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Supported ionic liquid phase (SILP) materials for removal of hazardous gas compounds – efficient and irreversible NH_3 adsorption†

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Novel supported ionic liquid phase (SILP) gas purification materials have been developed to remove ammonia irreversibly from an ambient gas flow of nitrogen (1000 ppm NH_3 in N_2 , wet and dry). In the applied SILP materials, thin films of imidazolium based ionic liquids and ionic solutions of metal complexes, namely $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]$, $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Cu}(\text{NTf}_2)_2$, $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Co}(\text{NTf}_2)_2$ and $[\text{C}_n\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($n = 2, 4, 8$), were dispersed onto the large surface area of polymer-based spherical activated carbon supports. For the $[\text{C}_n\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($n = 2, 4, 8$) based SILP materials the use of a humid gas flow significantly enhances NH_3 absorption as demonstrated by a clear increase of breakthrough times. The irreversibility of the ammonia sorption and the broadband capability (e.g. Cl_2 , H_2S and cyclohexane) of the prepared SILP absorber materials are reported and compared to typical standards for gas purification adsorber materials (ABEK regulations).

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Introduction

Gas purification is an important unit operation in many industries and is typically related to product quality, reliability, environmental and health aspects. The removal of troublesome compounds from gas streams can be achieved using either adsorption on solid surfaces, absorption in liquids, condensation, permeation or chemical reaction.^{1–5} Especially for safety applications (e.g. fire fighters, first responders) the irreversible removal of toxic and hazardous compounds is crucial.⁶ Today's gas filters are optimized for certain classes of compounds and color coded brown (for organic gasses and vapors), grey (for inorganic gasses and vapors), yellow (for SO_2 and HCl), green (for NH_3 and its derivatives), black (for CO), orange (Hg vapors), blue (NO_x) and white (for particles). Additionally, filters for radioactive compounds are available. From the variety of different filter materials it is obvious that broadband filters are highly desired. State-of-the-art gas filter materials consist of activated carbon which is chemically modified to guarantee irreversible fixation of the hazardous

compound by chemisorption.^{7–11} If only the carbon material would be used, a change in temperature or moisture could lead to desorption of the adsorbed hazardous molecules.

In recent years, we have developed the concept of supported ionic liquid phase (SILP) materials as platform technology for a variety of applications including catalysis and gas separation.¹² In SILP materials, a thin film of ionic liquid is dispersed over the inner surface of a porous material as shown in Fig. 1. The ionic liquid coating thereby modifies the surface properties of the support and constitutes, due to its negligible

Fig. 1 Schematic representation of supported ionic liquid phase (SILP) materials for removal of the hazardous gas compound B from a gas-mixture A + B. The ionic liquid film can contain a functionality M that binds B by chemisorption.

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Fig. 2 Ionic liquids used in the SILP facilitated NH₃ removal.

vapor pressure, a permanent modification of the solid surface that is stable in all typical gas-phase applications.^{13–16} By variation of anions and cations, solubility, reactivity and coordination properties of the ionic liquids can be modified according to the special requirements of the given process.^{17–19}

Note that gas removal with SILP materials is macroscopically an adsorption but microscopically an absorption process. In 2010 we reported on SILP materials based on alkylimidazolium dialkylphosphates of the general formula [C_nC₁Im]-[PO₂(OR')₂] as well as on chlorometallate salts of the general type [C_nC₁Im]Cl/MCl_x (*n* = 4, 8, 12, M = Sn, Zn, Cu, *x* = 1, 2) for the continuous gas-phase removal of *n*-butyl-mercaptan from nitrogen streams.¹⁹ Best purification performance was obtained for [C₁₂C₁Im]Cl/SnCl₂ based SILP systems with a clear trend for longer breakthrough times (*i.e.* better desulphurization performance) with increasing lipophilicity of the ionic liquid's cation. The S-loaded SILP material was regenerated by a combined pressure and temperature swing by heating the material for 3 h up to 130 °C while reducing the pressure down to 0.025 mbar. Afterwards, this reversible SILP absorber could be reused for three repetitive loading and unloading cycles.

1,1,3,3-Tetramethylguanidinium lactate [TMGH][Lac] dispersed on silica particles was used by Wu and Zhu in 2009 for SO₂ removal.²⁰ Reversible SO₂ removal was also reported by Riisager and Fehrmann using a similar task-specific ionic liquid 1,1,3,3-tetramethylguanidinium chloride [TMGH]Cl supported on silica gel.²¹ Wu *et al.* synthesized amino acid functionalized ionic liquids for SILP facilitated, reversible CO₂ absorption.²² Petronas, the Malayan petrochemical company, disclosed at the EUCHEM Molten Salt and Ionic Liquids Conference 2012 in Celtic manor, Wales, the commercial operation of a supported ionic liquid phase material for irreversible mercury removal from natural gas and other gaseous refinery streams in its plants.²³ To the best of our knowledge this marks the first publication of a commercial SILP application on a refinery scale, utilizing around 60 tons of SILP absorber material in the disclosed application.

In the present work we report on the use of hydrophobic and hydrophilic ionic liquids containing dissolved metal salts

(see Fig. 2) for the irreversible absorption of ammonia. This work is part of our on-going program for the development of broadband gas filter technologies based on supported ionic liquid materials.

Experimental

Materials

Copper chloride CuCl₂ (≥98.0%), 1-ethyl-3-methylimidazolium chloride [C₂C₁Im]Cl (for synthesis) and 1-methyl-3-octylimidazolium chloride [C₈C₁Im]Cl (for synthesis) were purchased from Merck and used without any further purification. 1-Butyl-3-methylimidazolium chloride [C₄C₁Im]Cl and ethanol (≥99.9%) were obtained from Aldrich (≥98.0%). 1-Methyl-3-octylimidazolium bis[(trifluoromethyl)sulfonyl]-amide [C₈C₁Im][NTf₂] was prepared and purified according to the literature.²⁴ NH₃ (99.5 vol%) and N₂ (99.5 vol%) were purchased from Linde Gas, Germany and used without further purification. The support material consisted of polymer-based spherical activated carbon beads (*S*_{BET} = 2004.5 m² g⁻¹, *V*_{pore} = 1.071 cm³ g⁻¹, *d*_{pore} = 2.47 nm) supplied by Blücher GmbH, Germany.

SILP preparation

For SILP preparation the desired amount of IL was dissolved in around 50 ml of pure ethanol at room temperature. The required amount of activated carbon support material was added subsequently and the suspension was stirred for 2 h. The solvent was evaporated at 50 °C using a vacuum of 2 × 10⁻³ mbar, assisted by ultra-sonic agitation. For additional information see ESI.† The formal pore filling α_{IL} of the SILP catalyst was calculated according to eqn (1).

$$\alpha_{\text{IL}} = \frac{V_{\text{IL, total}}}{V_{\text{pore, total}}} \cdot 100 \quad (1)$$

The metal content of metal salt *X*_{MS} dissolved in the particular IL was calculated according to eqn (2).

$$X_{\text{MS}} = \frac{n_{\text{MS}}}{n_{\text{MS}} + n_{\text{IL}}} \quad (2)$$

Ammonia solubility measurements

The gas solubility of ammonia in the ILs was determined in an isochoric pressure apparatus, consisting of two chambers (measurement chamber and receiver tank) each equipped with a thermocouple and electronic pressure transducer (GMH 3156 Greisinger electronics). A defined amount of the particular IL was placed inside the measurement chamber, while a defined volume of NH_3 was dosed in the second chamber. After closing the chambers the apparatus was evacuated for several hours. As soon as the temperature was equilibrated, the valve of the receiver tank was opened and the decrease of pressure recorded over time until the equilibrium was reached. By knowledge of the exact volumes of both chambers the uptake of ammonia and consequently the Henry coefficient could be calculated.²⁵ For additional information and a schematic view of the experimental set up see ESI.†

Breakthrough experiments

Fig. 3 shows a schematic view of the experimental set-up as applied in the here described gas sorption experiments with SILP absorber materials. For the breakthrough experiments nitrogen and ammonia streams were dosed separately *via* two MFCs (Bronkhorst) in order to adjust an ammonia contamination of 1000 ppm. The total volume flow was kept constant with a flow velocity of 2 cm s^{-1} in the absorber column. For experiments with a humid gas stream, the nitrogen stream was passed through a saturator before the carrier gas and

ammonia were mixed. The relative humidity of the gas stream was regulated by the temperature of the saturator and verified *via* a humidity sensor. The contaminated gas stream passed through the SILP fixed-bed absorber column containing around 2.8 g of absorber material. The test conditions were based on the DIN EN 14387 and the bed height was kept constant at $h_{\text{bed}} = 20 \text{ mm}$ throughout all experiments.⁶ The sorption temperature was kept constant at 30°C and the sorption column was operated under atmospheric pressure. The amount of ammonia at the column outlet was determined by an online gas chromatograph (Varian CP-3800, Volamine fused silica $60 \text{ m} \times 0.31 \text{ mm}$ capillary column) equipped with a thermal conductivity detector and a thermionic specific detector for detection of nitrogen and phosphorus compounds.

The breakthrough and saturation capacities reflected the absorbed amount of ammonia until breakthrough ($c_{\text{NH}_3} > 25 \text{ ppm}$) or saturation ($c = c_0$), respectively.²⁶ The breakthrough and saturation capacity x_b and x_s were calculated according to eqn (3) and (4) with t_h being the time when the c/c_0 ratio reached the value of 0.5.

$$x_b = \frac{\dot{m}_{\text{NH}_3}}{m_{\text{SILP}}} t_b \quad (3)$$

$$x_s = \frac{\dot{m}_{\text{NH}_3}}{m_{\text{SILP}}} t_h \quad (4)$$

All breakthrough curves were fitted using an empirical formula of a hyperbolic tangent function as shown in eqn (5).

Fig. 3 Schematic view of the experimental set up used for the breakthrough experiments.

$$y(t) = a \tanh(bt + c) + a \quad (5)$$

Details of the individual parameters can be found in the ESI†. It should be noted that the variable c , describing the horizontal alignment of the fit function, was directly influenced by the breakthrough time and the absorption rate. Thus, from this parameter, a mathematical breakthrough time can be calculated for any breakthrough concentration. Even concentrations below the threshold value of the gas chromatographic detector could be considered and respective breakthrough times extrapolated.

Results and discussion

In a first set of experiments the pure, hydrophobic ionic liquids, $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{eFAP}]$, and the metal containing ionic liquids $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Cu}(\text{NTf}_2)_2$ ($X_{\text{Cu}(\text{NTf}_2)_2} = 0.05$), $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Co}(\text{NTf}_2)_2$ ($X_{\text{Co}(\text{NTf}_2)_2} = 0.15$) and $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/[\text{CuCl}_2]$ ($X_{\text{CuCl}_2} = 0.5$), were tested in regard to their absorption capability of ammonia. The determined Henry coefficients k_{H} of the compounds are summarized in Table 1.

The measured values of k_{H} ranged from 3.075 to 0.033 bar, reflecting a very high solubility of ammonia in all tested ILs. High ammonia solubility was expected in the pure ionic liquids from previous work by Shiflett and coworkers studying ammonia solubility in RTILs namely $[\text{C}_6\text{C}_1\text{Im}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$.²⁷

Compared with the Henry coefficients of CO_2 in $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]$ at 298 K ($k_{\text{H}}(\text{CO}_2) = 30 \text{ bar}$)²⁸ the Henry coefficient for ammonia in the same IL was lowered by a factor of 10 indicating a much higher solubility of ammonia in this ionic liquid. Compared to the metal-free ILs, the ionic metal complex solutions showed again a significantly higher ammonia uptake, since the latter bind ammonia by physisorption and chemisorption. In analogy to aqueous metal solutions, the $\text{Cu}(\text{II})$ and $\text{Co}(\text{II})$ ions bind ammonia by complexation leading to $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}$, respectively. These complexation reactions could be monitored during ammonia uptake by a color change of the IL (see also ESI†).

In a consecutive experiment the described ILs were immobilized in the micro-porous network of activated spherical carbon supports with a pore filling degree of $\alpha_{\text{IL}} = 10 \text{ vol}\%$ and tested for the purification of a nitrogen stream with an ammonia contamination of 1000 ppm. The results of the

corresponding breakthrough experiments are summarized in Table 2.

Although the chlorometallate ILs $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Cu}(\text{NTf}_2)_2$ and $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Co}(\text{NTf}_2)_2$ showed a better solubility of ammonia compared to pure $[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]$, no measurable differences in the breakthrough times could be detected. All three ILs exhibited a breakthrough time of less than 5 min, identical to the one obtained for the uncoated carbon support. When using $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$, however, a very interesting gas cleaning performance was observed. For dry and humid gas feeds the breakthrough of ammonia was delayed to 43 min and 75 min, respectively. Based on these results the subsequent experiments focused on a more detailed investigation of the copper chloride based SILP-materials.

The reproducibility of the results was tested by using two different batches of SILP material (A and B) and testing these in consecutive experiments. Within a batch of SILP material the reproducibility was excellent, with all three runs giving similar results of 284, 284 and 295 min breakthrough time. However, for the two batches A and B slightly different absorption performance was observed, with the second batch having a lower breakthrough time of 259 min, thereby a deviation from the previous results of approx. 10%. This most probably stems from minor differences in the preparation of the SILP material on the small laboratory scale. Note that the wet impregnation of the ionic liquid has to be facilitated by means of an ultrasonication step (see ESI†). If minor amounts of the ionic liquid do not penetrate the support, the effective loading is different and hence the absorption capacity. We are currently working on a more reliable, large-scale preparation method.

The alkyl chain length R (see Fig. 2) of the imidazolium cation was varied to test the influence of the cation size against the ammonia absorption capability of the SILP materials. For these studies, the pore filling degree of the tested SILP materials was increased to $\alpha_{\text{IL}} = 40 \text{ vol}\%$, since we anticipated an extended breakthrough time in consequence of a higher copper amount in the absorber bed. Hence, the influence of different alkyl chain lengths on sorption behavior should become more visible. Moreover, the ammonia absorption behavior of the different SILP materials was compared against activated carbon with an impregnation of solid copper chloride (Fig. 4).

Table 1 Henry coefficients k_{H} of $[\text{C}_8\text{C}_1\text{Im}]$ -based ILs with different anions at 303 K

Anion	Metal salt content $X_{\text{MS}}/\text{mol mol}^{-1}$	k_{H}/bar
$[\text{NTf}_2]^-$	—	3.075 ^a
$[\text{eFAP}]^-$	—	2.429 ^a
$[\text{NTf}_2]^-$	$X_{\text{Cu}(\text{NTf}_2)_2} = 0.05$	1.905 ^b
$[\text{NTf}_2]^-$	$X_{\text{Co}(\text{NTf}_2)_2} = 0.15$	0.605 ^b
Cl^-	$X_{\text{CuCl}_2} = 0.5$	0.033 ^b

^a Pure physisorption. ^b Physisorption and chemisorption.

Table 2 Breakthrough times of ammonia with different SILP-materials at 303 K and a bed height of 20 mm

Material	$\alpha_{\text{IL}}/\text{vol}\%$	$r\text{H}^a/\%$	$t_{\text{b}}^b/\text{min}$
Activated carbon without IL	0	0	<5
Activated carbon without IL	0	80	<5
$[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]$	10	0	<5
$[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Cu}(\text{NTf}_2)_2$ ($X_{\text{Cu}(\text{NTf}_2)_2} = 0.05$)	10	0	<5
$[\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2]/\text{Co}(\text{NTf}_2)_2$ ($X_{\text{Co}(\text{NTf}_2)_2} = 0.15$)	10	0	<5
$[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$)	10	0	43
$[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$)	10	80	75

^a Relative humidity of feed gas. ^b Breakthrough time.

Fig. 4 Normalized breakthrough curves of ammonia recorded for SILP absorber materials based on chlorometallate ionic liquids ($X_{\text{CuCl}_2} = 0.5$) and a pore filling $\alpha_{\text{IL}} = 40$ vol% with different cations and activated carbon impregnated with CuCl_2 as reference; $T_{\text{absorber}} = 303$ K, $p_{\text{absorber}} = 1.21$ bar, $rH = 85\%$, $h_{\text{bed}} = 20$ mm, $V_{\text{N}_2} = 325.61$ Nml min^{-1} , $V_{\text{NH}_3} = 0.33$ Nml min^{-1} .

The system with CuCl_2 but without ionic liquid resulted in the shortest breakthrough time with $t_b = 242$ min. Even the SILP system with $[\text{C}_8\text{C}_1\text{Im}][\text{CuCl}_2]$ impregnation, having a lower molar amount of copper chloride in the absorber bed than the activated carbon with solid CuCl_2 , showed a longer breakthrough time. As a general trend the breakthrough time increased with decreasing chain-length of the cation and a larger total amount of copper in the absorber bed. Table 3 lists different tested systems with respect to the breakthrough time and the copper fraction in the bed.

We assume that the main reason for the comparatively short breakthrough time with pure CuCl_2 is linked to the crystalline state of the CuCl_2 on the support with limited accessibility of all Cu ions for ammonia to undergo complexation. Additionally, the impregnated layer of CuCl_2 might not be very homogeneous in its distribution in the carbon spheres with a certain probability for spots in the materials where no Cu-salt is present and ammonia breakthrough is more likely.^{7a}

In contrast, the SILP materials provide the Cu(II) salt homogeneously dissolved in a liquid salt layer of negligible volatility.

In addition, the hygroscopic nature of the applied IL allows the dissolved Cu(II) species to get in contact with water, which usually promotes the formation of $[\text{Cu}(\text{NH}_3)_n]^{2+}$ complexes ($n = 1, 2, 3, 4$).²⁹ The molar ratio between absorbed NH_3 and amount of Cu at breakthrough suggests the presence of $\text{Cu}(\text{NH}_3)_2^{2+}$ as the dominant species being formed. Due to strong absorption of the carbon support, no clear evidence was found by means of FT-IR spectroscopy. The increasing breakthrough times with decreasing cation chain length are related to the higher molar amounts of Cu ions in the SILP-bed.

The following experiments focused on the influence of relative humidity rH and the interplay between humidity and ionic liquid loading α_{IL} for $[\text{C}_8\text{C}_1\text{Im}]$ -based SILP-materials mainly. It is important to understand the interplay of IL loading and humidity since a potential swelling of the IL film in presence of water could reduce the gas-liquid interface and could harm effective adsorption of other contaminants, such as *e.g.* cyclohexane, at the carbon surface.

Therefore, the pore filling degree α_{IL} was systematically varied from 10 to 40 vol% for two different absorption conditions, namely dry and humid nitrogen stream with relative humidity of $rH = 0\%$ and 80% , respectively. The results of the corresponding breakthrough experiments are depicted in Fig. 5. They indicate a strong correlation between the ionic liquid loading on the support and the sorption performance of the SILP material. In both experiment (dry and humid) the breakthrough time of the SILP material increased with increasing pore filling. Only the initial breakthrough time of the absorber material with 30 vol% loading differed slightly from this trend in the case of a dry stream, as the ammonia retention time was shorter than with a SILP material having 20 vol% loading. A possible explanation could be an inhomogeneous packing of the absorber bed in that experiment, whereby a tunnel stream of the gas formed and the breakthrough time was reduced accordingly.

Note that the experiments in Fig. 5 were performed at a relative humidity of 80% which differed slightly from the previous results for the material comprising $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$, $\alpha_{\text{IL}} = 40$ vol%, $rH = 85\%$), shown in Fig. 4. The saturation and breakthrough capacity of the different SILP materials (as specified in Table 4) showed a coherent behavior. Whereas the saturation capacity increased with increasing pore filling, the breakthrough capacity of the SILP absorber materials ($\alpha_{\text{IL}} > 10$ vol%) remained almost in the same range (around $13 \text{ mg}_{\text{NH}_3} \text{ g}_{\text{SILP}}^{-1}$ for dry gas and $21 \text{ mg}_{\text{NH}_3} \text{ g}_{\text{SILP}}^{-1}$ for

Table 3 Breakthrough times of ammonia for activated carbon coated with copper chloride and for different SILP materials $\alpha_{\text{IL}} = 40$ vol% at 303 K with a constant bed height of 20 mm

Coating	$n_{\text{Cu,bed}}/10^{-3} \text{ mol}^a$	t_b^b/min	$x_b/\text{mg}_{\text{NH}_3} \text{ g}_{\text{SILP}}^{-1}$	$x_s/\text{mg}_{\text{NH}_3} \text{ g}_{\text{SILP}}^{-1}$	$n_{\text{NH}_3} : n_{\text{Cu}}^c/\text{mol mol}^{-1}$
CuCl_2	3.3	242	23.9	54.8	0.9
$[\text{C}_2\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$)	5.8	409	27.5	56.6	0.9
$[\text{C}_4\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$)	4.6	373	26.6	47.9	1.0
$[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$)	3.2	316	24.2	37.0	1.2

^a Copper content in absorber bed. ^b Breakthrough time. Conditions: $T_{\text{absorber}} = 303$ K, $p_{\text{absorber}} = 1.21$ bar, $rH = 85\%$, $V_{\text{N}_2} = 325.61$ Nml min^{-1} , $V_{\text{NH}_3} = 0.33$ Nml min^{-1} . ^c Molar ratio of NH_3 to Cu at breakthrough.

Fig. 5 Normalized breakthrough curves of ammonia recorded for SILP absorber materials based on $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X = 0.5$) with different pore filling α_{IL} in (left) a dry ($\text{rH} = 0\%$) and (right) a humid ($\text{rH} = 80\%$) nitrogen stream; $T_{\text{absorber}} = 303 \text{ K}$, $p_{\text{absorber}} = 1.21 \text{ bar}$, $h_{\text{bed}} = 20 \text{ mm}$, $V_{\text{N}_2} = 325.61 \text{ Nml min}^{-1}$, $V_{\text{NH}_3} = 0.33 \text{ Nml min}^{-1}$.

Table 4 Breakthrough time and sorption capacities of $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$) based SILP materials at 303 K and with a bed height of 20 mm

rH/%	$\alpha_{\text{IL}}/\text{vol}\%$	t_{b}/min	$x_{\text{b}}/\text{mg}_{\text{NH}_3}^{-1} \text{ g}_{\text{SILP}}^{-1}$	$x_{\text{b,IL}}/\text{mg}_{\text{NH}_3}^{-1} \text{ g}_{\text{IL}}^{-1}$	$x_{\text{s}}/\text{mg}_{\text{NH}_3}^{-1} \text{ g}_{\text{SILP}}^{-1}$
0	0 ^a	348	34.5	n.a.	54.2
	10	43	4.47	36.43	8.51
	15	124	12.29	70.83	14.23
	20	153	14.28	65.28	17.41
	30	139	11.68	39.55	19.76
	40	192	14.72	41.05	27.14
80	0 ^b	242	23.9	n.a.	54.8
	10	75	7.83	63.75	11.13
	15	196	19.32	111.30	21.62
	20	231	21.59	98.68	26.87
	30	245	20.66	69.97	31.06
	40	291	22.35	62.34	33.47

Conditions: $T_{\text{absorber}} = 303 \text{ K}$, $p_{\text{absorber}} = 1.21 \text{ bar}$, $h_{\text{bed}} = 20 \text{ mm}$, $V_{\text{N}_2} = 325.61 \text{ Nml min}^{-1}$, $V_{\text{NH}_3} = 0.33 \text{ Nml min}^{-1}$. ^a $\text{rH} = 25\%$. ^b $\text{rH} = 85\%$.

Fig. 6 Normalized breakthrough curves of ammonia recorded for SILP absorber materials based on $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X = 0.5$) with different humidity. $T_{\text{absorber}} = 303 \text{ K}$, $p_{\text{absorber}} = 1.21 \text{ bar}$, $\alpha_{\text{IL}} = 40 \text{ vol}\%$, $h_{\text{bed}} = 20 \text{ mm}$, $V_{\text{N}_2} = 325.61 \text{ Nml min}^{-1}$, $V_{\text{NH}_3} = 0.33 \text{ Nml min}^{-1}$.

humid gas). This demonstrates that the SILP absorber material works very well for a wide range of humidity, a very important aspect for its practical use.

Due to the difference in the retention performance regarding a dry and a humid nitrogen stream, we examined the effect of water in the gas stream in more detail for a highly loaded SILP material ($\alpha_{\text{IL}} = 40 \text{ vol}\%$). Gas feeds with different relative humidity (dry, $\text{rH} = 62$, 78 and 85%) were additionally investigated and the results for breakthrough experiments are depicted in Fig. 6. Note that in the latter the previously shown breakthrough experiment of the SILP material coated with $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}$ and a pore filling of $\alpha_{\text{IL}} = 40 \text{ vol}\%$ at a relative humidity of 80% is not plotted again. Table 5 summarizes the measured and calculated breakthrough parameters of the $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ based SILP-materials with a pore filling of $\alpha_{\text{IL}} = 40 \text{ vol}\%$ at different relative humidity of the gas stream.

Furthermore the results are compared to the breakthrough behavior of a copper chloride impregnated activated carbon support.

The results showed a stringent retardation of the ammonia breakthrough and thus higher absorption capacity with increasing humidity of the nitrogen stream. The shortest breakthrough time of $t_{\text{b}} = 192 \text{ min}$ was recorded for the dry stream, whereas for a relative humidity of 83% an ammonia breakthrough occurred only after 316 min. Water was evaporated and the steam was passed over the SILP bed with the

Table 5 Breakthrough time and sorption capacities of $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$) based SILP materials with a pore filling of $\alpha_{\text{IL}} = 40$ vol% at different humidity in a dry gas stream at 303 K and with a bed height of 20 mm

rH/%	t_b/min	$x_b/\text{mg}_{\text{NH}_3}^{-1}\text{g}_{\text{SILP}}^{-1}$	$x_{b,\text{IL}}/\text{mg}_{\text{NH}_3}^{-1}\text{g}_{\text{IL}}^{-1}$	$x_s/\text{mg}_{\text{NH}_3}^{-1}\text{g}_{\text{SILP}}^{-1}$
85	316	24.23	65.74	37.04
80	291	22.35	62.34	33.47
78	270	20.72	57.77	33.47
62	238	18.26	50.93	28.99
0	192	14.72	41.05	27.14

water peak being detectable in the online GC. The water breakthrough of the experiment with rH = 62% demonstrates that the SILP absorber material is saturated with water long before the breakthrough of ammonia occurs. Moreover, around 90% of water was absorbed within the first hour of experiment. The enhanced sorption performance of the SILP materials by higher concentration of water can be understood by the strong solubility of ammonia in water and is in-line with observations with other ammonia complexing absorber systems, e.g. for the ammonia decontamination by aluminum–zirconium–polyacations and by activated carbon impregnated with ZnCl_2 .^{30,31} The activated carbon loaded with CuCl_2 also showed reasonable performance in both wet and dry gas streams. In a dry environment (rH = 25%) the breakthrough time was 348 min, while at 85% rH 242 min were observed (see Table 4). Interestingly, the influence of humidity, observed for the SILP materials, seems to follow a different trend for CuCl_2 systems. A detailed investigation on this phenomenon is currently carried out in our laboratory.

To further improve the irreversible ammonia absorption in the SILP materials, the molar fraction of CuCl_2 in the immobilized ionic liquid was increased. The absorption results for the variation of copper are shown in Table 6.

Raising the copper content in $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ based SILP systems from $X_{\text{CuCl}_2} = 0.5$ to 0.56 resulted in an increase of breakthrough time as well as breakthrough and saturation loadings. This is obviously related to the larger copper amount in the SILP bed. Due to the limited solubility of CuCl_2 in $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}$, no larger molar copper fractions could be tested. The experiments with $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ based SILP systems revealed a similar behavior. The increase of the molar copper amount from $X_{\text{CuCl}_2} = 0.5$ to 0.61 (solubility limit of CuCl_2 in $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}$) also led to higher breakthrough time. For the

Table 6 Breakthrough time and sorption capacities of $[\text{C}_n\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($n = 2, 8$) based SILP materials with $\alpha_{\text{IL}} = 40$ vol% at 303 K, rH = 85% and with a bed height of 20 mm

Alkyl n	X_{CuCl_2}	t_b/min	$n_{\text{Cu,bed}}/10^{-3}\text{mol}$	$x_b/\text{mg}_{\text{NH}_3}^{-1}\text{g}_{\text{SILP}}^{-1}$	$x_s/\text{mg}_{\text{NH}_3}^{-1}\text{g}_{\text{SILP}}^{-1}$
2	0.5	409	5.80	27.52	56.65
2	0.56	519	6.57	34.93	63.92
8	0.5	316	3.21	24.23	37.04
8	0.61	380	5.35	24.59	38.00

breakthrough respectively saturation loadings, there was just a minor improvement although the amount of copper was significantly raised. It is questionable whether inside the pores all CuCl_2 remains completely dissolved in the ionic liquid layer with the IL being very close to the solubility limit of CuCl_2 . Hence, formation of CuCl_2 precipitates at the pore walls could restrict the availability of these ions for the formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complexes. Based on these results, the best performing SILP system $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.56$) was selected for further measurements.

To determine whether ammonia complexation in the tested SILP materials is irreversible, the SILP material coated with $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.5$, $\alpha_{\text{IL}} = 0.2$) was first loaded with ammonia to saturation. The corresponding ammonia mass flow is depicted in Fig. 7 (white shaded area). After 1200 min, the material was heated to 85 °C while passing a flow of nitrogen through the adsorber unit. The amount of ammonia, desorbed in this procedure and detected *via* GC, is also depicted in Fig. 7 (black shaded area). Under these mild thermal conditions, the ionic liquid is highly stable, having an onset temperature for decomposition of 520 K. The SILP material also remained stable during an isothermal temperature treatment at 373 K for 10 h (see ESI†).

The applied desorption process removed ammonia from the SILP material within the first 300 minutes. After that, further flushing did not result in additional release of ammonia. In a final balance, the content of reversibly absorbed ammonia, either being chemi- or physisorbed, was determined by area analysis to 56% at 85 °C. While this value is far too high for an application in a gas mask, where high irreversibility of complexation is mandatory, an additional experiment has been conducted to simulate a desorption at 30 °C after ammonia loading below the breakthrough capacity. The same type of SILP material was loaded with ammonia for 206 min at 30 °C. The amount of ammonia desorbing at 30 °C

Fig. 7 Comparison of absorbed and desorbed amount of ammonia for the SILP absorber material coated with $[\text{C}_2\text{C}_1\text{Im}]\text{Cl}/\text{CuCl}_2$ ($X_{\text{CuCl}_2} = 0.57$) $\alpha_{\text{IL}} = 0.2$, $p_{\text{absorber}} = 1.21$ bar, $\alpha_{\text{IL}} = 0.2$, $h_{\text{bed}} = 20$ mm, $V_{\text{N}_2} = 325.61$ Nml min^{-1} , $V_{\text{NH}_3} = 0.33$ Nml min^{-1} .

Table 7 Benchmark test results for broadband applicability of pure carbon, impregnated carbon and a carbon based SILP absorber material ($T = 23\text{ }^{\circ}\text{C}$, $d_{\text{bed}} = 5\text{ cm}$, $h_{\text{bed}} = 2\text{ cm}$, $v_{\text{air}} = 0.1\text{ m s}^{-1}$, $c_{\text{NH}_3} = 1000\text{ ppm}$; $\text{rH} = 70\%$)

Class	Example	ABEK criteria/ min	Pure support/ min	ABEK impregnated support/min	SILP with [C ₂ C ₁ Im]Cl-CuCl ₂ /min	SILP performance
Organic	C ₆ H ₁₂	70	131	72	39	— —
Inorganic	Cl ₂	20	158	115	95	+++
Acidic	H ₂ S	20	1	22	83	+++
Ammonia	NH ₃	50	1	41	103	++

was much lower than in the previous experiment and accounted for less than 1% of total absorbed NH₃.

Finally, the broadband capability of the novel SILP filter materials was tested by exposing the SILP material coated with [C₂C₁Im]Cl/CuCl₂ ($X_{\text{CuCl}_2} = 0.5$) $\alpha_{\text{IL}} = 0.2$ to various other test gases. The reason for lowering the pore filling degree from 40 vol% to 20 vol% is related to the broadband capability of the SILP materials (see Table 7). Cyclohexane adsorbs best on the pure activated carbon surface. The reduction of the pore filling degree is a reasonable compromise between providing the exchange surface for cyclohexane adsorption on the pure carbon surface and ammonia absorption in the [C₂C₁Im]Cl/CuCl₂ layer. All of these measurements were carried out by the laboratory of ProQares B.V., the Netherlands, according to the DIN EN 14387 ABEK1 standard procedure.³² This allowed direct comparison of the results with commercial filter materials. As a very promising result, our new SILP absorber material exceeded the critical value for ammonia by more than 100% under the standardized ABEK test conditions (Table 7).

The new SILP absorber materials show also very good performance for chlorine (Cl₂) and hydrogen sulfide (H₂S) absorption. For these two gases criteria of the ABEK1 norm were significantly surpassed. With H₂S, the SILP material even outperformed the commercial broadband filter by a factor of 3.8.

With respect to cyclohexane our Cu-containing SILP material did not match the criteria of ABEK1. As cyclohexane is known to adsorb directly to the inner surface of the spherical activated carbon, the decrease in performance compared to pure activated carbon is due to the loss of accessible carbon surface by the ionic liquid impregnation. Since the absorption capacities for the other classes of gases are very high, the SILP material can be optimized to meet all ABEK criteria simply by decreasing the ionic liquid loading.

Conclusion

In this work we have shown the applicability of the supported ionic liquid phase (SILP) technology for efficient removal of hazardous compounds from gas streams. A SILP material consisting of a spherical activated carbon support material coated with 20 vol% [C₂C₁Im]Cl/CuCl₂ (molar ratio 1/1.3) was shown to remove very effectively the test compound ammonia from the gas stream by a combined chemi- and physisorption process. It is expected that chemisorption forms [Cu(NH₃)₄]²⁺ ions in the ionic liquid during absorption.

This complex formation process is facilitated in the presence of water and as a result the absorption capacity and performance of the SILP materials improve for humid feed gas streams. Nevertheless, the performance in dry gas streams is good. This is due to the high dispersion of ionic liquid with homogeneously dissolved copper salt on the large inner surface of the carbon spheres. Under specific desorption conditions (80 °C, nitrogen purge) of a fully saturated SILP material, the chemisorbed amount of ammonia remained bound in the SILP material while the physisorbed part of NH₃ could be removed. This behavior could allow for industrial ammonia filters that operate in modes of temperature swing or pressure swing adsorption. In this case, metal-free ionic liquids might allow for faster SILP regeneration. Pure [choline]-[NTf₂], for instance, was recently determined by Palomar *et al.* to exhibit good ammonia solubility.¹⁷

We could demonstrate that our Cu-based SILP material, though exclusively developed for ammonia absorption, shows also significant performance for gas cleaning of Cl₂ and H₂S. While certainly more gases need to be tested, this gives a strong hint that SILP materials could open a new way to design filter materials with very interesting broadband capabilities. The latter would have a significant potential to improve the safety of first responders. The troublesome and sometimes dangerous selection of the right filter in case of an unknown accident could become redundant by these new materials.

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