Alkyl chain length-dependent surface reaction of dodecahydro-N-alkylcarbazoles on Pt model catalysts

Christoph Gleichweit, Max Amende, Udo Bauer, Stefan Schernich, Oliver Höfert, Michael P. A. Lorenz, Wei Zhao, Michael Müller, Marcus Koch, Philipp Bachmann, Peter Wasserscheid, Jörg Libuda, Hans-Peter Steinrück, and Christian Papp

Citation: *The Journal of Chemical Physics* **140**, 204711 (2014); doi: 10.1063/1.4875921

View online: <http://dx.doi.org/10.1063/1.4875921>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/140/20?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Performance and characteristics of a high pressure, high temperature capillary cell with facile construction for operando x-ray absorption spectroscopy

Rev. Sci. Instrum. **85**, 084105 (2014); 10.1063/1.4893351

Methane dissociative chemisorption and detailed balance on Pt(111): Dynamical constraints and the modest influence of tunneling

J. Chem. Phys. **139**, 214707 (2013); 10.1063/1.4837697

Electron induced dissociation of trimethyl (methylcyclopentadienyl) platinum (IV): Total cross section as a function of incident electron energy

J. Appl. Phys. **106**, 074903 (2009); 10.1063/1.3225091

Kinetics of the CO oxidation reaction on Pt(111) studied by in situ high-resolution x-ray photoelectron spectroscopy

J. Chem. Phys. **120**, 7113 (2004); 10.1063/1.1669378

Reaction fronts in the oxidation of hydrogen on Pt(111): Scanning tunneling microscopy experiments and reaction-diffusion modeling

J. Chem. Phys. **116**, 5759 (2002); 10.1063/1.1453964

COMSOL
CONFERENCE
2014 BOSTON

The Multiphysics
Simulation
Event of the Year

LEARN MORE >>

COMSOL

Alkyl chain length-dependent surface reaction of dodecahydro-*N*-alkylcarbazoles on Pt model catalysts

Christoph Gleichweit,^{1,a)} Max Amende,^{1,a)} Udo Bauer,¹ Stefan Schernich,¹ Oliver Höfert,¹ Michael P. A. Lorenz,¹ Wei Zhao,¹ Michael Müller,² Marcus Koch,² Philipp Bachmann,¹ Peter Wasserscheid,^{2,3} Jörg Libuda,^{1,3} Hans-Peter Steinrück,^{1,3} and Christian Papp^{1,b)}

¹*Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany*

²*Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany*

³*Erlangen Catalysis Resource Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany*

(Received 11 February 2014; accepted 21 April 2014; published online 28 May 2014)

The concept of liquid organic hydrogen carriers (LOHC) holds the potential for large scale chemical storage of hydrogen at ambient conditions. Herein, we compare the dehydrogenation and decomposition of three alkylated carbazole-based LOHCs, dodecahydro-*N*-ethylcarbazole (H_{12} -NEC), dodecahydro-*N*-propylcarbazole (H_{12} -NPC), and dodecahydro-*N*-butylcarbazole (H_{12} -NBC), on Pt(111) and on Al_2O_3 -supported Pt nanoparticles. We follow the thermal evolution of these systems quantitatively by *in situ* high-resolution X-ray photoelectron spectroscopy. We show that on Pt(111) the relevant reaction steps are not affected by the different alkyl substituents: for all LOHCs, stepwise dehydrogenation to NEC, NPC, and NBC is followed by cleavage of the C–N bond of the alkyl chain starting at 380–390 K. On Pt/ Al_2O_3 , we discern dealkylation on defect sites already at 350 K, and on ordered, (111)-like facets at 390 K. The dealkylation process at the defects is most pronounced for NEC and least pronounced for NBC. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4875921>]

INTRODUCTION

Recent developments in energy politics show that in the near future renewable energy sources, such as wind or solar energy, will play an increasingly important role for electricity production. Unfortunately, these two very important technologies for a sustainable energy production are characterized by an unsteady energy output with fluctuations caused by seasonal, climatic, and weather effects. An increasing share of unsteady energy electricity output creates a demand for efficient energy distribution and storage systems.¹ Focusing on future energy storage systems, hydrogen is one of the most promising candidates. However, practical applications are hampered by the unfavorable physico-chemical properties of molecular hydrogen requiring high pressures (up to 700 bars) or cryogenic temperatures (typically -253°C) for storage at reasonable energy densities. Note that the volumetric energy capacity of gaseous hydrogen at standard conditions is as low as 3 Wh/l (compared to ca. 10.000 Wh for a liter of diesel).^{2–4}

One possible way to overcome these challenges is to store hydrogen chemically in an organic compound that is liquid under ambient conditions. Among the different concepts of chemical energy storage, the use of so-called liquid organic hydrogen carriers (LOHCs) is particularly attractive as no extra gas component is necessary (in contrast, e.g., to methanol

or formic acid production by CO_2 hydrogenation). Hydrogen storage in LOHC systems includes the reversible catalytic dehydrogenation and hydrogenation of alicyclic/aromatic organic compounds. The latter are typically characterized by diesel-like physico-chemical properties to ensure their operability in traditional infrastructures built for liquid energy carriers.^{3,5,6} Establishing a suitable storage system based on this concept requires the optimization of both the LOHC and the catalyst, which is used for the loading and unloading cycles. Regarding the catalyst, a balance between price and efficiency has to be found for a competitive storage technology. In this context, the evaluation of the performance of nano-sized catalysts with a large surface/bulk ratio is important, in particular in view of the fact that the presently used catalysts contain the precious metals Pt and Pd.

There are numerous requirements for an ideal LOHC compound, including storage density, liquid range, thermal stability, toxicity/ecotoxicity, and large-scale availability. Among the feasible systems, the most widely studied molecule is *N*-ethylcarbazole (NEC), which is able to store 5.8 wt.% hydrogen (H_2) when fully hydrogenated to dodecahydro-*N*-ethylcarbazole (H_{12} -NEC).^{7,8} However, NEC has a relatively high melting point of about 68°C , which is one of the shortcomings of this carrier. The melting point of the unloaded carrier can be lowered by using a longer alkyl chain, due to entropic reasons: by replacing the ethyl entity of NEC by an *n*-propyl group, one obtains *N*-propylcarbazole (NPC), with the melting point lowered to 48°C . The use of eutectic mixtures of NEC and NPC promises even lower

^{a)}C. Gleichweit and M. Amende contributed equally to this work.

^{b)}Author to whom correspondence should be addressed. Electronic mail: christian.papp@fau.de

FIG. 1. Schematic overview of the investigated molecules and model catalyst surfaces.

melting points.⁹ However, as the propyl chain does not participate in the dehydrogenation/hydrogenation cycle such structural modification reduces the gravimetric storage density of the system to 5.4%. On the other hand, NPC shows a lower activation barrier for full hydrogenation on Ru catalysts and thereby has an improved applicability.⁹

One important goal of fundamental studies concerning the applicability of LOHCs is the evaluation of the elementary steps of the involved surface reactions. Concerning the dehydrogenation reaction, one specifically relevant aspect is the avoidance of unwanted side reactions during unloading, such as dealkylation of the *N*-alkyl substituent that would lead to an unfavorable change in the liquidus range of the LOHC system. In this context, we extensively studied H₁₂-NEC regarding its dehydrogenation mechanism on various model catalysts including Pt(111),¹⁰ Pd(111),¹¹ and on both Al₂O₃-supported Pt¹² and Pd¹³ nanoparticles in ultra-high vacuum (UHV) using high-resolution X-ray photoelectron spectroscopy (HR-XPS), infrared reflection-absorption spectroscopy (IRAS), and temperature-programmed molecular beam methods (TPMB). The N 1s spectrum of the nitrogen atom of NEC and H₁₂-NEC is very suitable to monitor the C–N bond scission in HR-XPS. In fact, this reaction is observed to occur both on industrial catalysts (<2% dealkylation after heating NEC for 72 h at 543 K in contact with a commercial Pt on AlOx catalyst¹⁴) and on model catalytic surfaces. Dealkylation of H₁₂-NEC on a Pt(111) single crystal is observed starting at 390 K,^{10,15} while on Pd(111) the onset of dealkylation is found already at 350 K.¹¹ The same reaction was found to take place on supported Pt and Pd model systems, where the activation barrier of C–N bond scission is reduced as compared to single crystals.¹²

The aim of this work is to study modified LOHCs based on the carbazole system. Herein, we discuss the effect of the length of the alkyl chain on the dehydrogenation reaction and on the side reactions of the respective LOHC. We present a comparison between the reaction of dodecahydro-*N*-

ethylcarbazole (H₁₂-NEC), dodecahydro-*N*-propylcarbazole (H₁₂-NPC), and dodecahydro-*N*-butylcarbazole (H₁₂-NBC), on both Pt(111) and supported Pt nanoparticles under UHV conditions studied by *in situ* high-resolution X-ray photoelectron spectroscopy (HR-XPS); a schematic overview of the investigated LOHCs and substrates is given in Figure 1. On the single crystal surface, we obtain a detailed quantitative analysis of the reaction due to the highly defined nature of the substrate.^{10,11,15} On the other hand, the investigation of supported model catalysts provides a more realistic picture of reactions taking place on the complex surface of an industrial heterogeneous catalyst. Note that for the hydrogen-lean compounds, the abbreviations NEC, NPC, and NBC will be used (equivalent to H₀-NEC, H₀-NPC, H₀-NBC, respectively). When addressing all three carriers, hereinafter, the terms NXC and H₁₂-NXC are used.

EXPERIMENTAL

The HR-XPS experiments were conducted at the beamline U49/2-PGM1 of the 3rd generation synchrotron BESSY II of Helmholtz Zentrum Berlin using a transportable ultra-high vacuum (UHV) setup consisting of two chambers.¹⁶ The preparation chamber provides typical surface-science instruments such as low energy electron diffraction (LEED), electron beam evaporators for metal deposition (Focus EFM 3), and a sputter gun (Specs IQE 11/35). The measurement chamber is equipped with an electron energy analyzer (Omicron EA 125 HR U7) and is directly connected to a supersonic molecular beam and an evaporator unit for LOHC deposition, which allows us to dose substances while taking XP spectra. The differentially pumped evaporator is separated from the main chamber by a gate valve and can be baked out separately. A filament situated at the back of the sample allows us to heat without disturbing the emitted electrons by electric or magnetic stray fields. Measurement times of ~10 s per spectra were used.

The Pt(111) single crystal was cleaned by Ar⁺ bombardment (1 kV, 5×10^{-6} mbar) and annealing in vacuum prior to each experiment. The cleanliness of the surface was checked by XPS. For preparation of the supported catalyst, a NiAl(110) single crystal was cleaned by several cycles of Ar⁺ bombardment (1 kV, 5×10^{-6} mbar) and annealing in vacuum. On top of the clean substrate, the Al₂O₃ film was prepared by at least two cycles of O₂ exposure (550 K, 7×10^{-6} mbar) and subsequent annealing to 1150 K.¹⁷ The flux of the metal evaporator, which was equipped with a Pt wire (MaTecK, 99.95%), was calibrated using a quartz microbalance, yielding Pt deposition rates around 0.05 Å/min. While evaporating a total amount of 1 Å Pt, the sample was kept at 150 K to obtain defect-rich Pt aggregates. Based on an estimate of the densities in the order of 10^{13} particles cm⁻¹, we roughly estimate an average value of 70 atoms per particle at a nominal Pt coverage of 0.1 nm (6.8×10^{14} Pt atoms cm⁻²).

H₁₂-NEC, H₁₂-NPC, and H₁₂-NBC were deposited by physical vapor deposition (PVD). During H₁₂-NXC evaporation, the background pressure in the analysis chamber rises to approximately 1.3×10^{-8} mbar.

In order to avoid radiation induced damage of the surface, the X-ray spot on the sample was shifted prior to each measurement. The N 1s (C 1s) spectra were acquired at a photon energy of 500 eV (380 eV) with an overall resolution of approximately 300 meV (180 meV) at an emission angle of the photoelectrons of 0° with respect to the sample normal. The linear heating rate during TPXPS experiments was 0.5 K/s. For peak fitting we used Doniach-Sunjić functions to represent the peak shape after subtraction of the background. In the C 1s spectra two Doniach-Sunjić functions were used as envelopes to represent the surface species H₁₂-NXC, NXC, and carbazole. These two contributions were used solely to represent the envelope and do not have a physical meaning. In the N 1s region, one Doniach-Sunjić was used (see, for example, the supplementary material of Ref. 10).

NPC and NBC were produced by alkylation¹⁸ of carbazole using the precursors propyl iodide and butyl bromide, respectively. NEC was bought from Hydrogenius Technologies GmbH (www.hydrogenius.net) in sulfur-free quality. Hydrogenation was performed in cyclohexane at 150 °C at a hydrogen pressure of 50 bars using a Ru/AlO_x catalyst (5 wt.% Ru on AlO_x). Purity was ensured through vacuum distillation and consequent checks using gas chromatography–mass spectrometry (GC–MS).

RESULTS AND DISCUSSION

Adsorption and thermal evolution on Pt(111)

As a first step, the adsorption of H₁₂-NEC, H₁₂-NPC, and H₁₂-NBC on the Pt(111) single crystal surface at low temperature (140 K) was investigated by continuously measuring C 1s and N 1s spectra during adsorption (data not shown). This allows us to compare the spectra of the fully hydrogenated molecules at similar coverage prior to any reaction. The curves with open symbols in Figure 2 show spectra taken slightly above the monolayer coverage. For all three molecules, two signals are found in the N 1s region, which

are assigned to the chemisorbed monolayer at a binding energy of 401.3 eV and the physisorbed multilayer at 399.5 eV. In the C 1s region, one peak is observed at approximately 284.7 eV. With increasing coverage (not shown here), this peak shifts to higher binding energies and a broadening of the signal is observed, indicating multilayer adsorption. From these observations, we conclude that the behavior of H₁₂-NPC and H₁₂-NBC during adsorption is similar to the one of H₁₂-NEC that was already addressed in great detail in our previous studies.^{10–13,15}

Next, we discuss the reactions occurring during heating of the adsorbed layers. To eliminate any contributions of the multilayer signal, which are difficult to separate from peaks of the chemisorbed species, for these experiments adsorption was performed at ~250 K (except for the C 1s experiment for H₁₂-NPC, where the molecule was adsorbed at 140 K and then heated to 250 K). After saturation of the monolayer signal (at ~4 L), the crystal was heated linearly at a rate of 0.5 K/s. The spectra were taken continuously (Temperature Programmed XPS, TPXPS) to monitor the surface reaction *in situ*. Selected spectra at the denoted temperatures are displayed as curves (solid symbols) in Figure 2.

First, we briefly discuss the thermal evolution of H₁₂-NEC. At 250 K, the N 1s peak at 399.5 eV is caused by partial dehydrogenation already during the adsorption experiment (note that it has the same binding energy as the multilayer, by coincidence). In the initial reaction step, H₁₂-NEC partly dehydrogenates to H₈-NEC by abstraction of the four hydrogen atoms in the nitrogen-containing heterocycle. The nitrogen atom is strongly affected by these changes, which leads to the strong shift to lower binding energy from 401.3 to 399.5 eV. In the C 1s region, partial dehydrogenation is reflected by a lower binding energy shoulder appearing at 284.1 eV. At temperatures above 300 K this shoulder shifts to slightly higher energy (284.4 eV) and strongly increases at the expense of the signal at 285.2 eV due to dehydrogenation to H₈-NEC. This process continues, even when the N 1s signal at 401.3 eV has vanished at 330 K, indicating further dehydrogenation. Finally, it yields NEC at 380 K, as is evident from the quantitative analysis in Figures 3(a) and 3(d). Note that the N 1s signal of H₁₂-NEC already vanishes at 330 K, since the nitrogen atom in the pyrrole ring is not affected by the further dehydrogenation from H₈-NEC to NEC.

The data for H₁₂-NPC and H₁₂-NBC show a comparable behavior, with some differences, which are evident from the quantitative analysis of both the C 1s and N 1s levels for all three molecules in Figure 3. At 250 K, for all three LOHCs, comparable coverages of H₁₂-NXC and NXC are deduced from the N 1s spectra, indicating that dehydrogenation has occurred at this temperature to about the same extent. Also in the C 1s data, a very similar behavior is observed for the three LOHCs. One difference to the N 1s data is that in the C 1s spectra the H₁₂-NXC signals at 250 K are in all cases about a factor of 2.5 larger than the NXC signals (Figure 3). This at first sight puzzling behavior is due to the fact that in the N 1s spectra only the chemical surrounding of the nitrogen atom is probed, i.e., the dehydrogenation at the pyrrole ring, which results in a clear chemical shift; on the other hand, the C 1s peaks contain information on all carbon atoms in the

FIG. 2. Selected XP spectra of H_{12} -NEC, H_{12} -NPC, and H_{12} -NBC on Pt(111) at different temperatures for both the (a)–(c) C 1s and (d)–(f) N 1s core levels. The bottom spectra (open symbols) are taken during adsorption at 140 K at similar coverage, the other spectra (filled symbols) were recorded after adsorption at 250 K until saturation (a) and (c)–(f) and during subsequent heating to 600 K; in (b) heating was performed after adsorption at 140 K.

respective molecules, and due to the stepwise reaction the C 1s peak at 285.2 eV assigned to “ H_{12} -NXC” also contains intensity from the CH_2 subunits in H_y -NXC ($y \leq 8$). As a consequence, the amount of H_{12} -NXC is overestimated at coverages, where H_{12} -NXC and H_y -NXC coexist on the surface, as is the case at 250 K.

Overall, the thermal evolution shows the same behavior for all LOHCs. Upon heating, in both the N 1s and the C 1s regions, the H_{12} -NXC signals decrease and, simultaneously, the signals for the dehydrogenated species increase (note that the increase is less pronounced for the N 1s region of NPC).

In the N 1s region, starting from 330 K the NXC signal is the only peak. As the nitrogen atom is again mainly influenced by the nearby carbon atoms, only the dehydrogenation of the pyrrole ring, but not of the two six-membered rings, is reflected by the N 1s binding energy. The C 1s region, however, is sensitive to the latter process and, indeed, the signals of H_{12} -NXC vanish only at 375 ± 10 K, where the dehydrogenated species (NXC) reach their maximum intensities. This is deduced from a comparison of the C 1s signal of the dehydrogenated carrier molecule and the surface species at 380 K and additionally no further decrease of the

FIG. 3. Quantitative analysis of the heating experiments performed with H_{12} -NEC, H_{12} -NPC, and H_{12} -NBC on the Pt(111) single crystal (data from Figure 2). The right hand side (d)–(f) shows the N 1s, the left hand side (a)–(c) the C 1s analysis.

shoulder at 285.2 eV that coincides with the main peak of H_{12} -NXC is seen (see spectra at 380 K in Figure 2); this temperature is about 45 K higher than observed in the N 1s spectra, which indicates the further stepwise dehydrogenation of H_8 -NXC above 330 K. The dehydrogenation of the outer carbon rings is completed at ~ 375 K. At this temperature, the surface is dominated by the fully unloaded carrier molecules NXC.

The next reaction step occurring for all three molecules is the dealkylation, i.e., C–N bond scission and liberation of the alkyl group to form carbazole. In the N 1s core level, a new peak appears at 398.1 eV, while the one at 399.5 eV decreases,

see Figures 2(d)–2(f). The reaction starts at 380–390 K for NEC, NPC, and also for NBC. In the C 1s region, no new peak is observed, but only a gradual shift towards lower binding energies is seen upon dealkylation. The quantitative comparison of the decrease of the NXC N 1s signal (and also the increase of carbazole N 1s signal), which indicates the reactivity towards dealkylation, reveals a clear trend of lower reactivity with increasing alkyl chain length, when comparing the amount of carbazole to the total intensity at 450 K: NEC shows a conversion to carbazole of $\sim 70\%$, whereas NPC reacts slower, yielding $\sim 40\%$, and NBC yielding only 20%.

Above 500 K, the N 1s level shifts from 399.5 to 400.0 eV, and in the C 1s region a broadening of the peak occurs. This is probably due to further dehydrogenation and formation of other decomposition products, increasing the number of different surface species further.

Adsorption and thermal evolution on supported Pt particles

To bridge the gap between single crystals and real catalysts, we also investigated the reaction of the potential LOHCs H₁₂-NEC, H₁₂-NPC, and H₁₂-NBC on Al₂O₃-supported Pt model catalysts. Briefly, the model catalysts were prepared in UHV, starting from a well-defined Al₂O₃ film epitaxially grown on NiAl(110). This well-ordered oxide film is widely used as a support for model catalyst preparation.^{19–23} Due to its low thickness, charging effects during electron spectroscopy measurements are avoided. Pt is

deposited on top of the Al₂O₃ support via physical vapor deposition (PVD). Both the well-ordered oxide film^{19,24,25} and structural characterizations of Pt deposits^{17,24,26} have been subject of numerous investigations.

Recently, we could show that the dealkylation of H₁₂-NEC is promoted by the presence of low-coordinated Pt sites.¹² To obtain information on LOHC decomposition and the role of the alkyl LOHC chain length, we prepared highly dispersed Pt particles with an estimated size of 2 nm, which exhibit a high amount of defects and low-coordinated Pt sites. For details on the sample preparation and characterization, we refer to the experimental section.

After preparation, the model catalyst was exposed to the LOHC at 160 K. Subsequently, the sample was annealed stepwise up to 600 K. Figures 4(a)–4(c) display the N 1s spectra recorded after annealing of the LOHC-covered catalysts to the denoted temperatures. At the lowest temperature, we can distinguish between H₁₂-NXC adsorbed on Al₂O₃ (402.1 eV) and on the Pt clusters (399.8 eV). Note that in

FIG. 4. Thermal evolution of the N 1s region ($h\nu = 500$ eV) for (a) H₁₂-NEC, (b) H₁₂-NPC, and (c) H₁₂-NBC on highly dispersed Pt particles grown on Al₂O₃/NiAl(110). (d)–(f) Quantitative analysis of the N 1s peaks shown in (a)–(c) as a function of temperature. All data are referenced to the relative amount of H₁₂-NXC chemisorbed on the Pt surface at 300 K.

Figures 4(a) (H_{12} -NEC) and 4(b) (H_{12} -NPC) the latter peak is superimposed by the signal of the physisorbed multilayer, which cannot be separated unambiguously. Figure 4(c) does not show any multilayer contribution, since the amount of H_{12} -NBC deposited on the surface was significantly lower. Since we know from previous studies and from the experiments on Pt(111) that the multilayer desorbs up to 225 K,^{11,15} we can exclude any multilayer contribution above this temperature. Therefore, we chose the spectra recorded after annealing to 300 K to reference the data to the amount of adsorbate chemisorbed on the Pt particle surfaces. The desorption of the multilayers for H_{12} -NEC and H_{12} -NPC can also be followed from the quantitative analysis of the respective N 1s peaks as a function of temperature (see Figures 4(d)–4(f)). After multilayer desorption until 250 K, the intensity of the peak associated with H_{12} -NEC chemisorbed on Pt remains constant (Figure 4(d)) or even increases until 350 K for H_{12} -NPC (Figure 4(e)) and H_{12} -NBC (Figure 4(f)). The high binding energy signal (H_{12} -NXC adsorbed on Al_2O_3) shifts towards higher values by ~ 0.5 eV, while it decreases and vanishes at approximately 400 K. Previous studies suggest that the adsorbate is mobile in this temperature regime and migrates from the support towards the metal deposits. Similar observations were made on Pd/ Al_2O_3 both for H_{12} -NEC¹³ and other adsorbates.²⁷

The coexistence of various non-equivalent adsorption sites on highly dispersed Pt aggregates as compared to Pt(111) causes a general broadening of all peaks. This effect substantially hampers a more detailed analysis of dehydrogenation intermediates, which are formed on the surface, and accordingly, the denotation H_{12} -NXC is generalized to H_y -NXC ($y = 12, 8, 4, 0$) hereinafter. In contrast, the dealkylation of the adsorbed species can be followed without hindrance, since the respective N 1s signal is strongly shifted to lower binding energies (from 399.8 to 398.5 eV); all three molecules are undergoing dealkylation on the catalyst surface, which is reflected by the growth of the signal at 398.5 eV. Closer examination of the integrated intensities of H_y -NEC (Figure 4(d)) and H_y -NPC (Figure 4(e)) reveals that the respective signal develops in two steps. The first onset of dealkylation appears at ~ 350 K, while at ~ 390 K the signals substantially gain in intensity. For H_y -NBC, the first increase is not clearly evident from the fits, but we cannot exclude that minor amounts of H_y -NBC also start to dealkylate around 350 K. One could conceive that steric hindrance is responsible for a decreasing degree of adsorption and decomposition at defect sites with increasing length of the alkyl entity. One might speculate that fewer molecules are able to occupy the limited number of available low-coordinated Pt atoms, since a more bulky alkyl chain is expected to require more space on the surface.

Interestingly, the stepwise increase of the dealkylation with temperature is not observed on Pt(111) and also not on Pd(111),¹¹ while previous studies addressing the reaction of H_{12} -NEC on supported Pd¹³ and Pt¹² model catalysts clearly indicate a similar trend. Consequently, we assign the first step at ~ 350 K to dealkylation at highly reactive low-coordinated defect sites on the metal particles. Previous studies on the dehydrogenation of ethylene²⁸ and methane²⁹ show that

these low-coordinated sites are responsible for a substantial decrease of the activation barrier of dehydrogenation, as compared to Pt(111). The literature states that hydrocarbon activation is promoted by the presence of defect sites due to a stronger binding of the adsorbates.²⁹ As a consequence, the kinetics and thermodynamics of dehydrogenation and degradation are strongly affected. We suggest that these findings can be transferred to the present system, which is reflected by a lowered temperature threshold of H_x -NBC dealkylation on the supported Pt catalyst.

The second step at ~ 390 K, which perfectly matches the onset of dealkylation on Pt(111), is attributed to the ordered (111) facets on the particle surface that resemble the reactivity of a Pt(111) single crystal. Upon further heating, the maximum product concentration is reached at approximately 500 K and levels off subsequently.

Figure 5 compares the integrated intensities of the signals attributed to dealkylation of NEC, NPC, and NBC on Pt(111) and on supported nanoparticles. For Pt(111), it is evident that the onset of decomposition is observed at 380–390 K for all LOHCs and, thus, does not depend on the length of the alkyl chain. While the initial increase up to 450 K is strongest for the LOHC with the shortest alkyl chain (NEC) and weakest for the one with the longest chain (NBC), the final amount of product above 500 K does not show a clear trend. On the Pt nanoparticles, dealkylation occurs in

FIG. 5. Comparison of the integrated intensities of the N 1s peak assigned to the dealkylation product carbazole on (a) the Pt(111) single crystal and (b) highly dispersed Pt aggregates grown on $Al_2O_3/NiAl(110)$.

two steps; the first increase is strongest for NEC and not observed for NBC, with NPC being intermediate. The second step is observed at 390 K, i.e., at the same temperature as for Pt(111) for all LOHCs. While NPC shows the lowest quantity of dealkylation product, NEC and NBC do not exhibit any significant differences. Overall, no clear tendency concerning the stability of the investigated LOHCs is found in the data obtained; in particular, the decrease of the reactivity with chain length at 450 K that was observed on Pt(111) was not found on the nanoparticles. Due to the lower overall coverage of LOHCs on the nanoparticles a higher error bar has to be assumed and thus such effects might not be detected.

SUMMARY

In conclusion, we have studied the influence of the alkyl chain length of three different *N*-alkylcarbazoles on the surface reaction both on Pt(111) single crystal surface and on supported Pt nanoparticles by HR-XPS. On the single crystal, the reactions follow the same steps for all three molecules, i.e., H₁₂-NEC, H₁₂-NPC, and H₁₂-NBC. As a first reaction, the chemisorbed monolayer of H₁₂-NXC partially dehydrogenates to H₈-NXC up to 330 K by releasing hydrogen from the N heterocycle. The next step involves further dehydrogenation at the carbon atoms of the outer phenyl rings up to ~375 K, yielding NXC on the surface. Starting at 380–390 K, for all three LOHCs C–N bond scission, i.e., dealkylation occurs, yielding carbazole and the alkyl groups adsorbed separately on the surface.

Additionally, we investigated the adsorption and reaction of H₁₂-NEC, H₁₂-NPC, and H₁₂-NBC on Al₂O₃-supported Pt aggregates. For all three LOHCs, we again observed dealkylation. For H₁₂-NEC and H₁₂-NPC a pronounced two-step increase of the respective N 1s signal intensity due to formed carbazole is observed. The first step at ~350 K indicates that C–N bond scission first takes place at low-coordinated reaction sites. With increasing alkyl chain, the first step becomes less pronounced and is not present at all in case of H₁₂-NBC; this observation is tentatively assigned to steric hindrance due to the increasing length of the alkyl chain. At 390 K, the dealkylation reaction significantly accelerated for all three LOHCs. Since this onset temperature is identical to that found for the Pt(111) single crystal, we propose that the LOHCs undergo dealkylation in a similar way also on the ordered (111)-like facets on the nanoparticles in this temperature regime. The comparison of the amounts of dealkylated products formed on supported Pt aggregates does not show a clear correlation between alkyl chain length and LOHC stability.

Based on the results shown above, the implementation of *N*-alkylcarbazoles into the LOHC concept necessitates careful scrutinizing of various critical aspects. Finding the ideal balance between stability and storage capacity of the applied carrier substance certainly is an elemental step towards the development of structure-optimized LOHC-based hydrogen storage solutions. In our studies on single crystalline surfaces and on model catalysts, we found that all studied *N*-alkylcarbazoles show similar stability, rendering them all

as suitable LOHC candidates for practical use in hydrogen storage systems.

ACKNOWLEDGMENTS

We thank the BMW group and the Cluster of Excellence “Engineering of Advanced Materials” for funding. S.S. acknowledges a grant from the Fonds der Chemischen Industrie, W.Z. thanks the China Scholarship Council for financing his Ph.D. grant. P.W. and M.K. acknowledge support by the ERC through their Advanced Investigator Grant (Grant No. 267376). Furthermore, we gratefully thank the DFG and the DAAD for partly supporting the present work. Finally, the authors thank the BESSY staff especially T. Kachel for support during beam time and the HZB for travel support as well as the allocation of synchrotron beamtime.

- ¹P. J. Hall, *Energy Policy* **36**, 4363–4367 (2008).
- ²U. Eberle, M. Felderhoff, and F. Schüth, *Angew. Chem. Int. Ed.* **48**, 6608 (2009).
- ³B. Müller, W. Arlt, and P. Wasserscheid, *Energy Environ. Sci.* **4**, 4322–4331 (2011).
- ⁴A. Sartbaeva, V. L. Kuznetsov, S. A. Wells, and P. P. Edwards, *Energy Environ. Sci.* **1**, 79–85 (2008).
- ⁵D. Teichmann, W. Arlt, P. Wasserscheid, and R. Freymann, *Energy Environ. Sci.* **4**, 2767–2773 (2011).
- ⁶D. Teichmann, K. Stark, K. Müller, G. Zottl, P. Wasserscheid, and W. Arlt, *Energy Environ. Sci.* **5**, 9044–9054 (2012).
- ⁷K. M. Eblagon, D. Rentsch, O. Friedrichs, A. Remhof, A. Züttel, A. J. Ramirez-Cuesta, and S. C. Tsang, *Int. J. Hydrogen Energy* **35**, 11609–11621 (2010).
- ⁸K. M. Eblagon, K. Tam, K. M. K. Yu, S.-L. Zhao, X.-Q. Gong, H. He, L. Ye, L.-C. Wang, A. J. Ramirez-Cuesta, and S. C. E. Tsang, *J. Phys. Chem. C* **114**, 9720 (2010).
- ⁹M. Yang, Y. Dong, S. Fei, Q. Pan, G. Ni, C. Han, H. Ke, Q. Fang, and H. Cheng, *RSC Adv.* **3**, 24877–24881 (2013).
- ¹⁰C. Gleichweit, M. Amende, S. Schernich, W. Zhao, M. P. A. Lorenz, O. Höfert, N. Brückner, P. Wasserscheid, J. Libuda, H.-P. Steinrück, and C. Papp, *ChemSusChem* **6**, 974–977 (2013).
- ¹¹M. Amende, S. Schernich, M. Sobota, I. Nikiforidis, W. Hieringer, D. Assenbaum, C. Gleichweit, H.-J. Drescher, C. Papp, H.-P. Steinrück, A. Görling, P. Wasserscheid, M. Laurin, and J. Libuda, *Chem. Eur. J.* **19**, 10854–10865 (2013).
- ¹²M. Amende, C. Gleichweit, S. Schernich, O. Höfert, M. P. A. Lorenz, W. Zhao, M. Koch, K. Obesser, C. Papp, P. Wasserscheid, H.-P. Steinrück, and J. Libuda, *J. Phys. Chem. Lett.* **5**, 1498–1504 (2014).
- ¹³M. Sobota, I. Nikiforidis, M. Amende, B. S. Zanón, T. Staudt, O. Höfert, Y. Lykhach, C. Papp, W. Hieringer, M. Laurin, D. Assenbaum, P. Wasserscheid, H.-P. Steinrück, A. Görling, and J. Libuda, *Chem. Eur. J.* **17**, 11542–11552 (2011).
- ¹⁴N. Brückner, K. Obesser, A. Bösmann, D. Teichmann, W. Arlt, J. Dungs, and P. Wasserscheid, *ChemSusChem* **7**, 229–235 (2014).
- ¹⁵M. Amende, C. Gleichweit, K. Werner, S. Schernich, W. Zhao, M. P. A. Lorenz, O. Höfert, C. Papp, M. Koch, P. Wasserscheid, M. Laurin, H.-P. Steinrück, and J. Libuda, *ACS Catal.* **4**, 657–665 (2014).
- ¹⁶R. Denecke, M. Kinne, C. M. Whelan, and H. P. Steinrück, *Surf. Rev. Lett.* **09**, 797–801 (2002).
- ¹⁷T. Bertrams, F. Winkelmann, T. Uttich, H.-J. Freund, and H. Neddermeyer, *Surf. Sci.* **331–333**, 1515–1519 (1995).
- ¹⁸H. Nishi, H. Kohno, and T. Kano, *Bull. Chem. Soc. Jpn.* **54**, 1897–1898 (1981).
- ¹⁹J. Libuda and H.-J. Freund, *Surf. Sci. Rep.* **57**, 157–298 (2005).
- ²⁰V. Johánek, S. Schauermaier, M. Laurin, J. Libuda, and H.-J. Freund, *Angew. Chem. Int. Ed.* **42**, 3035 (2003).
- ²¹M. Sobota, S. Schernich, H. Schulz, W. Hieringer, N. Paape, P. Wasserscheid, A. Görling, M. Laurin, and J. Libuda, *Phys. Chem. Chem. Phys.* **14**, 10603–10612 (2012).
- ²²M. Sobota, M. Happel, M. Amende, N. Paape, P. Wasserscheid, M. Laurin, and J. Libuda, *Adv. Mater.* **23**, 2617–2621 (2011).

- ²³M. Sobota, I. Nikiforidis, W. Hieringer, N. Paape, M. Happel, H.-P. Steinrück, A. Görling, P. Wasserscheid, M. Laurin, and J. Libuda, *Langmuir* **26**, 7199 (2010).
- ²⁴J. Libuda, M. Bäumer, and H.-J. Freund, *J. Vac. Sci. Technol. A* **12**, 2259–2264 (1994).
- ²⁵G. Kresse, M. Schmid, E. Napetschnig, M. Shishkin, L. Köhler, and P. Varga, *Science* **308**, 1440 (2005).
- ²⁶M. Bäumer and H.-J. Freund, *Prog. Surf. Sci.* **61**, 127–198 (1999).
- ²⁷S. Schauerermann, J. Hoffmann, V. Johánek, J. Hartmann, and J. Libuda, *Phys. Chem. Chem. Phys.* **4**, 3909 (2002).
- ²⁸Y. Lykhach, T. Staudt, N. Tsud, T. Skála, K. C. Prince, V. Matolín, and J. Libuda, *Phys. Chem. Chem. Phys.* **13**, 253–261 (2011).
- ²⁹F. Viñes, Y. Lykhach, T. Staudt, M. P. A. Lorenz, J. Libuda, C. Papp, H.-P. Steinrück, K. M. Neyman, and A. Görling, *Chem. Eur. J.* **16**, 6530–6539 (2010).