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Transition metal exchanged β zeolites: Characterization of the metal state and catalytic application in the methanol conversion to hydrocarbons

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Various first-row transition metal cations (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) have been introduced to zeolite beta using ion exchange procedures. Both aluminum and transition metal sites were studied by UV–Vis spectroscopy, XPS and ^{27}Al NMR. Generally, ion exchange favored the incorporation of Al defects into the zeolite framework. The effect of the divalent and trivalent cations on the final zeolite beta structure was found to be considerably different. While divalent cations were mainly exchanged for Bronsted acid sites after calcination, trivalent cations such as Fe^{3+} were mostly transformed into oxide-like species whilst Cr^{3+} species were oxidized to Cr^{6+} species. Their surface properties were quite distinct since only divalent cations generated strong Lewis acid sites, even though the Brönsted acidity decreased in all cases. Their catalytic performance was evaluated in the transformation of methanol to hydrocarbons. Various metal species, i.e., Cr^{6+}, Mn^{2+}, Fe^{3+} and Zn^{2+} were found to act as promoters of polymerization or aromatization reactions. In particular, Cr species were found to enhance the catalytic activity in the conversion of methanol and dimethyl ether into higher order hydrocarbons.

1. Introduction

Zeolites are widely used as catalysts for a variety of organic reactions [1]. Apart from their different topologies and pore architectures, they possess different acidities depending on their Si to Al ratio. The bridging hydroxyl groups are responsible for the Brönsted acidity of these materials. Ion exchange has been used to introduce different metal cations in zeolites [2]. These species can act as Lewis acid sites and redox active centers, thus providing new functionalities to zeolites [3]. Whilst the catalytic activity in acid catalysis is usually related to the Brönsted acid sites, the influence of the Lewis acid sites cannot be overruled and is still widely debated [4]. For instance, the presence of Lewis acid sites, generated by dealumination or incorporation of BF_3 [5], increased the acid strength of Brönsted sites, whereas zeolites exchanged with Zn^{2+} exhibited no increased Brönsted acid strength [6].

Zeolites exchanged with transition metals are useful in many reactions. For example, Zn^{2+} exchanged zeolites effectively catalyze hydroamination reactions [7], aromatization of ethylene [8], dehydrogenation of propane [9] and synthesis of 2-methylpyrazine from ethylene diamine and propylene glycol [10], among others. Also, zeolites exchanged with Co^{2+}, Fe^{3+}, and Cu^{2+} are excellent catalysts for the selective catalytic reduction (SCR) of NO by ammonia [11,12]. The SCR of NO is also catalyzed by zeolite beta exchanged with Co^{2+} cations using propane as the best reductant [13]. An analogous catalyst was used for the dehydrogenation and dehydrocyclization of alkanes [14]. During the ethanol steam reforming on Na-Y zeolite, the exchange with Co^{2+} or Ni^{2+} cations led to ethylene by dehydration [15]. Ni^{2+} exchanged on mordenite is used as catalyst for the isomerization and ring-opening of styrene oxide [16]. The catalytic reforming of methane by carbon dioxide is also observed on different Ni^{2+} exchanged zeolites [17]. A Cu-exchanged USY zeolite synthesized by vapor-phase exchange with CuCl afforded diynes through homocoupling of terminal alkynes [18]. The catalytic oxidation of pyridine pollutant over various zeolites exchanged with Cu^{2+} has also been reported [19]. Mn^{2+} exchanged CaA zeolites are promising catalysts for the abatement of volatile organic compounds [20] and Mn^{2+} exchanged beta zeolite has been used as heterogeneous catalyst for the liquid phase epoxidation of alkenes with aqueous hydrogen peroxide (30% H_2O_2) [21]. The performance of Fe^{3+}, as well as Co^{2+} and Mn^{2+}, exchanged LTA zeolites

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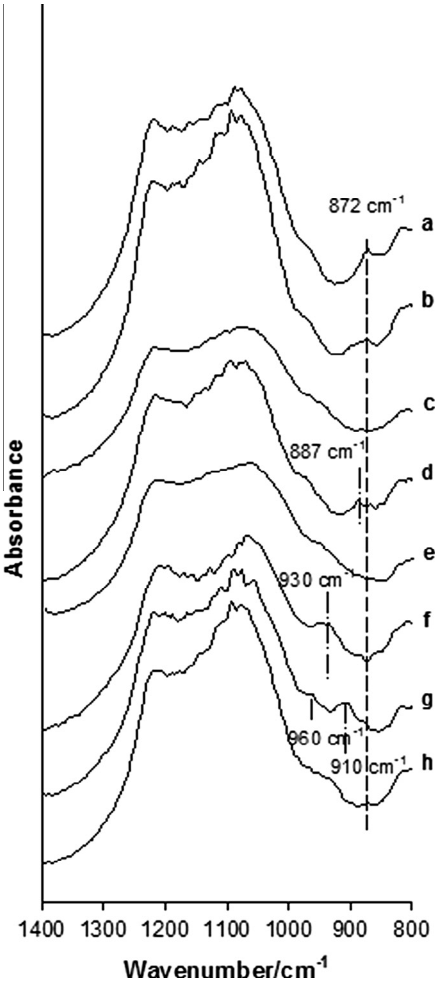

Fig. 1. DRIFT spectra of zeolites: (a) H-β, (b) Cr-β, (c) Mn-β, (d) Fe-β, (e) Co-β, (f) Ni-β, (g) Cu-β and (h) Zn-β in the characteristic region of structural vibrations.

for the catalytic combustion of lean methane–air mixtures has recently been studied [22]. Also, the oxidative dehydrogenation of propane has been carried out over chromium-containing beta zeolites [23].

Zeolite beta is an outstanding catalyst for a great variety of organic processes [24]. Although less studied than for other zeolites, ion exchange has been used for the introduction of different metal cations in this material to improve its activity and/or selectivity. Beside some previously referred examples, alkaline and alkaline-earth metals have been usually chosen for that purpose. Generally, they reduce the concentration of Brönsted acid sites, thus favoring the selectivity toward different products [25–28]. The highly interesting methanol to hydrocarbons process proceeds by a complex mechanism which remains controversial in some aspects [29,30]. However, it is well known that it requires the presence of Brönsted acid sites and indeed it has been proposed as a test reaction for different molecular sieves [31,32]. We have previously reported that the conversion to hydrocarbons over alkaline and alkaline-earth exchanged beta zeolite is mostly dependent on the exchange degree and that the Lewis acidity generated by the exchanged cations does not influence the reaction but it modulates the materials acid strength and product selectivity [33]. Various transition metal exchanged beta zeolites were also reported to be active in the transformation of acetone into hydrocarbons [28,34]. Selectivity and activity were closely related but none of the exchanged catalysts surpassed the activity of the protonic zeolite. Herein, we study different transition metal exchanged beta zeolites using complementary techniques such as FTIR, UV–Vis, XPS, ^{27}Al NMR and chemisorption experiments, in order to determine the nature of the metal species. We also test the materials performance as catalysts in the methanol conversion to hydrocarbons and elucidate the possible participation of the exchanged metals (Lewis acid sites) in this reaction.

2. Experimental section

Zeolite β was exchanged with different metal cations (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) according to previously reported procedures [34]. Briefly, the protonic form of zeolite β (Si/Al = 12.5) was stirred in a 0.3 M aqueous solution of the metal salt (6 ml/g) at 80 °C during 24 h. The exchanged zeolites were calcined at 600 °C for 3 h.

Several structural techniques were used for the characterization of the exchanged zeolites. XRD analyses and N_2 adsorption isotherms were reported elsewhere [34]. Diffuse reflectance infrared spectra were recorded on a FT-IR PerkinElmer Spectrum 100 spectrometer at 300 °C. Also, diffuse reflectance UV–Vis spectroscopy studies were carried out at room temperature using a PerkinElmer Lambda 650 S spectrophotometer ($BaSO_4$ as reference). XPS spectra were recorded with a SPECS Phoibos HAS 3500 150 MCD. The residual pressure in the analysis chamber was 5×10^{-9} Pa. The X-ray source was generated by a Mg anode ($h\nu = 1253.6$ eV) powered at 12 kV and with an emission current of 25 mA. The powdered sample was pressed and introduced into the spectrometer without previous thermal treatment. They were outgassed overnight and analyzed at room temperature. Accurate binding energies (BE) have been determined with respect to the position of the Si 2p peak at 103.4 eV. The peaks were decomposed using a least squares fitting routine (Casa XPS software) with a Gauss/Lorenz ratio of 70/30 and after subtraction of a linear background. The surface atomic concentration ratios were calculated using sensitivity factors from the Casa XPS element library. ^{27}Al MAS NMR spectra were recorded at room temperature in a Bruker Avance-400 WB spectrometer (9.4 T) at a spin rate of 12 kHz. A resonance frequency of 104.2 MHz, pulse of 10°, a recycle delay of 0.5 s and a number of scans of 6000 were applied. Chemical shifts were measured relative to $Al(H_2O)_6^{3+}$ (0 ppm).

Temperature programmed desorption of pyridine and acetonitrile was used to determine the acidity of the zeolites studied in this work. For this, 80 mg of zeolite were calcined in the reactor at 580 °C using a heating rate of 10 °C/min in a N_2 flow. Subsequently, pyridine (or acetonitrile) was chemisorbed by injecting several pulses of 1 μl until saturation of the catalyst at 140 °C (or 110 °C for acetonitrile). After 12 h in a N_2 flow, desorption was carried out at a rate of 5 °C/min up to 650 °C.

Catalytic reactions were carried out at 400 °C in a microanalytical pulse reactor as reported elsewhere [33]. 10 mg of catalyst and 0.2 μl of pulse size were used. The analyses were performed on a Petrocol 100 m × 0.25 mm ID capillary column with the following program: 15 min at 40 °C and then 5 °C min^{-1} up to 220 °C. The identity of each reaction product was determined by mass spectrometry using a Hewlett Packard 5971A mass selective detector. Conversions and selectivities were calculated on a carbon basis. The configuration of the system avoids the condensation of heavy aromatic products in the transmission lines.

3. Results and discussion

3.1. Aluminum sites in metal-exchanged zeolites

The DRIFT spectra in the framework region of β-type zeolites (Fig. 1) revealed a small band at ca. 872 cm^{-1}, assigned to O–Al–