Fate of Brønsted Acid Sites and Benzene-Based Carbenium Ions During Methanol-to-Olefin Conversion on SAPO-34

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The silicoaluminophosphate SAPO-34 with chabazite-cages and 8-ring windows is the most interesting candidate for application as shape-selective acidic catalyst in the conversion of methanol to olefins (MTO).[1] As an important advantage, SAPO-34 has a high selectivity to light olefins, such as ethene and propene. On the other hand, this catalyst shows a rapid deactivation depending on the weight hourly space velocity of the reactant methanol. A number of studies focused on the mechanism of the MTO reaction on SAPO-34, which indicated that a hydrocarbon pool consisting mainly of polyalkylaromatics formed during an induction period.[1] In the steady-state of the MTO reaction, carbenium ions, formed from polyalkylaromatics on Brønsted acidic SAPO-34 catalysts, were suggested to act as catalytically active compounds, which reacted with methanol to form larger hydrocarbons and split-off olefins. Polycyclic aromatics, which formed upon long times-on-stream by the above-mentioned aromatics, were discussed as being responsible for the catalyst deactivation as demonstrated, for example, by analyzing the GC-MS data of coke compounds upon dissolution of the catalyst framework.[1,2]

The work presented here focused on the investigation of the number of accessible Brønsted acid sites and benzene-based carbenium ions on working SAPO-34 catalysts after different MTO reaction times by applying a novel method consisting of ammonia adsorption and quantitative solid-state NMR spectroscopy of the different types of formed ammonium ions. Catalyst samples were taken from the fixed-bed reactor for ^1H and ^{13}C solid-state NMR studies after various MTO conversion times until the catalyst was deactivated. For this purpose, the MTO reaction was quenched after different times-on-stream, and then the catalyst samples were transferred from the fixed-bed reactor to the MAS NMR rotors, without contact to air, and loaded with ammonia. An important prerequisite for this study was the application of ^1H high-speed MAS NMR spectroscopy, which led to a significant improvement of the resolution of ^1H MAS NMR spectra and a high sensitivity for the different surface species under study.

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Silicoaluminophophate SAPO-34, which had an $n_{Si}/(n_{Al}+n_{Si}+n_P)$ ratio of 0.11, was used.[3] Upon preparation and calcination of this catalyst (see the Supporting Information), the methanol conversion was performed in a standard fixed-bed reactor connected to a glass fiber UV/Vis spectrometer. Figure 1 shows the conversion of methanol and selectivities to
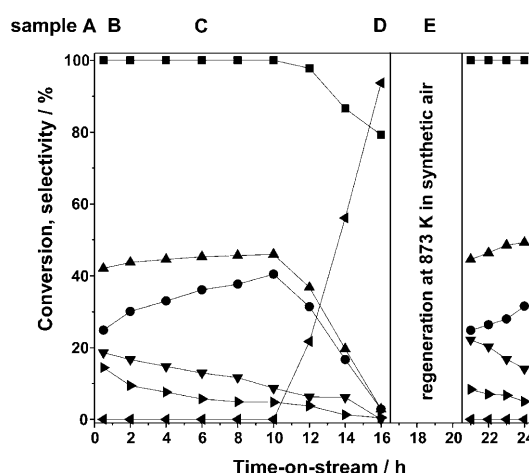

Figure 1. Conversion of methanol (■) and selectivities to ethene (●), propene (▲), butenes (▼), DME (◄), and others (►) for the MTO reaction on SAPO-34 at 673 K with WHSV = 0.5 h^{-1}. After times-on-stream of 1, 6, and 16 h, samples B, C, and D, respectively, were taken for further solid-state NMR investigations. Samples A and E correspond to the calcined and the regenerated materials, respectively. For experimental details, see the Supporting Information.

ethene, propene, butenes, dimethyl ether (DME), and others determined as a function of time-on-stream (TOS) at a reaction temperature of 673 K and a weight hourly space velocity of WHSV = 0.5 h^{-1}. For TOS ≤ 10 h, a methanol conversion of 100% and selectivities to propene and ethene of 42 to 45% and 25 to 40%, respectively, were reached. In the same period, the selectivities to butenes decreased from 19 to 8%. At TOS = 16 h, exclusively DME was produced, indicating a deactivation of the SAPO-34 catalyst. After regeneration of the deactivated catalyst in synthetic air at 873 K for 4 h, the catalytic performance was the same as that of the fresh material at TOS = 30 min (Figure 1, left and right).

Simultaneous to the catalytic studies summarized in Figure 1, the in situ UV/Vis spectra shown in Figure S1 were recorded. Already at TOS = 30 min, weak bands appeared at 240, 270, and approximately 390 nm, an indication for the formation of dienes (e.g., cyclopenta- and cyclohexadienes),[4] aromatics,[4] and benzene-based carbenium ions,[5,6] respectively. At TOS = 4 and 10 h, additional bands of bicyclic aromatics at 330 nm and polycyclic aromatics at 400–475 nm appeared.[4]

At TOS = 1, 6, and 16 h, samples B, C, and D (Figure 1, top), respectively, were taken for solid-state NMR studies on Brønsted acid sites, hydrocarbon-pool compounds, and carbenium ions formed on the SAPO-34 catalyst after reaching the steady-state of the MTO reaction (B), the highly active state of the MTO catalyst (C), and after deactivation of the catalyst (D). In addition, the calcined catalyst before starting the methanol conversion (sample A) and the regenerated catalyst (sample E), prepared by treating sample D in synthetic air at 873 K for 4 h, were investigated (Figure 1, top). The ^{1}H MAS NMR spectra of samples A to C are shown in Figure 2, left, whereas those of samples D and E are given in Figure S2, left.
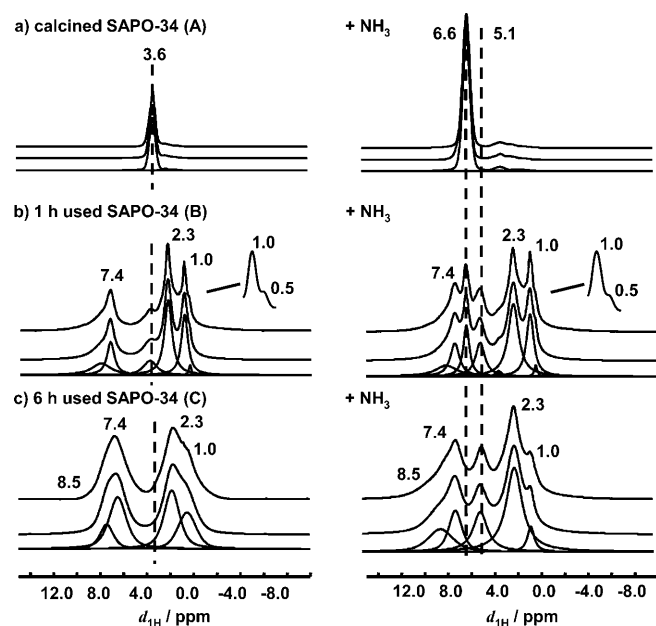
Table 1. Numbers of non-accessible bridging OH groups, n_{nonOH}, accessible Brønsted acidic Si(OH)Al groups, $n_{Si(OH)Al}$, and benzene-based carbenium ions, $n_{benzenium}$, formed upon loading ammonia on the calcined, used, and regenerated SAPO-34 catalysts, as determined by using quantitative ^{1}H MAS NMR spectroscopy.

Catalyst samples	n_{nonOH}[a] [mmol g^{-1}]	$n_{Si(OH)Al}$[a] [mmol g^{-1}]	$n_{benzenium}$[a] [mmol g^{-1}]
Calcined SAPO-34 (A)+NH$_3$	0.15	1.30	0
1 h used SAPO-34 (B)+NH$_3$	0.13	0.33	0.40
6 h used SAPO-34 (C)+NH$_3$	0	0	0.82
16 h used SAPO-34 (D)+NH$_3$	0	0	0
Regenerated SAPO-34 (E)+NH$_3$	0.10	1.15	0

[a] experimental accuracy: ±5%

Figure 2. ^{1}H high-speed MAS NMR spectra ($\nu_0 = 400.1$ MHz, $\nu_{rot} = 25$ kHz) recorded before (left) and after (right) adsorption of ammonia. a) Calcined SAPO-34 (sample A); b) and c) Catalyst samples B and C taken after methanol conversion times of 1 and 6 h, respectively. From top to bottom, the experimental spectra, the simulated spectra, and the signal components utilized for the simulation are shown. For experimental details, see the Supporting Information.

The ^{1}H MAS NMR spectrum of the calcined SAPO-34 sample A in Figure 2a, left, is dominated by a signal at 3.6 ppm, which is characteristic for Brønsted acidic bridging OH groups (Si(OH)Al).[7] Adsorption of ammonia on this catalyst and subsequent desorption of the physisorbed probe molecules lead to an ammonium signal at 6.6 ppm, the intensity of which (5.20 mmol g^{-1}) corresponds to 1.30 mmol g^{-1} (divided by four) accessible Brønsted acid sites (Figure 2a, right). The weak high-field signal at 3.6 ppm is caused by non-accessible Si(OH)Al groups (0.15 mmol g^{-1}) on the calcined SAPO-34 sample A (see Table 1). The ^{1}H MAS NMR spectrum of the SAPO-34 sample B taken at TOS = 1 h shows a weak signal corresponding to the Si(OH)Al groups at 3.6 ppm and strong signals at 1.0–2.3 ppm and 7.4–8.5 ppm, the latter two being attributable to hydrogen atoms bound to aliphatic and aromatic carbon atoms, respectively (Figure 2b, left).[8] Interestingly, the weak

signal at approximately 0.5 ppm may be an indication for organic three-ring compounds, such as trimethylcyclopropane ($\delta_{1H} = 0.57$ and 0.89 ppm),[9] formed on the SAPO-34 catalyst after short times-on-stream.

After loading samples B and C with ammonia, additional ^{1}H MAS NMR signals appeared at 5.1 and 6.6 ppm (Figures 2b and c, right). The latter one can be attributed to protonation of the probe molecules, caused by accessible Si(OH)Al groups, leading to the formation of ammonium ions.[10] The signal at 5.1 ppm is an indication for the formation of polymethylphenylammonium ions (Scheme 1), formed by the reaction of ammonia with benzene-based carbenium ions. The chemical shift of this signal is not affected by the number of methyl groups bound to the aromatic ring.
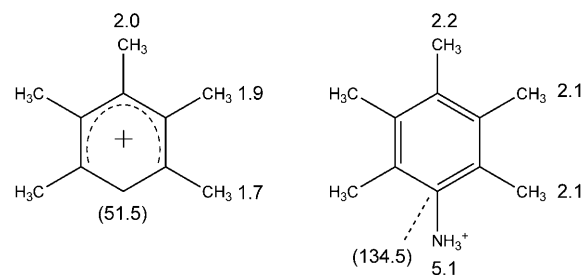
Scheme 1. Polymethylbenzenium ions (left) reacting with ammonia to polymethylphenylammonium ions (right). ^{1}H and ^{13}C NMR shift values (in ppm) are given without and with brackets, respectively.[9,13]

In a number of studies, the formation of benzene-based carbenium ions on acidic zeolite catalysts was suggested.[6,11,12] Bjørgen et al.[6] performed UV/Vis studies of benzene-based carbenium ions after loading an acidic H-beta zeolite ($n_{Si}/n_{Al} = 12$) with hexamethylbenzene (HMB). For the HMB-loaded H-beta zeolite, a UV/Vis band at 390 nm (25600 cm^{-1}) was detected, which disappeared after adsorption of ammonia. This result was explained by the formation of hexamethylbenzenium ions (band at 390 nm) on the HMB-loaded H-beta zeolite, which were converted into neutral moieties and ammonium ions in the presence of ammonia. In the present work, therefore, the SAPO-34 sample B (TOS = 1 h) was studied by using UV/Vis spectroscopy before and after loading the sample with

ammonia (Figure 3 a). The UV/Vis spectrum of sample B in Figure 3 a, top, is dominated by a band centered at 390 nm, which strongly decreases upon loading the sample with am-
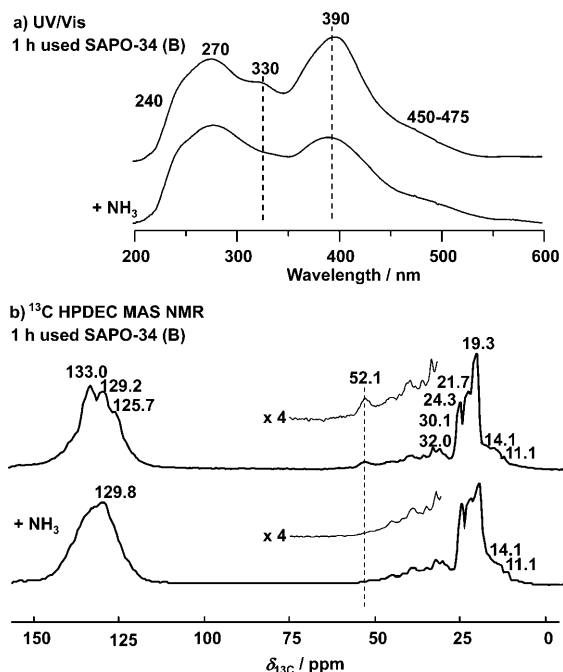

Figure 3. a) UV/Vis and b) ^{13}C HPDEC MAS NMR spectra of SAPO-34 sample B, obtained after a time-on-stream of 1 h and recorded before (top) and after (bottom) adsorption of ammonia. For experimental details, see the Supporting Information.

monia (Figure 3 a, bottom). This ammonia-induced decrease of the band at 390 nm indicates the presence of benzene-based carbenium ions. Polycyclic aromatics formed on the SAPO-34 catalyst are responsible for the UV/Vis intensities occurring at 380–420 nm in the spectrum recorded after loading (Figure 3 a, bottom).

To study the carbenium ions formed on sample B by using high-power decoupled magic angle spinning ^{13}C NMR (HPDEC MAS NMR) spectroscopy, a SAPO-34 catalyst prepared by conversion of ^{13}C-enriched methanol after TOS = 1 h was investigated. In Figure 3 b, the ^{13}C HPDEC MAS NMR spectra of this catalyst, recorded before (top) and after (bottom) adsorption of ammonia, are shown. The UV/Vis spectra of the same SAPO-34 catalyst are shown in Figure 3 a. The ^{13}C HPDEC MAS NMR spectrum of sample B in Figure 3 b, top, is dominated by strong signals of aliphatic and aromatic carbon atoms at 19–24 ppm and 126–133 ppm[8,13], respectively, and shows very broad signals at 140–180 ppm. The latter signals, which could not be resolved, are attributable to C_2 and C_6 atoms of benzene-type carbenium ions.[14,15] Weak signals at approximately 11 and 14 ppm point to the formation of organic three-ring compounds, such as trimethylcyclopropane ($\delta_{13C} = 9.8$ and 14.7 ppm).[13] More importantly, the well-resolved ^{13}C HPDEC MAS NMR signal at 52 ppm in Figure 3 b, top, is attributable to C_1 carbon atoms of benzene-based carbenium ions, which are approximately 75 ppm shifted upfield from the resonance posi-

tions of ring carbon atoms.[14] For benzenium ions and 2,4,6-trimethylbenzenium ions in superacidic solvents, ^{13}C NMR shift values of 52.2 and 53.3 ppm,[14,15] respectively, are detected.

After adsorption of ammonia on sample B, prepared by conversion of ^{13}C-enriched methanol for 1 h, the ^{13}C MAS NMR signal of C_1 atoms at 52 ppm completely disappeared (Figure 3 b, bottom). This result indicated that a reaction of ammonia with benzene-based carbenium ions occurred, leading to the formation of phenylammonium ions (see Scheme 1, right). The latter supports the assignment of the ^{1}H MAS NMR signal at 5.1 ppm to phenylammonium ions detected after ammonia adsorption on SAPO-34 samples B and C (Figures 2 b and c, right).

Based of the assignment of the ^{1}H MAS NMR signals at 5.1 and 6.6 ppm to ammonium ions formed on accessible benzene-based carbenium ions and Si(OH)Al groups, respectively, the determination of the numbers of these surface species is possible by evaluating the corresponding ^{1}H MAS NMR intensities of used MTO catalysts loaded with ammonia. In columns 2, 3, and 4 of Table 1, the numbers of non-accessible Si(OH)Al groups, n_{nonOH}, accessible Si(OH)Al groups protonating ammonia to ammonium ions, $n_{Si(OH)Al}$, and accessible polyalkylbenzenium ions able to form polyalkylphenylammonium ions, $n_{benzenium}$, respectively, are given. According to these values, the calcined SAPO-34 sample A had 1.30 mmol g^{-1} accessible Brønsted acid sites, which decreased to 0.33 mmol g^{-1} after TOS = 1 h (sample B). Furthermore, 0.40 mmol g^{-1} accessible benzene-based carbenium ions existed on sample B. After TOS = 6 h (sample C), no accessible Si(OH)Al groups were detected. However, the number of accessible polyalkylbenzenium ions increased to a value of 0.82 mmol g^{-1}. For the deactivated SAPO-34 sample D (TOS = 16 h), neither accessible Si(OH)Al groups nor benzene-based carbenium ions were detected upon ammonia adsorption. This catalyst produced exclusively dimethyl ether, which was formed on POH and AlOH groups, as was found for AlPO$_4$ catalysts.[16] After regeneration of the deactivated SAPO-34 sample D, the resulting sample E had 1.15 mmol g^{-1} accessible Si(OH)Al groups and a MTO activity comparable to that of the calcined and non-used SAPO-34 sample A (compare Figure 1, left and right).

Summarizing, the adsorption of ammonia on SAPO-34, which was used as an MTO catalyst, and subsequent ^{1}H high-speed MAS NMR spectroscopy is a useful tool for quantifying the number of accessible Brønsted acid sites and polyalkylbenzenium ions as a function of the reaction time. Based on the present study, the significant change of the product selectivity of SAPO-34 from light olefins to dimethyl ether at long MTO conversion times can be explained by a complete absence of accessible Brønsted acid sites and benzene-based carbenium ions. In this situation, conversion of methanol occurs exclusively on AlOH, POH, or SiOH groups, for example, on the surface of a particle. As known from earlier studies, the low acidity of these surface sites leads to the formation of dimethyl ether. Further investigations must clarify the potential of the method demonstrated in this communication to study the fate of surface sites and carbenium ions on solid catalysts applied to a larger variety of acid-catalyzed reactions.

[1] M. Stöcker in *Zeolite and Catalysis: Synthesis Reactions and Applications* (Eds: J. Čejka, A. Corma, S. Zones), Wiley-VCH, Weinheim, **2010**, p. 687.

[2] B. Arstad, S. Kolboe, *Catal. Lett.* **2001**, *71*, 209–212.

[3] M. Kang, T. Inui, *J. Mol. Catal. A: Chem* **1999**, *140*, 55–63.

[4] P. Crews, J. Rodriguez, M. Jaspars, *Organic Structure Analysis*, Oxford University Press, USA, **1998**.

[5] I. Kiricsi, H. Förster, G. Tasi, J. B. Nagy, *Chem. Rev.* **1999**, *99*, 2085–2114.

[6] M. Bjørgen, F. Bonino, S. Kolboe, K.-P. Lillerud, A. Zecchina, S. Bordiga, *J. Am. Chem. Soc.* **2003**, *125*, 15863–15868.

[7] A. Buchholz, W. Wang, M. Xu, A. Arnold, M. Hunger, *Microporous Mesoporous Mater.* **2002**, *56*, 267–278.

[8] H. Friebolin, *Ein- und zweidimensionale NMR-Spektroskopie*, Wiley-VCH, Weinheim, **1999**.

[9] *H NMR Predictor*, Product Version 9.08, Advanced Chemistry Development Inc., **2006**.

[10] M. Hunger, J. Weitkamp in *In-situ Spectroscopy of Catalysts* (Ed.: B. M. Weckhuysen), American Scientific Publishers, Stevenson Ranch, USA, **2004**.

[11] B. Arstad, S. Kolboe, *J. Am. Chem. Soc.* **2001**, *123*, 8137–8138.

[12] S. Svelle, M. Bjørgen, S. Kolboe, D. Kuck, M. Letzel, U. Olsbye, O. Sekiguchi, E. Uggerud, *Catal. Lett.* **2006**, *109*, 25–35.

[13] *C NMR*, Version 1.1, Advanced Chemistry Development Inc., USA, **1995**.

[14] G. A. Olah, H. C. Lin, D. A. Forsyth, *J. Am. Chem. Soc.* **1974**, *96*, 6908–6911.

[15] G. A. Olah, J. S. Staral, G. Asencio, G. Liang, D. A. Forsyth, G. D. Mateescu, *J. Am. Chem. Soc.* **1978**, *100*, 6299–6308.

[16] K. Lertjiamratn, P. Praserthdam, M. Arai, J. Panpranot, *Appl. Catal. A* **2010**, *378*, 119–123.