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Zn-promoted hydrogen exchange for methane and ethane on Zn/H-BEA zeolite: In situ ^{1}H MAS NMR kinetic study

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Abstract

Hydrogen (H/D) exchange between Brønsted acid sites of both the acidic form of zeolite beta (H-BEA) and Zn-loaded zeolite beta (Zn/H-BEA) and small alkanes (methane and ethane) has been studied by monitoring the kinetics of the exchange in situ with ^{1}H MAS NMR spectroscopy within the temperature range of 433–563 K. On Zn/H-BEA, the exchange has been found to be more than two orders of magnitude faster compared to that on H-BEA. The decrease of reaction temperature and activation energy of the exchange on Zn/H-BEA (86–88 kJ mol^{-1}) compared to the acidic form of zeolite H-BEA (138 kJ mol^{-1}) has been rationalized by the promoting effect of zinc. We propose that the mechanism of the H/D exchange on Zn/H-BEA involves Zn-alkyl species as intermediates.

Keywords: Methane; Ethane; Zn/H-BEA zeolite; H/D exchange; Kinetics; Promoting effect; ^{1}H MAS NMR spectroscopy

1. Introduction

Zn-modified zeolites are effective catalysts for light alkanes aromatization [1–4]. The enhanced selectivity of alkane conversion (ethane [5–7] and propane [8,9]) towards aromatics is attributed to dehydrogenation ability of the loaded zinc species. It has been claimed [2,3] that strong Lewis sites, which are generated by zinc, change the mechanism of alkane activation and transformation from the beta scission to a dehydrogenation step. The alkenes formed under dehydrogenation then undergo a dehydrocyclooligomerization. Both Brønsted acid sites and Zn sites are involved in dehydrocyclooligomerization and produce finally the aromatic compounds [3,8,10,11].

Kazansky et al. [12–14] demonstrated the formation of strong adsorption complexes between small alkanes and Zn^{2+} cations by IR spectroscopy. They claimed that the activation of the alkane molecules in zeolite occurred on Zn^{2+} cations. But a combined IR and NMR study by Ivanova et al. [15] indicated that the activation could alternatively occur on small ZnO clusters, which were located in the pores of the zeolite. Formation of Zn-alkyl species during alkane activation has been reported in both cases [12–15].

The role of possibly formed Zn-alkyl species, as well as the Brønsted acid sites, in small alkane activation requires further clarification. A reaction of hydrogen H/D exchange between acid sites of the zeolite and alkane molecule could help to establish the mechanism of alkane activation on Zn-loaded zeolites. Indeed, a hydrogen exchange between the acid sites of solid catalysts and alkane molecules, which precedes usually the chemical transformation of alkane on acid catalysts [16], is often used to characterize the activation of alkanes and acidity of the catalysts [17–28]. A combination of experimental H/D exchange kinetics data with theoretical analysis of the possible intermediates of the exchange reaction provides valuable information on the mechanisms of the alkane molecule activation and the H/D exchange on solid acid catalysts [17–19]. In this

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paper, we consider the hydrogen H/D exchange between small alkanes (methane and ethane) and Brønsted acid sites of both Zn-loaded zeolite beta (Zn/H-BEA) and its pure acidic form (H-BEA).

2. Experimental

2.1. Materials characterization and samples preparation

The acidic form of the zeolite beta (H-BEA) (Si/Al = 18, average crystal size 0.1–0.2 μm) was synthesized using tetraethyl-ammonium hydroxide as template with subsequent calcination at 823 K in an air flow for 6 h [29]. Chemical analysis yielded the chemical composition: $Na_{0.475}H_{2.845}Al_{3.32}Si_{60.68}O_{128}$.

Zinc-loaded zeolite beta (Zn/H-BEA) was prepared by impregnation of the zeolite H-BEA with a saturated solution of zinc formate, subsequent drying at 473 K for 14 h and further calcination at 673 K for 4 h in a flow of air. The Zn content in the obtained zeolite Zn/H-BEA was 7.2 wt%. Zeolites were characterized by XRD, SEM, TEM, UV–vis and IR diffuse reflectance spectroscopy, and ^{1}H, ^{27}Al, ^{29}Si MAS NMR spectroscopy. A silicon-to-aluminum ratio of 18 in the zeolite framework obtained by ^{29}Si MAS NMR analysis [30], was in agreement with chemical analysis. The ^{27}Al MAS NMR spectrum exhibited only a signal at 54 ppm due to tetra-coordinated framework aluminum atoms for both H-BEA and Zn/H-BEA samples. The residual quantity of the acidic SiOHAl groups in a final Zn/H-BEA was 320 $\mu mol\,g^{-1}$, whereas the quantity of these groups was 480 $\mu mol\,g^{-1}$ in the parent zeolite H-BEA. 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 Zn/H-BEA or H-BEA by comparing their intensities with that of methane as internal standard.

XRD analysis has demonstrated the presence of bulk ZnO phase in Zn/H-BEA. UV–vis diffuse reflectance spectrum of Zn/H-BEA exhibits the bands at 265 and 370 nm due to subnanometric ZnO clusters inside zeolite pores and due to macrocrystalline particles of ZnO on the external surface of the zeolite, respectively [31].

Methane-d_4 (99% D) and ethane-d_6 (99% D) purchased from Aldrich Chemical Company Inc. were used without further purification. The samples for NMR measurements were prepared by heating 80 mg of the zeolite sample in the glass tubes of 5.5 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). The loading was performed at room temperature with 1.15 molecules (ca. 300 $\mu mol\,g^{-1}$) of alkane per unit cell and each sample was then sealed off (length of the glass tube = 10 mm). This glass tube could be tightly inserted in 7 mm zirconia rotors. Before acquisition of the signal, the NMR probe with the sample was preheated for 20 min at the temperature at which the H/D exchange did not yet occur at notable rate. This temperature was 400 K for Zn/H-BEA and 473 K for H-BEA zeolite samples, respectively. Then the temperature was rapidly increased within 3–10 min by 40–100 K to the reaction temperature, equilibrated for 1–2 min, and then the acquisition of NMR signal started. It should be noted here that any noticeable chemical conversion of methane or ethane did not occur under conditions of our experiment, so the H/D exchange was the main transformation of the alkanes.

2.2. NMR measurements

NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer equipped with high temperature broad-band double-resonance MAS probe. Zirconia rotors (7 mm outer diameter) with the inserted sealed glass tube were spun at 3–5 kHz by dried compressed air at 300–568 K. ^{1}H MAS spectra were recorded by the Hahn-echo pulse sequence ($\pi/2$–τ–π–τ–acquire), where τ equals to one rotor period (200–333 μs). The excitation pulse length was 4.5 μs ($\pi/2$), and typically 6–24 scans were accumulated with a 6–26 s delay. In double-resonance $^{1}H\{^{27}Al\}$ TRAPDOR experiments [32,33] a Hahn-echo sequence was applied to the ^{1}H channel with irradiation of aluminum during the both τ periods. The ^{27}Al nutation frequency of the irradiation field was about 70 kHz. ^{27}Al MAS 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 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. The sample temperature was controlled by the Bruker BVT-2000 variable-temperature unit. The calibration of the temperature inside the rotor was performed with an accuracy of ±2 K by using lead nitrate, located inside the rotor, as a ^{207}Pb MAS NMR chemical shift thermometer [34].

2.3. IR measurements

IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a DTGS detector and 2 cm^{-1} resolution and 50 scans for signal accumulation. Zeolite samples were pressed in self-supporting discs (diameter: 1.5 cm, 10–20 $mg\,cm^{-2}$) and activated in the IR cell, attached to a vacuum line, at 723 K for 2 h at 10^{-2}–10^{-3} Pa. The adsorption of CO for testing the Lewis acidity was performed at 77 K at 13–1333 Pa CO pressure. Assessment of Lewis acidity was performed on the base of the absorbance bands at 2170–2230 cm^{-1} belonging to CO coordinated to Lewis site [35]. Among the bands observed for Zn/H-BEA at 2170–2230 cm^{-1}, the band at 2212 cm^{-1} was attributed to CO coordinated to isolated Zn^{2+} cations, the band at 2190 cm^{-1} to CO coordinated to small ZnO clusters and the band at 2170 cm^{-1} to CO on bulk ZnO phase. Quantitative estimations of Lewis sites in accordance to procedure described in Ref. [35] have shown that concentration of Lewis acid sites was ca. 30 $\mu mol\,g^{-1}$ for H-BEA and ca. 110 $\mu mol\,g^{-1}$ for Zn/H-BEA.