_{\text{n-decane}}\) was plotted against the ratio of the measured peak areas from the chromatograms \(A_{\text{product}} : A_{\text{n-decane}}\). The slope of the linear regression through the zero point was then used as a conversion factor.
3.5.2 Continuous-flow experiments

For the continuous experiments, Al-MIL-101-NH₂-ba was pelletized with a pressure of 640 kPa crushed and sieved. 125 mg of the fraction with a particle size between 0.4 and 1 mm were filled into a stainless steel tubular mini reactor with an inner diameter of 4 mm and a usable length of 60 mm. The voids in the reactor were filled with glass wool on both sides. The reactor was mounted vertically in a Jetstream II Plus column oven with a flow direction from bottom to top. The flow was adjusted using a Merck/Hitachi655A-11 liquid chromatograph pump. Samples were withdrawn at the outlet tubing at room temperature, treated and analyzed as described for the batch experiments.
4 Results and Discussion

4.1 Synthesis and characterization of different MOFs

4.1.1 Fe-MIL-101-NH$_2$

Materials with MIL-101 topology were chosen as promising catalysts for this study, due to their unique properties described in chapter 2.4.1. Mainly the very large pore volume and internal surface area, and the fairly high stability, combined with the large variety of functionalized terephthalic acid derivatives available on the market, make this class of materials an interesting choice for functional catalysts in liquid phase applications. Unfortunately the amino-functionalized derivative of the chromium-based variant Cr-MIL-101-NH$_2$ is not accessible by direct synthesis, using 2-aminoterephthalic acid as linker source. The complicated post-synthetic functionalization of Cr-MIL-101 by nitrulation of the aromatic ring and subsequent reduction of the nitro moiety to form the amine function, unfortunately is accompanied by a decrease of porosity. Moreover, the uniformity and equal distribution of the catalytically active sites cannot be guaranteed. For this reason the iron-based derivative Fe-MIL-101-NH$_2$ was chosen as an alternative.

An optimized synthesis procedure for Fe-MIL-101-NH$_2$ was published in 2008 by Bauer et al. [107] which was scaled up by a factor of four in this work. In contrast to the procedure described in the literature, it was found that longer contact with ambient air leads to an X-ray amorphous material with drastically reduced porosity. The workup procedure was therefore adapted to the air sensitivity of the material. Especially the activated material obtained by Soxhlet extraction with ethanol must be prevented from exposure to air. The comparison of the powder X-ray diffraction patterns measured at ambient conditions after different exposure times (Figure 4.1) and the one measured in transmittance mode in a sealed glass capillary (Figure 4.2), shows that the crystalline material decomposes into a X-ray amorphous phase within minutes if contacted with air. This decomposition of the sample also leads to drastic decrease of the porosity of the material as evident from the nitrogen adsorption
Results and Discussion

Isotherms shown in figure 4.3, revealing a significant reduction of the total pore volume.

The carefully handled material, which was stored under inert argon atmosphere until further use, exhibits a very high porosity as expected for a MIL-101 type MOF. The total pore volume amounts to 1.63 cm$^3$ g$^{-1}$ and the specific BET area is calculated to 3452 m$^2$ g$^{-1}$. The nitrogen adsorption isotherm clearly shows the characteristic three step shape in the relative pressure region up to $p/p_0 = 0.3$, typical for a MIL-101 type material. These three steps are due to the successive filling of the micropores and the two different types of mesoporous cages (see chapter 2.4.1). The analysis of the isotherm of Fe-MIL-101-NH$_2$ after partial decomposition shows that all these types of cavities are still present after exposure to air but the total pore volume is decreased by 43 % to 0.93 cm$^3$ g$^{-1}$ and the specific BET area declines by 46 % to 1851 m$^2$ g$^{-1}$. Hence, it is concluded that the material doesn’t decompose completely, but porous fragments of the network, which are too small for powder X-ray diffraction analysis, remain in the sample.

Figure 4.1: Powder X-ray diffraction patterns of Fe-MIL-101-NH$_2$ directly after sample preparation (bottom) and after 1 h of air contact (top) (same sample).
Results and Discussion

Figure 4.2: Powder X-ray diffraction pattern of Fe-MIL-101-NH$_2$ measured in a sealed glass capillary under inert atmosphere in transmittance mode compared to the simulated pattern from single crystal data of Cr-MIL-101 [29] (bottom).

Figure 4.3: Nitrogen adsorption isotherms of Fe-MIL-101-NH$_2$ handled under inert atmosphere (top) and the resulting X-ray amorphous decomposition products after 20 minutes (center) and 40 minutes (bottom) of exposure to humid air.
4.1.2 Fe-MIL-101

In order to study the influence of the amino groups on the catalytic activity of Fe-MIL-101-NH$_2$, a non-functionalized variant was synthesized based on terephthalate anions as organic linkers. The unfunctionalized derivative Fe-MIL-101 was synthesized and activated under the same conditions as the amine-containing analogue. The resulting dark yellow to light brown material possesses a comparable crystallinity as Fe-MIL-101-NH$_2$, as evident from the powder X-ray diffraction patterns shown in figure 4.4. The nitrogen adsorption isotherm shows the same characteristic three step shape (Figure 4.5) and the comparison of the total pore volumes (1.74 vs. 1.63 cm$^3$ g$^{-1}$, +6.9 %) and the specific BET areas (3791 vs. 3452 m$^2$ g$^{-1}$, +9.8 %) of Fe-MIL-101 and Fe-MIL-101-NH$_2$, respectively, shows that for this type of highly porous material, the incorporation of amino groups only slightly reduces the overall porosity. Thus, the dimensions and the accessibility of the pore system can be regarded as equal.

Figure 4.4: Comparison of X-ray diffraction patterns of Fe-MIL-101-NH$_2$ (top) and non-functionalized Fe-MIL-101 (bottom) measured in sealed glass capillaries under inert atmosphere in transmittance mode.
CAU-1 was chosen for testing as a catalyst in the base-catalyzed Knoevenagel condensation due to its comparably high chemical and thermal stability as compared to other amino-functionalized MOFs. In contrast to the original procedure [111] stainless steel autoclaves quipped with PTFE liners were used as reaction vessels instead of glass bottles for safety reasons because the methanol used as solvent develops a fairly high vapor pressure of around 7 bar at the reaction temperature of 125 °C. Handling such a high pressure in a glass bottle filled with a toxic and highly flammable liquid was considered unacceptable! Furthermore, the activation procedure using large amounts of water (three times two liters for 0.5 g of solid) was replaced by extraction with ethanol in a Soxhlet apparatus overnight.

The powder X-ray diffraction pattern of the activated material and the comparison to the pattern simulated from published crystal structure data (Figure 4.6), reveals that phase pure CAU-1 was successfully synthesized with very good crystallinity.
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Figure 4.6: Measured (top) and simulated (bottom) X-ray diffraction patterns of CAU-1.

The nitrogen adsorption isotherm shown in figure 4.7 is of type I according to the IUPAC classification, as expected for a highly crystalline microporous solid. With a specific BET area of 1485 m$^2$ g$^{-1}$, a total pore volume of 0.61 cm$^3$ g$^{-1}$ and a micropore volume of 0.50 cm$^3$ g$^{-1}$, the synthesized sample of CAU-1 exhibits a porosity which is fully in line with the data published by Ahnfeld et al. [111].

Figure 4.7: Nitrogen adsorption isotherm at 77 K of CAU-1.
4.1.4 UiO-66-NH₂

The synthesis conditions for UiO-66-NH₂ were adapted from the original conditions published by the group of K. P. Lillerud for the synthesis of unfunctionalized UiO-66 [30]. Due to the fast hydrolysis of ZrCl₄ at ambient conditions, it was quickly transferred into the reaction vessel which was immediately sealed air tight. The amounts of the other components were then calculated according to the exact amount of ZrCl₄ present in the reactor and rapidly added to the reaction vessel. The nitrogen adsorption isotherm is also of type I shape as expected for a MOF with UiO-66 topology, being a purely microporous crystalline material (Figure 4.8). Interestingly, the specific BET area of 1081 m² g⁻¹ by far exceeds the theoretical and experimental values of 700 and 830 m² g⁻¹, respectively derived for UiO-66-NH₂, synthesized under similar conditions by Katz et al. [121]. It is suggested that the thorough extraction of the material with ethanol in a Soxhlet apparatus causes leaching of linker molecules from the structure. A similar linker-deficient form of UiO-66-NH₂ is proposed to be formed when hydrochloric acid is added to the synthesis mixture [121]. This is considered to be beneficial for the application of UiO-66-NH₂ as a heterogeneous catalyst, since the pore system should be more easily accessible if a fraction of the linkers is missing. In addition, the thereby generated defects at the SBUs might provide additional and / or different catalytically active sites which can by beneficial for the activity but can also negatively influence the selectivity of the catalyst.
Results and Discussion

Figure 4.8: Nitrogen adsorption isotherm at 77 K of UiO-66-NH₂.

The comparison of the powder X-ray diffraction pattern of the synthesized UiO-66-NH₂ with the simulated pattern from crystal structure data for UiO-66 reported in the literature (Figure 4.9) reveals that this MOF was synthesized in good crystallinity and without phase impurities. The additional line at 2θ = 12.0° (# in Figure 4.9) is typical for solvated UiO-66-type MOFs and hence not present in the simulated pattern of the desolvated structure [119].

Figure 4.9: Measured (top) and simulated (bottom) X-ray diffraction patterns of UiO-66-NH₂. The lines indicated with asterisks are assigned to the aluminum sample holder.
4.1.5 Al-MIL-101-NH$_2$

Fe-MIL-101-NH$_2$ was found to be unstable at ambient conditions even for the time needed for typical handling as a solid catalyst on bench scale. While the chromium derivative is not directly accessible and post-synthetic functionalization leads to a material with insufficient porosity, the aluminum based derivative was considered a promising alternative. There are numerous examples reported in literature for aluminum(III) based MOFs showing high thermal and chemical stability including Al-MIL-53 [19] and CAU-1 [111].

The existence of Al-MIL-101-NH$_2$ was already suggested by the group of N. Stock [111]. In a high throughput investigation, it was shown that this material can be synthesized when $N,N$-dimethylformamide is used as solvent with a metal : linker ratio of 2:1 and with low starting concentrations (not specified) at a temperature of 125 °C within 5 hours. Detailed characterization of this material was not provided. Based on this report, the following conditions for the successful synthesis of Al-MIL-101-NH$_2$-ba were identified:

- In order to slow down the reaction and allow the formation of large crystallites, the temperature was reduced to 110 °C, similar to the synthesis of the iron-based derivative.
- As an adaption to the expected slower reaction the synthesis time was extended to 24 hours.
- The reactants were applied in concentrations of 0.05 mol L$^{-1}$ and 0.025 mol L$^{-1}$ for aluminum(III)chloride hexahydrate and 2-aminotherephthalic acid respectively. This matches half of the concentrations reported by Ahnfeld et al. for a synthesis that results in a mixture of MIL-101 and MIL-53 phases.
- The synthesis size was adjusted to 60 mL of solvent in order to yield enough material for thorough characterization.

The synthesis under these conditions results, after filtration, washing and Soxhlet extraction, in a bright yellow crystalline material with MIL-101 structure. The powder X-ray diffraction pattern matches the one simulated for Cr-MIL-101 as shown in figure 4.10 a. However, a closer look shows a shift of all reflections to higher angles (Figure 4.10 b). This corresponds to a shortening of the d-spacing by 1.4 to 2.3 % and is
explained by the smaller ionic radius of aluminum compared to chromium or iron (Table 4.1).

Figure 4.10: a) Comparison of powder X-ray diffraction patterns of Al-MIL-101-NH$_2$-ba measured in transmittance mode in a sealed capillary (top), and in a standard reflectance measurement of a flat sample (center) and the theoretical pattern simulated from crystal structure data of Cr-MIL-101. b): Detailed view of the shift of the powder XRD pattern of Al-MIL-101-NH$_2$ with respect to Cr-MIL-101.
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Table 4.1: Atomic and ionic radii metals used for the synthesis of MOFs with MIL-101 topology.\(^{(1)}\)

<table>
<thead>
<tr>
<th></th>
<th>atomic radius / Å</th>
<th>Ionic (M(^{3+})) radius / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum (Al)</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>chromium (Cr)</td>
<td>1.66</td>
<td>1.40</td>
</tr>
<tr>
<td>iron (Fe)</td>
<td>1.56</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The X-ray diffraction pattern of the sample measured in reflectance mode does not show any obvious phase impurities. Only if measured in transmittance mode, viz. in a sealed capillary, an additional broad reflection is visible around 12.3 °, indicating that an additional amorphous side product is formed under the static synthesis conditions used here.

The existence of an unwanted impurity is also suggested by the nitrogen sorption data. The isotherm shown in figure 4.12 shows the characteristic shape for a MIL-101-type material, but the resulting total pore volume of 1.11 cm\(^3\) g\(^{-1}\) and specific BET area of 2225 m\(^2\) g\(^{-1}\) are only 64 % and 68 %, respectively, of the values found for Fe-MIL-101-NH\(_2\) (\(V_{\text{pore}} = 1.63 \text{ cm}^3 \text{ g}^{-1}\), \(A_{\text{BET}} = 3452 \text{ m}^2 \text{ g}^{-1}\)). This lack of porosity cannot solely be explained by the reduction of the pore volume due to smaller aluminum ions. Similar results for a comparable Al-MIL-101-NH\(_2\) material with even lower porosity were published while this work was underway by Serra-Crespo et al. [99]. Unfortunately this synthesis was, at first, not easily reproducible. It was found that the batch synthesis does not work, when the aluminum salt is dissolved prior to, or during the heating step. Even short shaking of the reaction vessel results in lower porosity and crystallinity. Best results are obtained when the aluminum chloride hexahydrate is added to the 2-aminoterephthalic acid solution in \(N,N\)-dimethylformamide directly before transferring the reaction vessel to the preheated oven with minimum internal motion.

When this procedure is carefully followed and the synthesis is carried out in a transparent glass vessel, it was observed that in addition to the yellow powder in the bulk liquid, an almost white material is formed, predominantly at the internal glass

\(^{(1)}\) Values are taken from the Crystalmaker software documentation.
surface of the reaction vessel in the lower third of the volume occupied by the liquid phase.

Collection of only the bulk yellow solid without scratching material off the glass wall results in a material with MIL-101 structure (further denoted as Al-MIL-101-NH$_2$-bb) and an enhancement of the total pore volume by 15 % to 1.27 cm$^3$ g$^{-1}$ (calculated from the nitrogen adsorption isotherm shown in figure 4.12. Unfortunately attempts to isolate the byproduct from the glass wall did not yield enough material for structural or textural characterization. But the scanning electron microscope image (figure 4.11) clearly reveals that particles with at least two different morphologies are present in this fraction.

![SEM image of Al-MIL-101-NH$_2$ synthesized under solvothermal conditions.](image)

As a conclusion from the phenomena described above, the following hypothesis was developed: The concentration of dissolved aluminum in the synthesis mixture has an enormous influence on the sensitive formation process of the MIL-101 phase. Different local concentrations due to slow dissolution and diffusion of AlCl$_3$ during the temperature adjustment period lead to different products. Since it can be assumed that concentration of free dissolved aluminum is highest in the lower region of the reaction mixture where the unwanted byproduct is preferably formed, a strategy for a
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material synthesis with low local and/or temporal concentration but acceptable space yield has to be developed.

To prevent the formation of aluminum-containing byproducts which are favored by high aluminum concentrations in the solution, a continuous addition of the aluminum source would be an appropriate procedure. But the continuous addition of a hygroscopic crystalline solid to a solution at a temperature of 110 °C is quite difficult and hard to realize with standard laboratory equipment.

Another option is the addition of the aluminum salt as a solution in the solvent used for the synthesis. This technique provides a very controllable way for continuous addition of one reaction partner. However, the major drawback of this strategy is the ongoing dilution of the reaction system with respect to the linker concentration.

As a compromise, a semi-batch procedure based on stepwise addition of the aluminum salt in seven small portions to the preheated and vigorously stirred solution of 2-aminoterephthalic acid in N,N-dimethylformamide at 110 °C in an open round bottom flask was established. Formation of particles can be observed approximately 10 min after the first addition, so the time delay between two additions was set to 15 min to prevent accumulation of free unreacted aluminum chloride. After the last addition of the aluminum source, the flask was capped to prevent evaporation of the solvent and kept at 110 °C for three hours with stirring and for additional 16 hours without stirring to allow the growth of larger particles by a longer crystallization time and the formation of agglomerates to facilitate product separation. This synthesis strategy results in a very fine, yellow powder which is identified as highly crystalline Al-MIL-101-NH₂-s as evident from the powder X-ray diffraction pattern shown in figure 4.15. The comparison of the nitrogen adsorption isotherm to the ones of the materials synthesized in a classical batch synthesis (Figure 4.12) shows again the characteristic three step shape. In addition, the uptake is significantly increased, especially in the mesopore region at relative pressures between p/p₀ = 0.05 and 0.3. This implies that the byproduct of the batch syntheses might not only be formed as separate particles, it could also be present in the mesoporous cavities of the MIL-101 structure. The specific BET area of Al-MIL-101-NH₂-s is calculated to 3095 m² g⁻¹, while a total pore volume of 1.48 cm³ g⁻¹ is determined. That represents a gain of 39 % and 33 %, respectively, compared to the values obtained for Al-MIL-101-NH₂-ba.
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Figure 4.12: Nitrogen adsorption isotherms at 77 K of Al-MIL-101-NH₂ samples synthesized under solvothermal conditions with recovery of the complete solid (Al-MIL-101-NH₂-ba, bottom) and only the bulk powder (Al-MIL-101-NH₂-bb, center) and synthesized via the semi-batch approach developed in this work (Al-MIL-101-NH₂-s, top).

For this material the composition found by elemental analysis (C: 40.60 wt.-%; H: 2.78 wt.-%; N: 5.55 wt.-%) perfectly matches the composition which was calculated for an ideal Al-MIL-101-NH₂ (Al₃OCl(H₂O)₂(bdc-NH₂)₃) (C: 40.84 wt.-%; H: 2.71 wt.-%; N: 5.95 wt.-%). It can, hence, be excluded, that significant amounts of organic or inorganic impurities are present in the sample.

A closer look to the mesopore region of the nitrogen ad- and desorption isotherms plotted on logarithmic scale (Figure 4.13) reveals that the adsorption and desorption isotherms exhibit the characteristic MIL-101 shape and are fully reversible so that no hysteresis is seen in the region where nitrogen is supposed to condense in the mesoporous cavities. Thus, those cavities are filled with and emptied from the nitrogen molecules without any effect of hindering phenomena like pore blocking in bottle-neck windows or cavitation [140].
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Figure 4.13: Logarithmic plot of the mesopore region of nitrogen adsorption and desorption isotherms of Al-MIL-101-NH$_2$-s.

The morphological uniformity of Al-MIL-101-NH$_2$-s is demonstrated in the scanning electron microscopic (SEM) image shown in figure 4.14. It is found that the rod-like particles, which are present after the batch synthesis (Figure 4.11), are absent in this sample. Only the lump shaped particles are present, even though their surfaces seem to possess more sharp edges instead of the smooth roundings seen in figure 4.11. This is most probably due to the fact that the synthesis mixture is vigorously stirred in the period where the initial particles are formed.
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Figure 4.14: SEM image of Al-MIL-101-NH₂-s synthesized by the semi-batch approach.

In order to further optimize the synthesis protocol, the influence of a shorter reaction time on the quality of the resulting Al-MIL-101-NH₂-s material has been studied.

As evident from the powder X-ray diffraction patterns shown in figure 4.15 and the nitrogen adsorption isotherms in figure 4.16, a reduction of the crystallization time to 30 minutes with stirring and another 5 hours without after the last addition of the aluminum salt does not result in a reduction of the porosity of the resulting Al-MIL-101-NH₂-s material. However, the crystallinity of the material is significantly lower compared to the above discussed material which is allowed to crystallize for 3 hours with and additional 16 hours without stirring. Further reduction of the crystallization time to only 30 minutes (with stirring) leads to a predominantly X-ray amorphous substance. Interestingly, this material already shows a significant porosity and the nitrogen adsorption isotherm shows the characteristic three-step shape, expected for a MIL-101-type structure. This potentially indicates that larger subunits of the MIL-101 motif including the mesoporous cavities of both dimensions are already formed, but do not possess the far distance order which is required for narrow X-ray diffraction lines of a material with such a large unit cell. It is hence concluded that the formation of the MIL-101 structure is not completed in the precipitate that is formed initially and additional synthesis time for further crystal growth or even recrystallization is needed.
Figure 4.15: Powder X-ray diffraction patterns of samples isolated from Al-MIL-101-NH₂-s syntheses after different crystallization times.

Figure 4.16: Nitrogen adsorption isotherms of samples isolated from Al-MIL-101-NH₂-s syntheses after different crystallization times.
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Detailed characterization of Al-MIL-101-NH₂

As outlined in chapter 4.1.1, the main driving force for the optimization of the synthesis of Al-MIL-101-NH₂ was the expectation that this material could combine the ultrahigh porosity with uniformly distributed and accessible amino moieties known from the iron derivative with the high chemical stability of well investigated aluminum(III) based MOFs like MIL-53 and CAU-1. The stability of the new MOF at ambient conditions is clearly demonstrated by comparison of the nitrogen adsorption isotherms in of the same sample, measured after different times (up to four days) of exposure to air while keeping it openly on the bench (Figure 4.17).

![Figure 4.17: Nitrogen adsorption isotherms of a Al-MIL-101-NH₂-s sample directly after synthesis and after up to four days of storage at ambient conditions.](image)

In addition, the crystal structure of the sample after storage at ambient conditions for four days is maintained as evident from the powder X-ray diffraction patterns shown in figure 4.18. Thus, it can be assured that the material at least does not decompose during the handling time and that it can be used as a catalyst in its here reported form. It must though be mentioned, that the moisture stability of this MOF is limited. Contact with liquid water for example leads to a rapid and complete decomposition.
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Figure 4.18: Powder X-ray diffraction patterns of a Al-MIL-101-NH$_2$-s sample directly after synthesis (top) and after 4 days of storage at ambient conditions (bottom).

An interesting effect is observed when Al-MIL-101-NH$_2$ is exposed to the Cu K$_\alpha$ radiation used for powder X-ray diffraction measurements. Since a collection of the diffraction pattern is of course impossible without exposure to X-rays, an investigation of the influence of the exposure to the radiation on the crystal structure of the material was not possible in this work. However, a comparison of the nitrogen adsorption isotherms demonstrates that the porosity of the material is drastically reduced during this treatment (Figure 4.19). The total pore volume and the specific BET area decrease by 31 % from 1.48 to 1.01 cm$^3$ g$^{-1}$ and from 3095 to 2123 m$^2$ g$^{-1}$, respectively. The change of porosity is not only detectable by instrumental characterization techniques, it is even directly visible for the eye! Figure 4.20 shows the appearance of three different samples after powder X-ray diffraction measurement. The samples represent the products of differently successful attempts to synthesize Al-MIL-101-NH$_2$. One being an almost amorphous material with very low porosity, the second being the complete solid isolated from a batch synthesis (Al-MIL-101-NH$_2$-ba) and finally a highly porous sample derived by the novel procedure reported above (Al-MIL-101-NH$_2$-s). All samples were prepared in the same way and at the same time applying gentle mechanical pressure. It is clearly seen that, the higher the initial porosity or the fraction of pure Al-MIL-101-NH$_2$ of the sample is, the more significant is the shrinking of the sample due to exposure to the
radiation. Since this textural conversion is not reversible by heating the material in vacuum, as evident from the nitrogen adsorption isotherm, it is considered to be due to irreversible irradiation induced partial decomposition rather than adsorption of water from air. It must therefore be assured that samples which have been used for crystallographic characterization shall not be used for further analyses or any other application.

Figure 4.19: Nitrogen adsorption isotherms of Al-MIL-101-NH₂-s before (top) and after (bottom) exposure to Cu Kα radiation during the powder X-ray diffraction measurement.

Figure 4.20: Change in bulk volume during powder X-ray diffraction analysis of an almost amorphous material (left) and Al-MIL-101-NH₂ samples of different qualities (batch synthesis (center) and semi-batch synthesis (right)).
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The chemical nature of the amines and other functional groups were investigated by FT-IR spectroscopy. FT-IR spectroscopy is an excellent tool to investigate the nature of functional groups i.e. amines, incorporated in a 3D porous framework. The infrared spectra of Al-MIL-101-NH$_2$ and Fe-MIL-101-NH$_2$ (Figure 4.21) show absorption bands at 3485 and 3375 cm$^{-1}$ which are assigned to the asymmetric and symmetric -NH$_2$ stretching vibrations of free unassociated amino moieties [120]. While the characteristic band at 1626 cm$^{-1}$, representing the -NH$_2$ scissoring vibration is not visible due to interference with other vibration bands, a typical C-N stretching band for aromatic amines is observed at 1356 cm$^{-1}$ in the spectra of both materials.

The shoulder / band appearing in the spectra of both materials at 1698 cm$^{-1}$, shows the presence of free carboxylic acid groups. This does not necessarily indicate free 2-aminoterephthalic acid molecules inside the pores, it can also be due to terminating carboxylic acid moieties from non-bridging linkers at the outer surface of the small crystallites.

![FT-IR spectra of Al-MIL-101-NH$_2$ (top) and Fe-MIL-101-NH$_2$ (bottom) measured in the attenuated total reflectance (ATR) mode.](image)

It turned out that the ATR technique is, due to the wavelength dependency of the penetration depth, not a proper technique to record infrared spectra in the high wavenumber range where the -NH$_2$ stretching vibrations are observed. Therefore, detailed investigations concerning the nature of the amino groups present in Al-MIL-101-NH$_2$ at different conditions have been performed in a DRIFTS cell equipped with
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a heatable reaction chamber that allows the adjustment of the temperature and measurements under controlled gas atmospheres. With this setup it is possible to either treat the sample with a probe gas by allowing it to flow though the sample packing or to purge the gas filled volume above the sample with inert gas. Figure 4.22 shows the infrared spectra in the high wavenumber region of Al-MIL-101-NH$_2$-s at ambient conditions and during heating under inert nitrogen atmosphere. At ambient conditions, not only the absorption bands of the asymmetric and symmetric -NH$_2$ stretching vibrations can be observed at 3485 and 3375 cm$^{-1}$, respectively, but another band is present at 3688 cm$^{-1}$. This band can be assigned to the stretching vibration of -OH groups which are attached to the coordinatively unsaturated metal centers of the MIL-101 structure. Similar –OH groups have been shown to be present in the hydrated form of unfunctionalized Cr-MIL-101 [99]. Upon heating, not only physisorbed water is desorbed from the porous framework, which causes a reduction in the intensity of the broad band observed between 2500 and 4000 cm$^{-1}$, but also the -OH signal at 3688 cm$^{-1}$ is gradually eliminated, which means that chemisorbed water is desorbed at elevated temperatures. Moreover, that the -NH$_2$ bands are redshifted with respect to the dehydrated form which is typical for amino groups that are associated to water or other polar moieties. Furthermore, another signal evolves as a shoulder next to the symmetric stretching band at 3400 cm$^{-1}$ accompanied by ongoing elimination of the O-H band. Thus it is assumed that the hydroxyl and the amino groups are in direct interaction with each other, most probably by means of weak hydrogen bonds, which might have an interesting influence on the catalytic properties of this highly functional MOF in condensation reactions (cf. chapter 2.2.1).
Figure 4.22: In-situ DRIFT spectra of Al-MIL-101-NH$_2$ during two cycles of heating under argon atmosphere.

Finally, the overlay of spectra measured under the same conditions in different heating cycles (Figure 4.23) reveal, that both, the dehydration and the rehydration is fully reversible with respect to the nature of the polar and protic functional groups discussed above.
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![Graph](image)

**Figure 4.23:** Overlay of the DRIFT spectra of Al-MIL-101-NH₂ in the hydrated and partially dehydrated form in different heating cycles.

Furthermore, DRIFT spectroscopy was utilized to monitor the interaction of the sample with carbon dioxide (CO₂). CO₂ is a Lewis-acid and is therefore frequently used as a probe molecule for the investigation of basic surfaces. It can hence be expected, that the interaction with CO₂ will influence the observed bands of the amino groups in the infrared spectra. The desorption of CO₂ is followed by the reduction of the absorption band around 2350 cm⁻¹ which is assigned to the asymmetric stretching vibration of the linear CO₂ molecules in the gas phase as well as in a physisorbed on the surface [141]. The additional bands at around 3615 cm⁻¹ and 3715 cm⁻¹ represent combinations of stretching and bending vibrations of gaseous CO₂ and are not regarded for this evaluation.

Surprisingly, although fairly high temperatures of more than 100 °C are required for the complete desorption of carbon dioxide, as evident from the spectra in figure 4.24, the presence of CO₂, even as pure gas phase at ambient pressure, does not affect the nature of the amino groups at all, as evident from the spectra overlay shown in figure 4.25 and no signals witnessing the formation of carbamate species by chemisorption are detected. Thus the strong interaction of the probe molecules with the surface, at least at low pressures, takes place exclusively at the open metal sites in agreement with reports in the literature [142].
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Figure 4.24: In-situ DRIFT spectra of Al-MIL-101-NH₂ during loading with and temperature programmed desorption of CO₂. Asterisks indicate absorption bands of gaseous CO₂.

Figure 4.25: Comparison of the CO₂-loading of Al-MIL-101-NH₂ during the temperature programmed desorption.
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The purity of the prepared Al-MIL-101-NH$_2$ sample was further confirmed by $^{13}$C and $^{27}$Al solid state nuclear magnetic resonance (NMR) spectroscopy. The $^{13}$C NMR spectrum of the sample is shown in figure 4.26. The sharp peak 175 ppm is assigned to the carboxylate carbon atoms of 2-aminoterephthalate and the one at 153 ppm to the amine-functionalized aromatic carbon atom. The peaks of the remaining aromatic carbon atoms interfere and form the multiple between 110 and 140 ppm. Additional peaks of carbon atoms from the solvents used for synthesis and activation as well as signals from free 2-aminoterephthalic acid molecules are clearly absent in this spectrum.

![Figure 4.26: Solid state $^{13}$C-CP-NMR spectrum of Al-MIL-101-NH$_2$.](image)

The $^{27}$Al NMR spectrum of Al-MIL-101-NH$_2$-s (Figure 4.27) shows only one resonance at a chemical shift of -1 ppm. This is typical for aluminum cations with a very symmetric octahedral coordination sphere as it is present in the case of the trinuclear secondary building unit of MIL-101. Aluminum hydroxides, which would be expected as inorganic impurities, exhibit peaks at slightly higher chemical shift of around 5 ppm as reported in the literature [143]. Surprisingly, the $^{27}$Al NMR spectrum of an Al-MIL-101-NH$_2$-ba sample with reduced porosity, does not show any hint for inorganic impurities as well.

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2 Assignment adapted from database spectrum for dimethyl 2-aminoterephthalate in the “Spectral Database for Organic Compounds” (SDBS).
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![Graph showing solid state $^{27}$Al NMR spectra of Al-MIL-101-NH$_2$-ba (top) and Al-MIL-101-NH$_2$-s (bottom).](image)

Figure 4.27: Solid state $^{27}$Al NMR spectra of Al-MIL-101-NH$_2$-ba (top) and Al-MIL-101-NH$_2$-s (bottom).

4.1.6 DUT-5-NH$_2$ (Al-bp-MIL-53-NH$_2$)

In order to find a route to an isoreticular variant of Al-MIL-101-NH$_2$ with an extended linker, 2-amino-1,1'-biphenyl-4,4'-dicarboxylate (bpdc-NH$_2$) was chosen as organic linker. The double functionalized 2,2'-diamino-1,1'-biphenyl-4,4'-dicarboxylate (bpdc(-NH$_2$)$_2$) was not considered due to the expected chelating effect for metal ions that would lead to less controllable synthesis conditions and, for the case of a successful MOF synthesis, to a reduced accessible pore volume. In addition, the catalytic performance of this material would not be comparable to aminoterephthalate MOFs since two amino groups in direct proximity may result in a different reaction pathway.

Since the linker precursor H$_2$bpdc-NH$_2$ is not commercially available, it was synthesized following the three step route described in scheme 4.1, starting from dimethyl-1,1'-biphenyl-4,4'-dicarboxylate (Me$_2$bpdc) via single nitration, subsequent reduction of the nitro groups and finally hydrolysis of the esters under alkaline conditions.
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Scheme 4.1: Three-step synthesis of H$_2$bpdc-NH$_2$, the linker used in the synthesis of DUT-5-NH$_2$.

This linker was first applied under the optimized synthesis conditions for Al-MIL-101-NH$_2$-s as described above with aluminum(III)chloride hexahydrate as metal source in $N,N$-dimethylformamide in very low concentrations. The isolated product was identified not as a MIL-101 type material but as a MOF with the DUT-5 structure with low crystallinity as evident from the powder X-ray diffraction pattern in figure 4.28. Adaption of the synthesis conditions reported for the unfunctionalized DUT-5 [132] with aluminum(III)nitrate nonahydrate as metal source yielded highly crystalline DUT-5-NH$_2$ as evident from the powder X-ray diffraction pattern in figure 4.28.
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Figure 4.28: Powder X-ray diffraction patterns of DUT-5-NH$_2$, prepared using aluminum chloride (top) and aluminum nitrate (center) as metal source and the pattern simulated from literature structural data for unfunctionalized DUT-5.

The nitrogen adsorption isotherm shown in figure 4.29 is of type I according to the IUPAC classification, as expected for this purely microporous MOF with uniform pore size distribution. The total pore volume amounts to 0.73 cm$^3$ g$^{-1}$ and a specific BET area of 1674 m$^2$ g$^{-1}$ was determined. This is in total agreement to the properties of a similar material published by Halis et al. while this work was in preparation [133].

Figure 4.29: Nitrogen adsorption isotherm of DUT-5-NH$_2$ at 77 K.
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4.1.7 is-MIL-53 (imidazolium salt)

As described in the examples above, usually the free carboxylic acids, such as terephthalic acid, are used as linker sources in state of the art MOF syntheses. Thus typically, very high temperatures are needed in hydrothermal syntheses especially of MOFs with non-functional linkers forming Al-MIL-53 [19] or Cr-MIL-101 [29] in order to increase their solubility. In this study, an organic imidazolium salt of terephthalic acid was utilized as precursor for the linker. The salt 1-ethyl-3-methylimidazolium hydrogen terephthalate [EMIM][Hbdc] was chosen for the synthesis of is-MIL-53 with the aim of enhancing the solubility and the availability of deprotonated terephthalate anions and thereby reducing the synthesis temperature and time, respectively. [EMIM][Hbdc] was provided by Ines Mertens and Johannes Schwegler from the group of Peter Schulz (chair of chemical reaction engineering at the Friedrich-Alexander-Universität Erlangen-Nürnberg). The synthesis procedure and detailed characterization of this organic salt can be found elsewhere [41].

The comparison of the textural properties of Al-MIL-53 and is-MIL-53 (Table 4.2), calculated from the nitrogen adsorption isotherms shown in figure 4.30, reveal that although the total pore volumes of the samples determined at a relative pressure of \( p/p_0 = 0.6 \) are almost identical, the micropore volume, calculated by the t-plot method, of is-MIL-53 is about 30 % lower than the micropore volume of hydrothermally synthesized Al-MIL-53. This discrepancy is not fully confirmed by the comparison of the apparent specific BET areas, which is less than 20 % lower for is-Al-MIL-53. While the isotherm of MIL-53 reaches the saturation plateau at a very low relative pressure, typical for a purely microporous solid with uniform pore geometry, the isotherm of is-MIL-53 has a constantly increasing shape with a significant rise at relative pressures above 0.7. This rise at higher pressures can be assigned to early vapor condensation, initiated by either interparticle porosity or the presence of an additional meso- or macroporous compound.
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Figure 4.30: Nitrogen adsorption isotherms at 77 K of hydrothermally synthesized Al-MIL-53 after calcination and the as-synthesized [EMIM]Hbdc derived is-MIL-53.

Table 4.2: Specific BET areas and pore volumes of Al-MIL-53 and is-MIL-53.

<table>
<thead>
<tr>
<th></th>
<th>$S_{BET}$ / m² g⁻¹</th>
<th>$V_{p, \text{total}}$ / cm³ g⁻¹</th>
<th>$V_{p, \text{micro}}$ / cm³ g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-MIL-53</td>
<td>1510</td>
<td>0.57</td>
<td>0.53</td>
</tr>
<tr>
<td>is-MIL-53</td>
<td>1228</td>
<td>0.56</td>
<td>0.37</td>
</tr>
</tbody>
</table>

a) calculated at $p/p_0 = 0.6$, b) derived by the t-plot method.

Both effects are conceivable, when the morphology of the is-MIL-53 particles, as shown is the SEM image in figure 4.31, is considered. While the Al-MIL-53 particles possess a totally plain surface and sharp edges, the surface of the is-MIL-53 crystallites is of a rough and irregular morphology which is, as a closer look reveals, due to the agglomeration of very small crystallites (Figure 4.31, right). This might lead to the formation of a mesoporous superstructure and surely forms randomly sized interparticular (macro-) pores.
Figure 4.31: SEM-images of hydrothermally synthesized Al-MIL-53 after calcination and as synthesized is-MIL-53.

Interestingly, the powder X-ray diffraction pattern of is-MIL-53 (Figure 4.32) shows, that the material is obtained in pure ht-phase directly from the synthesis without further activation at high temperature. This demonstrates a certain structure directing effect of the imidazolium cation since the conventional hydrothermal synthesis first of all results in the as-form of Al-MIL-53, which contains a defined amount of 0.7 equivalents of unreacted terephthalic acid. This material is subsequently activated at 330 °C by thermal removal of the excess linker molecules and is then, after exposure to ambient air, present in the water loaded It-form.
In contrast to the hydrothermally synthesized Al-MIL-53, which is known for its breathing effect, viz. the temperature or adsorptive induced phase transition between the narrow pore Lt-form (low temperature or adsorptive (H₂O) loaded) and the large pore ht-form (high temperature or adsorptive free), is-MIL-53 was only observed in the ht-form as evident from the powder X-ray diffraction pattern (Figure 4.32) and the solid state $^{27}$Al-NMR spectra (Figure 4.33), even after washing of the material with deionized water. That suggests, that the ht-form is stabilized either chemically, by reduced hydrophilicity, or by mechanical stabilization of the small crystallites due to
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incorporation into a matrix of extra-framework alumina, preventing the phase transformation.

The latter suggestion is supported by the $^{27}$Al-NMR spectrum of is-Al-MIL-53 (Figure 4.33), which shows the characteristic signal of Al-MIL-53(ht) with a quadrupolar coupling constant $C_Q = 8.55$ MHz and an asymmetry factor $\eta_Q = 0.0$ while the presence of the lt-phase ($C_Q = 10.70$ MHz, $\eta_Q = 0.12$) cannot be detected. In addition, a second signal at 9.2 ppm shows the presence of another octahedrally coordinated aluminum species and a small fraction of tetrahedrally coordinated aluminum, indicated by the weak signal at 67 ppm. The obvious suspicion that the additional signal is due to residual Al(NO$_3$)$_3$ can be disproved since the intensity of this peak is not effected by washing the sample with deionized water. The comparison of the SEM images of Al-MIL-53 and is-MIL-53 demonstrates that the particles of the latter material possess a much rougher outer surface, indicating a shell of differently structured material around the MIL-53 crystallites. A similar phenomenon was found by Bezverkhyy et al. for Al-MIL-53 after post-synthetic hydrothermal treatment. In their study, the shell material was identified as $\gamma$-AlO(OH) which is formed at the surface after partial hydrolysis of the MOF [144].

![Figure 4.33: Solid state $^{27}$Al-MAS NMR spectra of MIL-53(lt) and MIL-53(ht) and [EMIM][Hbdc] derived is-MIL-53 after several days at ambient conditions (is-MIL-53) and after washing with deionized water (is-MIL-53 washed). Asterisks indicate spinning sidebands.](image-url)
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Both samples, hydrothermally synthesized Al-MIL-53 and is-MIL-53, have been tested as potential candidates for the adsorptive storage of hydrogen at cryogenic temperatures of -196 °C (Figure 4.34). The hydrogen sorption isotherm of Al-MIL-53 shows a large step in the adsorption branch at approx. 10 bar, and a significant hysteresis. This can be explained by the sorbent induced transformation between the lt- and the ht-phase, often referred to as breathing effect. After activation in vacuum at 170 °C, Al-MIL-53 is present in the ht-form, as demonstrated by MAS-NMR-spectroscopy. By cooling to temperatures below -100 °C, it converts to the lt-form, even in absence of inducing adsorbates [125]. Upon adsorption of hydrogen, the material is reconverted into the ht-form, but this process is very slow since the diffusion of the adsorbate is highly restricted at low temperatures when the material is in the narrow-pore lt-state.

In contrast to this unusual behavior, is-MIL-53 shows a steadily rising hydrogen uptake, as expected for a rigid microporous solid. This is in full agreement with the results of MAS-NMR-spectroscopy and powder X-ray diffraction, respectively, showing that is-Al-MIL-53 is stabilized in the ht-form. Thus, this stabilization can not only be due to enhanced hydrophobicity, as claimed by Liu et al. for a similar material synthesized by an ionothermal approach [48]. This could only explain the absence of a phase transformation in the presence of a suitable adsorbate. The results of the hydrogen sorption experiments reported here also prove the suppression of the purely temperature induced breathing effect, typical for MIL-53 type materials.

Figure 4.34: Hydrogen sorption isotherms of hydrothermally-synthesized Al-MIL-53 after calcination and as-synthesized [EMIM][Hbdc] derived is-MIL-53.
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4.2 Catalytic Performance of the MOFs synthesized in this work in the Knoevenagel condensation

4.2.1 General considerations

The Knoevenagel condensation of benzaldehyde with malonic acid derivatives such as malononitrile, ethyl cyanoacetate and diethyl malonate (Scheme 4.2) is known to be catalyzed by basic organic groups such as amines and is therefore a frequently utilized test reaction for heterogeneous catalysts, possessing Brønsted-basic sites such as the here discussed amino-functionalized MOFs.

![Scheme 4.2: Proposed mechanism of the solely amine-catalyzed Knoevenagel condensation of benzaldehyde with a C-H acidic malonic acid derivative.](image)

4.2.1.1 Choice of the solvent

For initial testing, the conditions for the Knoevenagel condensation were adapted from Gascon et al. [10] (7 mmol ethyl cyanoacetate and 8 mmol benzaldehyde in 5 mL N,N-dimethylformamide; 0.2 mmol NH₂-cat. at 40 °C under static nitrogen atmosphere). N,N-dimethylformamide was identified to be the best solvent for this reaction by Gascon et al. In a preliminary blank experiment, a significant yield of ethyl α-E-cyanoacinnamate of 59 % without catalyst was detected after 24 hours (78 % at 80 °C). This is either due to catalytic activity of the solvent itself or of strongly basic decomposition products like dimethylamine. Very surprisingly it was found, that the addition of Al-MIL-101-NH₂ as a catalyst, results in a lower yield of only 33 % after 24 hours. This could be caused by partial adsorption and thereby deactivation (or
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masking) of the catalytically active molecular species at the MOF. Hence, it was
decided that N,N-dimethylformamide is not an appropriate solvent for the evaluation
of the catalytic activities of the materials under study.

Another solvent used in the work of Gascon et al. is ethanol [10]. In this solvent a
lower but still significant yield of ethyl α-E-cyanocinnamate of 18 % is observed in the
absence of a catalyst after 24 hours in the reaction of ethyl cyanoacetate with
benzaldehyde. In addition, a second product is evident from the chromatogram of the
reaction mixture, which was identified as benzaldehyde diethyl acetal (diethoxymethyl
benzene) by NMR spectroscopy. The yield of this side product is estimated to roughly
8 % (not calibrated) in the blank run. When Fe-MIL-101-NH₂, Al-MIL-101-NH₂ or
CAU-1 are used as catalysts, benzaldehyde diethyl acetal is formed as the main
product with ethyl α-E-cyanocinnamate : benzaldehyde diethyl acetal ratios of 0.83,
0.05 and 0.01, respectively. The highly favored formation of the acetal over the
desired product in the case of both aluminum based MOFs and the almost even ratio
when the iron based derivative is applied gives rise to the assumption, that the acetal
formation is mainly catalyzed by Lewis acidic metal sites. In the case of CAU-1, it can
even be speculated that the presence of methoxy ligands in the framework might
facilitate the acetal formation and lead to an exchange with ethoxy groups from the
solvent. Although this is a very interesting reaction system, it must be concluded that
ethanol is not qualified as a solvent for the investigation and comparison of the
activities of different catalysts in the Knoevenagel condensation.

As a nonpolar and aprotic solvent, toluene can be assumed to be inert towards the
materials used in this study, even the moisture sensitive ones. It was found, that
toluene shows only negligible conversions of benzaldehyde in the absence of a
catalyst, but quite fast conversion in the presence of Fe-MIL-101-NH₂. Furthermore,
no undesired products were detected either by gaschromatography or by liquid-state
NMR spectroscopy. And the comparably high boiling point of toluene (T_b = 111 °C)
allows a sufficiently high reaction temperature to even detect low catalytic activities.

4.2.1.2 Concentration of the reactants

For better comparability to results previously obtained in the group, the starting
concentrations have been adapted from the studies of S. Sauerbeck [95], being
4 mmol of each reactant in 10 mL of solvent. Due to the low yields of some of the MOF syntheses and losses of material for different characterization techniques, the catalyst mass used in the catalytic test runs was reduced from 200 to 70 mg.

4.2.1.3 Influence of the reaction temperature

A standard reaction temperature of $T_R = 80 \, ^\circ C$ was chosen for several reasons:

- $T_R$ is high enough for relatively fast conversion even with less active catalysts.
- $T_R$ is low enough to ensure the stability of all educts and products for the time under investigation.
- $T_R$ is far enough below the boiling point of toluene ($T_b = 111 \, ^\circ C$) and water ($T_b = 100 \, ^\circ C$) (formed as byproduct in the Knoevenagel condensation) and the used reactants benzaldehyde ($T_b = 179 \, ^\circ C$), ethyl cyanoacetate ($T_b = 209 \, ^\circ C$) and malononitrile ($T_b = 220 \, ^\circ C$) to prevent pressurization of the reaction vial and large influence on the composition of the liquid phase.
- The accuracy and stability of the temperature adjusted in the oil bath improves at higher temperatures and has less influence on the comparability of the results.

4.2.1.4 Quantitative value for activity comparison

The most frequently used quantity for the comparison of catalytic activities is the turnover frequency (TOF), which is defined as molar amount of converted educt molecules per time and molar amount of catalytically active centers.

$$TOF = \frac{n_0(A) - n(A)}{n(cat,act) \cdot t}$$

The problem with the application of this quantity for the comparison of the catalysts described in the following sections is, that the different catalysts contain different types of active sites. Some catalysts contain different types of active species, which are present in unknown states, numbers and accessibilities. It will furthermore be shown that the reaction might follow a different mechanism over different catalysts. Therefore, the turnover frequency seems not to be an appropriate quantity in this
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context. Hence the more general, mass related catalyst activity $\alpha$ will be used, which is defined as the molar amount of product produced per catalyst mass and time.

$$\alpha = \frac{n(product)}{m(cat) \cdot t}, \text{with } [\alpha] = mol \cdot g^{-1} \cdot s^{-1}$$

The catalytic activity can also be related to the specific BET area of the catalysts.

$$\alpha_A = \frac{\alpha}{A_{BET}}, \text{with } [\alpha_A] = mol \cdot m^{-2} \cdot s^{-1}$$

For the calculation of the activities only the points at relatively low yields, where the progress of the reaction can be assumed to be linear, were used.

4.2.2 Knoevenagel condensation of benzaldehyde and malononitrile

Malononitrile is the smallest and most acidic representative of the malonic acid derivatives used in this study. It can therefore easily be activated by basic amines and was hence used as a reactant in the Knoevenagel condensation of benzaldehyde to prove the general catalytic activity of amino-functionalized MOFs under the chosen conditions and to perform an termination experiment, since even small quantities of leached active components should lead to a detectable yield in this very fast reaction.

In order to disprove the leaching of active components, the very fast Knoevenagel condensation of benzaldehyde and malononitrile catalyzed by Al-MIL-101-NH$_2$ was investigated in a controlled termination experiment. Therefore, large agglomerates of the powder catalyst were used to facilitate quick separation of the solid from the liquid phase. To prevent destruction of the agglomerates, external shaking was applied instead of mixing with an internal stirring bar.

As shown in figure 4.35, the initial activities of this catalyst are almost identical when used as fine powder with vigorous stirring or as large agglomerates with only gentle shaking, respectively. Hence, it can be concluded that, even for this very fast reaction, there is no significant influence of external film diffusion of reactants or product molecules. Film diffusion would significantly lower the observed reaction rate in the case of slow shaking instead of vigorous internal stirring. An influence of internal pore diffusion cannot be excluded by the results of this experiment since the
large particles used are macroporous agglomerates, while the crystallite size and, hence, the diffusion paths in the micro- and mesopores can be assumed the same in both experiments.

After removal of the solid catalyst, no further formation of the product benzylidenemalononitrile was observed. This proves that the reaction is truly catalyzed by functional groups incorporated in the framework of the solid coordination polymer and not by soluble active components which leached into the liquid phase and work as homogeneous catalysts after removal of the solid.

In addition, the yield of benzylidenemalononitrile in a blank experiment without catalyst is shown in figure 4.35, confirming that only negligible non-catalytic conversion occurs under the chosen reaction conditions.

![Figure 4.35: Yields of benzylidenemalononitrile in the condensation of benzaldehyde and malononitrile catalyzed by Al-MIL-101-NH$_2$ with internal stirring (top) and with external shaking and separation of the liquid phase from the solid catalyst after 20 min (center).](image)

### 4.2.2.1 Influence of the metal

A comparison of the activities of the aluminum- and iron-based MIL-101-NH$_2$ derivatives (Figure 4.36) shows that the reaction is very fast in the presence of those two catalysts. Due to the time-demanding sample withdrawing and workup technique
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A discussion of the small differences in the catalytic activities will be presented in chapter 4.2.3 in the investigation of the more demanding Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate.

![Figure 4.36: Yields of benzylidene malononitrile in the Knoevenagel condensation of benzaldehyde and malononitrile catalyzed by different amino-functionalized metal-organic frameworks.](image)

4.2.2.2 Influence of the pore size

CAU-1 was tested in the Knoevenagel condensation of benzaldehyde and malononitrile in order to demonstrate the influence of the pore size on the catalytic activity. The catalytic activity of this amino-functionalized MOF is almost two orders of magnitude lower compared to Al-MIL-101-NH$_2$ ($\alpha = 3.26 \cdot 10^{-7}$ vs. $1.93 \cdot 10^{-5}$ mol g$^{-1}$ s$^{-1}$, respectively) under the same reaction conditions (Figure 4.35). The most obvious reason for this large discrepancy is the inaccessibility of the pores for the reactants and products in the case of CAU-1. A comparison of the dimensions of the catalyst pores and the reactant molecules (Table 4.3) reveals, the cavities of CAU-1 are only accessible by windows with a diameter of 0.4 to 0.5 nm, which is smaller than the dimensions of the reactants (0.87 x 0.67 nm for benzaldehyde). Thus, it has to be assumed that only the functional groups at the outer surface of the particles are utilized as catalytically active centers. In contrast, the MIL-101 structure possesses...
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windows that are large enough to allow free diffusion of even the large product molecule benzylidenemalononitrile.

Table 4.3: Dimensions of molecules and pore structures discussed in this work.

<table>
<thead>
<tr>
<th>Molecule dimensions</th>
<th>length / Å</th>
<th>width / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>8.7</td>
<td>6.7</td>
</tr>
<tr>
<td>malononitrile</td>
<td>7.5</td>
<td>3.2</td>
</tr>
<tr>
<td>ethyl cyanoacetate</td>
<td>11</td>
<td>5.3</td>
</tr>
<tr>
<td>diethyl malonate</td>
<td>13.3</td>
<td>5.9</td>
</tr>
<tr>
<td>BzMN</td>
<td>11.3</td>
<td>7.2</td>
</tr>
<tr>
<td>EtCC</td>
<td>14.3</td>
<td>7.7</td>
</tr>
<tr>
<td>DEBzM</td>
<td>13.5</td>
<td>10.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pore dimensions</th>
<th>window diameter / Å</th>
<th>cavity diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101</td>
<td>12 to 16</td>
<td>29 to 34</td>
</tr>
<tr>
<td>CAU-1</td>
<td>3 to 4</td>
<td>5.5 to 10</td>
</tr>
<tr>
<td>Cu₃btc₂</td>
<td>9.5 to 13.3</td>
<td></td>
</tr>
<tr>
<td>MIL-53 (ht)</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td>DUT-5</td>
<td>11.1</td>
<td>-</td>
</tr>
<tr>
<td>UiO-66</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Surprisingly, Cu₃(btc-NH₂)₂ (HKUST-1-NH₂, provided by K. Peikert from the group of Prof. Michael Fröba from the University of Hamburg, detailed information concerning the synthesis procedure and characterization of the material are published elsewhere [138]) exhibits an even lower catalytic activity of $\alpha = 1.83 \cdot 10^{-7}$ mol g⁻¹ s⁻¹ although the pore window dimensions suggest that the diffusion of educt and product molecules into and out of the inner pore volume should be possible. The most obvious difference in the case of Cu₃(btc-NH₂)₂ compared to the other MOFs discussed above is the electronic and steric environment of the amino moieties. The electron density at the nitrogen atom and thereby its basicity is reduced due to the presence
of an additional electron withdrawing carboxylate group at the aromatic ring. Moreover, the presence of two bulky carboxylate groups at both neighboring aromatic carbon atoms might reduce the accessibility of the amine nitrogen.

![Diagram]

Scheme 4.3: Environment of the amino moieties present in 2-aminoterephthalate (left) and 2-aminotrimasate (right) linkers.

4.2.3 Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate

For a detailed investigation of the influence of different factors on the catalytic activities of the basic catalysts, the more demanding Knoevenagel condensation of benzaldehyde and the, compared to malononitrile, larger and less acidic malonic acid derivative ethyl cyanoacetate was investigated.

4.2.3.1 Influence of the amine-functionalization

In order to study the influence of the amino moieties as basic functional groups on the catalytic activity of a MIL-101-type MOF, Fe-MIL-101-NH₂ and Fe-MIL-101 are compared as catalysts in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. Fe-MIL-101-NH₂ shows an almost five times higher yield of ethyl α-E-cyanocinnamate than the non-functionalized Fe-MIL-101 (α = 1.62·10⁶ and
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$3.44 \cdot 10^{-7}$ mol g$^{-1}$ s$^{-1}$, respectively) (Figure 4.37). The activity of Fe-MIL-101 reveals, that the amino moieties of the organic linkers are one, but not the only catalytically active species. In addition, coordinatively unsaturated metal sites, which are known to be present at the trinuclear SBU of MIL-101-type MOFs, could act as Lewis-acidic single site catalytic centers by activating the C=O double bond of the aldehyde for the nucleophilic attack of the carbanion. Another possibility would be the formation of hydroxides as discussed earlier (cf. chapters 2.3 and 4.1.5), which can also act either as proton donors or electron acceptors and induce an activation of the electrophilic compound. Both mechanisms have been proposed in literature [93,145,146].

A physical 1:1 (wt : wt) mixture of Fe-MIL-101 and Fe-MIL-101-NH$_2$ has also been applied as catalyst in the same test reaction. The catalytic activity of the physical mixture ($\alpha = 1.22 \cdot 10^{-6}$ mol g$^{-1}$ s$^{-1}$), is not exactly half of the sum of the activities of the pure compounds ($\alpha = 0.98 \cdot 10^{-6}$ mol g$^{-1}$ s$^{-1}$) but notably higher. This indicates a certain cooperative effect of the active species of non-functionalized Fe-MIL-101 and the amino groups even if they are not in direct proximity. Most probably, an activated intermediate is formed at one of the active sites that can enter the second catalytic cycle as an educt.

Figure 4.37: Yield of ethyl $\alpha$-E-cyanocinnamate in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in toluene at 80 °C catalyzed by different Fe-MIL-101-type catalysts.
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4.2.3.2 Influence of the metal

To reveal the influence of the structure building metal, the catalytic activities of Fe-MIL-101-NH$_2$ and Al-MIL-101-NH$_2$ are compared (Figure 4.38). Since equal masses of 70 mg of both catalysts have been used, the Fe derivative possesses a higher absolute BET area due to its higher specific BET area. On the other hand, the Al catalyst brings, due to the lower atomic weight of the metal, a larger absolute amount of amino groups and other possible active centers. This leads to the trend, that although the mass related activities $\alpha$ are almost identical, Al-MIL-101-NH$_2$ shows a higher surface related activity $\alpha_A$, while Fe-MIL-101-NH$_2$ exhibits a higher turnover frequency (TOF), as shown in table 4.4. Thus, it is concluded that the nature of the metal centers of MIL-101-NH$_2$-type metal-organic frameworks only has a minor influence on its catalytic activity in the Knoevenagel condensation.

![Graph](image)

Figure 4.38: Yield of ethyl $\alpha$-E-cyanocinnamate yield in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in toluene at 80 °C catalyzed by Fe-MIL-101-NH$_2$ and Al-MIL-101-NH$_2$, respectively.
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Table 4.4: Comparison of different activity quantities for Al- and Fe-MIL-101-NH₂.

<table>
<thead>
<tr>
<th></th>
<th>α / mol g⁻¹ s⁻¹</th>
<th>αₐ / mol m² s⁻¹</th>
<th>TOF⁽⁽⁽⁾⁾ / h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-MIL-101-NH₂</td>
<td>1.71·10⁻⁶</td>
<td>5.51·10⁻¹⁰</td>
<td>1.44</td>
</tr>
<tr>
<td>Fe-MIL-101-NH₂</td>
<td>1.62·10⁻⁶</td>
<td>4.69·10⁻¹⁰</td>
<td>1.54</td>
</tr>
</tbody>
</table>

4.2.3.3 Stability and recyclability of Al-MIL-101-NH₂

The stability of Al-MIL-101-NH₂ under ambient conditions has been demonstrated and discussed in chapter 4.1.5. In addition, the stability of the material under reaction conditions in the catalytic tests and the resulting reusability as a catalyst is shown here. For catalyst recycling experiments, samples were taken in the same manner as described for the batch catalytic experiments. Attempts to take the samples without stirring after sedimentation of the catalyst in order to maintain the amount of catalyst constant for each run were not successful and suggested yields of more than 100 %. This is because the sedimentation of the catalyst comes along with the separation of the aqueous phase as soon as the stirring is stopped. This results in a reaction mixture with an inhomogeneous product distribution. In between two runs, the catalyst has been reactivated by thorough washing with ethanol in order to remove all reactants and products and, most importantly, the water which is formed as a byproduct of the reaction, and with toluene to remove the ethanol which has been shown earlier to react with benzaldehyde itself. Afterwards the catalyst was dried in vacuum to ensure defined starting concentrations.

In figure 4.39, the yields of five subsequent runs with the same catalyst for 17 hours are shown. It can be concluded that the activity of the catalyst remains unchanged during these repetitions. The rise of EtCC yield at higher repetitions is most probably due to ongoing permeabilization of the septum by the needles used to exchange the reaction solution and solvents used to clean and reactivate the catalyst. This leads to a higher evaporation rate of toluene and thereby higher apparent yields.

³ Based on the theoretical total amount of amino groups. Accessibility is not considered.
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![Graph showing yield of EtCC after 17 h](image)

**Figure 4.39:** Yield of ethyl α-E-cyanocinnamate after 17 h in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in toluene at 80 °C catalyzed by Al-MIL-101-NH₂.

The powder X-ray diffraction patterns shown in figure 4.40 demonstrate that not only the catalytic activity is preserved, but also the crystal structure of the MOF stays fully intact during this treatment although water is formed in significant quantities. This water forms an aqueous phase due to its low solubility in toluene and contact with liquid water has been found to cause a rapid decomposition of Al-MIL-101-NH₂ even at room temperature. Nevertheless, the presence of toluene seems to protect the framework against the attack of water even at the reaction temperature of 80 °C.
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Figure 4.40: Comparison of powder X-ray diffraction patterns of Al-MIL-101-NH$_2$ before (top) and after use as catalyst in five subsequent runs (bottom).

4.2.3.4 Comparison of different amino-functionalized MOFs and soluble analogues

The activity of MIL-101-NH$_2$ type catalysts was compared to amino-functionalized MOFs with different structural and textural properties in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate under the same conditions. The product yields shown in figure 4.41 clearly demonstrate the outstanding performance of Al-MIL-101-NH$_2$ in comparison to all other materials, which is most probably due to the smaller pore dimensions for Cu$_3$(btc-NH$_2$)$_2$ and UiO-66-NH$_2$ and, in addition, to the one dimensional pores of Al-MIL-53-NH$_2$ and DUT-5-NH$_2$. Nevertheless, a closer look exhibits interesting differences between the activities of the catalysts.
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Figure 4.41: Yields of ethyl α-E-cyanocinnamate of different amino-functionalized metal-organic framework catalysts and the soluble linker analogue dimethyl 2-aminoterephthalate.

Cu$_3$(btc-NH$_2$)$_2$ is the least active catalyst tested in this context although it provides the largest open apertures through which the 3D-pore system can be entered, except for the MIL-101-type materials. Since all other catalysts are known for providing, at least under some conditions, bridging hydroxyl anions in the SBUs, it is concluded in agreement with the IR spectroscopic results discussed in chapter 4.1.5 that this feature has a strong influence on the activity of amino-functionalized MOFs as basic catalysts. Most probably the –OH groups act as acid sites that activate the aldehyde component as electron acceptors and thus facilitate the nucleophilic attack of either the –NH$_2$ group or the deprotonated methylene compound to form a surface bound imine intermediate or the condensation product, respectively (Scheme 4.4).
Results and Discussion

Scheme 4.4: Proposed mechanisms for the bifunctional surface-catalyzed Knoevenagel condensation with –OH induced activation of the aldehyde.

The difference in activity between the two isoreticular MOFs Al-MIL-53-NH$_2$ ($d_p = 0.85$ nm) and Al-DUT-5-NH$_2$ ($d_p = 1.11$ nm), which possess the same types of functional groups, clearly demonstrates the influence of diffusion on the activity of the catalyst. Although the channel like pores of Al-DUT-5-NH$_2$ are not much larger than the dimensions of the desired product molecule (Table 4.3), the detected activity of $\alpha = 7.12 \times 10^{-8}$ mol g$^{-1}$ s$^{-1}$ is more than twice as high as the activity of Al-MIL-53-NH$_2$ ($\alpha = 3.17 \times 10^{-8}$ mol g$^{-1}$ s$^{-1}$).

The influence of the incorporation of the aromatic amino group into a porous structure was explored by the comparison of the catalytic activity of the linker itself. Since 2-aminoterephthalic acid is not soluble in toluene, no product yield was detected when it was added to the test reaction. As a soluble alternative the ester dimethyl 2-aminoterephthalate was used. It was expected, that this homogeneous catalyst would show a very high activity due to the unhindered accessibility of all active centers. Interestingly, only a very low activity with a turnover frequency of only TOF $= 0.0187$ h$^{-1}$ was observed which is almost a hundred times lower than the ones found for the MIL-101-NH$_2$ derivatives. That clearly proves that the amino groups, incorporated in the porous skeleton of metal-organic frameworks, need the support of
polar agents like hydroxyl groups or open metal sites to fully exploit their potential as solid basic catalysts in non-polar and aprotic solvents such as toluene.

### 4.2.4 Comparison of MOF catalysts to inorganic basic materials

For a classification of the here discussed catalysts in a general context, purely inorganic basic materials were tested as catalysts under the same conditions. In comparison to classical solid bases such as MgO and hydrotalcite (Figure 4.42), the novel amino-containing MOFs with MIL-101 structure are significantly more active. But it has to be noted, that the oxidic materials were activated under the same conditions as the MOFs at 100 °C in vacuum and must therefore be considered to be non-porous.

![Graph showing yield of ethyl α-E-cyanocinnamate of different MIL-101-type materials in comparison to conventional inorganic solid basic catalysts.](image)

**Figure 4.42:** Yield of ethyl α-E-cyanocinnamate of different MIL-101-type materials in comparison to conventional inorganic solid basic catalysts.

A comparison of the yields of benzylidenemalononitrile in the Knoevenagel condensation of benzaldehyde and malononitrile achieved by Al- and Fe-MIL-101-NH$_2$ to the activities of amorphous AlPON and the nitridated zeolites NaY-850N and Beta-600N, which have been studied earlier in the group of S. Ernst, reveals the
superior catalytic activity of the MOF catalysts over inorganic basic materials also for this fairly easily catalyzed reaction (Table 4.5).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\alpha$ / mol g$^{-1}$ s$^{-1}$</th>
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<tr>
<td>Al-MIL-101-NH$_2$</td>
<td>1.94 $\cdot$ 10$^{-5}$</td>
<td>this work</td>
</tr>
<tr>
<td>Fe-MIL-101-NH$_2$</td>
<td>2.48 $\cdot$ 10$^{-5}$</td>
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<td>AlPON</td>
<td>0.37 $\cdot$ 10$^{-5}$</td>
<td>[7]</td>
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<tr>
<td>NaY-850N</td>
<td>0.44 $\cdot$ 10$^{-5}$</td>
<td>“</td>
</tr>
<tr>
<td>Beta-650N</td>
<td>0.92 $\cdot$ 10$^{-5}$</td>
<td>[147]</td>
</tr>
</tbody>
</table>

4.2.5 Knoevenagel condensation of benzaldehyde and diethyl malonate

The formation of diethyl benzylidenemalonate was not detected even when Al-MIL-101-NH$_2$ was applied as catalyst. This is in agreement with findings reported in literature that the basicity of aromatic amines is insufficient for the deprotonation of the weakly acidic methylene group of diethyl malonate [92].

4.2.6 Knoevenagel condensation in a fixed bed reactor

Since Al-MIL-101-NH$_2$ has been proven to be a highly active, stable and reusable catalyst in the Knoevenagel condensation in toluene, this test reaction has been chosen to demonstrate the applicability of an amino-functionalized MOF as catalyst in a continuously-operated fixed bed reactor. In order to reduce the pressure drop in the
reactor, this material cannot be used in its parent form as a very fine powder. Since it was found that Al-MIL-101-NH₂-ba synthesized in the batch mode forms more stable agglomerated particles, this variant was chosen for catalytic tests in a fixed bed reactor.

Pelletization tests were carried out with a longitudinal force gauge to determine the minimum pressure that has to be applied to form rigid pellets of Al-MIL-101-NH₂-ba that can be crushed and sieved to the required grain size. Although only the minimum required pressure of 640 kPa was applied, this shaping process results in a significant decrease of the porosity of the material (Figure 4.43). However, the crystal structure of the MOF stays virtually intact (Figure 4.44), while the worse signal : noise ratio of the diffraction pattern indicates that the crystallinity of the material is also reduced.

Figure 4.43: Nitrogen adsorption isotherms of Al-MIL-101-NH₂-ba synthesized in batch mode before (top) and after (bottom) pelletization at 640 kPa.
Figure 4.44: Powder X-ray diffraction patterns of Al-MIL-101-NH₂-ba before (top) and after (bottom) pelletization at 640 kPa.

For reproducible results, the catalyst was activated in-situ by rinsing it first with ethanol and subsequently with toluene for 30 minutes at 60 °C. The breakthrough curve recorded during this solvent displacement procedure is shown in figure 4.45. A mean residence time of the whole system of 5 min at a volume flow of 0.5 cm³ min⁻¹ is observed. However, it takes another 10 minutes for complete displacement of the ethanol.
Results and Discussion

![Graph showing the displacement of ethanol by toluene in a packed bed of pelletized Al-MIL-101-NH₂-ba at $\dot{V} = 0.5 \text{ cm}^3 \text{ min}^{-1}$ and $T = 60 \degree \text{C}$.](image1)

**Figure 4.45:** Displacement experiment of ethanol by toluene in a packed bed of pelletized Al-MIL-101-NH₂-ba at $\dot{V} = 0.5 \text{ cm}^3 \text{ min}^{-1}$ and $T = 60 \degree \text{C}$.

The single component breakthrough curves of the reactants benzaldehyde and malononitrile from different 0.4 molar solutions in toluene reveals a sharp breakthrough of both substances after five minutes (Figure 4.46). It is also shown that the steady state concentrations of both reactants are reached after ca. 10 minutes which is in agreement with the results of the solvent displacement experiment.

![Graph showing the breakthrough of benzaldehyde and malononitrile through a packed bed of pelletized Al-MIL-101-NH₂ at $\dot{V} = 0.5 \text{ cm}^3 \text{ min}^{-1}$ and $T = 60 \degree \text{C}$.](image2)

**Figure 4.46:** Breakthrough curves of the educts benzaldehyde and malononitrile through a packed bed of pelletized Al-MIL-101-NH₂ at $\dot{V} = 0.5 \text{ cm}^3 \text{ min}^{-1}$ and $T = 60 \degree \text{C}$. 
Results and Discussion

The blank yield of benzylidene malononitrile in the reactor filled with glass wool at \( T = 80 \, ^\circ\text{C} \) and \( V = 0.5 \, \text{cm}^3 \text{min}^{-1} \) was found to be stable at 6 % which is, considering the short residence time in the reactor, significantly higher than in the batch experiment in a glass vial.

In figure 4.47 the yield of the Knoevenagel condensation of benzaldehyde and malononitrile catalyzed by 125 mg of pelletized Al-MIL-101-NH\textsubscript{2}-ba is shown. It is demonstrated that a stable yields of benzylidene malononitrile for several hours of time-on-stream at different temperatures is achieved. The activity of \( 1.20 \cdot 10^{-5} \, \text{mol-g}^{-1} \text{s}^{-1} \) at 80 °C at constant yield is 38 % lower than the one detected for Al-MIL-101-NH\textsubscript{2} in the batch experiment. However, the yield in the continuous experiment is higher in the beginning compared to steady state conditions. The freshly activated catalyst shows for a short time a significantly higher activity of \( 2.10 \cdot 10^{-5} \, \text{mol g}^{-1} \text{s}^{-1} \) which is even 9 % higher than in the batch experiment, which can be explained by the high background activity of the stainless steel reactor itself.

![Figure 4.47](image.png)

Figure 4.47: Initiation period and steady-state yields of BzMN in the Knoevenagel condensation of benzaldehyde and malononitrile catalyzed by a pelletized Al-MIL-101-N\textsubscript{2}-ba catalyst in a continuously-operated tubular fixed bed reactor at different temperatures and a volume flow of 0.5 cm\(^3\) min\(^{-1}\).
Results and Discussion

The fast decrease of the yield in the initiation period of a freshly activated Al-MIL-101-NH$_2$-ba catalyst is reproducible after reactivation of the catalyst by washing with ethanol and toluene and occurs at different reaction temperatures as evident from figure 4.48.

![Graph showing yield of BzMN over time-on-stream](image)

**Figure 4.48**: Initiation period of a pelletized Al-MIL-101-NH$_2$-ba catalyst in the continuous Knoevenagel condensation of benzaldehyde and malononitrile at a volume flow of 0.5 cm$^3$ min$^{-1}$ at 60 °C (bottom) and 80 °C (top), respectively.

Figure 4.49 shows the yields of benzylidenemalononitrile in the initiation period of the same Al-MIL-101-NH$_2$-ba catalyst after different reactivation procedures at 60 °C. While the maximum yield after washing with dry toluene is around 70 %, it reaches only 52 % when the catalyst is pretreated with toluene that has been saturated with water at room temperature. Finally, after the equilibrium state is reached, both runs exhibit the same constant yield. This behavior clearly indicates that the rapid deactivation of the catalytic activity in the initiation period is due to the saturation of the catalyst with water, formed as a byproduct of the condensation reaction.
Figure 4.49: Initiation period of a pelletized Al-MIL-101-NH₂ catalyst in the continuous condensation reaction of benzaldehyde and malononitrile at 60 °C and a volume flow of 0.5 cm³ min⁻¹ with different initial water loadings.
5 Summary

To overcome the drawbacks of homogeneous catalysis, which is state of the art for many base catalyzed reactions on industrial scale, the development of new basic solids for the use as heterogeneous basic catalysts is of high scientific interest. In the last decades, several types of basic solids were investigated for this purpose, including metal oxides, ion-exchanged zeolites, amino-functionalized mesoporous silica and nitridated aluminosilicate and aluminophosphate materials. In recent years, the investigation of functional metal-organic framework materials in this field has gained much attention and several highly active and selective MOF-based catalysts have been described in the literature. The high porosity, the variability of the pore geometry and the customizability of the chemical and electronic properties of the internal surface of this new class of functional materials are in the focus of the ongoing research.

The scope of this work was the identification, preparation and characterization of suitable NH$_2$-containing MOFs, the optimization of the synthesis procedures and the evaluation of their eligibility as solid basic catalysts in comparison to conventional basic solids in the Knoevenagel condensation. For the investigation of different influences, the catalytic activities of isoreticular MOFs with different pore sizes and geometries and isostructural MOFs based on different metals have been compared as well as MOFs of the same type with and without amino groups.

The syntheses and activation procedures of Fe-MIL-101-NH$_2$, Fe-MIL-101, CAU-1, Zr-Uio-66-NH$_2$ were optimized for the preparation of the materials in the desired amount and purity. In the case of the iron-based MIL-101 derivatives it was found that the materials have to be handled without air contact since this results in a fast decomposition of the crystal structures.

For Al-MIL-101-NH$_2$ a new synthetic route was developed based on a semi-batch approach with stepwise addition of the aluminum component in order to avoid the formation of impurities that reduce the overall porosity of the compound synthesized under static solvothermal conditions. By this approach the first successful synthesis
Summary

of an aluminum-based MOF with MIL-101 structure and the awaited porosity was achieved. It was further demonstrated that the initial precipitate of this synthesis, although already showing significant porosity, cannot be identified as MIL-101 phase and additional aging of the synthesis mixture is required to allow the growth of phase pure particles with MIL-101 structure. Al-MIL-101-NH₂ was intensely characterized and it was shown, that the replacement of iron by aluminum in this open framework drastically enhances the stability of the MOF at ambient conditions. The phase purity of the material was confirmed by powder X-ray diffraction and solid state 

NMR spectroscopy. DRIFT spectroscopy measurements revealed the presence of a hydroxyl species in the structure in its hydrated form and a strong interaction of the material with CO₂ although chemisorption at the –NH₂ sites was not observed.

Furthermore an amine-functionalized version of DUT-5, Al-DUT-5-NH₂ was synthesized for the first time. It was shown that this new material exhibits a high permanent porosity and the total pore volume is only slightly reduced, compared to the parent DUT-5 material. It was shown that Al-DUT-5-NH₂ possesses a rigid framework in the open pore form and does not show the structural flexibility known from the isoreticular Al-MIL-53 derivative.

For the synthesis of Al-MIL-53, the organic imidazolium salt [EMIM][hbdc] was used for the first time as a linker source. It was shown that this replacement of the conventionally used terephthalic acid leads to the formation of a hybrid material containing nanocrystalline Al-MIL-53, which is stabilized in the open pore high-temperature phase, in a hydrated alumina matrix. This novel AL-MIL-53 material does not show the characteristic breathing effect induced by water sorption or low temperatures which was demonstrated by its unprecedented behavior in nitrogen and hydrogen sorption experiments.

For the testing of the metal-organic frameworks as catalysts in the base-catalyzed Knoevenagel condensation of benzaldehyde with different malonic acid derivatives, proper reaction conditions and a sophisticated workup procedure were developed to assure the accurate and reliable analysis of the reaction mixtures and thereby allow a meaningful comparison of the catalytic activities of the catalysts employed in this study.
Summary

It was shown that amine-functionalized MOFs are qualified catalysts for this important reaction. Even materials with narrow pore sizes such as UiO-66-NH$_2$ or CAU-1 that potentially don’t allow the diffusion of the product molecules show a detectable acceleration of the reaction. However, for high catalytic activities the use of structures providing large open apertures like MIL-101 derivatives is inevitable. While the comparison of Al- and Fe-MIL-101-NH$_2$ shows that the nature of the metal in this structure does not have a significant influence on the catalytic activity, the comparison of Fe-MIL-101 and Fe-MIL-101-NH$_2$ clearly proves that the amino moieties are primarily responsible for the promoting effect of these catalysts. Nevertheless, it could be shown that the coordinatively unsaturated metal sites, present in MOFs with MIL-101 topology, or metal hydroxide species formed by their reaction with water, also act as catalytically active centers even in the absence of basic amines. The investigation of Al-MIL-53-NH$_2$ as catalyst in the Knoevenagel condensation substantiated the conclusion, that the presence of hydroxides in proximity of the amino groups is beneficial, while the comparison of its activity to the isoreticular Al-DUT-5-NH$_2$ clearly demonstrates that restrictive diffusion limitations are observed. Al-MIL-101-NH$_2$ was found to be the ideal metal-organic framework for the application as a basic catalyst in the Knoevenagel condensation. Besides its activity, the stability of the structure under reaction conditions even in the presence of water at 80 °C was demonstrated and it has been reused in five consequent runs without a decrease of product yield. The effect of the incorporation of the basic amino groups into the porous frameworks was explored by comparison of the catalytic activities of the MOFs and the soluble linker analogue dimethyl 2-aminoterephthalate which was found to be less active under the same conditions. The comparison of the catalytic activities of the MOFs with those of MgO and hydrotalcite has shown that amino-functionalized metal-organic frameworks can successfully compete against conventional solid basic catalysts.

Finally, it was shown that Al-MIL-101-NH$_2$ can be used is a fixed bed catalyst in a continuously operated tubular reactor. After an initiation period with a rapid decrease of the steady-state product yield, which can be assigned to the saturation of the metal-organic framework with water, the productivity of the catalyst was stable for several hours of time on stream at temperatures between 40 and 80 °C.
6 Perspectives

The formation mechanism of most metal-organic framework materials is still not well understood. Since it was shown that the formation of Al-MIL-101-NH₂ is based on a fast precipitation followed by a long recrystallization period, in-situ investigation of particle formation and development with techniques like ultrasound attenuation or dynamic light scattering might give new insights to the influence of parameters like temperature, concentrations and water content on the crystallization process.

Since it was shown that Al-MIL-101-NH₂ is a highly active and fairly stable basic catalyst for liquid phase reactions, further modifications of this material should be investigated. It has been shown by Wittmann et al. that post-synthetic modification of the NH₂ groups with hydrophobic moieties can further enhance the moisture stability of this MOF [148]. In addition more active or more specialized catalysts in the fashion of immobilized organocatalysts or highly selective adsorbents for the removal of specific molecules from a liquid or gaseous medium might be accessible by this approach.

A very interesting modification would be the alkylation of the -NH₂ groups to generate secondary amines. This modification could be interesting for the investigation of the dominating reaction mechanism of the Knoevenagel condensation. The higher basicity of secondary amines compared to the unsubstituted derivatives should cause a higher reaction rate in the case of a mechanism in which the amine only acts as a base, while the formation of an imine intermediate by the condensation of the aldehyde with the amine would be suppressed.

The diffusion restriction of large molecules in the narrow pore MOFs could be utilized for the size selective promotion of the reaction of smaller but less reactive reactants like small alkyl aldehydes. Furthermore the formation of benzaldehyde diethyl acetal, which is observed when ethanol is used as the solvent, should be examined in detail.

The concept of employing imidazolium salts or other ionic liquids as linker precursors in the syntheses of metal-organic frameworks should be transferred to different systems including terephthalate, trimesate and imidazolate based MOFs. Of specific
interest is the influence of the degree of deprotonation of the organic linker on the resulting structure.
7 Zusammenfassung


Die Zielsetzung dieser Arbeit war die Auswahl, Herstellung und Charakterisierung geeigneter NH$_2$-funktionalisierterer MOFs sowie die Optimierung ihrer Synthesen und die Untersuchung ihrer Eignung als feste basische Katalysatoren in der Knoevenagel Kondensation im Vergleich zu konventionellen basischen Feststoffen. Zur Untersuchung verschiedener Einflussfaktoren wurden die katalytischen Aktivitäten von isoretikulären MOFs mit unterschiedlichen Porenabmessungen und -Geometrien, sowie metallorganische Gerüstverbindungen des gleichen Typs mit verschiedenen strukturbildenden Metallen mit und ohne Aminogruppen miteinander verglichen.


Zusammenfassung


Für die Untersuchungen der metallorganischen Gerüstverbindungen als Katalysatoren für die basenkatalysierte Knoevenagel Kondensation von Benzaldehyd mit verschiedenen Malonsäurederivaten wurden geeignete Reaktionsbedingungen sowie ein ausgeklügeltes Aufarbeitungsverfahren erarbeitet, um sämtliche unerwünschten Einflüsse ausschließen und die genaue und verlässliche Analyse der Reaktionsmischungen sicherzustellen und dadurch einen aussagekräftigen Vergleich der katalytischen Aktivitäten der in dieser Arbeit verwendeten Katalysatoren zuzulassen.

Zusammenfassung

wurde die Stabilität dieser Struktur unter Reaktionsbedingungen bei 80 °C sogar in Anwesenheit des als Koppelprodukt entstehenden Wassers demonstriert indem der Katalysator in fünf aufeinanderfolgenden Durchläufen wiederverwendet wurde ohne eine Abnahme der Produktausbeute erkennen zu lassen. Der Effekt der Einbindung der basischen Aminogruppen in die porösen Netzwerke wurde anhand eines Vergleichs zwischen den katalytischen Aktivitäten der MOFs und des löslichen Linkeranalogons Dimethyl-2-aminoterephthalam schwierig, welches sich unter den gleichen Bedingungen als deutlich weniger aktiv herausgestellt hatte. Der Vergleich der katalytischen Aktivitäten der MOFs mit denen von MgO und Hydrotalcit hat gezeigt, dass sich aminfunktionalisierte metallorganische Gerüstverbindungen durchaus erfolgreich mit konventionellen basischen Feststoffkatalysatoren messen können.

8 References


References


References


References


References


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## 9 Appendix

### List of Abbreviations and Symbols

**Latin**

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A\textsubscript{BET}</td>
<td>specific surface area according to the BET model</td>
</tr>
<tr>
<td>AlPON</td>
<td>aluminophosphate oxinitride</td>
</tr>
<tr>
<td>arb.</td>
<td>arbitrary</td>
</tr>
<tr>
<td>as</td>
<td>as-synthesized</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
</tr>
<tr>
<td>ba</td>
<td>batch all</td>
</tr>
<tr>
<td>bb</td>
<td>batch bulk</td>
</tr>
<tr>
<td>bdc</td>
<td>1,4-benzenedicarboxylate, terephthalate</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>bpdc</td>
<td>4,4′-biphenyl-1,1′-dicarboxylate</td>
</tr>
<tr>
<td>bpy</td>
<td>bipyridyl</td>
</tr>
<tr>
<td>btc</td>
<td>1,3,5-benzenetricarboxylate, trimesate</td>
</tr>
<tr>
<td>BzMN</td>
<td>benzylidenemalononitrile</td>
</tr>
<tr>
<td>cat</td>
<td>catalyst</td>
</tr>
<tr>
<td>CAU</td>
<td>Christian-Albrechts-University</td>
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<tr>
<td>CCP</td>
<td>cubic close packed</td>
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<tr>
<td>CP</td>
<td>cross polarization</td>
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<td>CPO</td>
<td>Coordination Polymer of Oslo</td>
</tr>
<tr>
<td>C\textsubscript{Q}</td>
<td>quadrupolar coupling constant</td>
</tr>
<tr>
<td>CUS</td>
<td>coordinatively unsaturated site</td>
</tr>
<tr>
<td>DAY</td>
<td>dealuminated zeolite Y</td>
</tr>
<tr>
<td>DEBzM</td>
<td>diethyl benzylidenemalonate</td>
</tr>
<tr>
<td>DLaTGS</td>
<td>deuterated and L-alanine-doped triglycine sulfate</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DRIFT(S)</td>
<td>diffuse reflectance infrared Fourier transform (spectroscopy)</td>
</tr>
<tr>
<td>DUT</td>
<td>Desden University of Technology</td>
</tr>
<tr>
<td>[EMIM]</td>
<td>1-ethyl-3-methylimidazolium</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>EtCC</td>
<td>ethyl α-E-cyanocinnamate</td>
</tr>
<tr>
<td>(FT-\textsubscript{IR})</td>
<td>(Fourier transform-) infrared</td>
</tr>
<tr>
<td>HKUST</td>
<td>Hong Kong University of Science and Technology</td>
</tr>
<tr>
<td>ht</td>
<td>high temperature</td>
</tr>
<tr>
<td>IRMOF</td>
<td>isoreticular metal-organic framework</td>
</tr>
<tr>
<td>is</td>
<td>imidazolium salt</td>
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Appendix

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>It</td>
<td>low temperature</td>
</tr>
<tr>
<td>MAS</td>
<td>magic angle spinning</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>MIL</td>
<td>Matérial Institut Lavoisier</td>
</tr>
<tr>
<td>MNP</td>
<td>metal nano particle</td>
</tr>
<tr>
<td>MOF</td>
<td>metal-organic framework</td>
</tr>
<tr>
<td>MTN</td>
<td>Mobil Thirty-Nine</td>
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<tr>
<td>NaX</td>
<td>sodium-form of zeolite X</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NU</td>
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<tr>
<td>PCP</td>
<td>porous coordination polymer</td>
</tr>
<tr>
<td>POM</td>
<td>polyoxometallate</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>pw</td>
<td>pulse width</td>
</tr>
<tr>
<td>rf</td>
<td>radio frequency</td>
</tr>
<tr>
<td>s</td>
<td>semi-batch</td>
</tr>
<tr>
<td>SBA</td>
<td>Santa Barbara Amorphous</td>
</tr>
<tr>
<td>SBU</td>
<td>secondary building unit</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>T&lt;sub&gt;b&lt;/sub&gt;</td>
<td>boiling point</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature programmed desorption</td>
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<td>TPDC</td>
<td>terphenyl-4,4''-dicarboxylate</td>
</tr>
<tr>
<td>T&lt;sub&gt;R&lt;/sub&gt;</td>
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<td>UHM</td>
<td>University of Hamburg Material</td>
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<tr>
<td>UiO</td>
<td>Universitetet I Oslo</td>
</tr>
<tr>
<td>V&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>volume of adsorbed gas at standard conditions</td>
</tr>
<tr>
<td>V&lt;sub&gt;pore&lt;/sub&gt;</td>
<td>pore volume</td>
</tr>
<tr>
<td>wt.</td>
<td>weight</td>
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<tr>
<td>ZIF</td>
<td>zeolitic imidazolate framework</td>
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**Greek**

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Danksagung

Die Danksagung ist in der elektronischen Version nicht enthalten.