

Low-Temperature Modification of Mesoporous MCM-41 Material with Sublimated Aluminum Chloride in Vacuum

Mingcan Xu, Andreas Arnold, Andreas Buchholz, Wei Wang, and Michael Hunger*

Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

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Treatment of siliceous MCM-41 with aluminum chloride was performed in a vacuum at a temperature of 403 K. The obtained $\text{AlCl}_3/\text{MCM-41}$ material was characterized by multinuclear solid-state NMR spectroscopy and by application of probe molecules. The results of NMR spectroscopy indicate a reaction of aluminum chloride with vicinal silanol groups at the surface of conditioned MCM-41 and the formation of tetrahedrally coordinated aluminum species bound to chlorine and framework oxygen atoms. In the local structures of 3% of these aluminum atoms, strong Brønsted acid sites are formed causing a ^1H MAS NMR signal at 6.0 ppm. According to ^{13}C MAS NMR spectroscopy of acetone- $2\text{-}^{13}\text{C}$ adsorbed on $\text{AlCl}_3/\text{MCM-41}$ (241 and 245 ppm), these Brønsted acid sites are characterized by an acid strength higher than that of bridging OH groups in H-ZSM-5 (223 ppm).

Introduction

Due to the uniform mesopores and extensive specific surface area of MCM-41,^{1,2} this material has attracted wide attention for applications in chemical technology.³ Unlike zeolites, however, the weak acid strength of hydroxyl groups in MCM-41 limits the application of this material in heterogeneous catalysis. Consequently, much effort has been devoted to introduce strong acid sites into MCM-41 materials.^{4–11}

Very recently, progress has been reached in enhancing the acidity of MCM-41 by modification with aluminum chloride. Ghanbari-Siahkali et al. studied the incorporation of aluminum into MCM-41 material by vapor phase alumination.⁸ Siliceous MCM-41 was modified with aluminum chloride sublimated at 634 K in a stream of nitrogen, then calcined at 773 K and ion-exchanged with ammonium nitrate solution. Compared to the directly synthesized $[\text{Al}]\text{MCM-41}$, a higher catalytic activity in the cracking of triisopropylbenzene was found for the former material. Zhao et al. immobilized aluminum chloride on the mesopores of MCM-41 silica by refluxing it in benzene containing anhydrous aluminum chloride.⁹ A substantial density of acid sites was created, which were catalytically active for liquid-phase isopropylation of naphthalene. Choudhary and Mantri studied the incorporation of tetrahedral aluminum in MCM-41 by refluxing a mixture of siliceous MCM-41 and anhydrous aluminum chloride in carbon tetrachloride, followed by different thermal treatments.¹⁰ In all these approaches, however, preparation and unequivocal identification of the strong Brønsted acid sites in mesoporous material MCM-41 have not been reported.

In this work, siliceous MCM-41 material was modified with aluminum chloride at a temperature of 403 K in a vacuum, avoiding the use of any organic solvents. On this modified MCM-41 material, strong Brønsted acid sites were identified by solid-state NMR spectroscopy.

Experimental Section

Siliceous MCM-41 material was synthesized as described in ref 11, but without addition of sodium aluminate. The template was removed by calcination under flowing air (~ 1000 mL/min) at 823 K. The 3-fold ammonium ion exchange was performed in a 0.1 M aqueous solution of ammonium nitrate at 353 K for 3 h, followed by a calcination at 823 K for 12 h. The MCM-41 was conditioned as described in ref 12, i.e., washed by a 1 M aqueous solution of HCl, deionized water, 30% aqueous solution of H_2O_2 , and deionized water in sequence and dried in a vacuum at 373 K for 18 h (conditioned MCM-41). The modification was performed in a vacuum ($p \leq 10^{-2}$ mbar). Aluminum chloride was put at the bottom of a glass tube with a diameter of 0.4 cm connected with a vacuum line. Above, the same mass of conditioned siliceous MCM-41 material was situated. During the heating of this glass tube at 403 K under vacuum, the aluminum chloride was sublimated into the vapor phase. It slowly diffused upward and reacted with the conditioned MCM-41 material. This thermal treatment was performed for 36 h until no aluminum chloride was left at the bottom of the glass tube. The surplus of aluminum chloride simply passed the MCM-41 powder and condensed in the upper part of the glass tube, which was at room temperature. As determined by AES, the obtained $\text{AlCl}_3/\text{MCM-41}$ material has an aluminum content of 4.8 mmol/g.

NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 MHz for ^1H , 104.2 MHz for ^{27}Al , 100.6 MHz for ^{13}C , and 79.5 MHz for ^{29}Si , respectively. Quantitative ^1H MAS NMR measurements were carried out using an external intensity standard consisting of dehydrated zeolite H,Na-Y (exchange degree of 35%) with a pulse delay of 10 s. To record ^{29}Si CP/MAS NMR spectra, a contact time of 1.5 ms and a repetition time of 5 s were used. ^{13}C CP/MAS NMR measurements were performed with a contact time of 5 ms and a repetition time of 3 s. ^1H , ^{13}C , and ^{29}Si NMR spectra were referenced to TMS (tetramethylsilane), and ^{27}Al NMR shifts were referenced to a 0.5 M aqueous solution of aluminum nitrate. Adsorption of ammonia (0.15 mmol/g) on $\text{AlCl}_3/\text{MCM-41}$ was quantitatively carried out using

* Corresponding author. Fax: +49/711/6584081. E-mail: michael.hunger@po.uni-stuttgart.de.

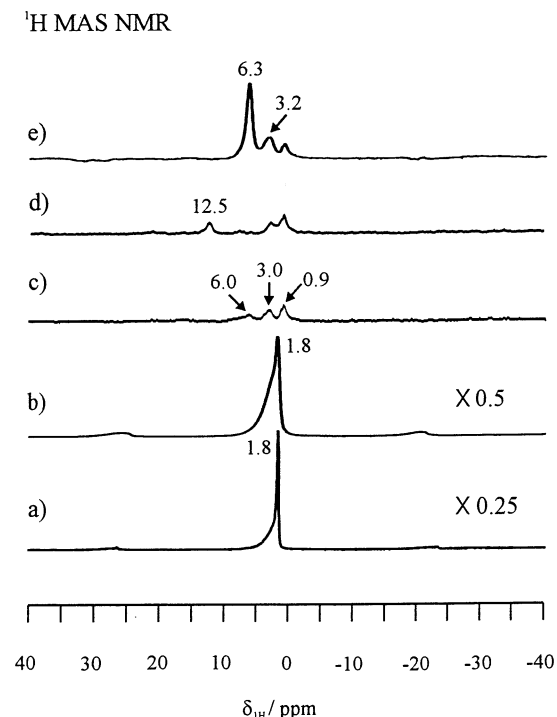


Figure 1. ^1H MAS NMR spectra of dehydrated samples of as-synthesized MCM-41 (a), conditioned MCM-41 (b), $\text{AlCl}_3/\text{MCM-41}$ (c), $\text{AlCl}_3/\text{MCM-41}$ loaded with pyridine- d_5 (d), and $\text{AlCl}_3/\text{MCM-41}$ loaded with ammonia (0.15 mmol/g) (e).

a standard volume connected to a vacuum line. In the case of pyridine- d_5 adsorption (0.10 mmol/g), the sample was evacuated for 60 min after loading the probe molecules at room temperature. Acetone- $2\text{-}^{13}\text{C}$ was quantitatively adsorbed without subsequent evacuation. All loadings of probe molecules and NMR measurements were performed at room temperature.

The results of nitrogen adsorption/desorption experiments, made on a Micrometrics ASAP 2010 instrument, showed a slight decrease of BET surface area after modification, from $1351\text{ m}^2\text{ g}^{-1}$ for the conditioned MCM-41 material to $1088\text{ m}^2\text{ g}^{-1}$ for the $\text{AlCl}_3/\text{MCM-41}$ material, and a decrease of the pore diameter from 25 to 19 nm, respectively, accompanied by a broader pore size distribution. XRD patterns recorded on a Siemens D5000 instrument confirmed the long-range-order in the modified MCM-41 materials.

Results and Discussion

The ^1H MAS NMR spectrum of the as-synthesized and calcined siliceous MCM-41 shown in Figure 1a consists of a single signal at 1.8 ppm and a broad shoulder on the low-field side, which are due to the isolated groups and silanol groups involved in internal hydrogen bondings, respectively. Using an external intensity standard, a SiOH concentration of 5.2 ± 0.5 mmol/g was determined. The conditioning of this material led to an increase of the signal of silanol groups corresponding to a concentration of 7.6 ± 0.7 mmol/g (Figure 1b). This variation of the total SiOH concentration is accompanied by a strong increase of the broad low-field shoulder due to silanol groups involved in internal hydrogen bondings. This is an indication of the formation of neighboring hydroxyl groups such as vicinal silanol groups. After the treatment of the conditioned MCM-41 with aluminum chloride, the ^1H MAS NMR signal of silanol groups at 1.8 ppm disappeared (Figure 1c). As evidenced by ^{29}Si and ^{27}Al NMR spectroscopy and in agreement with the

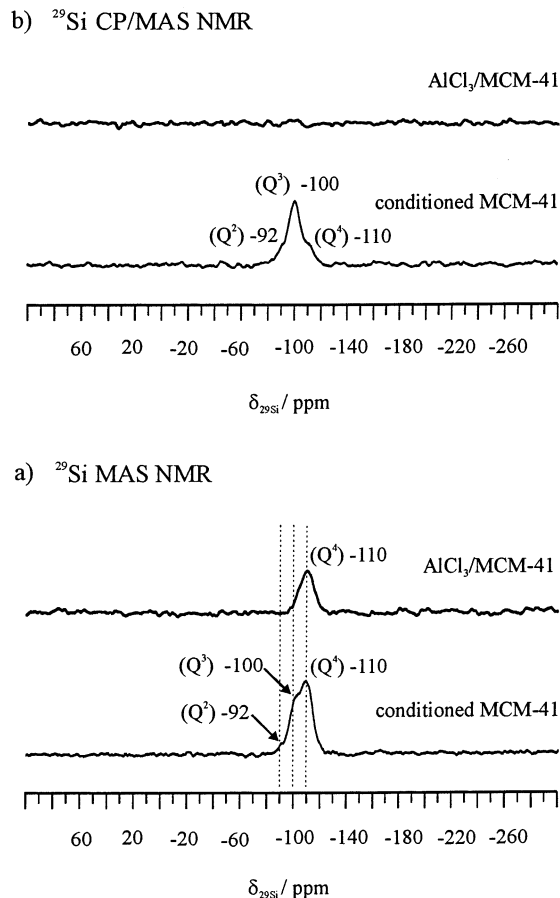


Figure 2. ^{29}Si MAS NMR (a) and CP/MAS NMR spectra (b) of dehydrated samples of the conditioned MCM-41 (bottom) and $\text{AlCl}_3/\text{MCM-41}$ materials (top).

studies of Choudhary and Mantri,¹⁰ this effect is caused by a reaction of the sublimated aluminum chloride with the silanol groups.

The ^{29}Si MAS NMR spectrum of the conditioned MCM-41 shows signals of Q^4 species ($\text{Si}(\text{4OSi})$) at -110 ppm, Q^3 species ($\text{Si}(\text{3OSi}, \text{1OH})$) at -100 ppm, and Q^2 species ($\text{Si}(\text{2OSi}, \text{2OH})$) at -92 ppm (Figure 2a, bottom). In contrast, the spectrum of $\text{AlCl}_3/\text{MCM-41}$ consists only of a broad signal at -110 ppm (Figure 2a, top). Hence, due to the substitution of the hydroxyl protons of silanol groups by aluminum species, the Q^3 and Q^2 species were transformed into Q^4 species appearing at -110 ppm. This finding is supported by the ^{29}Si CP/MAS NMR spectra shown in Figure 2b. Whereas the ^{29}Si CP/MAS NMR spectrum of the conditioned MCM-41 shows a strong signal of Q^3 species at -100 ppm with weak shoulders of Q^2 and Q^4 species at -92 and -110 ppm (Figure 2b, bottom), respectively, no signal was obtained for the $\text{AlCl}_3/\text{MCM-41}$ material (Figure 2b, top). This indicates that most of the silanol groups in the conditioned MCM-41 were removed by the treatment with aluminum chloride.

The conditioning of the parent MCM-41 material with H_2O_2 was found to be an important prerequisite for the formation of strong Brønsted acid sites by the treatment with aluminum chloride. As mentioned above, this conditioning leads preferentially to the formation of vicinal silanol groups. The reaction of aluminum chloride with these vicinal silanol groups causes local structures consisting of surface aluminum atoms bound via at least two oxygen atoms with the MCM-41 framework. This suggestion is supported by the ratio of the numbers of silanol groups (7.6 mmol/g) and aluminum atoms (4.8 mmol/

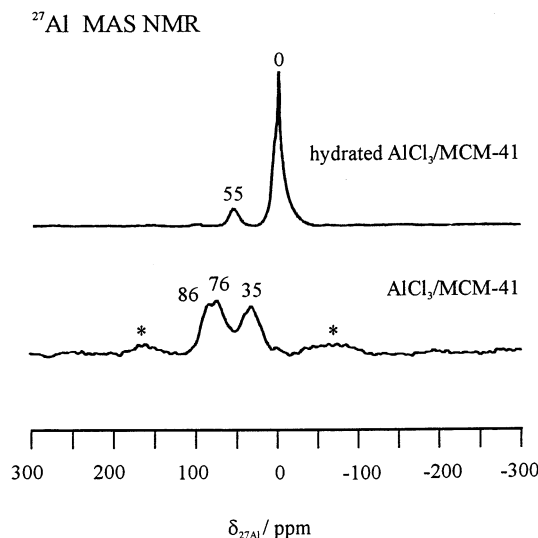
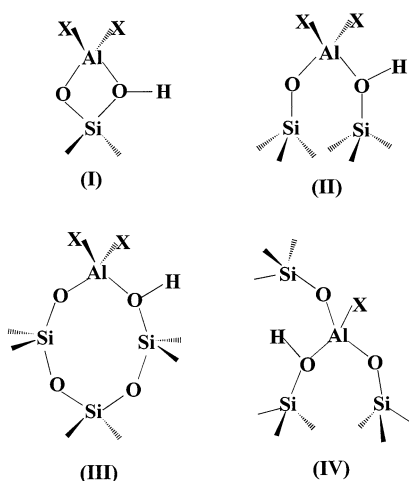


Figure 3. ^{27}Al MAS NMR spectra of $\text{AlCl}_3/\text{MCM-41}$ before (bottom) and after (top) hydration. Asterisks denote spinning sidebands.

CHART 1



g) that react with each other. Due to the fact that only a weak signal of Q^2 silicon species was found in the ^{29}Si MAS NMR spectrum of the conditioned MCM-41, the local structure I in Chart 1 corresponding to a reaction of aluminum chloride with geminal SiOH groups can be neglected. Most of the aluminum atoms should be bound at the MCM-41 surface according to structures II and III in Chart 1. However, also a bonding of a small number of surface aluminum species at the MCM-41 framework according to structure IV in Chart 1 is probable.

^{27}Al MAS NMR spectroscopy allows a direct observation of the aluminum species introduced by treatment of the conditioned MCM-41 material with aluminum chloride. In the ^{27}Al MAS NMR spectrum of the as-modified $\text{AlCl}_3/\text{MCM-41}$ (Figure 3, bottom), signals occur at 86 and 76 ppm, which are tentatively ascribed to tetrahedrally coordinated aluminum species with different local structures. Studying aluminum chloride deposited on silica gel, Drago and co-workers^{13,14} and Xu et al.¹² observed signals at 55–70 ppm assigned to tetrahedrally coordinated aluminum species and suggested the local structures I, II, and III in Chart 1 with $\text{X} = \text{Cl}$. The weak splitting of these signals may be due to different numbers of chlorine atoms in the first coordination sphere.¹⁵ The broad signal occurring in the present study at 35 ppm possibly indicates the formation of hydroxy-chloroaluminum species such as octahedral aluminum atoms coordinated to chlorine atoms as well as hydroxyl groups

($\text{Al}(\text{OH})_6-x\text{Cl}_x$).¹⁴ It is interesting to note that no signal of aluminum chloride (105 ppm) appeared in the ^{27}Al MAS NMR spectrum of $\text{AlCl}_3/\text{MCM-41}$. However, the presence of aluminum species invisible for ^{27}Al MAS NMR spectroscopy cannot be excluded. Upon hydration of $\text{AlCl}_3/\text{MCM-41}$ for 24 h at ambient conditions (Figure 3, top), a small signal appeared at 55 ppm. This signal indicates the presence of aluminum atoms in a tetrahedral oxygen coordination, caused by an incorporation of these species into the MCM-41 framework.¹⁰ A second signal occurring at 0 ppm is assigned to the octahedral aluminum species formed during the hydration process. The local structure IV in Chart 1 is an indispensable step to the formation of framework aluminum species with a tetrahedral oxygen coordination. Upon hydration of $\text{AlCl}_3/\text{MCM-41}$, these aluminum species may be transformed into tetrahedrally coordinated framework aluminum species causing the weak ^{27}Al MAS NMR signal at 55 ppm.

The nature of hydroxyl groups formed on dehydrated $\text{AlCl}_3/\text{MCM-41}$ was studied by ^1H and ^{13}C MAS NMR spectroscopy by applying various probe molecules. The ^1H MAS NMR spectrum of the unloaded $\text{AlCl}_3/\text{MCM-41}$ (Figure 1c) consists of signals at 0.9, 3.0, and 6.0 ppm. The signal at 0.9 ppm is caused by hydroxyl groups connected to aluminum species.¹⁶ A small number of SiOH or AlOH groups involved in hydrogen bondings are responsible for the signal at 3.0 ppm.¹⁶ However, the assignment of the signal at 6.0 ppm required further investigation. Generally, this signal may be due to hydroxyl species involved in hydrogen bondings or to strongly acidic OH groups formed during the treatment of conditioned MCM-41 with aluminum chloride. Modifying conditioned silica gel with aluminum chloride in CCl_4 , Xu et al. prepared strong Brønsted acid sites causing a ^1H MAS NMR signal at 5.7 ppm.¹²

According to the literature,^{17–19} strong Brønsted acid sites in solid catalysts can be identified by adsorption of deuterated pyridine ($\text{pyridine-}d_5$) and ammonia. Because these probe molecules are strong bases, an adsorption at Brønsted acid sites leads to the formation of pyridinium and ammonium ions, respectively. As shown in Figure 1d, after adsorption of $\text{pyridine-}d_5$, the signal at 6.0 ppm disappeared whereas the signals at 0.9 and 3.0 ppm were almost unchanged. Simultaneously, a new signal occurred at 12.5 ppm, due to the formation of pyridinium ions (12–20 ppm).^{16,19} Hence, the signal appearing at 6.0 ppm in the ^1H MAS NMR spectrum of the unloaded $\text{AlCl}_3/\text{MCM-41}$ is caused by strongly acidic hydroxyl groups. Adsorption of 0.15 mmol of ammonia/g of $\text{AlCl}_3/\text{MCM-41}$ leads to a signal of ammonium ions at 6.3 ppm (Figure 1e). Because the signal of physisorbed ammonia molecules occurring at ca. 3.0 ppm increased only slightly,²⁰ the number of Brønsted acid sites responsible for the protonation of adsorbed ammonia is about 0.15 mmol/g.

A more quantitative comparison of the acid strength of Brønsted acid sites formed on $\text{AlCl}_3/\text{MCM-41}$ with that of other solid acids was performed by adsorption of acetone- $2-^{13}\text{C}$.^{21,22} The isotropic chemical shift of the ^{13}C NMR of the carbonyl atoms is sensitive to the interaction between the carbonyl group of the acetone and acid sites. A downfield shift of this ^{13}C NMR signal indicates an interaction of acetone with strong Brønsted acid sites and vice versa. As shown in Figure 4a, the ^{13}C MAS NMR spectrum recorded after loading of $\text{AlCl}_3/\text{MCM-41}$ with 0.15 mmol of acetone- $2-^{13}\text{C}$ /g consists of a signal at 241 ppm with a small shoulder at 245 ppm. The signal at 34 ppm is ascribed to carbon atoms of the methyl groups in acetone. The well-defined sideband pattern indicates the formation of rigidly bound adsorbate complexes. An increase of the acetone loading

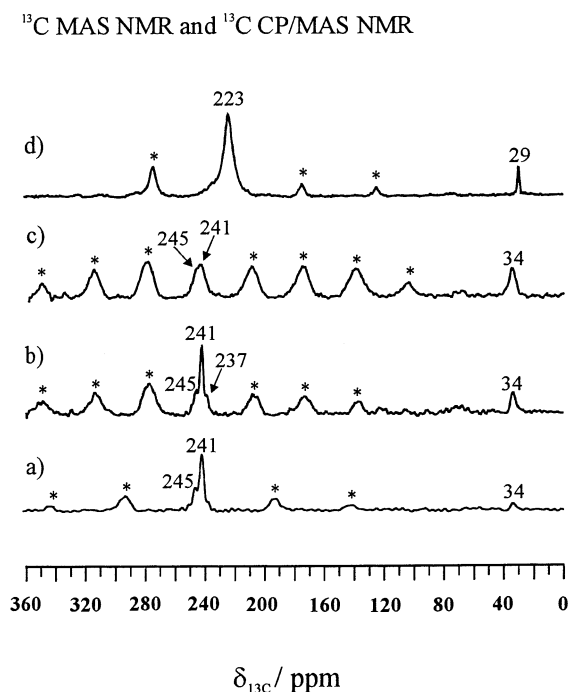


Figure 4. ^{13}C MAS NMR spectra of $\text{AlCl}_3/\text{MCM-41}$ loaded with 0.15 mmol (a) and 0.3 mmol (b) of acetone- $2\text{-}^{13}\text{C}$ per gram. In (c), the ^{13}C CP/MAS NMR spectrum of $\text{AlCl}_3/\text{MCM-41}$ loaded with 0.3 mmol of acetone- $2\text{-}^{13}\text{C}$ per gram is shown. For a comparison, the ^{13}C MAS NMR spectrum of zeolite H-ZSM-5 loaded with 0.4 mmol of acetone- $2\text{-}^{13}\text{C}$ per gram is shown in (d). Asterisks denote spinning sidebands.

to 0.30 mmol/g led to a shoulder at 237 ppm (Figure 4b). However, the latter signal is absent in the spectrum recorded with application of cross polarization (CP/MAS) (Figure 4c). This indicates that the shoulder at 237 ppm is due to acetone molecules adsorbed on Lewis sites, which is supported by studies of Biaglow et al.²³ Therefore, both the ^{13}C CP/MAS NMR signals at 241 and 245 ppm are caused by acetone molecules interacting with Brønsted acid sites. In the study of the silica gel supported aluminum chloride, Xu et al. also reported signals at 242 and 245 ppm, attributed to the interaction of acetone with strong Brønsted acid sites.¹² Compared with acetone adsorbed on acidic zeolites,^{21,22} such as acetone on zeolite H-ZSM-5 with a chemical shift of 223 ppm (Figure 4d), the resonance positions of 241 and 245 ppm of acetone adsorbed on $\text{AlCl}_3/\text{MCM-41}$ indicate a higher acid strength of the Brønsted acid sites in the latter material.

In comparison with the concentration of silanol groups on conditioned MCM-41 (7.6 mmol/g) and with the number of surface aluminum atoms (4.8 mmol/g) introduced by the low-temperature treatment with aluminum chloride in a vacuum, only a small number of strong Brønsted acid sites is formed on $\text{AlCl}_3/\text{MCM-41}$ (ca. 0.15 mmol/g), i.e., in the local structures of 3% of all surface aluminum species. On the basis of quantum-chemical investigations of $\text{H}_7\text{AlSi}_3\text{O}_4\text{Cl}_2$ clusters, which were used to describe the surface sites formed by a treatment of silica gel with aluminum chloride, Xu et al. proposed that strongly acidic bridging OH groups are caused by arrangements with large Al-O(H)-Si angles.¹² These authors suggested a formation of strong Brønsted acid sites at Al-O-Si bridges in the local structure III in Chart 1. Similarly, a bonding of a surface aluminum species on $\text{AlCl}_3/\text{MCM-41}$ via three oxygen bridges (structure IV in Chart 1) would also cause oxygen bridges with large Si-O-Al angles, leading to strong Brønsted acid sites.

Conclusions

The ^{27}Al MAS NMR spectra of the as-modified $\text{AlCl}_3/\text{MCM-41}$ material, prepared by the low-temperature treatment of conditioned MCM-41 with aluminum chloride in a vacuum, indicate the presence of tetrahedrally coordinated aluminum species with different numbers of chlorine atoms in their local structure. The large electron-withdrawing ability of the chlorine atoms enhances the acid strength of the hydroxyl groups existing in their local structures. A weak ^{27}Al MAS NMR signal occurring at 55 ppm in the spectrum of the hydrated $\text{AlCl}_3/\text{MCM-41}$ is caused by aluminum species incorporated into the MCM-41 framework in a tetrahedral oxygen coordination. This may be an indication for a bonding of a small number of surface aluminum atoms of the as-modified $\text{AlCl}_3/\text{MCM-41}$ material via more than two oxygen bridges.

As shown by ^1H MAS NMR spectroscopy, strong Brønsted acid sites are formed on the as-modified $\text{AlCl}_3/\text{MCM-41}$ material. These Brønsted acid sites are able to protonate ammonia and pyridine and cause a low-field shift of the ^{13}C MAS NMR signal of the carbonyl atoms in adsorbed acetone molecules corresponding to a higher acid strength than bridging OH groups in zeolite H-ZSM-5. Because Brønsted acid sites in aluminosilicate materials, such as in zeolites, are directly related to the presence of aluminum atoms in a tetrahedral oxygen coordination, the strong Brønsted acid sites in the $\text{AlCl}_3/\text{MCM-41}$ material may be due to hydroxyl groups in the local structure of tetrahedrally coordinated surface aluminum species bonded to at least one chlorine atom.

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