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Strong acidity of silanol groups of zeolite beta: Evidence from the studies by IR spectroscopy of adsorbed CO and ^{1}H MAS NMR

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ABSTRACT

Acidic OH groups of acid-form and Zn and Ga-modified zeolite beta (BEA) have been characterized with ^{1}H MAS NMR and by IR spectroscopy of adsorbed carbon monoxide. It is demonstrated that OH groups, which exhibit a vibration band at 3740 cm^{-1}, reveal acidity, which is similar to that of the OH groups with the band at 3610 cm^{-1} according to the value of the low frequency shift of OH vibrations with adsorbed CO ($\Delta\nu_{OH/CO}$ = 300 cm^{-1}). The IR band 3740 cm^{-1} corresponds to the signal at ca. 2.1 ppm in ^{1}H MAS NMR spectrum. The OH groups with signal 2.1 ppm are involved in H/D exchange with methane-d_4 similar to acidic OH groups with the signals 4.0–5.1 ppm. The signals at 2.1 ppm in ^{1}H MAS NMR and at 3740 cm^{-1} in IR are attributed to the strongly acidic silanol groups of the faulted structure of the zeolite. The silanols with the signals at 1.8 ppm and 3745 cm^{-1} are weakly acidic ($\Delta\nu_{OH/CO}$ = 85 cm^{-1}) and are not involved in the H/D exchange. Loading of the zeolite with Zn affords a notable decrease of the concentration of strongly acidic SiOHAl groups, whereas the quantity of these groups does not decrease upon loading the zeolite with Ga.

1. Introduction

Zeolite β (BEA) possesses a three-dimensional channel system with 12-membered ring apertures of 5.6–7.3 Å [1,2]. The protonic form of the high-silica zeolite BEA is an active catalyst in a variety of reactions, like hydrocarbon cracking [3], alkylation [4–7] and acylation of aromatics [8], alkane hydroisomerization [9] etc. Zn- and Ga-modified zeolites BEA were used for performance of Knoevenagel condensation reaction [10,11] and finds its application in aromatization of small alkanes [12]. The high catalytic activity frequently observed for zeolite BEA might be related to its open pore structure, high concentration of defects [1,2] and high acidity of Brønsted sites [13,14].

Acidic OH groups of zeolite BEA were earlier characterized with IR and ^{1}H MAS NMR spectroscopy [14–27]. Mainly two intense bands were identified in IR spectrum: at 3608–3620 cm^{-1} from the strong acidic bridged SiOHAl and at 3735–3745 cm^{-1} from weak-acidic terminal SiOH groups. Two vibrational bands of small intensities at 3660 cm^{-1} and 3785 cm^{-1} were assigned to OH groups of extra-framework aluminium species. Contrary to the acidic SiOHAl groups, weak-acidic OH groups are not involved in any catalytic transformations. However, we have recently identified an involvement of OH groups of zeolite BEA with the signal at ca. 1.8 ppm in ^{1}H MAS NMR spectrum (the position of the signal corresponds to that of weak-acidic terminal SiOH groups) in the reaction of H/D hydrogen exchange with small alkanes [28]. This finding prompted us to revisit the acid characteristics of OH groups of zeolite BEA.

In this paper we perform an analysis of the acid properties of OH groups of the acid-form and the Zn- and Ga-modified zeolites BEA with ^{1}H MAS NMR and IR of adsorbed CO with the aim of clarifying an involvement of OH groups with conventional weak-acidic characteristics in the reaction of H/D exchange.

2. Experimental

2.1. Materials characterization and samples preparation

The acid-forms of the zeolite beta (H-BEA-54, Si/Al = 19) and (H-BEA-59, Si/Al = 18), were synthesized using tetraethylammonium hydroxide as template with subsequent calcination at 823 K in air flow for 6 h [29]. The zeolite samples used in our experiments are characterized by an average crystallites size of 0.1–0.2 μm, which form the rounded agglomerates of 0.5–2 μm diameter.

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Zn- and Ga-modified zeolite beta samples were prepared by incipient wetness impregnation method of the parent samples of zeolite H-BEA with aqueous solution of zinc formate or gallium nitrate, subsequent drying at 473 K for 14 h and further calcination at 673 K for 4 h in a flow of air. Two samples of metal-modified zeolite, different in a metal loading were prepared. The Zn-modified samples of zeolite beta contained 5.6 wt.% of Zn (Zn/H-BEA-54). Ga-modified zeolite samples contained 1.26 wt.% of Ga (Ga/H-BEA-59). A detailed composition of the zeolite unit cell for the used zeolite samples was established (Table 1) taking into account the chemical analyses, quantitative analyses of acidic SiOHAl groups with ^{1}H MAS NMR, the Al^{IV} and Al^{VI} states by ^{27}Al MAS NMR, Si/Al ratio in zeolite lattice by ^{29}Si MAS NMR [30], and qualitative analysis of the states of Al, Zn and Ga in these materials, based on XRD, ^{1}H{^{27}Al} spin-echo double resonance (TRAPDOR [31,32]), ^{71}Ga MAS NMR, UV–vis diffuse reflectance and IR spectroscopy.

The ^{27}Al MAS NMR has shown that all zeolite samples, except for Zn-modified zeolite, contained the signals from octahedrally coordinated extra-framework aluminium species (ca. 20% of signal intensity) in vicinity of 0 ppm, besides the signal at 54 ppm (ca. 80% of signal intensity) due to tetrahedrally coordinated framework aluminium atoms (see Fig. S3). Concentrations of the acidic groups were obtained by the analysis of the intensities of signals of SiOHAl groups in ^{1}H MAS NMR spectra of all zeolite samples by comparing their intensities with that of methane as internal standard. Their concentration has not exceeded the expected one, estimated on the basis of the framework Si/Al ratio derived from ^{29}Si MAS NMR spectra of the zeolite samples [30].

XRD analysis has demonstrated the presence of bulk ZnO phase in Zn/H-BEA-54 (see Fig. S1). UV–vis diffuse reflectance spectrum of Zn/H-BEA-54 exhibits the bands at 260 nm and 370 nm due to sub-nanometric ZnO clusters inside zeolite pores and due to macrocrystalline particles of ZnO on the external surface of the zeolite crystals, respectively [33] (see Fig. S2). No any gallium oxide bulk phase was revealed with XRD analysis for Ga/H-BEA-59 (see Fig. S1). ^{71}Ga MAS NMR of this sample has shown the signal at 159 ppm from the Ga sites tetrahedrally coordinated by oxygen (Ga^{IV}) and the signal at 0 ppm from the Ga sites octahedrally coordinated by oxygen (Ga^{VI}). These data indicate that the signal at 0 ppm arises from the Ga^{VI} in Ga_2O_3 species, which is however not detected by XRD possibly due to its small dimension, while the signal at 159 ppm could belong to a tetrahedrally coordinated Ga species in the zeolite framework or in Ga_2O_3 species [34–37].

The samples for ^{1}H MAS NMR measurements were prepared by heating 80 mg or 30 mg of the zeolite sample in the glass tubes of 5.5 mm or 3.0 mm outer diameter. The samples were activated by an increase of the temperature from 300 to 673 K at the rate of 10 K h^{-1} under vacuum. Further, the samples were maintained at 673 K for 24 h under vacuum (less than 10^{-2} Pa) and then sealed off (length of the glass tube = 10 mm). The glass tubes could be tightly inserted in 7 or 4 mm zirconia rotors.

2.2. NMR measurements

NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer equipped with broad-band double-resonance-MAS probe. Zirconia rotors (4 or 7 mm outer diameter) with the inserted sealed glass tube were spun at 3–10 kHz by dried compressed air at 300 K. ^{1}H MAS NMR spectra were recorded by the Hahn-echo pulse sequence ($\pi/2-\tau-\pi-\tau$-acquisition), where τ equals to one rotor period (100–333 μs). The excitation pulse length was 4.5 μs ($\pi/2$), and typically 6–24 scans were accumulated with a 4–60 s delay. In double-resonance ^{1}H{^{27}Al} TRAPDOR experiments [31,32], Hahn-echo sequence was applied to the ^{1}H channel with irradiation of aluminium during the both τ periods. The ^{27}Al nutation frequency of the irradiation field was about 60 kHz. ^{27}Al MAS NMR spectra were acquired with a short $\pi/12$ radio-frequency pulse (0.6 μs), and about 1000 scans were accumulated with a 0.5 s recycle delay. ^{29}Si MAS NMR spectra were recorded with $\pi/2$ excitation pulse of 5.0 μs duration, and 10–15 s repetition time, and 1000 scans for signal accumulation. Both ^{27}Al and ^{29}Si NMR spectra were recorded using 4 mm rotors and a spinning rate of 10 kHz. The chemical shifts were referenced to TMS for ^{1}H and ^{29}Si NMR and to 0.1 M $Al(NO_3)_3$ solution for ^{27}Al NMR.

^{71}Ga MAS NMR studies were performed on Avance-750 spectrometer at resonance frequency of 228.8 MHz with sample spinning rates of 25 kHz (2 mm MAS NMR rotor). For obtaining the ^{71}Ga MAS NMR spectra, a single-pulse excitation of 0.5 μs, a repetition time of 0.5 s and 18,000 scans were used. The ^{71}Ga MAS NMR signals were referenced to saturated solution of $Ga(NO_3)_3$.

The sample temperature was controlled by the Bruker BVT-2000 variable-temperature unit.

2.3. IR measurements

IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer within the spectral range of 700–6000 cm^{-1} and 4 cm^{-1} resolution, 50 scans were acquired for each spectrum. Zeolite samples were pressed in self-supporting wafers (diameter: 0.5–1.0 cm, ρ = 8–12 mg cm^{-2}) and activated in the IR cell at 773 K for 1 h in air and further 1 h at 773 K in dynamic vacuum of 10^{-2} Pa. The adsorption of CO for testing the Brønsted acidity was performed at 77 K at 60–600 Pa of CO pressure. In the recorded spectra, the absorbance was normalized to zeolite wafer density ρ. The spectra were recorded at 298 and 77 K.

3. Results and discussion

3.1. Characterization of hydroxyl groups with IR

The IR spectra of OH groups of the studied samples of zeolite BEA exhibit five clearly distinguished signals (Fig. 1), which were also identified in earlier publications about BEA zeolites

Table 1
Concentration of different OH group of zeolite BEA samples.

Zeolite sample	Si/Al[a]	Concentration of OH groups[b] (μmol/g)				Zeolite unit cell
		AlOHSi, 4.0, 5.1 ppm	AlOH, 2.2–2.7 ppm	SiOH, 2.1 ppm	SiOH, 1.8 ppm	
H-BEA-54	19	680	250	270	700	$Al^{oct}_{0.827}$ $[Na^+]_{0.578}$ $H_{2.623}$ $Al^{tetr}_{3.201}$ $Si_{59.972}$ O_{128}
H-BEA-59	18	890	230	520	520	$Al^{oct}_{0.707}$ $[Na^+]_{0.031}$ $H_{3.422}$ $Al^{tetr}_{3.453}$ $Si_{59.840}$ O_{128}
Zn/H-BEA-54 (5.6% Zn)	19	420	175	175	555	$[ZnO]_{4.856}$ $[Na^+]_{0.578}$ $[Zn^{2+}]_{0.821}$ $H_{1.808}$ ${Al^{tetr}}_{4.029}$ $Si_{59.972}$ O_{128}
Ga/H-BEA-59 (1.26% Ga)	18	800	245	445	440	$[Ga_2O_3]_{0.573}$ $Al^{oct}_{0.790}$ $[Na^+]_{0.031}$ $H_{3.422}$ $Ga^{tetr}_{0.083}$ $Al^{tetr}_{3.370}$ $Si_{59.840}$ O_{128}

[a] Estimated based on ^{29}Si MAS NMR spectra with accuracy of ca. 6%.

[b] Error in estimation of concentration is 10–17%.