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Influence of dealumination and treatments on the chromium speciation in zeolite CrBEA

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ABSTRACT

Two samples of chromium-containing BEA zeolite, CrAlBEA and CrSiBEA prepared by different methods, are investigated by XRD, TPR and FTIR of CO adsorbed at 100 K and NO at ambient temperature. CrAlBEA is prepared by conventional ion exchange, and CrSiBEA, by a two-step post-synthesis method (dealumination of TEABEA zeolite by treatment with nitric acid followed by incorporation of chromium into resulting SiBEA by impregnation with $Cr(NO_3)_3$ aqueous solution). In both calcined and activated samples, the major part of chromium is in the form of Cr^{6+}. A small amount of Cr^{3+} is also detected in CrAlBEA by adsorption of CO (a Cr^{3+}–CO band at 2189 cm^{-1}) and NO (a Cr^{3+}–NO band at 1875 cm^{-1}).

The TPR pattern of CrSiBEA exhibits a main peak at 726 K, while two main peaks, at 520 and 760 K are observed with CrAlBEA. All these peaks are due to reduction of Cr^{6+} species. In line with the TPR results, the speciation of chromium in CrSiBEA does not change upon treatment of the sample at 573 K in H_2. In contrast, the same treatment leads to the reduction of CrAlBEA with creation of Cr^{3+} as shown by the appearance, after CO adsorption, of Cr^{3+}–CO bands at 2208–2202 cm^{-1}. When CrAlBEA is treated with H_2 at 773 K, some Cr^{2+} appear which can form tricarbonyls (as evidenced by IR bands at 2214, 2206 and 2179 cm^{-1}). The treatment of CrSiBEA with H_2 at 773 K leads to the formation of similar Cr^{2+} sites. However, with this sample, some Cr^{3+} is also present, as shown by a Cr^{3+}–CO band at 2198 cm^{-1} appearing after CO adsorption. In the presence of NO, Cr^{2+} ions are slowly oxidized to Cr^{3+}. These results demonstrate the important effect of dealumination of BEA zeolite and the treatment of Cr-containing BEA on the chromium speciation.

1. Introduction

Metal-containing zeolites have found wide applications in adsorption and catalysis. It is now well established that the zeolite matrix strongly affects the state and the properties of the metal cations. For instance, the cations exchanged in zeolites are characterized by a low coordination number with respect to the framework oxygen which allows coordination of more than one guest molecule [1–10]. However, the metal cation properties are determined by many factors, such as the nature of the exchanged cation, its oxidation state, its radius and its position in the zeolite.

The presence of aluminum in zeolites is a reason for their low hydrothermal stability, explaining why, in some cases, siliceous zeolites can be advantageous as compared to Al-containing zeolites. However, dealumination of the latter suppresses their ion-exchange capacity and the cations introduced in different ways are generally characterized by properties differing from those of exchanged cations. However, in some cases cations in siliceous zeolites can also be highly coordinatively unsaturated [11,12]. Moreover, cations introduced into siliceous zeolites can occupy framework positions and generate new properties of the zeolite [12–17].

We compared earlier the speciation of nickel and cobalt cations in two BEA zeolites: HAlBEA and dealuminated SiBEA [8,18]. It was found that the presence of aluminum strongly affected the cation speciation and, in consequence, also the properties of Ni- and Co-containing BEA zeolites.

Chromium-containing zeolites have important application in catalysis [19–22]. For instance, it has been reported that Cr-ZSM-5 is active in the elimination of chlorinated VOCs and oxidation of alcohols leading to a high yield of ketones [19,20]. Cr/SiO_2 catalysts are well known to be active in polymerization of ethylene and

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existence of low-coordinated Cr^{2+} ions is necessary in this case [21,22]. Because the catalytic performance depends on the state of chromium ions, in this work we determine the chromium speciation in two chromium-containing BEA zeolites subjected to different redox treatments: one of the samples, CrAlBEA, was prepared by conventional ion exchange, and the other, CrSiBEA, by a two-step post-synthesis method [23–27]. Although applying different techniques, we concentrated mainly on IR spectroscopy of probe molecules.

The most used probe molecules for characterization of supported chromium catalysts are CO and NO. However, most studies are performed with using only CO or only NO and the results are difficult to compare. Here, we use both, CO and NO as molecular probes for both zeolites in order to obtain information on the speciation of chromium. The combined use of the two molecular probes allows distinguishing between the various carbonyl and nitrosyl species due to the presence of various chromium species in the samples prepared by different methods. In order to be able to compare the results, exactly the same pretreatments were used for the two samples in the different experiments. Other techniques, such as TPR and XRD, were also used to provide complementary information.

2. Experimental

2.1. Materials

Tetraethylammonium BEA (TEABEA) zeolite was provided by RIPP (China). A portion of it was calcined (15 h, 823 K) to obtain the organic-free HAlBEA (Si/Al = 11). CrAlBEA was prepared by conventional ion exchange: HAlBEA was contacted in air at 343 K with a 2×10^{-3} mol dm^{-3} aqueous solution of $Cr(NO_3)_3{\cdot}9H_2O$ (pH = 2.4). The exchange procedure was repeated twice. The solid was then filtered and washed with distilled water. The resulting green solid, dried in air at 353 K for 24 h and containing 1.65 wt.% of Cr, was labelled CrAlBEA.

A second portion of TEABEA was treated, as described earlier [23–27], by a 13 mol L^{-1} HNO_3 solution (4 h, 353 K) to obtain the dealuminated organic-free BEA zeolite. The resulting SiBEA zeolite (Si/Al > 1300) with vacant T-sites was recovered by centrifugation, washed with distilled water and dried overnight at 353 K. Then, in order to introduce chromium ions into vacant T-sites, SiBEA was impregnated under aerobic conditions by a 3.8×10^{-3} mol dm^{-3} aqueous solution of $Cr(NO_3)_3{\cdot}9H_2O$ (pH = 2.6). First, 2 g of SiBEA were stirred for 24 h at 298 K in excess solvent using 200 ml of the chromium nitrate solution and the suspension (pH = 2.6) was stirred for 2 h in air at 353 K until the complete evaporation of water. The resulting light-green solid, dried in air at 353 K for 24 h and containing 0.9 wt.% of Cr was labelled as CrSiBEA.

CrAlBEA and CrSiBEA were characterized by different techniques after various specific treatments as described below.

2.2. Techniques

Chemical analysis of the samples was performed with inductively coupled plasma atom emission spectroscopy at the CNRS Centre of Chemical Analysis (Vernaison, France).

Powder X-ray diffractograms (XRD) were recorded in ambient atmosphere on a Siemens D5000 apparatus using Cu Kα radiation (λ = 154.05 pm).

Temperature-programmed reduction (TPR) experiments were performed in a U-shaped tubular quartz reactor, using a flow of 5% H_2 in Ar (1.8 L h^{-1}). The sample was heated from room temperature to 1220 K (450 K h^{-1}) and the H_2 consumption was monitored by a thermal conductivity detector (TCD). Prior to reduction, the samples were treated at 773 K (100 K h^{-1}) in flowing air for 3 h and then rehydrated at ambient atmosphere for 24 h. The corresponding samples will hereafter be referred to as calcined samples.

FTIR spectra were recorded in transmission mode on a Nicolet Avatar 360 spectrometer averaging 128 scans at a spectral resolution of 2 cm^{-1}. Before the experiments, the samples were treated at 773 K (100 K h^{-1}) in flowing air for 3 h in order to be able to compare the results with the TPR data. Then self-supporting pellets (ca. 10 mg cm^{-2}) were prepared from sample powders and treated directly in a purpose-made IR cell allowing measurements at ambient and low temperatures. The cell was connected to a vacuum-adsorption apparatus with a residual pressure below 10^{-3} Pa. Prior to the experiments, the samples were treated *in situ* first in oxygen (13.3 kPa) for 1 h at 673 K and then in dynamic vacuum (10^{-3} Pa) for 1 h at the same temperature. The procedure aimed at removal of adsorbed water, carbonates and eventual organic contaminants. The corresponding samples will hereafter be referred to as activated samples. After characterization of the samples by probe molecules (first by CO and then by NO) they were subjected to treatment with hydrogen at different temperatures. After each treatment the samples were characterized again by probe molecules in the same sequence.

Carbon monoxide (>99.997 purity) was supplied by Linde AG and nitrogen monoxide was purchased from Messer Griesheim GmbH. Before adsorption, CO was passed through a liquid nitrogen trap, while NO was additionally purified by fraction distillation.

3. Results and discussion

3.1. Initial characterization of the samples

3.1.1. X-ray diffraction

Neither calcination of TEABEA (at 853 K for 15 h in air) nor its dealumination by nitric acid affect the zeolite crystallinity, as indicated by similar X-ray diffraction line widths of the patterns of HAlBEA and SiBEA (Fig. 1, patterns a–c). It has been reported [28]

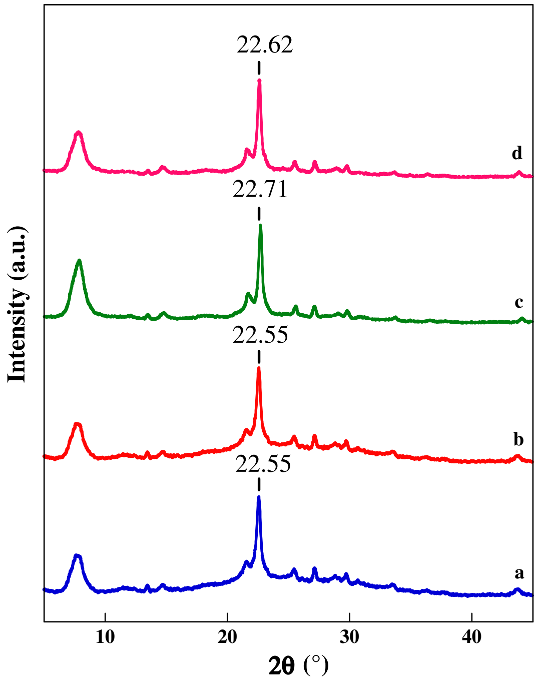

Fig. 1. X-ray diffractograms recorded at ambient atmosphere of (a) HAlBEA, (b) CrAlBEA obtained by the conventional ion exchange method, (c) SiBEA obtained by dealumination, and (d) CrSiBEA obtained by the two-step post synthesis method.