from the refined effective number of electrons at each T site by taking advantage of the high contrast between the scattering powers of Si and Ge.

Solid state NMR spectroscopy: The spectra were recorded under magic angle spinning (MAS) at room temperature. ^{19}F spectra were was measured in a Bruker Av-400 spectrometer at 376.8 MHz in 2.5 mm diameter zirconia rotors at spinning rate of 30 kHz. The ^{19}F spectra were collected using pulses of 3 μs corresponding to a magnetization flip angle of $\pi/2$ rad and a recycle delay of 100 s to ensure the complete recovery of the magnetization. The ^{19}F spectra were referred to $CFCl_3$.

Computational chemistry: methodology and model. All calculations were performed using lattice-energy minimization techniques and the GULP code,[14] employing the Ewald method for summation of the long-range Coulombic interactions, and direct summation of the short-range interactions with a cutoff distance of 12 Å. The RFO (rational function optimiser) technique was used as the cell minimization scheme with a convergence criterion of a gradient norm below 0.001 eV Å^{-1}. The empirical shell model forcefield for zeolites[15] was used throughout, with the inclusion of the forcefields for Ge[16] and F[17] atoms. The force-fields by Kiselev et al.,[18] and by Oie et al.[19] were used for the SDA–zeolite and SDA–SDA interactions, respectively. In the organic SDA, the charge distribution has been obtained by means of the quantum chemistry Hartree–Fock method by using a 6-31G** basis set and the calculations have been performed by means of the NWCHEM package.

Received: May 22, 2002
Revised: September 24, 2002 [Z19356]

[1] J. A. Rabo, P. H. Kasai, *Prog. Solid State Chem.* **1975**, *9*, 1.
[2] D. Barthomeuf, *J. Phys. Chem.* **1979**, *83*, 249.
[3] P. A. Jacobs, *Catal. Rev. Sci. Eng.* **1982**, *24*, 415.
[4] R. F. Lobo, S. I. Zones, M. E. Davis, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *21*, 47.
[5] A. Corma, M. J. Díaz-Cabañas, V. Fornés, *Angew. Chem.* **2000**, *112*, 2436; *Angew. Chem. Int. Ed.* **2000**, *39*, 2346.
[6] T. Blasco, A. Corma, M. J. Diaz-Cabañas, F. Rey, J. A. Vidal-Moya, C. M. Zicovich-Wilson, *J. Phys. Chem. B* **2002**, *106*, 2634.
[7] a) C. Baerlocher, W. M. Meier, D. H. Olson, *Atlas of Zeolite Framework Types*. 5th revised edition, Elsevier, Amsterdam, **2001**. Also in http://www.iza-structure.org/; b) T. Conradsson, M. S. Dadachov, X. D. Zou, *Microporous Mesoporous Mater.* **2000**, *41*, 183.
[8] a) A. Corma, M. T. Navarro, F. Rey, J. Rius, S. Valencia, *Angew. Chem.* **2001**, *113*, 2337; *Angew. Chem. Int. Ed.* **2001**, *40*, 2277; b) A. Corma, M. T. Navarro, F. Rey, S. Valencia, *Chem. Commun.* **2001**, 1486.
[9] P. Caullet, J. L. Guth, J. Hazm, J. M. Lamblin, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 359.
[10] L. A. Villaescusa, P. A. Barrett, M. A. Camblor, *Angew. Chem.* **1999**, *111*, 2164; *Angew. Chem. Int. Ed.* **1999**, *38*, 1997.
[11] A. Corma, M. J. Díaz-Cabañas, J. Martínez-Triguero, F. Rey, J. Rius, *Nature* **2002**, *418*, 514.
[12] J. Rius, J. L. Jordá, AJUST/01, Institut de Ciència de Materials de Barcelona (CSIC).
[13] J. Rodríguez-Carvajal, T. Roisnel, FULLPROF 98 and WinPLOTR: New Windows 95/NT Applications for Diffraction Commission For Powder Diffraction, International Union for Crystallography, Newletter No. 20 (May-August) **1998**.
[14] J. D. Gale, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 629.
[15] R. A. Jackson, C. R. A. Catlow, *Mol. Simul.* **1988**, *1*, 207.
[16] G. Sastre, J. D. Gale, *Chem. Mater.*, submitted.
[17] A. R. George, C. R. A. Catlow, *Zeolites* **1997**, *18*, 67.
[18] A. V. Kiselev, A. A. Lopatkin, A. A. Shulga, *Zeolites* **1985**, *5*, 261.
[19] T. Oie, T. M. Maggiora, R. E. Christoffersen, D. J. Duchamp, *Int. J. Quantum Chem. Quantum Biol. Symp.* **1981**, *8*, 1.
[20] G. Sastre, J. D. Gale, *Microporous Mesoporous Mater.* **2001**, *43*, 27.

Solid-State NMR Studies of MCM-41 Supported with a Highly Catalytically Active Cluster**

Matthew D. Jones, Melinda J. Duer,*
Sophie Hermans, Yaroslav Z. Khimyak,
Brian F. G. Johnson, and John Meurig Thomas

In 1992, Beck et al.[1] reported the first synthesis of a new classification of silicate/aluminosilicate materials. The topic of this work, MCM-41, is one such member of this extensive family of mesoporous materials.[1] The high surface area, typically up to 1000 $m^2 g^{-1}$, and the high concentration of silanol groups has led to the exploitation of this material as a support for anchored catalysts, in particular the highly promising catalysts derived from bimetallic clusters.[2,3] Bimetallic nanoparticles are becoming increasingly important in modern heterogeneous catalysis,[4] because of enhanced catalytic activity arising from the synergetic effects between the two metallic moieties. Further enhancement of activity is brought about by the small size of the particles. Recently, highly effective hydrogenation catalysts based on bimetallic clusters encapsulated in the channels of MCM-41 have been developed.[3,5–7] For example, the nanocatalyst derived from the cluster $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ is highly effective in the conversion of naphthalene to *cis*-decalin under mild conditions.[7] The formation of these nanocatalysts involves first the deposition of the anionic cluster within the pores of MCM-41 followed by removal of CO ligands, which produces the supported "naked" nanoparticles. Significantly, we have been able to establish, by FT-IR and EXAFS spectroscopy, that the structural motif of the cluster is maintained in the mesopore.[7,8] The further development of these very important catalytic systems depends crucially on understanding how the clusters are supported in the mesopore. We have recently completed a study which demonstrates the importance of the counterion in the binding process. We show that the counterion is intrinsically linked to the walls of the mesopore, acting like a molecular "glue" binding the cluster.

In particular we have studied the interactions between the surface of MCM-41 and the highly effective catalyst derived from the $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ cluster, by solid-state NMR spectroscopy. We have used $^{29}Si\{^1H\}$ cross polarization (CP)

[*] Dr. M. J. Duer, M. D. Jones, Dr. S. Hermans, Dr. Y. Z. Khimyak, Prof. B. F. G. Johnson
Department of Chemistry
University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44) 1223-336017
E-mail: mjd13@cam.ac.uk
Prof. Sir J. M. Thomas
The Royal Institution of Great Britain
Davy Faraday Research Laboratory
21 Albermarle Street, London W1X 4BS (UK)

[**] We thank the EPSRC for a studentship to M.D.J. and for their general financial support, ICI for financial support, Newnham College Cambridge for a research fellowship to S.H., and an Oppenheimer Research Fellowship for Y.K.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  0044-8249/02/4124-4726 $ 20.00+.50/0

magic angle spinning (MAS) for the main characterization. This selects the ^{29}Si sites that are close to the silanol groups, that is, predominantly ^{29}Si sites on the MCM-41 channel surfaces. A ^{1}H–^{29}Si two-dimensional heteronuclear correlation (HETCOR) experiment and $^{13}C\{^{1}H\}$ CP/MAS gives a compelling picture of the nature of the counterion binding. The combined results of these experiments leads to unusually detailed conclusions about the location and structure of the deposited cluster in MCM-41, which raises new questions about the possible catalytic activity of a catalyst formed in this way.

Initial $^{29}Si\{^{1}H\}$ CP/MAS NMR studies on freshly prepared dehydrated MCM-41 yielded three distinct Gaussian peaks (Figure 1) with centers at $\delta = -91$ ppm, $Si(OSi)_2(OH)_2$, (Q^2), $\delta = -100$ ppm, $Si(OSi)_3OH$, (Q^3), and $\delta = -109$ ppm $Si(OSi)_4$, (Q^4), wholly consistent with literature data.[9,10]

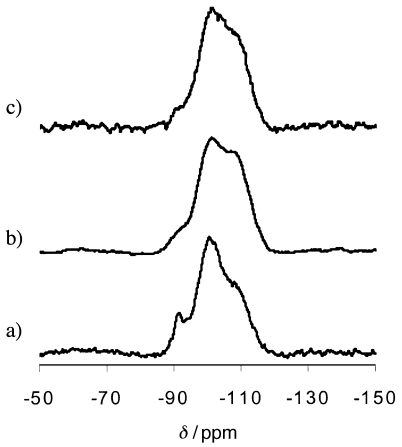


Figure 1. $^{29}Si\{^{1}H\}$ CP/MAS spectra: a) calcined dehydrated MCM-41 (6000), b) fuctionalized with $[Pd_6Ru_6(CO)_{24}]NEt_4]_2$ (6708), and c) activated cluster on MCM-41 (6116). Contact time = 8 ms and a recycle delay of 8 s. Spinning rate = 4 kHz. Numbers in brackets represent the number of scans taken per spectrum.

Deposition of $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ within the channels reduces the relative intensity of the signals from the Q^2 and Q^3 sites compared with the Q^4, as indicated by the ^{29}Si CP/MAS NMR spectra recorded under the same experimental conditions (Figure 1). We have also studied the catalytically active species, generated by removing the protective CO ligand sheath by gentle thermolysis in a vacuum.[6] This process is known from previous studies to form discrete bimetallic particles highly dispersed on the internal surface of MCM-41.[3,8] Comparison of the spectra in Figure 1 shows that the change in the relative intensity of the Q^2/Q^3/Q^4 peaks upon forming the "naked" metallic particle is not substantial. The elemental analysis of the activated and nonactivated forms are given in the Experimental Section. They show that a significant amount of the counterion is still present after the thermal treatment; this might explain why there is no significant change once activated.

The peak intensity of a cross polarization (CP) spectrum depends not only on the occupancy of ^{29}Si sites but on cross polarization dynamics. The CP dynamics are affected by changes in the structure and number of ^{1}H sites in close proximity to the ^{29}Si site as well as by any molecular motion in the system. CP/MAS ^{29}Si spectra were recorded for contact times in the range 0.5–15.0 ms for both pure MCM-41 and MCM-41 deposited with $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$. The CP dynamic curves for the two systems (Figure 2) were fitted according to Equation (1).[11,12]

The curves show a significant change in the $^{29}Si\{^{1}H\}$ CP/MAS dynamics once the MCM-41 is impregnated with the cluster. In particular, the rate of cross polarization transfer increases dramatically for the Q^4 site, and both Q^2 and Q^3 curves show pronounced ^{1}H $T_{1\rho}$ relaxation effects, which are not observed for the pure MCM-41. For the Q^3 sites the parameter T_{cp} changes from 1.2 ms for MCM-41 to 1.4 ms for that of the supported species (within experimental error bounds of the experiment), whilst for the Q^4 site T_{cp} decreases significantly from 27 ms to 5.3 ms for the supported species. The Supporting Information contains a full analysis of the CP dynamics. This parameter, T_{cp}, is a measure of polarization transfer rate, and effectively the closer the source of ^{1}H is to the ^{29}Si site the shorter the T_{cp}. The much stronger $T_{1\rho}$ relaxation effect in the MCM-41 impregnated with the cluster suggests that in this system there is a much more extensive ^{1}H network contributing to the cross polarization to ^{29}Si than in the pure MCM-41. Very slow $T_{1\rho}$ relaxation for pure MCM-41 suggests that the ^{1}H source is very mobile or that there is a weakly coupled ^{1}H network. For MCM-41 the cross polarization proceeds from the SiOH groups within the mesopore. It is clear that upon deposition of the cluster, a new polarization source occurs. The most obvious explanation of this phenomenon is that the counterion of the cluster is in close proximity to the surface of MCM-41 and participates in

$$M(t_m) = M_0\left(1 - T_{CP}/T_{1\rho H}\right)^{-1}\left[\exp\left(-t_m/T_{1\rho H}\right) - \exp\left(-t_m/T_{CP}\right)\right] \qquad (1)$$

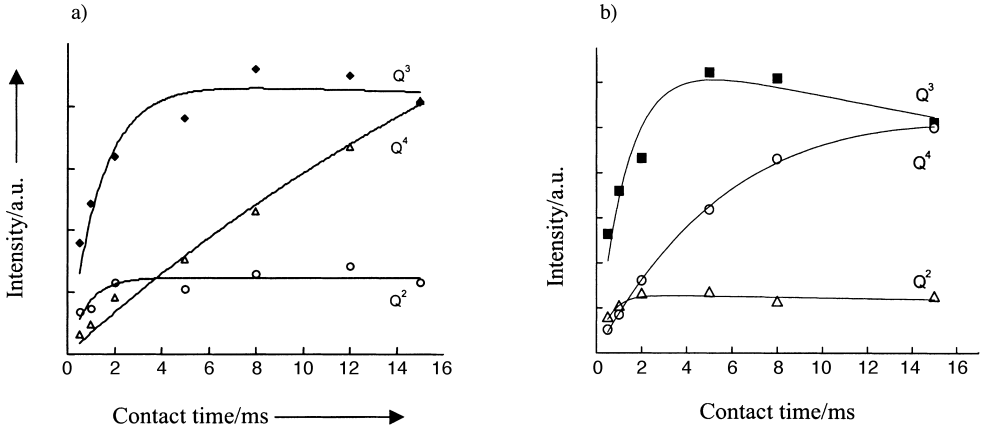
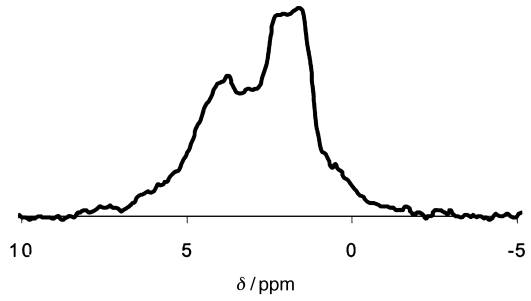


Figure 2. CP dynamic curves for a) MCM-41 and b) MCM-41 impregnated with $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$.

  0044-8249/02/4124-4727 $ 20.00+.50/0

the polarization transfer to the ^{29}Si sites at the surface from the counterions' ^{1}H moieties.To further probe the interaction between the cluster and the surface a two-dimensional ^{1}H–^{29}Si HETCOR experiment was performed on the supported $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ system (Figure 3). It is clear from the HETCOR spectrum (Figure 3) that the ^{29}Si groups of MCM-



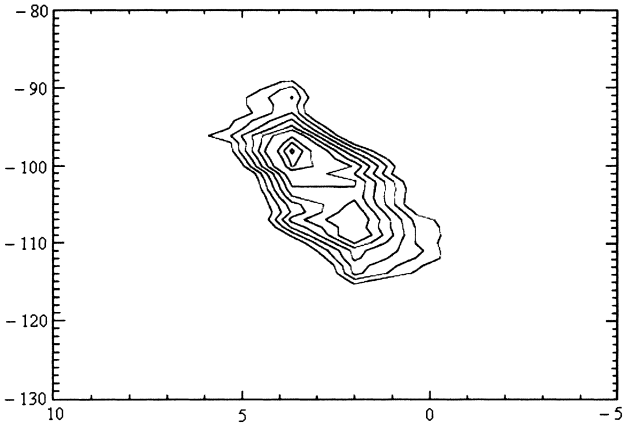


Figure 3. Top: ^{1}H NMR spectrum of MCM-41 impregnated with $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$, showing two ^{1}H resonance signals for the counterion, corresponding to CH_2 and CH_3 groups. Spinning rate = 4 kHz. Bottom: Two-dimensional correlation spectrum between ^{29}Si (vertical axis) and ^{1}H (horizontal axis) sites for MCM-41 impregnated with $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$.

41 with the cluster derive a considerable proportion of their intensity from the counterion, NEt_4^+. This infers, as we surmized from analysis of the cross polarization dynamic curves, that the counterion must be located at or very near the channel surfaces in the mesoporous material. This is the first direct evidence for this phenomenon. It is also noteworthy that the signal generated from the Q^4 site obtains a greater degree of enhancement from the $-CH_3$ moieties of the counterion, as opposed to the Q^2 and Q^3 sites, which obtain most of their intensity from the $-CH_2-$ groups within an ethyl group of the counterion. None of the ^{29}Si resonance signals derive significant cross polarization intensity from the surface silanol groups. The only structure of the impregnated mesopore, which is consistent with these observations, is one in which the ethyl group of the NEt_4^+ ion is embedded within the channel wall. We therefore conclude that an ethyl group is inserted into the channel wall of MCM-41. This structure brings a methyl group in close proximity with the Q^4 sites of the bulk MCM-41, whilst the CH_2 group of the embedded

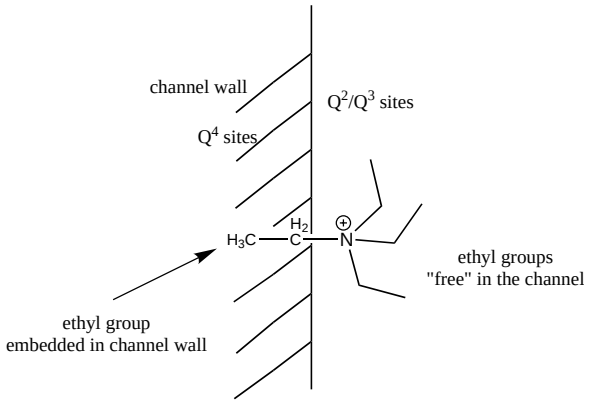


Figure 4. Schematic diagram illustrating the interaction between the NEt_4^+ ion and the channel wall of MCM-41.

ethyl group is brought in close proximity to the surface Q^2/Q^3 sites (Figure 4).

There is precedent for such an interaction: in the kaolinite/DMSO (dimethyl sulfoxide) intercalation compound where the methyl group of the DMSO molecule is inserted into the six-membered $-(SiO)_3-$ rings of the silicate layer in the kaolinite structure.[13]

To verify this conclusion, we have examined the $^{13}C\{^{1}H\}$ CP/MAS NMR spectrum of MCM-41 impregnated with $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$, (Figure 5a). The spectrum for the unsupported cluster (Figure 5b) affords two distinct reso-

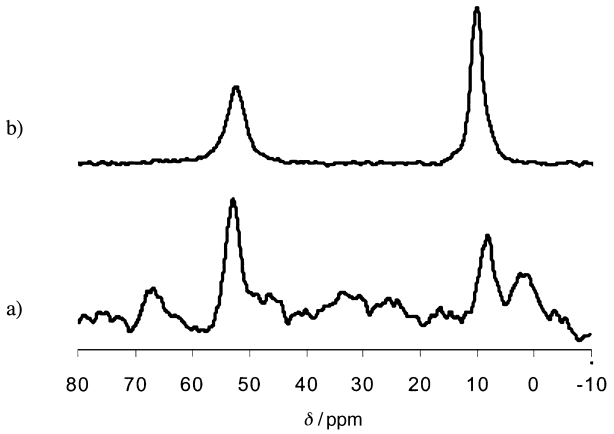


Figure 5. $^{13}C\{^{1}H\}$ CP/MAS spectra: a) MCM-41 impregnated with $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ (9668), and b) pure unsupported $[Pd_6Ru_6(CO)_{24}]$-$[NEt_4]_2$ cluster (1000). Contact time = 5 ms, and a recycle delay of 8 s. Spinning rate = 4.0 kHz.

nance signals at $\delta = 52$ and 10 ppm, respectively, originating from the methylene and methyl carbon atoms of the counterion, respectively. When the cross-polarization pulse sequence was used, signals for the CO ligands were not detected. Upon impregnation of the bimetallic cluster into MCM-41, both the methyl and methylene ^{13}C resonance signals split into two components; we thus infer a loss in the symmetry of the counterion. The principal methyl resonance signal shifts to $\delta = 6$ ppm, and a new lower intensity signal appears at $\delta = 3$ ppm. The methylene resonance signal shifts slightly to

  0044-8249/02/4124-4728 $ 20.00+.50/0 *Angew. Chem. Int. Ed.* **2002**, *41*, No. 24

$\delta = 54$ ppm and a new, lower intensity component appears at $\delta = 65$ ppm. The very low shift (to $\delta = 3$ ppm) of a component of the methyl signal is consistent for a methyl group close to Si moieties. The shift to higher frequency ($\delta = 65$ ppm) of a component of the CH_2 signal is consistent with this component being close to a more electron-withdrawing group that is, an oxygen moiety of MCM-41. This is consistent with the CH_2 being close to surface Q^2/Q^3 groups, which can (albeit weakly) interact with the CH_2 groups. It is worth noting that the two methyl and two methylene signals occur in approximately a 3:1 ratio. These relative intensities of course depend upon cross polarization dynamics of the groups concerned as well as on the relative number of sites of each. However, the cross polarization dynamics are not expected to be very different between the two different CH_3/CH_2 groups and so the 3:1 intensity ratio is entirely consistent with the proposed structure, in which one ethyl group of the NEt_4^+ ion is in a different environment to the other three.[1]

We have demonstrated that the counterion, often ignored in previous studies, plays a pivotal role in the adsorption of the mixed-metal clusters to the walls of MCM-41. We have shown, by means of a ^1H–^{29}Si HETCOR experiment that when the cluster $[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ is deposited in MCM-41 the cation becomes embedded in the MCM-41 channel walls through one ethyl group. There is a substantial change in the ^{13}C chemical shifts of the ethyl group compared with those which remain "free" in the channel space. This implies a significant rearrangement of the electron density in this ethyl group and would suggest a significant interaction with the channel wall. Further work will be published in due course to fully investigate this complex paradigm and to probe the vital role the counterion plays and to examine how general these findings are in related systems.

Experimental Section

$[Pd_6Ru_6(CO)_{24}][NEt_4]_2$ was prepared by using a standard literature preparation.[14] The MCM-41 was synthesized by using a previously reported methodology, and was characterized by powder X-ray diffraction.[15] Patterns were recorded on a Philips 1710 powder diffractometer with $Cu_{K\alpha}$ radiation (40 kV, 40 mA), 0.02° step size, and 1 s step time. The d_{100} spacing for MCM-41 was found to be 32.5 Å. The BET surface area, as determined by N_2 adsorption measurements, of the MCM-41, was found to be 880 $m^2 g^{-1}$, which is entirely consistent with the literature precedent.[15] The cluster was anchored to MCM-41 using a previously proven method:[7] MCM-41 (200 mg) was initially dried by heating at 190 °C for 24 h in a dynamic vacuum to remove any surface water. ^1H MAS NMR spectroscopy of the resulting MCM-41 showed no signs of any water being present. The anionic cluster (100 mg) was mixed with the MCM-41, to which a small amount of solvent (0.1 mL) in which the cluster is soluble (CH_2Cl_2) and a large volume of solvent (15 mL) in which the cluster is insoluble (Et_2O) were added. The mixture was stirred for 72 h, in the absence of light, after which time the solid was filtered off, washed with diethyl ether until the washings became clear, and then dried at 30 °C in a dynamic vacuum for 24 h. The presence of the carbonyl cluster was verified by using Nujol mull IR spectroscopy, on a Perkin Elmer Paragon 1000 FT-IR spectrometer. Elemental analysis (%): C 10.41, H 1.30, N 0.67. The removal of CO was achieved by heating the sample at 190 °C in vacuum for 2 h, the absence of CO stretching frequencies being verified by solid-state IR spectroscopy. Elemental analysis (%): C 4.67, H 0.62, N 0.31.

[1] A ^{13}C CP/MAS spectrum is available as Supporting Information for $[NEt_4]Br$ adsorbed onto MCM-41. This greatly improves the signal-to-noise ratio.

$^{29}Si\{^1H\}$ CP/MAS solid-state NMR spectra were recorded on a Chemagnetics CMX 400 MHz and a 500 MHz Varian Infinity Plus spectrometer. The 400 MHz spectrometer operated at 399.875 MHz for ^1H and 79.437 MHz for ^{29}Si and the 500 MHz spectrometer at 499.871 MHz and 99.303 MHz, respectively. Samples were placed in zirconia rotors 4 mm/7.5 mm in diameter and spun in nitrogen at 4 kHz. The ^1H–^{29}Si Hartmann–Hahn match was optimized by using kaolinite. All ^{29}Si spectra were externally referenced to liquid tetramethylsilane (TMS) at 0 ppm. A pulse delay of 8 s between scans and a contact time of 8 ms were used for the majority of ^{29}Si NMR experiments with a 90° pulse of 4.0 μs. For the ^1H–^{29}Si variable contact time experiments, the contact time was varied in the range 0.5–15.0 ms. The ^1H–^{29}Si HETCOR NMR experiment was performed on the 400 MHz NMR instrument, using the experimental conditions detailed above. The $^{13}C\{^1H\}$ CP/MAS spectra were recorded on the CMX-400 MHz NMR spectrometer operating at 100.561 MHz for ^{13}C. The ^1H–^{13}C Hartmann–Hahn match was optimized by using hexamethylbenzene (HMB). All ^{13}C spectra were referenced to external TMS at 0 ppm. A delay of 8 s between scans and a contact time of 5.0 ms was employed, with a 90° pulse of 4.2 μs.

Received: June 3, 2002
Revised: September 30, 2002 [Z19428]

[1] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.
[2] S. A. Raynor, J. M. Thomas, R. Raja, B. F. G. Johnson, R. G. Bell. M. D. Mantle, *Chem. Commun.* **2000**, 1925.
[3] S. Hermans, R. Raja, J. M. Thomas, B. F. G. Johnson, G. Sankar, D. Gleeson, *Angew. Chem.* **2001**, *113*, 1251; *Angew. Chem. Int. Ed.* **2001**, *40*, 1211.
[4] J. M. Thomas, W. J. Thomas, *Principles and Practice of Heterogeneous Catalysts*, Wiley-VCH, Weinheim, **1997**.
[5] D. S. Shephard, T. Maschmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R. D. Oldroyd, R. G. Bell, *Angew. Chem.* **1997**, *109*, 2337; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2242.
[6] D. S. Shephard, T. Maschmeyer, G. Sankar, J. M. Thomas, D. Ozkaya, B. F. G. Johnson, R. Raja, R. D. Oldroyd, R. G. Bell, *Chem. Eur. J.* **1998**, *4*, 1214.
[7] R. Raja, G. Sankar, S. Hermans, D. S. Shephard, S. Bromley, J. M. Thomas, B. F. G. Johnson, *Chem. Commun.* **1999**, 1571.
[8] W. Zhou, J. M. Thomas, D. S. Shephard, B. F. G. Johnson, D. Ozkaya, T. Maschmeyer, R. G. Bell, Q. Ge, *Science* **1998**, *280*, 1998.
[9] C.-F. Cheng, W. Zhou, J. Klinowski, *Chem. Phys. Lett.* **1996**, *263*, 247.
[10] X. S. Zhao, G. Q. Lu, A. K. Whittaker, G. J. Millar, H. Y. Zhu, *J. Phys. Chem. B* **1997**, *101*, 6525.
[11] R. Voelkel, *Angew. Chem.* **1988**, *100*, 1525; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1468.
[12] W. Kolodziejski, J. Klinowski, *Chem. Rev.* **2002**, *102*, 613.
[13] M. J. Duer, J. Rocha, J. Klinowski, *J. Am. Chem. Soc.* **1992**, *114*, 6867.
[14] E. Brivio, A. Ceriotti, R. D. Pergola, L. Garaschelli, F. Demartin, M. Manassero, M. Sansoni, P. Zanello, F. Lushi, B. T. Heaton, *J. Chem. Soc. Dalton Trans.* **1994**, 3247.
[15] C. Cheng, W. Zhou, D. Park, J. Klinowski, M. Hargreaves, L. F. Gladden, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 359.

  0044-8249/02/4124-4729 $ 20.00+.50/0