Angewandte Chemie International Edition

Zeolites

DOI: 10.1002/anie.201004007

Insights into the Dealumination of Zeolite HY Revealed by Sensitivity-Enhanced ^{27}Al DQ-MAS NMR Spectroscopy at High Field**

Zhiwu Yu, Anmin Zheng, Qiang Wang, Lei Chen, Jun Xu, Jean-Paul Amoureux, and Feng Deng**

Zeolites are widely used in various acid-catalyzed reactions (e.g., cracking, disproportionation, isomerization, and alkylation) in the chemical and petrochemical industry due to their peculiar pore structure, strong acidity, and high selectivity.[1–4] Since the catalytic activity and selectivity of dealuminated zeolites are much higher than those of their respective parents, zeolite modification by dealumination has received considerable attention.[5–7] In zeolites, four-coordinate framework aluminum (FAL) is associated with a Brønsted acid site (SiOHAl), while extra-framework aluminum (EFAL) species generated during the dealumination process acts as a Lewis acid site. The existence of EFAL species is crucial for a favorable influence on the catalytic properties of zeolites.[8] Although enormous progress has been made in the studies of the nature of both FAL and EFAL by various methods, including solid-state NMR spectroscopy,[9] X-ray standing waves,[10] X-ray absorption near edge structure,[11] and theoretical calculations,[12] the detailed structure of EFAL species and the spatial proximities (or interactions) of various Al species in dealuminated zeolites are poorly understood. This strongly hampers the understanding of structure–activity relationship in numerous zeolites.

One-dimensional single-pulse ^{27}Al MAS NMR and two-dimensional multiple-quantum magic angle spinning (MQ-MAS) NMR have been used extensively to study the local symmetry and coordination state of aluminum species in zeolites.[13–15] However, both are unable to obtain information on the spatial correlation of different aluminum species. Two-dimensional ^{27}Al double-quantum MAS NMR (DQ-MAS NMR) is a powerful technique for probing aluminum–aluminum proximities in solid materials. However, the ^{27}Al DQ-MAS NMR technique still remains a great challenge because of the quadrupolar nature of the aluminum nucleus ($I = 5/2$), which leads to low efficiency of DQ excitation ($< 5\%$). So far, the ^{27}Al DQ-MAS NMR technique has been successfully applied to systems with high Al content, such as aluminophosphate molecular sieves,[16–18] glasses,[19] and minerals,[20] but for aluminosilicate zeolites with low Al content, the technique was less successful due to its extremely low sensitivity.[21]

Homonuclear dipolar recoupling of quadrupolar nuclei under MAS is difficult because of the intricate nuclear spin dynamics of the quadrupolar nuclei in the presence of an rf field and sample rotation. Mali et al. first demonstrated that the rotary resonance recoupling (R^3) technique with HORROR condition[22] can be used for DQ recoupling of half-integer quadrupolar nuclei.[16,23] As an improvement, Edén et al. then showed that symmetry-based pulse sequences display superior rf error tolerance than HORROR recoupling, and these sequences were incorporated into DQ-MAS experiments.[17,20] Recently, we developed a new homonuclear ^{27}Al DQ-MAS NMR correlation method based on the rotor-synchronized and symmetry-based $BR2_2^1$ pulse sequence and achieved a two- to threefold sensitivity enhancement (Supporting Information, Figure S1).[24] We have now employed this sensitivity-enhanced ^{27}Al DQ-MAS NMR technique at high field (18.8 T) to study the evolution of EFAL species in HY zeolite with dealumination temperature. On the basis of the ^{27}Al NMR experimental results, a new dealumination mechanism is proposed, which was further supported by DFT calculations.

Figure 1 shows the ^{27}Al MAS and ^{27}Al DQ-MAS NMR spectra of parent HY and HY zeolites calcined at 500, 600, and 700 °C (denoted HY-500, HY-600, and HY-700, respectively). For the parent HY, only one signal at 61 ppm due to four-coordinate FAL is observable in the ^{27}Al MAS NMR spectrum (Figure 1a). The signal exhibits a single auto-correlation peak (on the diagonal) at (61, 122) ppm in the ^{27}Al DQ-MAS NMR spectrum, which indicates that these four-coordinate FAL species, which are associated with bridging hydroxyl groups (SiOHAl, Brønsted acid site), are in close proximity to one another. For the HY-500 zeolite, an additional peak at $\delta = 0$ ppm due to six-coordinate Al appears in the ^{27}Al MAS NMR spectrum (Figure 1b). Besides two auto-correlation peaks at (61, 122) and (0, 0) ppm, one cross-peak pair at (61, 61) and (0, 61) ppm is observed in the ^{27}Al DQ-MAS NMR spectrum (Figure 1b), corresponding to spatial proximity between the four-coordinate FAL and the

---

[*] Z. W. Yu, Dr. A. M. Zheng, Q. Wang, Dr. L. Chen, Dr. J. Xu, Dr. F. Deng
State Key Laboratory Magnetic Resonance and Atomic Molecular Physics, Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences
Wuhan 430071 (P. R. China)
Fax: (+86) 27-8719-9291
E-mail: dengf@wipm.ac.cn

Prof. J. P. Amoureux
Batiment C7, ENSCL Lille-1 University
Villeneuve d'Ascq 59652 (France)
Fax: (+33) 320-43-6814
E-mail: jean-paul.amoureux@univ-lille1.fr

[**] This work was supported by the National Natural Science Foundation of China (Grants 20933009, 20921004, and 20773159) and the Ministry of Science and Technology of China (2009IM030700). Financial support from the TGE RMN THC Fr3050 for conducting research is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004007.

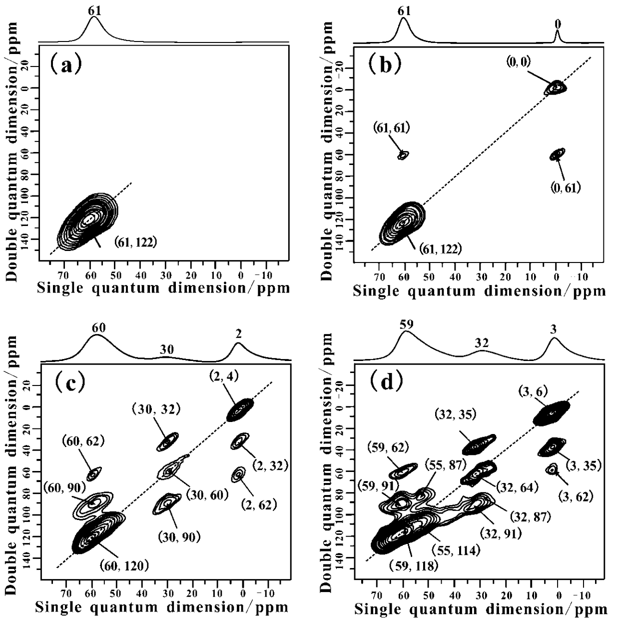
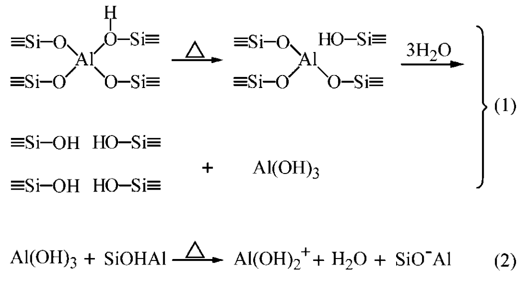


Figure 1. ^{27}Al MAS and DQ-MAS NMR spectra of a) parent HY, b) HY-500, c) HY-600, and d) HY-700 zeolites. One-dimensional ^{27}Al MAS spectra are plotted on top of the two-dimensional ^{27}Al DQ MAS spectra. All spectra were recorded on hydrated samples at 18.8 T with a 3.2 mm probe at a sample rotation rate of 21.5 kHz. About 45 h were required to record one ^{27}Al DQ-MAS NMR spectrum.

six-coordinate Al. As revealed by previous research,[25,26] during the initial stage of the dealumination of zeolite Y, three-coordinate FAL in the vicinity of an SiOH group is formed due to breaking of framework Si-O-Al bridges (see step 1 in Scheme 1), and it can host water molecules, which give rise to octahedrally coordinated Al species at about 0 ppm. Adsorption of ammonia can convert the coordination of the Al species from octahedral to tetrahedral, which is accompanied by a subsequent healing of the framework Si-O-Al bridges. Increasing the degree of dealumination of zeolite Y causes successive hydrolysis of three-coordinate FAL and subsequent formation of extra-framework octahedral Al species, such as $Al(OH)_3$ (see step 1 in Scheme 1).[9,27] The existence of $Al(OH)_3$ EFAL species in dealuminated HY zeolite was confirmed by our previous ^1H DQ-MAS NMR experiments and DFT calculations.[28] Here we also recorded ^{27}Al, ^{29}Si, and ^1H MAS NMR spectra of the dealuminated HY zeolites before and after adsorption of ammonia (Supporting Information, Figures S2–S4 and Table S1). Partial conversion of Al coordination from octahedral to tetrahedral and partial healing of the framework Si-O-Al bridges after adsorption of ammonia are observed by ^{27}Al MAS NMR and ^1H MAS NMR, respectively. Based on the NMR results, we conclude that besides the six-coordinate EFAL species, such as $Al(OH)_3{\cdot}3H_2O$, three-coordinate FAL species with three adsorbed water molecules may also contribute to the signal at $\delta = 0$ ppm.



Scheme 1. Proposed dealumination mechanism of zeolite HY.

On further increasing the calcination temperature to 600 °C, apart from the two signals from four-coordinate FAL and six-coordinate Al, a new signal at about $\delta = 30$ ppm due to five-coordinate EFAL is visible in the ^{27}Al MAS spectrum (Figure 1 c).[30,31] Interestingly, the signal at about $\delta = 30$ ppm remains almost unchanged after adsorption of ammonia (Supporting Information, Figure S3), and this implies that it should be associated with EFAL species. Since the four-coordinate FAL (SiOHAl) is in close proximity to the six-coordinate EFAL species $Al(OH)_3$ (see Figure 1 b), it is reasonable to expect that the acidic nature of the former and the basic nature of the latter would lead to easy elimination of a water molecule between them on further increasing the calcination temperature to 600 °C (see step 2 in Scheme 1) with formation of $Al(OH)_2^+$, which gives rise to the signal at $\delta = 30$ ppm. The existence of this EFAL species was also proposed by Hunger et al.[25] In the ^{27}Al DQ-MAS spectrum of HY-600 (Figure 1 c), besides three diagonal peaks, three distinct cross-peak pairs between: 1) four-coordinate FAL and five-coordinate EFAL ((60, 90), (30, 90) ppm), 2) four-coordinate FAL and six-coordinate Al ((60, 62), (2, 62) ppm), and 3) five-coordinate EFAL and six-coordinate Al ((30, 32), (2, 32) ppm) are present, that is, the three kinds of aluminum species are in close proximity one another. It is noteworthy that the cross-peak pair ((60, 90), (30, 90) ppm) between the four-coordinate FAL (SiOHAl) and the five-coordinate EFAL ($Al(OH)_2^+$) are most intense, which implies that the distance between these two species is the shortest. Further increasing the calcination temperature may readily result in removal of another molecule of water between them.

For the HY-700 zeolite, the four-coordinate FAL signal at $\delta = 59$ ppm becomes broadened and exhibits an unsymmetrical line shape in the ^{27}Al MAS spectrum (Figure 1 d). The existence of a new signal at about $\delta = 55$ ppm is confirmed by ^{27}Al triple-quantum MAS spectra (Figure 2). According to its chemical shift and following theoretical calculation, we can assign this signal to four-coordinate EFAL species $AlOH^{2+}$, which is formed by elimination of one water molecule between SiOHAl and $Al(OH)_2^+$ (see step 3 in Scheme 1). Compared with the ^{27}Al DQ-MAS NMR spectrum of HY-600 zeolite (Figure 1 c), a new strong cross-peak pair at (55, 87) and (32, 87) ppm is observed in this case (Figure 1 d), which suggests spatial proximity between the four-coordinate EFAL species $AlOH^{2+}$ and the five-coordinate EFAL species $Al(OH)_2^+$. In addition, a cross-peak at (55, 114) ppm corresponds to spatial correlation between the four-coordinate

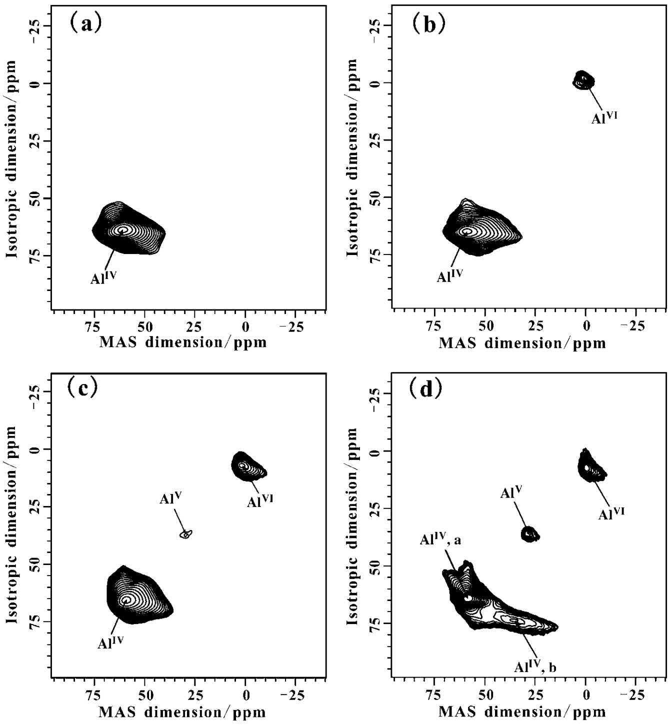


Figure 2. ^{27}Al triple-quantum MAS spectra of a) HY, b) HY-500, c) HY-600, and d) HY-700 zeolites, recorded on hydrated samples at 9.4 T.

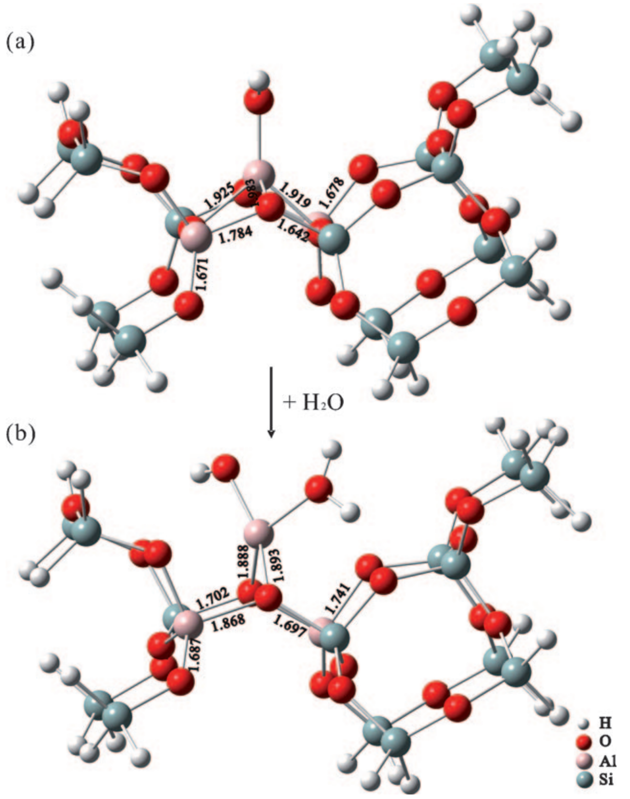


Figure 3. Optimized geometries of EFAL species $AlOH^{2+}$ (a) and $AlOH^{2+}$-H_2O (b) coordinated to the oxygen atom near the framework Al in HY zeolite. Selected interatomic distances [Å] are indicated.

FAL (SiOHAl) and four-coordinate EFAL ($AlOH^{2+}$) species. Interestingly, the $AlOH^{2+}$ species exhibits no spatial correlation with the six-coordinate Al. Clearly, two-dimensional ^{27}Al DQ-MAS NMR experiments are capable of revealing the detailed spatial correlations among various aluminum species in hydrated HY zeolites with different extents of dealumination. Note that it is impossible to determine where the EFAL species are located in dealuminated HY zeolite by the ^{27}Al DQ-MAS NMR experiment. However, the location of the EFAL species could be determined by ^{1}H DQ-MAS NMR experiment.[28] It was found that a small amount (5.5–11 %) of the EFAL species are located in the sodalite cages of HY zeolites calcined at different temperatures (500, 600, and 700 °C).[29] Recently, in situ XRD experiments also showed that the EFAL species enter the sodalite cages.[11]

Based on the ^{27}Al NMR experimental results, a dealumination mechanism with evolution of EFAL species is proposed in Scheme 1. To confirm this proposed dealumination mechanism, we performed quantum chemical calculations to obtain detailed structural information on the EFAL species in hydrated HY zeolites. On the basis of the ^{27}Al DQ-MAS NMR data, all of the EFAL species are in close proximity to FAL. Thus, we optimized the structures (Figure 3 and Supporting Information, Figures S5 and S6) of the three EFAL species (i.e., $Al(OH)_3$, $Al(OH)_2^{+}$ and $AlOH^{2+}$) connected to the oxygen atom near the framework Al of HY zeolite and then calculated the ^{27}Al chemical shift of the corresponding system. In the calculations, water molecules were allowed to coordinate to the EFAL species. Our DFT calculations indicate that hydration would only change the coordination number rather than the structure of EFAL species. For example, in the dehydrated state, the $AlOH^{2+}$ species is located near the center of four-membered ring and is coordinated to four framework oxygen atoms (Figure 3 a). In this case, the four Al–O distances in the coordination complex are about 1.9 Å, slightly longer than the framework Al–O bond (ca. 1.8 Å), that is, the $AlOH^{2+}$ species is tightly coordinated with the zeolite framework and has fivefold oxygen coordination. This is in agreement with previous ^{27}Al NMR observations in which Jiao et al. found that the appearance of ^{27}Al signal at about $\delta = 35$ ppm could be an indication of fivefold oxygen coordination of EFAL species.[31] After adsorption of a water molecule (Figure 3 b), the $AlOH^{2+}$ species moves away from the center of the four-membered ring, although it is still coordinated to two framework oxygen atoms. In this case, the coordination of the $AlOH^{2+}$ species becomes tetrahedral. Similarly, for the other two EFAL species, $Al(OH)_3$ and $Al(OH)_2^{+}$, adsorption of water molecules changes the coordination number from four to six and five, respectively (Supporting Information, Figures S5 and S6). On the basis of the optimized structure, the ^{27}Al NMR chemical shifts of both FAL and EFAL species were calculated (Table 1). Their excellent agreement with the corresponding experimental ^{27}Al NMR data supports the proposed dealumination mechanism of zeolite HY.

In summary, the results present herein show the power of sensitivity-enhanced ^{27}Al DQ-MAS NMR spectroscopy at high field, which is capable of revealing detailed spatial correlations among various aluminum species in zeolites, and

Table 1: Calculated and experimental ^{27}Al chemical shifts[a] [ppm]

Hydrated EFAL species	Chemical shift of EFAL species		Chemical shift of FAL species[b]		Coordination state of EFAL species
	calcd	exptl	calcd	exptl	
$Al(OH)_3$	7	ca. 4	61	62.5	six-coordinate
$Al(OH)_2^+$	35	ca. 34	64	62.5	five-coordinate
$AlOH^{2+}$	58	58.6	63	61.1	four-coordinate

[a] All ^{27}Al chemical shifts are isotropic chemical shifts, and the experimental values were obtained from the ^{27}Al triple-quantum MAS NMR spectra (Supporting Information, Table S2). [b] In the presence of the EFAL species nearby (Figure 3 and Supporting Information, Figures S5 and S6).

is expected to be applicable to other Al-containing solid functional materials (e.g., minerals, ceramics, glasses, catalysts). Based on our experimental and theoretical results, we propose a new dealumination mechanism. In particular, the nature and the configuration of EFAL species are rather different for samples modified at different calcination temperatures. Further work on a wider range of zeolite topologies and with varying Si/Al ratios is currently underway. The main limitation of the present DQ-MAS NMR method remains its weak sensitivity, and this method would presently be difficult to apply to dehydrated zeolites, as the quadrupolar interactions are too large (Supporting Information, Figure S7). However, the sensitivity of the present ^{27}Al DQ-MAS NMR method may be increased in the future by using higher-field magnets, better recoupling pulse sequences, and/or the dynamic nuclear polarization technique.

Experimental Section

Parent HY and dealuminated HY zeolites were prepared as described in references [28,29].

^{27}Al MAS and ^{27}Al DQ-MAS NMR experiments were carried out on a Bruker AVANCE III 800 spectrometer at a resonance frequency of 208.6 MHz with a 3.2 mm HXY triple-resonance MAS probe at a sample spinning rate of 21.5 kHz. The chemical shift of ^{27}Al was referenced to 1 M aqueous $Al(NO_3)_3$. ^{27}Al MAS NMR spectra were recorded by small-flip-angle technique with a pulse length of 0.5 μs ($<\pi/12$) and a recycle delay of 1 s. A CT-selective $\pi/2$ pulse of 19 μs and π pulse of 38 μs were used for the DQ-MAS experiments, and the signal sensitivity was enhanced by initiating each transient by the FAM scheme.[32] DQ coherences were excited and reconverted by using the BR2_2^1 pulse sequence[24] with $\tau_{exc} = \tau_{rec} = 1116.30$ μs, following the general scheme of 2D multiple-quantum spectroscopy of dipolar-coupled quadrupolar spins. The rotor-synchronized increment interval in the indirect dimension was set to 46.51 μs, and the two-dimensional data sets consisted of $30\,t_1 \times 400\,t_2$ points. 13056, 14080, 13056, and 12032 FIDs were acquired for each t_1 increment with a recycle delay of 0.4 s for HY, HY-500, HY-600, and HY-700 respectively.

^{27}Al triple-quantum MAS NMR experiments were performed on a Varian Infinity-plus 400 spectrometer by using Z-filtering[33] and hyper-complex acquisition scheme on a 4 mm double-resonance probe at a sample spinning rate of 15 kHz. The pulse durations were set to 3.8 and 1.3 μs for the first and the second hard pulses, respectively, and 20 μs for the third CT-selective $\pi/2$ pulse. Two-dimensional data sets consisted of $64\,t_1 \times 512\,t_2$ points. 480, 1200, 2400, and 4800 FIDs were acquired for each t_1 increment with a recycle delay of 0.5 s for HY, HY-500, HY-600, and HY-700 samples, respectively.

Received: July 1, 2010
Revised: August 11, 2010
Published online: October 7, 2010

Keywords: aluminum · dealumination · density functional calculations · NMR spectroscopy · zeolites

---

[1] B. Smit, T. L. M. Maesen, *Nature* **2008**, *451*, 671.
[2] J. Huang, Y. J. Jiang, V. R. R. Marthala, M. Hunger, *J. Am. Chem. Soc.* **2008**, *130*, 12642.
[3] R. Rachwalik, Z. Olejniczak, J. Jiao, J. Huang, M. Hunger, B. Sulikowski, *J. Catal.* **2007**, *252*, 161.
[4] A. Feller, A. Guzman, I. Zuazo, J. A. Lercher, *J. Catal.* **2004**, *224*, 80.
[5] S. J. DeCanio, J. R. Sohn, P. O. Fritz, J. H. Lunsford, *J. Catal.* **1986**, *101*, 132.
[6] R. López-Fonseca, J. I. Gutiérrez-Ortiz, M. A. Gutiérrez-Ortiz, J. R. González-Velasco, *J. Catal.* **2002**, *209*, 145.
[7] J. Kanellopoulos, A. Unger, W. Schwieger, D. Freude, *J. Catal.* **2006**, *237*, 416.
[8] a) M. J. Remy, D. Stanica, G. Poncelet, E. J. P. Feijen, P. Grobet, *J. Phys. Chem.* **1996**, *100*, 12440; b) M. A. Kuehne, H. H. Kung, J. T. Miller, *J. Catal.* **1997**, *161*, 338.
[9] B. H. Wouters, T. H. Chen, P. J. Grobet, *J. Am. Chem. Soc.* **1998**, *120*, 11419.
[10] J. A. van Bokhoven, T. L. Lee, M. Drakopoulos, C. Lamberti, S. Thie, J. Zegenhagen, *Nat. Mater.* **2008**, *7*, 551.
[11] G. Agostini, C. Lamberti, L. Palin, M. Milanesio, N. Danilina, B. Xu, M. Janousch, J. A. van Bokhoven, *J. Am. Chem. Soc.* **2010**, *132*, 667.
[12] a) U. Eichler, M. Brandle, J. Sauer, *J. Phys. Chem. B* **1997**, *101*, 10035; b) D. L. Bhering, A. Ramirez-Solis, C. J. A. Mota, *J. Phys. Chem. B* **2003**, *107*, 4342.
[13] Y. Cai, R. Kumar, W. Huang, B. G. Trewyn, J. W. Wiench, M. Pruski, V. S.-Y. Lin, *J. Phys. Chem. C* **2007**, *111*, 1480.
[14] S. Antonijevic, S. E. Ashbrook, S. Biedasek, R. I. Walton, S. Wimperis, H. X. Yang, *J. Am. Chem. Soc.* **2006**, *128*, 8054.
[15] S. Stepan, J. Dedecek, C. B. Li, B. Wichterlova, V. Gabova, M. Sierka, J. Sauer, *Angew. Chem.* **2007**, *119*, 7424; *Angew. Chem. Int. Ed.* **2007**, *46*, 7286.
[16] a) G. Mali, F. Taulelle, *Chem. Commun.* **2004**, 868; b) G. Mali, G. Fink, F. Taulelle, *J. Chem. Phys.* **2004**, *120*, 2835.
[17] M. Edén, D. Zhou, J. H. Yu, *Chem. Phys. Lett.* **2006**, *431*, 397.
[18] C. M. Morais, V. Montouillout, M. Deschamps, D. Luga, F. Fayon, F. A. A. Paz, J. Rocha, C. Fernandez, D. Massiot, *Magn. Reson. Chem.* **2009**, *47*, 942.
[19] a) S. K. Lee, M. Deschamps, J. Hiet, D. Massiot, S. Y. Park, *J. Phys. Chem. B* **2009**, *113*, 5162; b) Y. H. Lo, M. Eden, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6635.
[20] M. Edén, H. Annersten, A. Zazzi, *Chem. Phys. Lett.* **2005**, *410*, 24.
[21] N. Malicki, G. Mali, A. A. Quoineaud, P. Bourges, L. J. Simon, F. Thibault-Starzyk, C. Fernandez, *Microporous Mesoporous Mater.* **2010**, *129*, 100.
[22] T. G. Oas, R. G. Griffin, M. H. Levitt, *J. Chem. Phys.* **1988**, *89*, 692.
[23] G. Mali, V. Kaucic, *J. Magn. Reson.* **2004**, *171*, 48.
[24] Q. Wang, B. Hu, O. Lafon, J. Trébosc, F. Deng, J. P. Amoureux, *J. Magn. Reson.* **2009**, *200*, 251.
[25] S. Altwasser, J. Jiao, S. Steuernagel, J. Weitkamp, M. Hunger, *Stud. Surf. Sci. Catal.* **2004**, *154*, 3098.
[26] J. A. van Bokhoven, Ad. M. J. Van der Eerden, D. C. Koningsberge, *J. Am. Chem. Soc.* **2003**, *125*, 7435.

[27] Q. L. Wang, G. Giannetto, M. Torrealba, G. Perot, C. Kappenstein, M. Guisnet, *J. Catal.* **1991**, *130*, 459.
[28] S. H. Li, A. M. Zheng, Y. C. Su, H. L. Zhang, L. Chen, J. Yang, C. H. Ye, F. Deng, *J. Am. Chem. Soc.* **2007**, *129*, 11161.
[29] S. H. Li, S. J. Hung, W. L. Shen, H. L. Zhang, H. J. Fang, A. M. Zheng, S. B. Liu, F. Deng, *J. Phys. Chem. C* **2008**, *112*, 14486.
[30] C. A. Fyfe, J. L. Bretherton, L. Y. Lam, *J. Am. Chem. Soc.* **2001**, *123*, 5285.
[31] J. Jiao, J. Kanellopoulos, W. Wang, S. S. Ray, H. Foerster, D. Freude, M. Hunger, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3221.
[32] P. K. Madhu, A. Goldbourt, L. Frydman, S. Vega, *Chem. Phys. Lett.* **1999**, *307*, 41.
[33] J. P. Amoureux, C. Fernandez, S. Steuernagel, *J. Magn. Reson. Ser. A* **1996**, *123*, 116.