Even though compound **6** is extremely sensitive towards air it is thermally very stable and melts without decomposition at 237 °C. An irreversible rearrangement or decomposition reaction only occurs at above 267 °C and is indicated by a change in color from red to yellow. We will next investigate whether compound **6** can participate in typical reactions for 1,3-dienes, especially cycloadditions of the Diels–Alder type.

Experimental Section

Lithium (60 mg, 8.7 mmol) was added to a solution of **3** (700 mg, 0.81 mmol) in dimethoxyethane (30 mL) and the initially blue-green, later red, mixture was stirred for 2 h at room temperature. After separation of insoluble materials, the remaining solution was cooled to −30 °C and treated with mesityl bromide (80 mg, 0.40 mmol). After the solution had been allowed to warm to room temperature, it was stirred for 16 h. The precipitated solid was filtered off and recrystallized from toluene to furnish **6** (280 mg, 53% yield) as reddish brown crystals; m.p. 237–238 °C; ^{1}H NMR (Bruker AM300, [D$_6$]benzene, 25 °C): δ = 0.16 (d, 3H, J = 6.6 Hz), 0.24 (d, 3H, J = 6.5 Hz), 0.34 (d, 3H, J = 6.5 Hz), 0.45 (d, 3H, J = 6.6 Hz), 0.52 (d, 3H, J = 6.5 Hz), 0.85 (d, 3H, J = 6.5 Hz), 1.02 (d, 3H, J = 7 Hz), 1.08 (d, 3H, J = 6.8 Hz), 1.09 (d, 3H, J = 6.8 Hz), 1.14 (d, 3H, J = 6.8 Hz), 1.15 (d, 3H, J = 6.8 Hz), 1.34 (d, 3H, J = 6.5 Hz), 1.35 (d, 3H, J = 6.5 Hz), 1.37 (d, 3H, J = 6.5 Hz), 1.64 (d, 3H, J = 6.5 Hz), 1.69 (d, 3H, J = 6.5 Hz), 1.78 (d, 3H, J = 6.6 Hz), 1.88 (d, 3H, J = 6.5 Hz), 2.55 (sept., 1H, J = 6.5 Hz), 2.64 (sept., 1H, J = 6.5 Hz), 2.65 (sept., 1H, J = 6.5 Hz), 3.44 (sept., 2H, J = 6.5 Hz), 3,56 (sept., 1H, J = 6.8 Hz), 3.86 (sept., 1H, J = 6.5 Hz), 4.42 (sept., 1H, J = 6.6 Hz), 4.99 (sept., 1H, J = 6.6 Hz), 6.68 (d, 1H, J = 1.5 Hz), 6.84 (d, 1H, J = 1.5 Hz), 6.86 (d, 1H, J = 1.5 Hz), 6.94 (d, 1H, J = 1.5 Hz), 6.98 (d, 1H, J = 1.5 Hz), 7.20 (d, 1H, J = 1.5 Hz); ^{13}C NMR ([D$_6$]benzene, 25 °C): δ = 23.81 (C$_p$), 23.90 (C$_p$), 24.09 (C$_p$), 24.22 (C$_p$), 24.48 (C$_p$), 24.66 (C$_p$), 24.79 (C$_p$), 25.12 (C$_p$), 25.31 (C$_p$), 25.50 (C$_p$), 31.12 (C$_t$), 34.21 (C$_t$), 34.47 (C$_t$), 34.85 (C$_t$), 37.46 (C$_t$), 37.79 (C$_t$), 38.08 (C$_t$), 38.31 (C$_t$), 39.41 (C$_t$), 121.74, 121.97, 122.50, 122.80, 123.69, 125.66, 129.29, 132.79, 135.64, 136.39, 150.44, 153.36, 153.84, 154.21, 154.44, 156.30; ^{29}Si NMR (Bruker AMX300, [D$_6$]benzene, 25 °C): δ = 52.3 (s), 89.5 (s); MS (CI, NH$_3$): m/z (%): 1349 (4, MNH$_4^+$), 1332 (9, MH$^+$); UV/Vis (THF): λ_{max} (lgε) = 392 (4.48), 518 (4.41) nm.

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[12] **6**: Single crystals from diisopropyl ether; diffractometer: Siemens P4RA, radiation Mo$_{K\alpha}$ (λ = 71.073 pm), graphite-monochromated, rotating anode, scintillation counter, T = 150 K, empirical absorption correction, SHELXTL-PLUS program system, direct methods, least-squares refinement, one scaling factor, one isotropic extinction parameter; **6**·(C$_3$H$_7$)$_2$O; formula C$_{96}$H$_{152}$OSi$_4$, formula weight 1434.54; monoclinic, space group $C2/c$, a = 2275.9(6), b = 2105.7(5), c = 2003.1(6) pm, β = 106.32(2)°, V = 9212.8 × 10^6 pm^3, Z = 4, ρ_{calcd} = 1.034 g cm^{-3}, μ(Mo$_{K\alpha}$) = 0.11 mm^{-1}, transmission range 0.986–0.958, crystal dimensions 0.52 × 0.22 × 0.19 mm, ω scan, $2\theta_{max}$ = 48°, unique reflections 7217, $R(R_w)$ = 0.0629 (0.0547) for 4418 observed reflections [$I > 2\sigma(I)$], 480 parameters. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically. Further details of the crystal structure determination may be obtained from the. Fachinformationsdienst Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59437.

Synergism between the Guest Compound and the Host Framework in Zeolite CsNaY after Impregnation with Cesium Hydroxide**

Michael Hunger,* Udo Schenk, Beate Burger, and Jens Weitkamp

Over the past decades acid zeolites have found numerous applications as catalysts in industrial chemistry. In contrast, only scarce attention has been paid to basic zeolite catalysts, even though such materials show great potential for a number of industrially important reactions—such as dehydrogenation of alcohols, isomerization of olefins, side-chain alkylation of toluene, or the synthesis of 4-methylthiazol.[1] The chemical properties of basic zeolites are determined by the alkali metal cations, which act as weak Lewis acid sites, and the basic framework oxygen atoms. Exchanging sodium ions in the synthesized zeolites with rubidium or cesium ions brings about a decrease in the mean electronegativity of the framework, and the basicity of the oxygen atoms increases.[2] Strongly basic sites can be created by incorporating alkali metal oxides into the zeolite pores.[3, 4] Inside the zeolite host, such oxide guests can occur with a high dispersion. We have now applied multinuclear NMR spectroscopy to investigate the host–guest interactions of oxidic nanoparticles in a Y-type zeolite prepared by exchange with cesium cations followed by impregnation with cesium hydroxide and calcination (see Experimental Section).

According to Hathaway and Davis,[3] the selectivity for acetone formation in the conversion of propan-2-ol can be used as a measure of catalyst basicity. Propan-2-ol was converted at atmospheric pressure in a flow-type unit made of glass with a saturator, a fixed-bed reactor, and an on-line capillary gas chromatograph. All zeolites were first calcined in a flow of dry nitrogen for 12 h at 673 K. At this temperature and a modified residence time of W/F_{P-2-ol} = 450 g h mol^{-1}, conversions between 70 and 90% were achieved, and the acetone selectivities amounted to 0, 9, and 61% for NaY, CsNaY-70, and CsNaY-70/16CsOH, respectively. These figures clearly demonstrate the increase in catalyst basicity.

Prior to the NMR measurements the zeolites were heated in a glass tube at a rate of 10 K per hour and calcined for 12 h at 673 K and 10^{-2} Pa. Figure 1 shows the ^{27}Al NMR spectra of the dehydrated zeolites recorded with a spin-echo sequence.[5] The dominating solid-state interaction of the aluminum atoms in the framework of the dehydrated zeolites is that between the electric quadrupole moment Q and the z component of the electric field gradient V_{zz} at the sites of the resonating aluminum nuclei. The strength of this quadrupolar interaction is described by the quadrupole coupling constant $QCC = eQV_{zz}/h$, where e is the elementary charge, and h Planck's constant. In a strained framework-AlO$_4$ tetrahedron, the charge distribution directly surrounding the resonating Al nucleus is unsymmetrical; hence, there is a high electric field gradient and a high ^{27}Al quadrupolar coupling constant. In other words, QCC furnishes information on the chemical bonds inside the zeolitic host framework, and the aluminum atoms represent internal probes for detecting changes in the framework bonds. Previous ^{27}Al NMR investiga-

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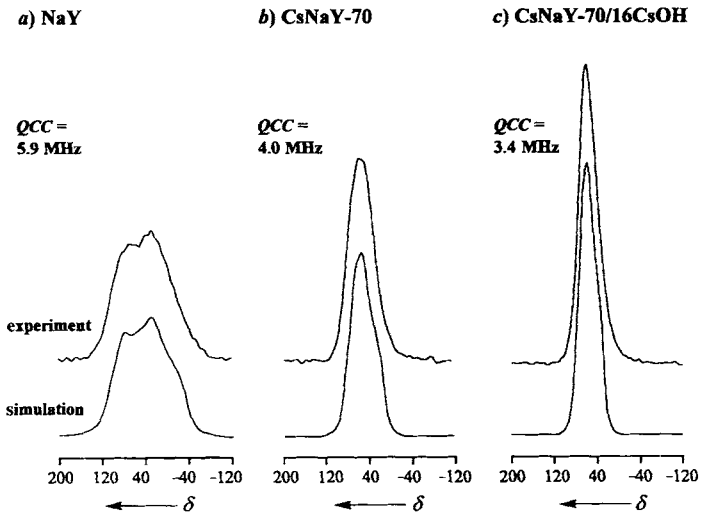


Figure 1. ^{27}Al NMR spectra (104.2 MHz) of dehydrated (673 K) zeolites a) NaY, b) CsNaY-70, and c) CsNaY-70/16CsOH. The quadrupole coupling constants QCC (see text) were determined by simulating the experimental spectra with the Bruker WINFIT software.

tions revealed a relationship between the chemical properties of dehydrated zeolites and the QCC values of the framework-AlO_4 tetrahedra.[5, 6] For acidic zeolites such as HZSM-5 ($n_{Si}/n_{Al} = 22.0$, $QCC = 15.5-16.0$ MHz),[5, 6] HMOR ($n_{Si}/n_{Al} = 8.0$, $QCC = 13.7$ MHz),[5] HY ($n_{Si}/n_{Al} = 3.1$, $QCC = 12.7-13.5$ MHz),[5, 6] and HNaX ($n_{Si}/n_{Al} = 1.4$, $QCC = 10.8$ MHz),[6] the ^{27}Al quadrupole coupling constant decreased with increasing aluminum content in the framework. Even more pronounced variations in QCC occur upon doing from an acidic form of zeolite Y ($QCC = 12.7-13.5$ MHz)[5, 6] to the basic sodium form ($QCC = 5.5$ MHz).[6] A simulation of the ^{27}Al spin-echo NMR spectra depicted in Figure 1 gives quadrupole coupling constants of 5.9 MHz, 4.0 MHz, and 3.4 MHz for zeolites NaY, CsNaY-70 and CsNaY-70/16CsOH, respectively. These values unambiguously show that the chemical bonds of the zeolite host are affected not only by ion exchange (NaY → CsNaY-70), but also by impregnation with cesium hydroxide.

The cesium oxide guest compound was directly investigated with ^{1}H and ^{133}Cs MAS NMR spectroscopy (MAS = magic angle spinning). The ^{1}H MAS NMR spectra of the three zeolites are shown in Figure 2. The concentrations of the hydroxyl groups were determined quantitatively by applying the absolute

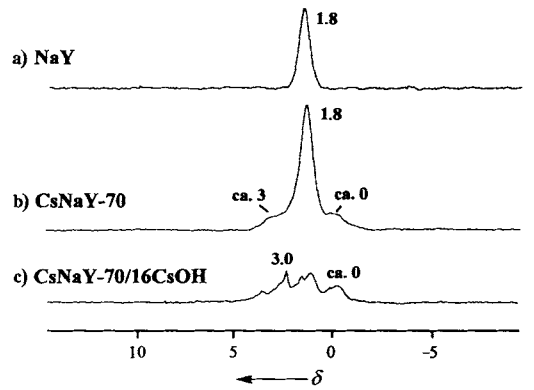


Figure 2. ^{1}H MAS NMR spectra (400.1 MHz) of dehydrated (673 K) zeolites a) NaY, b) CsNaY-70, and c) CsNaY-70/16CsOH; sample spinning rate about 10 kHz.

intensity mode with an external intensity standard (zeolite HNaY-35). The spectrum of zeolite NaY (Figure 2a) consists of one signal at $\delta = 1.8$ (referenced to TMS), which is caused by 1.4 ± 0.2 SiOH groups per unit cell (u.c.) at the framework defects and at the external surface of the zeolite crystallites.[7] Exchanging the sodium ions with cesium ions leads to an increase in the intensity of this signal (Figure 2b), corresponding now to 1.8 ± 0.2 SiOH/u.c. In addition, weak signals appear at $\delta \approx 0$ and 3, which can be assigned to undisturbed and hydrogen-bonded metal OH groups, respectively.[7] Upon impregnating zeolite CsNaY-70 with cesium hydroxide (Figure 2c), the concentration of the silanol groups drops to 0.4 ± 0.2 SiOH/u.c. However, there is no significant change in the signals at $\delta \approx 0$ and 3. Therefore, impregnation of CsNaY-70 does not result in the formation of hydroxyl groups bound to the alkali metal; that is, the guest compound exists as an oxide. On the other hand, the decrease in the concentration of the silanol groups indicates that the guest compound chemically interacts with the framework defect sites.

The ^{133}Cs MAS NMR spectra of the dehydrated zeolites CsNaY-70 and CsNaY-70/16CsOH are shown in Figure 3.

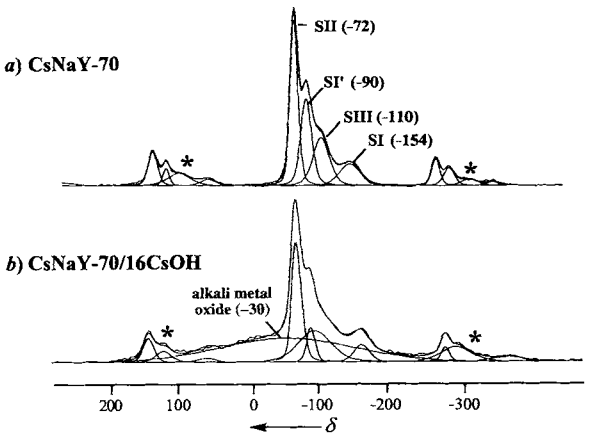


Figure 3. ^{133}Cs MAS NMR spectra (52.5 MHz) of dehydrated (673 K) zeolites a) CsNaY-70 and b) CsNaY-70/16CsOH; sample spinning rate about 10 kHz (*: MAS sidebands).

A modified 4-mm Bruker MAS NMR probe head was used. By applying a sample spinning rate of $\nu_{rot} \approx 10$ kHz ($\nu_{rot} \approx 4$ kHz was employed in earlier work),[8] the spectral resolution was significantly enhanced. This, in turn, was a prerequisite for investigating cesium oxide in zeolite CsNaY-70/16CsOH. The spectrum of dehydrated zeolite CsNaY-70 (Figure 3a) consists of signals at $\delta = -154$, -110, -90, and -72 (referenced to 1 M CsCl) due to cesium cations (37.3 Cs^+/u.c.) located at positions SI, SIII, SI', and SII, respectively.[8] For the impregnated zeolite (Figure 3b), an additional signal is observed with a linewidth of $\Delta\nu_{1/2} = 10 \pm 1$ kHz and a center of gravity at $\delta \approx -30 \pm 2$. Its intensity contribution of $30 \pm 5\%$ agrees well with the amount of cesium oxide introduced in the impregnation step (see below). To interpret the signal at $\delta = -30$, it is important to notice that pure cesium hydroxide (dehydrated for 12 h at 673 K) gives a narrow ^{133}Cs MAS NMR sideband pattern with an isotropic chemical shift of $\delta = 146$ (not shown). Consequently, the cesium oxide in CsNaY-70/16CsOH does not exist as pure isolated clusters. The strong broadening of the signal at $\delta = -30$ may originate in a distribution of chemical shifts for highly dispersed cesium oxide species bound in different ways to the framework.

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Bosacek recently proposed a new method for characterizing the mean electronegativity and basicity of the zeolite lattice.[9] He found a correlation between the isotropic ^{13}C NMR shift of the methoxy groups formed upon adsorption of methyl iodide on dehydrated zeolites and the mean Sanderson electronegativity, S^m, of the lattice. Varying S^m from 3.04 for zeolite HZSM-5 ($n_{Si}/n_{Al} = 21.8$) to 2.26 for zeolite CsNaX-49 ($n_{Si}/n_{Al} = 1.2$) resulted in a change in the shift for the methoxy groups from $\delta(^{13}C) = 59.4$ to 54.1 ($\delta(^{13}C)/S^m \approx 6.8$).[9] Bosacek proposed ^{13}C cross-polarization (CP)/MAS NMR spectroscopy of the methoxy groups bound to the zeolite as a new method for determining the basicity of the framework oxygen atoms in zeolites. Figure 4 shows the ^{13}C CP/MAS NMR spectra of the dehydrated zeolites NaY, CsNaY-70, and CsNaY-70/16CsOH after adsorption of $16\,CH_3I$/u.c. The signals at $\delta = -20 \pm 0.5$ are due to physisorbed CH_3I.[9] The chemical shifts of the methoxy groups in zeolites NaY ($\delta = 56.7$, Figure 4a) and CsNaY-70 ($\delta = 56.1$, Figure 4b) correlate well with their mean Sanderson electronegativities ($S^m = 2.60$ and 2.46, respectively). The spectrum of zeolite CsNaY-70/16CsOH (Figure 4c) consists of signals at $\delta = 55.4$ and 50.3 due to methoxy groups and a narrow signal at $\delta = 61.0$. This latter signal has an intensity contribution of about 10% and is due to dimethyl ether.[9] Since there is no signal at $\delta = 56.1$ (for methoxy groups in zeolite CsNaY-70), the whole framework of zeolite CsNaY-70/16CsOH must have been uniformly affected by CsOH impregnation. The change in the ^{13}C shift from $\delta = 56.1$ for methoxy groups in zeolite CsNaY-70 to $\delta = 55.4$ for methoxy groups in zeolite CsNaY-70/16CsOH corresponds to an increased framework basicity of the latter. The high-field signal at $\delta = 50.3$ (Figure 4c), with MAS sidebands comparable to those of the signal at $\delta = 55.4$, indicates the existence of an additional strongly basic compound. Apparently, the methoxy groups responsible for this signal are bound to the alkali metal guest introduced upon impregnation. The high intensity of this signal ($32 \pm 5\%$ of the total intensity) points to a large surface and, hence, to a high dispersion of this alkali metal guest compound in CsNaY-70/16CsOH.

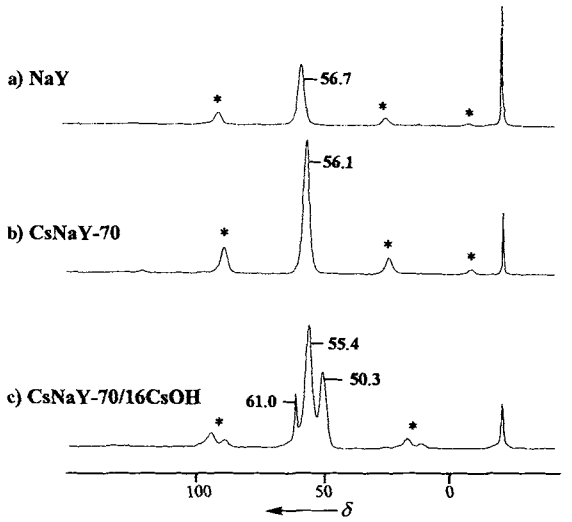


Figure 4. ^{13}C CP/MAS NMR spectra (100.6 MHz) of dehydrated (673 K) zeolites a) NaY, b) CsNaY-70, and c) CsNaY-70/16CsOH loaded with $16\,CH_3I$/u.c.; recorded with a contact time of 3 ms and a sample spinning rate of about 3 kHz (*: MAS sidebands).

In conclusion, impregnation and calcination of zeolite CsNaY-70 with cesium hydroxide not only creates a cesium oxide guest with a high dispersion, but it also affects the chemical properties of the zeolite framework. By using the methoxy groups as an NMR spectroscopic probe, a significant decrease in the mean electronegativity of the zeolite framework was detected upon impregnation with CsOH. Spin-echo NMR spectra of framework aluminum atoms functioning as internal probes revealed an impregnation-induced variation of the ^{27}Al quadrupole coupling constant and, hence, of the chemical bonding inside the dehydrated zeolite framework. A signal of the guest species was observed in the ^{133}Cs MAS NMR spectrum of the dehydrated zeolite CsNaY-70/16CsOH, which differs significantly from that of the pure dehydrated alkali metal hydroxide. The pronounced broadening of this signal points to a high dispersion of the guest inside the pores of zeolite CsNaY-70/16CsOH. The significant decrease in the intensity of the ^1H MAS NMR signal for defect SiOH groups accompanying impregnation is due to deprotonation of these sites by the alkali oxide, and possibly indicates that at least a part of the guest compound is bound to defect sites of the zeolite framework.

Experimental Section

The parent zeolite NaY (Union Carbide Corp., Tarrytown, NY, USA, $n_{Si}/n_{Al} = 2.6$) was ion-exchanged five times in a 0.4 M aqueous solution of CsCl at 353 K, which led to 70% exchange of sodium (zeolite CsNaY-70). Part of this material was then suspended in a 0.2 M solution of CsOH which contained exactly the amount of CsOH need for the final material. The suspension was stirred overnight to dryness at 353 K and calcined for 12 h at 673 K. The material coded CsNaY-70/16CsOH was impregnated with 16 CsOH/u.c. The chemical compositions of the samples were analyzed with inductively coupled plasma atomic emission spectrometry (ICPAES) and atomic absorption spectrometry (AAS). ^{27}Al and ^{29}Si MAS NMR spectroscopy (Bruker MSL 400) of the hydrated zeolites NaY, CsNaY-70 and CsNaY-70/16CsOH showed that no dealumination of the zeolite framework took place as a result of cesium exchange, impregnation with CsOH, and calcination.

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