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Microporous and Mesoporous Materials 99 (2007) 86–90
MICROPOROUS AND MESOPOROUS MATERIALS
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In situ ^{1}H MAS NMR investigations of the H/D exchange of alkylaromatic hydrocarbons on zeolites H-Y, La,Na-Y, and H-ZSM-5

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Received 28 April 2006; received in revised form 26 June 2006; accepted 28 June 2006
Available online 31 October 2006

Abstract

In situ ^{1}H MAS NMR spectroscopy was used to investigate the H/D exchange behavior of benzene-d_6, ethylbenzene-d_{10}, toluene-d_8, and *p*-xylene-d_{10} with Brønsted acid sites in different zeolite catalysts. In the temperature range of 303 to 393 K, the H/D exchange takes place exclusively between zeolitic bridging OH groups and deuterons bound to the aromatic rings of adsorbed compounds. The activation energies E_a of the H/D exchange of same deuterated aromatics adsorbed on different zeolites have the sequence: H-Y $\geqslant$ La,Na-Y > H-ZSM-5. The decrease of the E_a values correlates well with the increase of the strength of Brønsted acid sites determined via the low-field shift of the ^{1}H MAS NMR signal of bridging OH groups upon adsorption of deuterated acetonitrile (CD_3CN). The E_a values determined for the different deuterated aromatic hydrocarbons adsorbed on the zeolites under study show the sequence: benzene ($E_a = 46$–76 kJ/mol) > ethylbenzene ($E_a = 29$–41 kJ/mol) > toluene ($E_a = 25$–32 kJ/mol) >*p*-xylene ($E_a = 20$–27 kJ/mol). Generally, this sequence demonstrates the electron donation effect of alkyl groups bound to the aromatic rings (+I effect). The larger E_a value of ethylbenzene in comparison with that of toluene indicates an interaction of ethylbenzene with the zeolite framework via its ethyl group leading to a lower electron density and a decrease of the +I effect of this alkyl group towards the aromatic ring.

Keywords: H/D exchange; Alkylaromatic hydrocarbons; Zeolites; Acid strength; *In situ* ^{1}H MAS NMR

1. Introduction

Since a large number of chemical reactions in industrial processes are initiated or promoted by proton transfer steps, Brønsted acidic zeolites have an obvious importance as solid acid catalysts [1]. In a general manner, the rate of the proton transfer between acidic surface sites and reactants or probe molecules can be utilized as a dynamic measure of the Brønsted acidity of solid acids. As an experimental approach, the activation energy of the H/D exchange between deuterated reactants or probe molecules, such as benzene, and bridging OH groups in different dehydrated zeolites was investigated by ^{1}H MAS NMR spectroscopy [2,3]. Moreover, increasing efforts have been devoted to the determination of the H/D exchange of hydrocarbons adsorbed on zeolite catalysts with the aim of clarifying intermediates formed and reaction pathways [4–10]. The alkylation of aromatic hydrocabons and the alkylbenzene transalkylation on acidic zeolite catalysts have great potentials for the industrial chemistry [1]. In addition, the protonation and methylation of polyalkylaromatic hydrocarbons are important steps in the methanol-to-olefin (MTO) conversion process on zeolites [11]. To shed more light on these acid catalyzed reactions, the H/D exchange behavior of aromatic compounds in

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1387-1811/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2006.06.041

dependence on the number and type of alkyl groups has been studied in the present work.

A further aim of this work is the correlation of the experimentally obtained activations energies of the H/D exchange with the chemical behavior of surface acid sites in zeolites. In the past decades, a number of probe molecules were suggested for the NMR characterization of the strength of Brønsted acid sites on solid catalysts (see [12] and references therein). Acetonitrile was found to be a suitable probe molecule to discriminate between acid centres of different strength in zeolite catalysts by the low-field shift $\Delta\delta_{1H}$ of the ^{1}H MAS NMR signals of Brønsted acid sites [13–17]. A strong low-field shift corresponds to a high acid strength. The interaction of acetonitrile with the acid surface sites in zeolite catalysts occurs via an O–H···N-type hydrogen bonding [15,16]. The application of deuterated acetonitrile (CD_3CN) for ^{1}H MAS NMR studies of dehydrated zeolites allows the study of the signals of Brønsted acid sites without overlapping signals of the probe molecules. In the present study zeolites H-Y, La,Na-Y, and H-ZSM-5 were applied as model catalysts exhibiting acid centres of different strength.

2. Experimental

2.1. Sample preparation

Zeolite Na-Y ($n_{Si}/n_{Al} = 2.7$) was purchased from Degussa AG, Hanau, Germany. The NH_4^+-form material was prepared by a fourfold ion exchange of zeolite Na-Y at 353 K in a 1.0 M aqueous solution of NH_4NO_3 leading to an ion-exchange degree of 91% as determined by AES-ICP. Subsequently, the material was washed with demineralized water and dried at room temperature. Zeolite H-Y was obtained by heating the NH_4^+-form material in vacuum with a rate of 20 K/h up to 723 K and calcination at a pressure of $p < 10^{-2}$ mbar for 12 h. Zeolite La,Na-Y was prepared by an ion-exchange of zeolite Na-Y for three times with a 0.1 M aqueous solution of $La(NO_3)_3$ at 353 K leading to an ion-exchange degree of 73%. Then, the material was washed with demineralized water and dried at room temperature. For the dehydration, zeolite La,Na-Y was heated in vacuum with a rate of 20 K/h up to 473 K and evacuated at a pressure of $p < 10^{-2}$ mbar for 12 h.

Zeolite Na-ZSM-5 (MFI) with an n_{Si}/n_{Al} ratio of 26 was synthesized according to Ref. [18]. To remove the template, the assynthesized material was heated with a rate of 60 K/h to 823 K in dry nitrogen and calcined at this temperature for 6 h in synthetic air (20 vol.% oxygen, 60 l/h). The NH_4^+-form material was prepared by a fourfold ion exchange of zeolite Na-ZSM-5 at 353 K in a 1.0 M aqueous solution of NH_4NO_3 leading to an ion-exchange degree of 98%. Subsequently, the material was washed with demineralized water and dried at room temperature. Finally, zeolite H-ZSM-5 was obtained by heating the NH_4^+-form material in vacuum with a rate of 20 K/h up 723 K and a calcination at this temperature at a pressure of $p < 10^{-2}$ mbar for 12 h.

All zeolite catalysts were characterized by AES-ICP, XRD, and solid-state ^{1}H, ^{27}Al, and ^{29}Si MAS NMR spectroscopy, indicating that the materials obtained after cation exchange and calcination were neither damaged nor dealuminated.

Benzene-d_6, ethylbenzene-d_{10}, toluene-d_8, and p-xylene-d_{10} with a deuteration degree of 99.6%, 98.0%, 99.6%, and 99.5% were purchased from Dr. Ehrenstorfer GmbH, Augsburg. Using a vacuum line, the dehydrated zeolite catalysts were quantitatively loaded with 0.5 molecules of deuterated aromatics per bridging OH group in the supercages or 10-ring channels. Acetonitrile-d_3 with a deuteration degree of 99.9% was obtained from ACROS. CD_3CN was quantitatively loaded with 1 molecule per OH group on the dehydrated zeolites.

2.2. ^{1}H MAS NMR measurements

All ^{1}H MAS NMR studies were carried out on a Bruker MSL-400 spectrometer at a resonance frequency of 400.1 MHz with a sample spinning rate of ca. 9 kHz. The spectra were recorded after $\pi/2$-pulse excitation, with a repetition time of 10 s, and were referenced to tetramethylsilane (TMS). Before starting the ^{1}H MAS NMR experiments, the samples were filled into 4 mm MAS rotors in a glove box purged with dry nitrogen. The H/D exchange was initiated by heating the MAS rotor in a variable-temperature MAS NMR probe. The investigations of CD_3CN adsorbed on the dehydrated zeolites were performed at room temperature.

The decomposition and simulation of the NMR spectra were performed using the Bruker software WINNMR and WINFIT.

3. Results and discussion

3.1. In situ ^{1}H MAS NMR investigations of the H/D exchange of aromatic hydrocarbons adsorbed on dehydrated zeolite catalysts

As an example, Fig. 1 shows the stack plot of the ^{1}H MAS NMR spectra recorded at 358 K during the H/D exchange of deuterated ethylbenzene on H-Y as a function of time. The increasing intensity of the signal at 7.3 ppm of hydrogen atoms bound to the aromatic rings of ethylbenzene molecules and the simultaneous decrease of the signal of bridging OH groups in the supercages of zeolite H-Y at 3.9 ppm indicates a H/D exchange between the zeolitic Brønsted acid site and the adsorbates. On the other hand, the high-field signals at 1.2 and 2.6 ppm caused by residual hydrogen atoms in methyl and methylene groups, respectively, of ethylbenzene (deuteration degree of 98.0%) show no change in their intensity. This finding implies that deuterons bound to aromatic rings rather than those in the ethyl groups of the ethylbenzene molecules are involved in the H/D exchange. The same selective H/D exchange with deuterons bound to the aromatic rings was found