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Characterization of basic guest compounds on solid catalysts by ^{13}C CP/MAS NMR spectroscopy of surface methoxy groups†

Udo Schenk, Michael Hunger* and Jens Weitkamp

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

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ABSTRACT: Silica gel, dealuminated zeolite USY and cesium-exchanged zeolite Y were impregnated with alkali metal hydroxides or acetates followed by calcination. Surface methoxy groups formed upon loading these samples with methyl iodide were applied as ^{13}C NMR spectroscopic probes to investigate the formation of well dispersed basic guest compounds. The variation of the isotropic ^{13}C NMR shifts of methoxy groups bound to different guest compounds on silica gel (49.6–48.7 ppm) shows the same tendency as the electronegativities of alkali metal atoms introduced by impregnation. ^{13}C CP/MAS NMR studies of surface methoxy groups bound to guest compounds on silica gel and zeolites Y revealed an influence of the support on the ^{13}C chemical shift tensor. The application of this NMR spectroscopic method on cesium-exchanged zeolite Y impregnated with cesium hydroxide allows one to distinguish at least two types of oxidic guest compounds. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C CP/MAS NMR; surface methoxy groups; basic catalysts; guest compounds

INTRODUCTION

Although zeolites are widely used as solid acids in heterogeneous catalysis,[1] they have so far received much less attention as solid bases. A variety of industrially important reactions, such as the dehydrogenation of alcohols, the double bond isomerization of olefins, the side-chain alkylation of toluene with methanol and the synthesis of 4-methylthiazole can be catalyzed, in an environmentally friendly manner, by basic zeolites.[2] However, basic zeolites are difficult to prepare and a prerequisite for their industrial application is a better understanding of the steps in their manufacture and of the nature of their basic sites. A commonly employed method to create basic zeolites is the exchange of their sodium cations by cations with lower electronegativities such as rubidium or cesium. This modification effects a decrease in the mean electronegativity of the zeolite framework and, therefore, of the framework oxygen atoms acting as weak Lewis base sites.[3] Strong Lewis bases can be created by incorporating alkali metal oxides into the zeolite pores via a method proposed by Hathaway and Davis:[4,5] the zeolitic host is impregnated by a solution of alkali metal hydroxides or acetates and subsequently calcined at 673–773 K.

To investigate the catalytic behavior of basic zeolites, various test reactions have been proposed, such as the dehydrogenation of 2-propanol,[6,7] the isomerization of 1-butene,[8] the cyclization of acetonylacetone[9] and Knoevenagel condensations.[10] The base strength of solid catalysts has been studied by Fourier transform IR and x-ray photoelectron spectroscopy with pyrrole, chloroform, acetylene or methanol as probe molecules.[11–14] Finally, quantification of strong base sites on solids can be performed by temperature-programmed desorption (TPD) of CO_2.[15]

Recently, Bosacek *et al.*[16–18] applied ^{13}C magic angle spinning (MAS) NMR spectroscopy to investigate the mean electronegativity and base strength of different cation-exchanged zeolites. After the formation of methoxy groups by loading methyl iodide, Bosacek *et al.*[16–18] found a correlation between the isotropic chemical shift of surface methoxy groups bound to framework oxygen atoms in bridging position and the mean Sanderson electronegativity S^{m19} of the zeolite framework. According to this correlation, a low ^{13}C NMR shift of methoxy groups corresponds to a high base strength of the framework oxygen atoms. We applied this method to investigate cesium-exchanged zeolites X and Y impregnated with cesium hydroxide.[7,20,21] In those studies,[7,20,21] the ^{13}C NMR chemical shifts of surface methoxy groups bound to framework oxygen atoms of the zeolitic host were found to be 54–56 ppm, in good agreement with the values reported by Bosacek.[16] Additional ^{13}C cross-polarization (CP) MAS NMR signals were observed to occur at a chemical shift of ca 50 ppm, and these signals were assigned to methoxy groups bound to guest compounds.[7,20,21] In the present work, different guest compounds on silica gel, dealuminated zeolite USY and cesium-exchanged zeolite Y were studied by NMR spectroscopy. The principal aim was to study the influence

* *Correspondence to*: M. Hunger, Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany.
E-mail: michael.hunger@po.uni-stuttgart.de
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of the supports and host materials on the ^{13}C chemical shift tensor of methoxy groups bound to these guest compounds.

EXPERIMENTAL

The parent zeolite NaY (Union Carbide, Tarrytown, NY, USA, $n_{Si}/n_{Al} = 2.6$) was fivefold ion-exchanged with a 0.4 M aqueous solution of CsCl (Aldrich, Steinheim, Germany; 19,831-5) at 353 K leading to an exchange degree of 70% (zeolite CsNaY-70). Dealuminated zeolite USY was prepared according the method described by Beyer *et al.*[22] by treating zeolite NaY with $SiCl_4$ up to $n_{Si}/n_{Al} \approx$ 950. Silica gel was purchased from Fluka (Buchs, Switzerland) (980911). To impregnate these samples, the materials were suspended in 0.2 M aqueous solutions of alkali metal hydroxides (MeOH) or acetates (MeAc): NaOH (Merck, Darmstadt, Germany; 6498.5000), KOH (Riedel-de Haën, Hannover, Germany; 1813), RbOH (Aldrich; 40,129-3), CsOH (Aldrich; 19,833-1), sodium acetate (Merck; 6267.0500) and cesium acetate (Aldrich; 32,982-7). Subsequently, the suspensions were stirred for 12 h at room temperature and then heated to dryness at 353 K. To designate the samples, the amounts of incorporated alkali metal hydroxide or acetate are given in wt% on silica gel (SG) or by the number of MeOH or MeAc per unit cell (u.c.), e.g. SG/16NaOH or CsNaY-70/16CsOH. Finally, the samples were calcined in dry air at 673 K for 6 h. The chemical compositions of the samples were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS). The quality of all zeolites were verified by ^{27}Al and ^{29}Si MAS NMR spectroscopy and by x-ray diffraction.

Prior to the NMR measurements, the samples were heated in vacuum at a rate of 1 K min^{-1} up to the final temperature of 673 K and then calcined for 12 h at a pressure below 10^{-2} Pa. The adsorption of methyl iodide (C^*H_3I, Aldrich; 27,718-5; the asterisk indicates the ^{13}C-enriched carbon atom) on the calcined samples was carried out using a vacuum line. Subsequently, the samples were filled into MAS rotors under dry nitrogen gas using a glove-box.

^{13}C CP/MAS NMR spectra were recorded on a Bruker MSL 400 spectrometer at a resonance frequency of 100.5 MHz. The measurements were performed with a 7 mm double-bearing Bruker MAS standard probe applying sample spinning rates of 1.0 and 2.5 kHz. CP/MAS experiments were carried out with a contact time of $\tau = 3$ ms and high-power proton decoupling. At least 1000 scans with a recycle delay of 10 s were accumulated for each spectrum. The ^{13}C NMR shifts were referenced to TMS.

RESULTS AND DISCUSSION

Silica gel impregnated with alkali metal hydroxides

Figure 1 shows ^{13}C CP/MAS NMR spectra of surface methoxy groups formed on the dehydrated silica gels

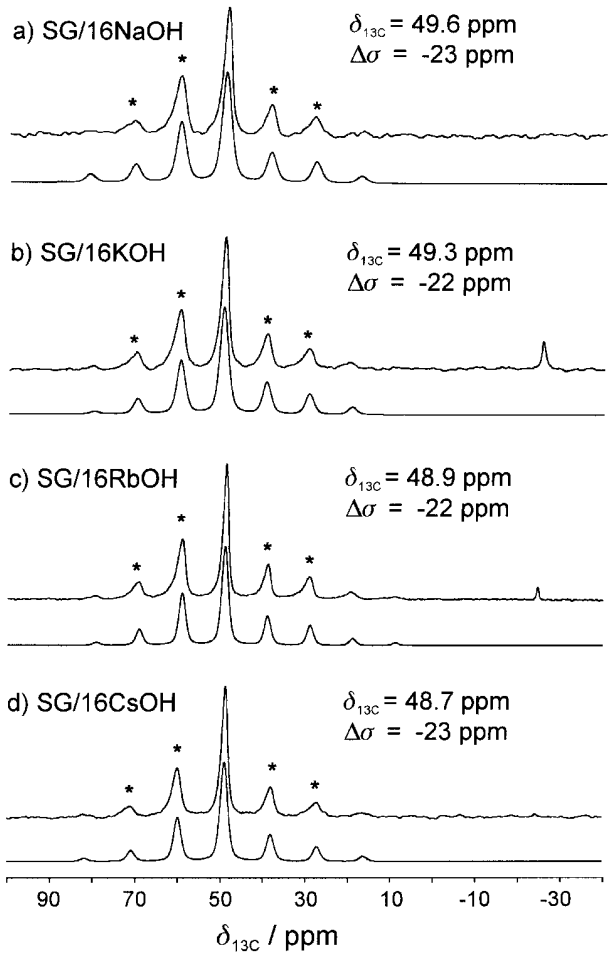

Figure 1. ^{13}C CP/MAS NMR spectra of calcined silica gel (SG) impregnated with 16 wt% NaOH (a), KOH (b), RbOH (c) and CsOH (d), loaded with 0.2 mmol of C^*H_3I per gram and recorded with a sample spinning rate of 1.0 kHz. Asterisks denote spinning sidebands.

SG/16NaOH (a), SG/16KOH (b), SG/16RbOH (c) and SG/16CsOH (d) upon loading with 0.2 mmol of C^*H_3I per gram. The spectra which were recorded using a sample spinning rate of 1 kHz consist of MAS patterns with central lines at 49.6–48.7 ppm. The signals at the isotropic chemical shift of -24 ± 2 ppm are due to physisorbed methyl iodide.[17] Quantitative evaluation of the sideband intensities according to Herzfeld and Berger[23] yields a chemical shift anisotropy of $\Delta\sigma = -23 \pm 2$ ppm. This $\Delta\sigma$ value indicates the formation of rigidly bound species, which is characteristic for surface methoxy groups. The isotropic ^{13}C NMR shifts of surface methoxy groups bound to the alkali metal oxide compounds on silica gel (48.7–49.6 ppm, see Fig. 1) are low in comparison with those of methoxy groups in zeolites (ca 54–59 ppm[16–18]). In a preliminary experiment it was proved that loading of methyl iodide on pure and dehydrated silica gel does not lead to the formation of methoxy groups. The tendency of the resonance shift from 49.6 ppm for methoxy groups on SG/16NaOH to 48.7 ppm for methoxy groups on SG/16CsOH agrees with the variation of the electronegativities of alkali metal atoms introduced by the oxidic guest compounds ($S_{Na} = 0.560$, $S_K = 0.445$; $S_{Rb} = 0.312$ and $S_{Cs} = 0.220$).

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Zeolite USY impregnated with alkali metal acetates

The observation of the chemical shift anisotropy is characteristic of rigidly bound species.[24] In previously published studies,[16–18,20,21] for methoxy groups bound to framework oxygen atoms and guest compounds in zeolites, a chemical shift anisotropy of $\Delta\sigma = -42 \pm 2$ ppm was found. Since this value differs from that obtained for methoxy groups on impregnated silica gel ($\Delta\sigma = -23 \pm 2$ ppm, see above), in the following experiments the influence of the support on the ^{13}C chemical shift tensor of methoxy groups was explored.

Impregnation of zeolite USY ($n_{Si}/n_{Al} \approx 950$) with alkali metal hydroxides led to considerable damage to the zeolite framework. Therefore, this material was impregnated with sodium acetate (USY/16NaAc) or cesium acetate (USY/16CsAc) and subsequently calcined as described by Lasperas *et al.*[25] Figure 2 shows the ^{13}C CP/MAS NMR spectra of surface methoxy groups formed upon loading 2 C*H$_3$I/u.c. on zeolites USY/16NaAc (a) and USY/16CsAc (b). The spectra of zeolites USY/16NaAc and USY/16CsAc consist of MAS patterns with asymmetric central lines at 49.4 ppm. This chemical shift agrees well with that found for methoxy groups on impregnated silica gel. A simulation of the ^{13}C CP/MAS NMR spectra in Fig. 2(a) and (b), however, reveals that at least two MAS patterns have to be invoked: a first one with MAS central lines at 49.0 ± 0.5 ppm and a second one with a MAS central line at 52.0 ± 1.0 ppm. The chemical shift anisotropy of $\Delta\sigma = -32 \pm 6$ ppm obtained by this quantitative evalution is significantly higher than that of methoxy groups bound to guest compounds on impregnated silica gel. This fact and the slight resonance shift of the ^{13}C CP/MAS NMR signals due to methoxy groups bound to cesium oxidic compounds on silica gel (48.7 ppm), zeolite USY (49.4 ppm) and zeolite CsNaY-70 (50.0 ppm[20]) are a hint at the influence of the support on the ^{13}C chemical shift tensor of surface methoxy groups.

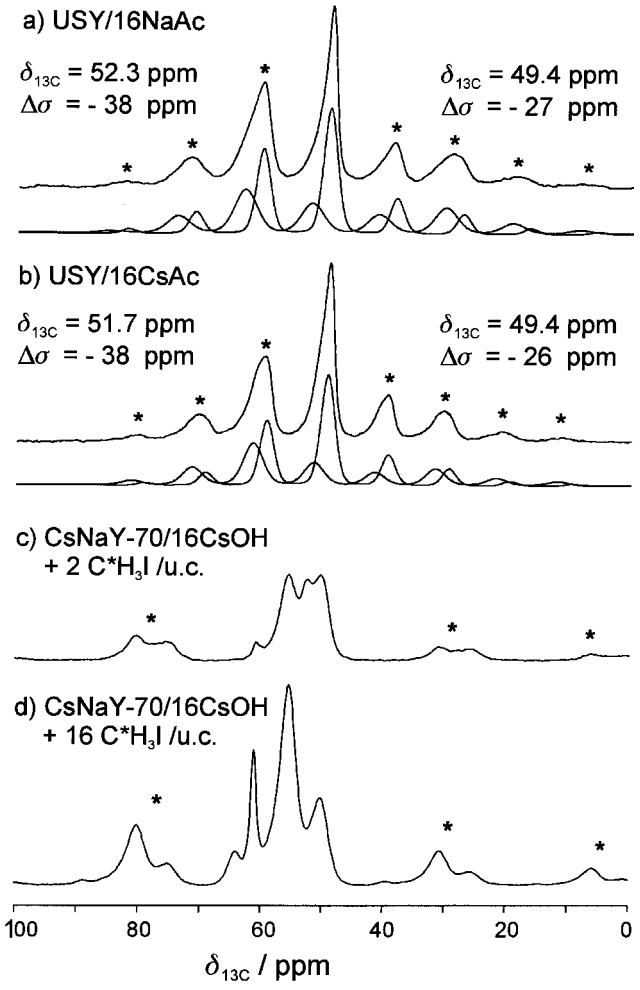

Figure 2. ^{13}C CP/MAS NMR spectra of calcined zeolite USY impregnated with 16 sodium acetate (a) and 16 cesium acetate (b) molecules per unit cell, loaded with 2 C*H$_3$I/u.c. and recorded with a sample spinning rate of 1 kHz and of calcined zeolite CsNaY-70/16CsOH loaded with 2 C*H$_3$I/u.c. (c) and 16 C*H$_3$I/u.c. (d) and recorded with a sample spinning rate of 2.5 kHz. Asterisks denote spinning sidebands.

Zeolite CsNaY-70 impregnated with cesium hydroxide

To investigate the affinity of methoxy groups to the different base sites in zeolite CsNaY-70 impregnated with cesium hydroxide, samples loaded with different amounts of methyl iodide were studied by ^{13}C CP/MAS NMR spectroscopy. Figure 2(c) and (d) show ^{13}C CP/MAS NMR spectra of zeolite CsNaY-70/16CsOH loaded with 2 C*H$_3$I/u.c. and 16 C*H$_3$I/u.c., respectively. The MAS central lines of both spectra consist of signals due to methoxy groups bound to guest compounds (50–52 ppm[7,20,21]), methoxy groups bound to zeolitic framework oxygen atoms (55.3 ppm[7,16–18,20,21]) and dimethyl ether (61.0 ppm[16,20]). On the sample loaded with 2 C*H$_3$I/u.c., about 50% of the methoxy groups are bound to guest compounds (signals at 50–52 ppm). A higher loading with methyl iodide leads to a significant increase in the signal due to methoxy groups bound to zeolitic framework oxygen atoms (55.3 ppm) and to its overlap with the signal at ca 52 ppm [Fig. 2(d)]. The observation that methoxy groups are preferentially formed at guest compounds after the loading of a small amount of methyl iodide is a strong indication for the high base strength of these alkali metal oxides.

In Fig. 3, the components and the simulation of the ^{13}C CP/MAS NMR spectrum of zeolite CsNaY-70/16CsOH loaded with 2 C*H$_3$I/u.c. are shown. The anisotropies of chemical shift of the components 1, 2 and 3 of $\Delta\sigma = -38$ (1), -35 (2) and -42 ppm (3) agree well with the value of -43 ppm determined for methoxy groups on zeolite NaX.[17] Comparing the isotropic chemical shifts of components 1 and 2 (50.0 and 52.3 ppm, respectively) with those observed for methoxy groups on impregnated zeolite USY [see Fig. 2(a) and (b)], both components 1 and 2 can be attributed to methoxy groups bound to guest compounds. According to Krawietz *et al.*,[26] guest compounds formed by impregnating a support with cesium hydroxide or acetate should be a mixture of a cesium oxide (Cs_2O), peroxide (Cs_2O_2) or superoxide (CsO_2). Whereas cesium

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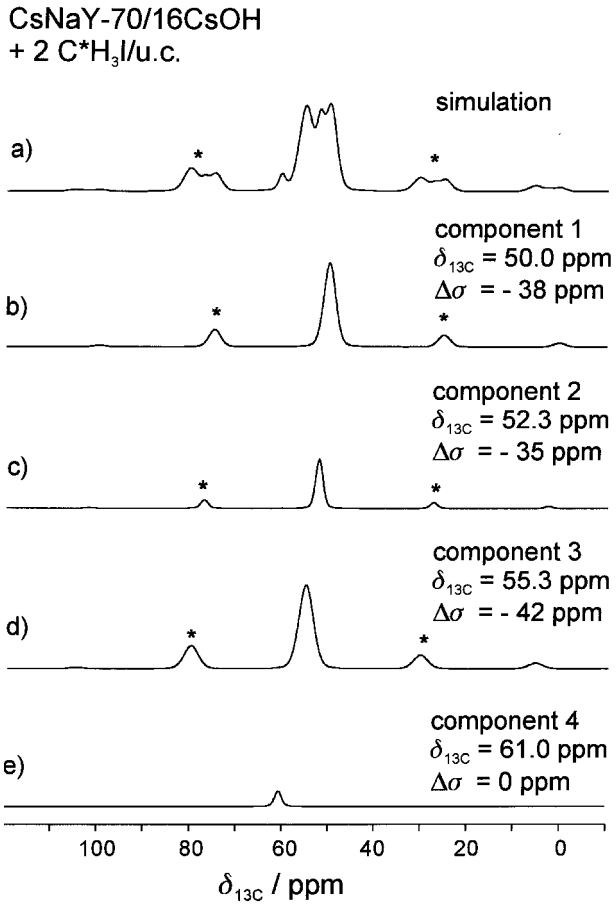

Figure 3. Decomposition and simulation of the ^{13}C CP/MAS NMR spectrum of zeolite CsNaY-70/16CsOH loaded with 2 C^*H_3I/u.c. [Fig. 2(c)] using the Bruker software WINFIT. Asterisks denote spinning sidebands.

oxide is a strong base, guest compounds consisting of peroxide or superoxide have a lower base strength.[26] The ^{13}C NMR signals at 50.0 and 52.3 ppm could, therefore, be a hint of the presence of different oxidic guest compounds on zeolite CsNaY-70/16CsOH.

CONCLUSIONS

Surface methoxy groups formed by loading methyl iodide on impregnated supports are useful ^{13}C NMR probes for the investigation of basic guest compounds. The chemical shift anisotropy of methoxy groups bound to the guest compounds depends on the support material and covers a range from $\Delta\sigma = -22$ to -42 ppm. The isotropic ^{13}C NMR shifts of these methoxy groups (48.7–50.0 ppm) are significantly lower than those observed for surface methoxy groups bound to zeolite framework oxygen atoms in bridging position (ca 54–59 ppm). The preferential formation of methoxy groups with these guest compounds is a strong indication of their high base strength. The observation of different methoxy groups on zeolite CsNaY-70 impregnated with cesium hydroxide at ^{13}C NMR shifts of ca 50 and 52 ppm could be a hint of guest compounds consisting of a mixture of different oxidic guest compounds.

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