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Novel Approach for the Characterization of Lewis Acidic Solid Catalysts by Solid-State NMR Spectroscopy

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Acetone-2-^{13}C, trimethylphosphine oxide (TMPO), and ammonia were applied as probe molecules for solid-state NMR investigations of Lewis acid sites on γ-Al_2O_3, TiO_2/anatase, and lithium-exchanged zeolite Na-Y. An indication for Lewis acid sites are the ^{31}P MAS NMR signals at 48–51 ppm for TMPO-loaded catalysts. The determination of the Lewis site density through the evaluation of these ^{31}P MAS NMR signals, however, is difficult owing to the demanding TMPO adsorption procedure. Upon ammonia adsorption, the formation of ammonium ions at Brønsted acid sites and the coordination of ammonia at Lewis acid sites cause ^{1}H MAS NMR signals at 6–7 ppm and −0.5–3 ppm, respectively. The integration of these signals results in the densities of Brønsted and Lewis acid sites. Future studies have to clarify whether the different ^{1}H chemical shifts in the range of −0.5–3 ppm for ammonia coordinated at Lewis acid sites on solid catalysts are a hint at the different strengths of these surface sites.

Introduction

To understand the mechanisms of heterogeneously catalyzed reactions, detailed characterization of the active surface sites is required. Over the past decades, solid-state NMR spectroscopy has demonstrated its high potential in the characterization of Brønsted acid sites, but Lewis acid sites have only been studied in a limited manner.[1–3] Often, the ^{13}C magic angle spinning (MAS) NMR signal of the carbonyl atom of adsorbed acetone-2-^{13}C is utilized to investigate the strength of Brønsted acid sites.[4,5] Owing to the large range of the adsorbate-induced chemical shifts between δ_{13C} = 210 ppm for silica and δ_{13C} = 235 ppm for heteropoly acids, acetone-2-^{13}C is a very useful probe molecule for the characterization of the strength of Brønsted acidic solid catalysts.[3,6,7] DFT calculations by Fang et al. demonstrated that the above-mentioned chemical shifts of acetone-2-^{13}C adsorbed at hydroxyl protons can be correlated with the deprotonation energy of these surface OH groups.[5]

Also, for the adsorption of acetone-2-^{13}C on Lewis acid sites, typical resonance positions of the carbonyl atom of δ_{13C} = 233–245 ppm are given in the literature.[1–3] The observation of these ^{13}C MAS NMR signals were described for acetone-2-^{13}C adsorption, for example, on $AlCl_3$-modified MCM-41 (δ_{13C} = 241 and 245 ppm)[8] and dealuminated zeolite H-Y (δ_{13C} = 242 ppm).[9,10] On the other hand, in the presence of very strong Lewis acid sites, adsorbed acetone-2-^{13}C is catalytically converted as described for γ-Al_2O_3[11] and for pure and modified ZrO_2.[12] However, this surface reaction is only an indirect hint at the presence of Lewis acid sites. Infrared studies of acetone adsorbed on TiO_2 also indicated a conversion of the probe molecules on this Lewis acidic material.[13]

Another probe molecule is trimethylphosphine (TMP), with typical ^{31}P MAS NMR signals at approximately −3 to −5 ppm for $(CH_3)_3P{-}H^+$ complexes at the former Brønsted acid sites and at approximately −24 to −58 ppm for $(CH_3)_3P$ coordinated at Lewis acid sites.[14–16] On the other hand, TMP is a toxic agent, which limits its application for routine characterization of solid catalysts. Therefore, more often, trialkylphosphine oxides, such as trimethylphosphine oxide (TMPO), are utilized as molecular probes for Brønsted acid sites on solid catalysts.[3,17] Also in this case, DFT calculations by Zheng et al. demonstrated that the ^{31}P chemical shift of TMPO adsorbed at hydroxyl protons correlates with the proton affinity of these surface OH groups.[17] Typically, the experimentally observed ^{31}P MAS NMR shift range of TMPO adsorbed at well accessible Brønsted acid sites is δ_{31P} = 60–70 ppm.[3,18–21] For TMPO-loaded heteropoly acids, ^{31}P MAS NMR signals at 87.7–92.1 ppm indicated the presence of superacidic Brønsted sites.[22] For adsorption of TMPO at Brønsted acid sites in small pores or cages, such as in the small sodalite cages of zeolite Y, a high-field shift by approximately 10 ppm to $\delta_{31P} \approx 55$ ppm occurs. Recently, Hayashi et al. observed a similar high-field shift of the ^{31}P MAS NMR signal of physisorbed TMPO at more stable sites with smaller spaces, leading to a signal at δ_{31P} = 37 ppm.[23] Based on ^{31}P MAS NMR studies of TMPO-loaded γ-Al_2O_3, Rakiewicz et al. explained the signal occurring at δ_{31P} = 37 ppm in the ^{31}P MAS NMR spectrum of TMPO-loaded dealuminated zeolite H-Y with TMPO at the Lewis acid sites.[24] To the best of our knowledge, the above-mentioned discrepancy in the assignment of the ^{31}P MAS NMR signals occurring at δ_{31P} = 37 ppm for TMPO-loaded solid catalysts was not clarified.

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In the present work, the interactions of TMPO and other probe molecules with Lewis acidic solids, such as γ-Al_2O_3 and TiO_2/anatase, were studied by solid-state NMR spectroscopy. As a third model compound, a lithium-exchanged zeolite Y was investigated. It is expected that the small radius and strong electrostatic field of the Li^+ cations make this material a weak Lewis acid. In the result of these investigations, a novel procedure for the identification and characterization of Lewis acid sites on solid catalysts has been suggested, which is based on the application of TMPO and ammonia as probe molecules in combination with solid-state NMR spectroscopy.

Results and Discussion

Chemical instability of acetone in the presence of Lewis acid sites

To clarify the chemical instability of acetone on Lewis acidic solids, the adsorption of acetone-2-^{13}C on γ-Al_2O_3, TiO_2/anatase, and zeolite 52Li,48Na-Y was investigated by ^{13}C CP MAS NMR spectroscopy (Figure 1a–c). Pure acetone-2-^{13}C gives a signal at $\delta_{13C}=208$ ppm,[4] which can be observed in the spectra in Figure 1a and b. Owing to the physisorption of acetone-2-^{13}C

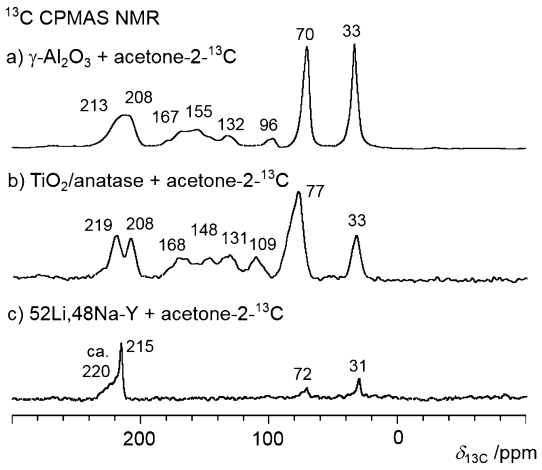


Figure 1. ^{13}C CP MAS NMR spectra of acetone-2-^{13}C-loaded γ-Al_2O_3 (a), TiO_2/anatase (b), and zeolite 52Li,48Na-Y (c).

at AlOH and SiOH groups, additional signals occur at $\delta_{13C}=$ 213–215 ppm in Figure 1a–c. The weak shoulder at $\delta_{13C}\approx220$ ppm in Figure 1c indicates the presence of a small amount of Brønsted acidic OH groups in zeolite 52Li,48Na-Y. The signals appearing at $\delta_{13C}=31$–33 ppm, 70–77 ppm, and 96–168 ppm indicate that, already at 295 K, a catalytic conversion of acetone at Lewis acid sites on the samples under study occurs. According to Biaglow et al.,[25] Xu et al.,[26] and Li et al.,[9,10] most of these signals are due to products of aldol condensation reactions. The low signal intensities of the reaction products for the acetone-2-^{13}C-loaded zeolite 52Li,48Na-Y in Figure 1c are probably due to the lower strength of the Lewis acid sites in this material in comparison with those of γ-Al_2O_3 and TiO_2/anatase.

Identification of Lewis acid sites by trimethylphosphine oxide

In the literature,[18–21,23,24] different procedures for the adsorption of TMPO onto solid catalysts are described, such as (i) loading the catalyst with TMPO dissolved, for example, in CH_2Cl_2[24] and subsequent evacuation of the solvent or (ii) mixing the catalyst with pure TMPO particles followed by heating of this mixture at 433 K[21] to distribute the probe molecules over the powder sample. To exclude problems with residual solvent molecules, in the present work procedure (ii) was applied for the TMPO loading. In the case of not well distributed TMPO, that is, in the presence of residual bulk TMPO, a ^{31}P MAS NMR signal at $\delta_{31P}=41$ ppm occurs in the spectra (see Figure 2a).

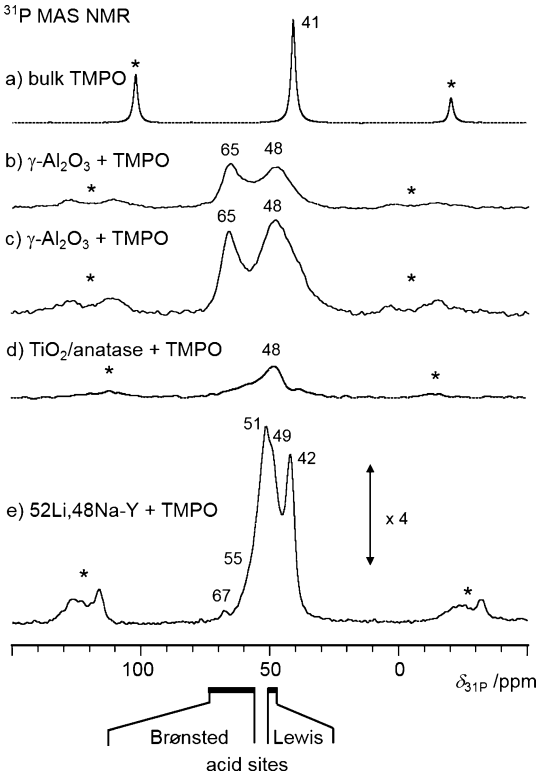


Figure 2. ^{31}P MAS NMR spectra of bulk TMPO (a), γ-Al_2O_3 loaded with approximately 2.5 and 5 mg TMPO (b and c, respectively), TMPO-loaded TiO_2/anatase (d), and TMPO-loaded zeolite 52Li,48Na-Y (e). Asterisks denote spinning sidebands.

To clarify the assignment of TMPO adsorbed at Lewis acid sites, studies were performed with TMPO adsorbed on γ-Al_2O_3, as also described by Rakiewicz et al.[24] The ^{31}P MAS NMR spectrum in Figure 2b clearly consists of two signals at $\delta_{31P}=48$ and 65 ppm, without any additional signal or shoulder at $\delta_{31P}=37$ ppm. Because the signal at $\delta_{31P}=65$ ppm is typical for TMPO interacting with Brønsted acid sites, the signal at $\delta_{31P}=$ 48 ppm must be due to TMPO adsorbed at Lewis acid sites. Only after an increase in the TMPO loading was a weak shoulder at $\delta_{31P}\approx40$ ppm observed (Figure 2c), but this signal should

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be caused by the remaining bulk TMPO (compare with Figure 2a). Probably, the earlier assignment of the ^{31}P MAS NMR signal at $\delta_{31P}=37$ ppm to TMPO at Lewis acid sites was caused by physisorbed TMPO in small pores at the surface of the γ-Al_2O_3 material used by Rakiewicz et al.[24] and the very high TMPO loading of this material. TMPO adsorption on TiO_2/anatase in the present work gave additional support for the new assignment of TMPO at Lewis acid sites, because the dominant ^{31}P MAS NMR signal for this Lewis acidic material appeared also at $\delta_{31P}=48$ ppm (Figure 2d). Additionally, only a very weak broad low-field shoulder occurs in Figure 2d, which hints at a very small number of TMPO at Brønsted acid sites on TiO_2/anatase. Also, the ^{31}P MAS NMR spectra of TiO_2/anatase with much higher TMPO loadings do not contain signals at $\delta_{31P}\approx37$ ppm (see Figure S1 in the Supporting Information), which supports the new assignment of the 48 ppm signal to TMPO at Lewis acid sites. Furthermore, the ^{31}P MAS NMR spectrum of TMPO loaded on zeolite 52Li,48Na-Y shows two signals at $\delta_{31P}=49$ and 51 ppm in the range of TMPO at Lewis acid sites (Figure 2e). As the relative intensities of these two signals are roughly 1:1, these signals can be explained by TMPO adsorption at Li^+ and Na^+ cations. The signal at $\delta_{31P}=42$ ppm in Figure 2e is caused by bulk TMPO, whereas the weak signal and shoulder at $\delta_{31P}=67$ and approximately 55 ppm are due to TMPO adsorbed at the very few Brønsted acidic OH groups in the supercages and sodalite cages of the zeolite Y, respectively.[21]

The above-mentioned ^{31}P MAS NMR studies of three very different and well-accepted Lewis acids support the new assignment of ^{31}P MAS NMR signals at $\delta_{31P}=48$–51 ppm to TMPO at Lewis acid sites on solid catalysts. Furthermore, these studies have shown that application of TMPO as a probe molecule in combination with ^{31}P MAS NMR spectroscopy is a very useful approach for indicating the presence of Lewis acid sites on solid catalysts. On the other hand, no significant and characteristic differences in the chemical shift values of the ^{31}P MAS NMR signals of TMPO at Lewis acid sites, which could be caused by differences in the strength of these surface sites were observed. Furthermore, the TMPO loading methods by the above-mentioned procedures (i) and (ii) make the determination of the density of Lewis acid sites by evaluating the signal intensity at $\delta_{31P}\approx48$ ppm difficult.

Quantification of Lewis acid sites by adsorption of ammonia

A number of studies in the past decade have demonstrated that ammonia is a very useful probe molecule for the determination of the density of Brønsted acid sites by solid-state NMR spectroscopy. Protonation of ammonia by Brønsted acid sites leads to the formation of ammonium ions causing an ^{1}H MAS NMR signal at $\delta_{1H}=6$–7 ppm, which is integrated to determine the number of Brønsted acid sites.[3] This method is comparable with the well-accepted temperature-programmed desorption of ammonia (NH_3-TPD).[27,28] In the NH_3-TPD curves of solid catalysts containing both Brønsted and Lewis acid sites, the high-temperature peak at 623–723 K is caused by ammonia desorbed from Brønsted as well as Lewis acid sites. Similarly, the ^{1}H MAS NMR spectra of ammonia-loaded catalysts should contain both types of signals owing to ammonia molecules chemisorbed at Brønsted acid sites and coordinated at Lewis acid sites. Only a few papers describe ^{1}H MAS NMR signals at $\delta_{1H}=2$–3 ppm in the spectra of ammonia-loaded solid catalysts, which may be due to ammonia coordinated at Lewis acid sites. But no systematic studies existed until now.[12,29,30]

In Figure 3a, the ^{1}H MAS NMR spectrum of the dehydrated and unloaded γ-Al_2O_3 is shown. In agreement with the literature,[31] the signals at $\delta_{1H}=-0.2$ and 1.7 ppm can be explained by different types of external and internal AlOH species. Loading of ammonia on γ-Al_2O_3 leads to a strong increase in the

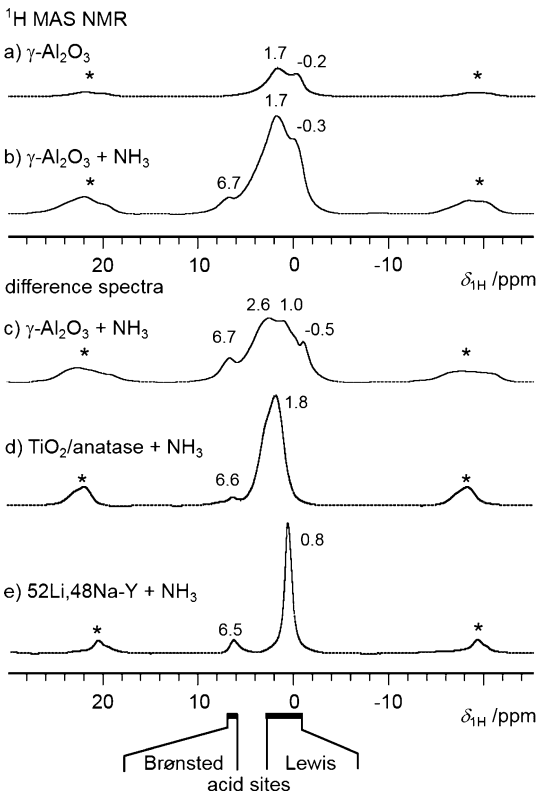


Figure 3. ^{1}H MAS NMR spectra of dehydrated γ-Al_2O_3 recorded before (a) and after (b) adsorption of ammonia. (c)–(e) The difference spectra obtained after subtraction of the ^{1}H MAS NMR spectra of dehydrated γ-Al_2O_3 (c), TiO_2/anatase (d), and zeolite 52Li,48Na-Y (e) from those of the ammonia-loaded samples. Asterisks denote spinning sidebands.

signal intensities in the shift range $\delta_{1H}=-0.3$–2.6 ppm (Figure 3b). These signals must be due to very strongly adsorbed ammonia, such as ammonia coordinated at Lewis acid sites, because these molecules do not desorb during evacuation at 453 K. Furthermore, a weak signal at $\delta_{1H}=6.7$ ppm hints at the formation of ammonium ions at Brønsted acidic OH groups. The spectrum in Figure 3c corresponds to the difference of the spectra in Figure 3a and b.

Evaluation of the signal intensities of this difference spectrum gives the number of ammonium ions formed at Brønsted acid sites (signal at $\delta_{1H}=6.7$ ppm) and the number of ammonia molecules coordinated at Lewis acid sites (signals at $\delta_{1H}=$

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Table 1. ^{31}P and ^{1}H MAS NMR investigations of the surface acid sites on γ-Al_2O_3, TiO_2/anatase, and zeolite 52Li,48Na-Y by using trimethylphosphine oxide (TMPO) and ammonia as probe molecules.

Catalyst	^{31}P MAS NMR after TMPO loading	^{1}H MAS NMR after ammonia loading
γ-Al_2O_3	**Signal at 48 ppm:** TMPO at Lewis acid sites **Signal at 65 ppm:** TMPO at Brønsted acid sites	**Signals at −0.5–3 ppm:** NH_3 at Lewis acid sites (0.088 mmol g^{-1})[a] **Signal at 6.7 ppm:** NH_4^+ at Brønsted acid sites (0.020 mmol g^{-1})[a]
TiO_2/anatase	**Signal at 48 ppm:** TMPO at Lewis acid sites **Shoulder at 55–60 ppm:** TMPO at very few Brønsted acid sites	**Signal at 1.8 ppm:** NH_3 at Lewis acid sites (0.051 mmol g^{-1})[a] **Signal at 6.6 ppm:** NH_4^+ at very few Brønsted acid sites (0.002 mmol g^{-1})[a]
52Li,48Na-Y	**Signal at 42 ppm:** Bulk TMPO **Signals at 49 and 51 ppm:** TMPO at different Lewis acid sites **Shoulder/signal at ca. 55 and 67 ppm:** TMPO at Brønsted acid sites	**Signal at 0.8 ppm:** NH_3 at Lewis acid sites (0.212 mmol g^{-1})[a] **Signal at 6.5 ppm:** NH_4^+ at Brønsted acid sites (0.018 mmol g^{-1})[a]

[a] Experimental accuracy of ±10%.

−0.5–3 ppm), summarized in column 3 of Table 1. The same ^{1}H MAS NMR studies of ammonia-loaded samples were also performed with TiO_2/anatase and zeolite 52Li,48Na-Y, leading to the difference spectra in Figure 3d and 3e. The evaluation of the results of these spectra are also given in Table 1, column 3.

For comparison, column 2 of Table 1 is a summary of the results obtained by ^{31}P MAS NMR spectroscopy of the TMPO-loaded model catalysts. In all cases, if ^{31}P MAS NMR spectroscopy of the TMPO-loaded catalyst indicates the presence of Lewis acid sites (signals at δ_{31P} = 48–51 ppm), the ^{1}H MAS NMR signals of ammonia coordinated at Lewis acid sites (signals at δ_{1H} = −0.5–3.0 ppm) occur in the spectrum of the ammonia-loaded material. Similarly, the appearance of ^{31}P MAS NMR signals at δ_{31P} = 55–67 ppm in the spectrum of the TMPO-loaded catalysts is accompanied by the observation of ^{1}H MAS NMR signals of ammonium ions at δ_{1H} = 6–7 ppm, which hints at the presence of Brønsted acid sites. Furthermore, evaluation of the ^{1}H MAS NMR difference spectra gave the densities of Lewis and Brønsted acid sites in column 3 of Table 1.

The observation of narrow spinning sidebands resulting from the signals of ammonia molecules coordinated at Lewis acid sites (signals at δ_{1H} = −0.5–3.0 ppm) is evidence that the correlation time of the thermal mobility of these ammonia molecules must be large in comparison with the MAS period of τ_{rot} = 0.125 ms (ν_{rot} = 8000 Hz). In addition, physisorbed ammonia and ammonia in the gas phase were removed by evacuation at 453 K. Hence, the rapid exchange of ammonia molecules can be excluded as a reason for the different ^{1}H chemical shift values of these molecules. Therefore, future studies should clarify whether the different ^{1}H chemical shifts of δ_{1H} = −0.5–3 ppm for ammonia coordinated at the Lewis acid sites hint at different acid strengths.

Conclusions

This work introduces a procedure for the identification and quantification of Lewis acid sites on solid catalysts. For this purpose, different probe molecules for the solid-state NMR characterization of Lewis acid sites on solid catalysts were investigated. The studies were performed by using γ-Al_2O_3, TiO_2/anatase, and a lithium-exchanged zeolite Na-Y (52Li,48Na-Y) as model compounds for Lewis acidic solid catalysts. In agreement with earlier studies, acetone (acetone-2-^{13}C) was found to be chemically unstable on Lewis acidic solid catalysts. Therefore, ^{13}C CP MAS NMR spectroscopic observation of the products of aldol condensation reactions after adsorption of acetone was found to give only an indirect hint of the presence of Lewis acid sites. Trimethylphosphine oxide (TMPO) was found to be a stable probe molecule for Lewis acidic solid catalysts. Characteristic ^{31}P MAS NMR signals at δ_{31P} = 48–51 ppm hint at the presence of TMPO adsorbed at Lewis acid sites. Therefore, TMPO adsorption in combination with ^{31}P MAS NMR spectroscopy is a suitable approach for the identification of these surface sites. Their quantification, that is, the determination of the density of Lewis acid sites from ^{31}P MAS NMR spectroscopy of TMPO-loaded materials, however, is difficult because of the demanding TMPO adsorption procedure.

As a suitable alternative pathway for the quantitative determination of Lewis acid sites on solid catalysts, the evaluation of the ^{1}H MAS NMR spectra of ammonia-loaded catalysts was utilized. As is well known, the high-temperature peak of NH_3-TPD curves can be due to ammonium ions at Brønsted acid sites and ammonia molecules being strongly coordinated at Lewis acid sites. Similarly, these two surface species, that is, ammonium ions at Brønsted acid sites and ammonia coordinated at Lewis acid sites, can be observed by ^{1}H MAS NMR spectroscopy, with the advantage that they have very different ^{1}H chemical shifts: δ_{1H} = 6–7 ppm and δ_{1H} = −0.5–3 ppm, respectively. The evaluation of the integral intensities of these ^{1}H MAS NMR signals allows the determination of the densities of Brønsted and Lewis acid sites.

Interestingly, coordinated ammonia in zeolite 52Li,48Na-Y, which was the material with the lowest tendency for aldol condensation reactions (see Figure 1) and, therefore, with the

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weakest Lewis acid sites, showed a ^{1}H chemical shift of $\delta_{1H}=$ 0.8 ppm. The majority of the ammonia molecules coordinated at Lewis acid site in γ-Al_2O_3 and TiO_2/anatase occurred at significantly higher ^{1}H chemical shifts. Therefore, future investigations should clarify whether the different ^{1}H chemical shifts in the range $\delta_{1H}=-0.5$–3 ppm for ammonia coordinated at Lewis acid sites indicate the different strengths of these surface sites.

Experimental Section

Catalysts and sample preparation

The γ-Al_2O_3 (CAS 2014750087) was delivered by Saint-Gobain, Cleveland, Ohio, USA, and had a particle size of 70 μm and a Brunauer–Emmett–Teller (BET) surface area of 259 m^2g^{-1}. The anatase-type TiO_2 was a commercial product (CAS 1317–70–0) from Alfa Aesar, Haverhill, Massachusetts, USA, with a BET surface of 45 m^2g^{-1}. Zeolite Na-Y ($n_{Si}/n_{Al}=2.7$) was purchased from Degussa AG, Hanau, Germany. For removing cationic impurities in the commercial zeolite Na-Y, the hydrated material (25 g) was exchanged in 750 mL of a 1 M aqueous solution of sodium nitrate at 353 K for 4 h. Subsequently, the suspension was washed with demineralized water until no nitrate was detected and dried at 353 K in air. The purified zeolite Na-Y (5 g) was suspended in 100 mL of 1 M aqueous solution of lithium nitrate and stirred for 12 h at 353 K. Subsequently, this suspension was washed and dried as mentioned above. By optical emission spectroscopy (ICP-OES, Varian Vista-MPX), an ion-exchange degree of the zeolite Li,Na-Y of 52% was determined (52Li,48Na-Y). The structural intactness was characterized by XRD (Bruker D8 diffractometer) as well as ^{27}Al and ^{29}Si MAS NMR spectroscopy.

Before the loading of the catalysts under study with probe molecules, they were dehydrated by evacuation ($p<10^{-2}$ mbar) at 623 K (TiO_2/anatase) or 723 K (γ-Al_2O_3, Li,Na-Y) for 12 h. For the adsorption of acetone-2-^{13}C (99.5% ^{13}C-enriched, Sigma–Aldrich) on the dehydrated catalysts, the sample tubes were connected with a vacuum line and 40 mbar of these probe molecules were adsorbed within 10 min. Subsequently, the acetone-2-^{13}C-loaded samples were evacuated ($p<10^{-2}$ mbar) at 295 K for 10 min to remove weakly hydrogen-bonded or physisorbed acetone-2-^{13}C. Loading of the dehydrated catalysts with TMPO (Alfa Aesar) was performed inside a glovebox purged with dry nitrogen gas by mixing the dehydrated catalysts (ca. 50 mg) with TMPO (2.5 or 5 mg) inside a rotor, which was sealed with an O-ring-containing Marcor-Cap. Subsequently, the TMPO-loaded samples inside the sealed rotors were heated at 433 K for 2 h. The ammonia loading of the dehydrated catalysts was performed on a vacuum line by adsorption of 100 mbar ammonia (Griesinger) at 298 K for 10 min, followed by evacuation ($p<10^{-2}$ mbar) at 453 K for 2 h.

Solid-state NMR spectroscopy

The ^{1}H, ^{13}C, and ^{31}P MAS NMR investigations were carried out on a Bruker Avance III 400 WB spectrometer at resonance frequencies of 400.1, 100.6, and 161.9 MHz, respectively, and with a sample spinning rate of 8 kHz (^{1}H) or 10 kHz (^{13}C, ^{31}P) using 4 mm rotors. The ^{31}P MAS NMR spectra were obtained with single $\pi/2$ pulse excitation, high-power proton decoupling, and a repetition time of 30 s. ^{13}C cross-polarization MAS NMR spectra (CP MAS NMR) were recorded with a contact time of 4 ms and a repetition time of 4 s. ^{1}H MAS NMR spectra were obtained after single-pulse $\pi/2$ excitation with a repetition time of 20 s. Quantitative ^{1}H MAS NMR measurements were performed by using zeolite 35 H,65Na-Y (decationization degree of 35%) as an external intensity standard. ^{1}H MAS NMR difference spectra of the unloaded and ammonia-loaded samples under study were utilized for the signal separation and the determination of the relative signal intensities. For the calculation of the number of NH_4^+ at former Brønsted acid sites and of NH_3 coordinated at Lewis acid sites, the integral intensities of the corresponding ^{1}H MAS NMR signals were divided by 4 and 3, respectively.

Acknowledgments

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Keywords: Lewis acid sites · probe molecules · quantitative characterization · solid catalysts · solid-state NMR

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