Method for the determination of the strength of base sites by formation of methoxy groups and ¹³C CPMAS NMR

Spectroscopic background: In contrast to the broad application of acidic zeolites as solid catalysts in chemical technology, only scarce attention has been paid to **basic zeolite catalysts**, even though such materials do **have a potential for industrial applications** [1]. 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 [1]. Therefore, the preparation and spectroscopic characterization of basic zeolites were in the focus of numerous studies [2-10]. It has been demonstrated that different cations and guest compounds strongly influences the chemical shift of the ¹³C CPMAS NMR signals of surface methoxy groups bound at framework oxygen atoms [2-8]. In the case of basic zeolites, such as cesium-exchanged zeolites Y (Cs,Na-Y), these surface methoxy groups are formed by chemisorption of methyl iodide [4]:

$$Cs^{+} \qquad CH_{3}$$

$$\equiv Si - O^{-} - Al \equiv + CH_{3}I \rightarrow \equiv Si - O^{-} Al \equiv + CsI \qquad (1)$$

After formation of methoxy groups at framework oxygen atoms by adsorption of methyl iodide, the isotropic ¹³C NMR shifts of these methoxy groups correlate with the base strength of the zeolite framework.

Fig. 1 shows the ¹³C CPMAS NMR spectra of dehydrated zeolites Na-Y (a), Cs,Na-Y-70 (b), Na-X (c), and Cs,Na-X-55 (d), recorded after chemisorption of 16 CH₃I molecules per unit cell and subsequent calcination at T = 673 K [6]. The signals marked by asterisks are due to spinning sidebands and indicate that the species causing the sideband pattern are rigidly bound to the zeolite framework, which is typical for methoxy groups. Simulation of the MAS sideband patterns [11], which are due to the ¹³C CPMAS NMR signals at $\delta_{13C} = 55$ to 57 ppm, leads to a chemical shift anisotropy of $\Delta \sigma = -41\pm 2$ ppm [6]. In faujasite-type zeolites, the corresponding methoxy groups are explained to be bound to different framework oxygen atoms, such as O1 and O4 [2].

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In Fig. 2, the isotropic chemical shifts δ_{13C} of methoxy groups at zeolite frameworks, published by Bosácek [2] and of the samples in Fig. 1, are depicted as a function of the mean Sanderson electronegativity S_m [12] of the zeolites under study [1]. According to this figure, the base strength of the zeolite framework increases with decreasing mean Sanderson electronegativity S_m and decreasing ¹³C chemical shifts δ_{13C} of the surface methoxy groups. Therefore, zeolites X with the higher aluminum content compared to zeolite Y ($S_{AI} < S_{Si}$) and cesium-exchanged zeolites compared to sodium-exchanged zeolites ($S_{Cs} < S_{Na}$), have the higher base strength due to their lower mean Sanderson electronegativity S_m .



Fig. 2

In the following, this method was applied to characterize zeolites X and Y impregnated with guest compounds, such as cesium hydroxide, for obtaining catalysts with further improved base strength [3, 5-7]. **Fig. 3** shows the ¹³C CPMAS NMR spectra of **zeolite CsNaY-70** impregnated with 4, 8, and 16 CsOH per unit **cell** and loaded with CH₃I [5]. These spectra consist of up to three signals at δ_{13C} = 50.3 ppm, 56.0 to 55.4 ppm, and 61.0 ppm. The signal at δ_{13C} = 61.0 ppm is caused by dimethyl ether. The signals at δ_{13C} = 56.0 to 55.4 ppm are due to methoxy groups formed at framework oxygen atoms of the faujasite structure (compare **Fig. 1**). The increasing amount of cesium hydroxide, impregnated on zeolite CsNaY-70, leads to a high-field shift of the ¹³C CPMAS NMR signal of methoxy groups at the framework oxygen atoms. This finding indicates an increased base strength of the host framework due to CsOH impregnation [5].

To clarify the assignment of the ¹³C CPMAS NMR signal at δ_{13C} = 50.3 ppm, pure silica gel (SG) was impregnated with cesium hydroxide and subsequently calcined at



Fig. 3

T = 673 K. The ¹³C CPMAS NMR spectrum of this SG/CsOH material, loaded with CH₃I, gave a single signal at δ_{13C} = 50.3 ppm [5]. Obviously, also the signals at δ_{13C} = **50.3 ppm** in the spectra of CsOH impregnated zeolites Cs,Na-Y in **Fig. 3** are **due to methoxy groups bound to CsOH guest compounds**. The low ¹³C chemical shift of these methoxy groups hint at a **very high base strength** of these guest compounds in zeolites Cs,Na-Y/*n*CsOH.

Catalyst preparation: The parent zeolite Na-Y ($n_{Si}/n_{AI} = 2.6$) was ion-exchanged in an aqueous solution of CsCI at T = 353 K (zeolites Cs,Na-Y-55 and Cs,Na-Y-70). Subsequently, these zeolites were suspended in a solution of CsOH, which contained the required amount of CsOH need for the final material. This suspension was stirred overnight to dryness at T = 353 K and calcined for 12 h at T = 673 K. The material denoted Cs,Na,Y-70/4CsOH was impregnated with 4CsOH/u.c. etc. The adsorption of CH₃I on the calcined samples was carried out at in a "sample tube system 1" at a "vacuum line 2" (see Sections "sample tube system 1" and "vacuum line 2", both accessible via link ""In Situ Solid-State NMR Techniques").

¹³*C CPMAS NMR studies:* The ¹³*C* CPMAS NMR spectra were recorded at a Bruker MSL-400 spectrometer, with a resonance frequencies of $v_0 = 100.6$ MHz and a contact time of 5 ms, and using a 7 mm Bruker MAS NMR probe with a sample spinning rate of $v_{rot} \approx 3$ kHz. The ¹³*C* chemical shifts are referenced to tetramethylsilane ($\delta_{13C} = 0$ ppm).

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