

Solid-state dealumination of zeolites for use as catalysts in alcohol dehydration



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ABSTRACT

The dealumination of zeolites has been studied to tune acidity, resulting in enhanced catalytic efficiency. MOR, FER, and ZSM-5 were dealuminated to remove 5, 10, 15, or 20 mol% of Al with $(\text{NH}_4)_2\text{SiF}_6$ (solid-state reaction at 80 °C). XRD, SEM, and FT-IR showed structural maintenance. Aluminum removal was confirmed by the total Si/Al ratio (XRF and AAS) and ^{27}Al MAS NMR. The dealuminated samples were tested in the dehydration of different alcohols and compared to the protonic parent zeolites. Dealuminated MOR samples exhibited a decrease in coke formation (maximum decrease of 18.3%, 18.2%, and 6.1% for methanol, ethanol, and 1-propanol dehydration, respectively), and an increase in conversion values (maximum increase of 29.0%, 13.9%, and 6.2% for methanol, ethanol, and 1-propanol dehydration). H-FER/20% showed an improvement in methanol (19.9%) and ethanol (3.8%) conversions and a reduction of coke (decrease of 8.6% and 5.6%, respectively), corroborating the highest value of acid sites (0.73 mmol g^{-1}). All catalysts showed 100% selectivity to each desired product. The mechanisms for all dehydrations were related to the presence of Brønsted acid sites. Methanol dehydration might involve the generation of methoxonium ion, and ethoxy groups might be formed for ethanol conversion. For ZSM-5, Lewis acid sites may also participate in the elimination mechanism. High reaction temperature (300 °C) favored intramolecular dehydration to ethylene, avoiding formation of diethyl ether and oligomers. Structural defects on H-ZSM-5/15% could facilitate the access of 1-propanol to active sites, leading to the best combination of TON (0.67), conversion (100%), and coke formation (0.35%).

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1. Introduction

Zeolites are crystalline microporous materials with a high specific surface area and nanometer channels that are used for many important industrial reactions such as cracking, hydrocracking, and isomerization [1–3]. Zeolites with higher Si/Al ratios exhibit higher selectivity, resistance to thermal or chemical treatments [4], and lower water affinity. To obtain these modified materials, a dealumination process can be used to remove an amount of aluminum atoms from the zeolitic framework without considerably affecting the microporous structure of the solid [5].

Severe dealumination can be accomplished using HCl [6], which removes Al and leaves the previously occupied spaces empty. Occasionally, this method can critically reduce crystallinity and

cause the destruction of the structure [1]. Using a controlled process, this type of dealumination can produce mesopores within the zeolite structure that improve molecule diffusion [7]. However, the creation of mesopores can also lead to the formation of extra framework aluminum (EFAL) species, such as Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, and $\text{Al}(\text{OH})_3$, which can then block pores and channels [6,8].

Ammonium hexafluorosilicate $((\text{NH}_4)_2\text{SiF}_6$, AHFS) is another dealuminating agent that is currently used. AHFS achieves a mild dealumination through the isomorphic substitution of aluminum with silicon [9], and it has the advantage of producing materials practically free of EFAL species [6]. Literature reports have shown that this dealumination process has limitations when performed with aqueous solution due to the difficulty of controlling the experimental parameters and degree of dealumination [10]. Solid-state dealumination was first used in 1994 [11] to overcome those limitations.

Dealuminated zeolites can be found in many applications, such as n-heptane hydroisomerization [12], catalytic cracking of cumene [13], methanol and ethanol dehydration [14–18], among

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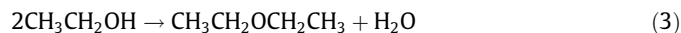
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others [19–22]. Dimethyl ether (DME), the main product of methanol dehydration, has been widely studied due to its potential to replace petroleum-based fuels [23]. Methanol dehydration provides better yields than the direct synthesis from syngas [24] and therefore is the most used commercially [25]. On the other hand, the main product of ethanol dehydration, ethylene, is used in the preparation of polyethylene, polyvinyl chloride (PVC), ethylene oxide, and ethylene dichloride [26]. When ethylene is obtained by bio-ethanol dehydration, it results in a net reduction of CO₂, producing the so-called green polyethylene [17,27,28], in contrast to its conventional production by naphtha thermal cracking or ethane dehydrogenation.

H-ZSM-5 zeolite and γ -Al₂O₃ are the most studied catalysts for both methanol and ethanol dehydration. Although γ -Al₂O₃ is active, it adsorbs large quantities of water, which is a byproduct of both methanol (reaction (1)) and ethanol dehydration (reactions (2) and (3)). The competition between alcohol and water molecules for the active sites on γ -Al₂O₃ results in decreased activity [29]. This is a problem, especially considering that water is also present in crude methanol (20–30% water) and bioethanol (10 wt.% ethanol, remainder is water and fermentation impurities) [29,30]. Zeolites such as ZSM-5 have high hydrophobicities, leading to better yields of the desired products.

The desired ethanol dehydration reaction (2) is favored at higher temperatures and produces ethylene. However, a side reaction (3) is favored at lower temperatures and produces diethyl ether (DEE) [29,30].



This paper addresses the dealumination of MOR, FER, and ZSM-5 by removing 5, 10, 15, or 20 mol% of Al with AHFS (solid-state reaction at 80 °C). To the best of our knowledge, there is no other systematic study on the degree of solid-state dealumination for any zeolite. In addition to structural, textural, and acidity characterizations, dehydration reactions with methanol, ethanol, and 1-propanol were used as catalytic tests for the developed materials. The aim of the dealumination was to decrease the deactivation of the catalysts and to investigate the relationship between the alcohol chain and the catalytic results such as conversion, turnover number, and coke formation.

2. Experimental

2.1. Dealumination of zeolites

All of the zeolites used in this study were obtained from Zeolyst. Sodium form MOR (mole ratio, SiO₂/Al₂O₃ = 13; Na₂O = 6.5 wt.%) underwent cation exchange three times with NH₄Cl solution (1 mol L⁻¹) to convert it to the ammoniacal form (NH₄-MOR). FER (mole ratio, SiO₂/Al₂O₃ = 20) and ZSM-5 (mole ratio, SiO₂/Al₂O₃ = 50), supplied in the ammoniacal form, and NH₄-MOR were all dealuminated through the solid-state reaction with dealuminating agent AHFS (Aldrich) to remove different molar percentages of Al (5, 10, 15, or 20 mol%). The nomenclature used to identify samples was H-XXX/Y%, where XXX represents the zeolite (MOR, FER or ZSM-5), and Y% represents the percentage of Al that was removed. Each zeolite was weighed (12.0 g) with the specific amount of AHFS to result in the desired percentage of dealumination and then heated at 80 °C for 2 h in a vacuum oven. Then, the samples were washed with 800 mL of hot water (80 °C) and dried. After dealumination, all of the samples were calcined at 550 °C for

8 h to remove ammonium, turning the zeolitic materials into their protonic forms.

2.2. X-ray diffraction (XRD)

XRD data were obtained with a Bruker powder diffractometer (model D8 Focus, θ - 2θ) with radiation from a copper tube ($K\alpha = 1.5406 \text{ \AA}$), operating at 40 kV and 30 mA. The scanning rate used was 1° min⁻¹ in the region of 2θ from 2 to 50°. To determine the variation of the zeolite crystallinities (%C) with dealumination, the following calculation was performed using the recommended reflections from the ASTM D 5758 for ZSM-5: (051), (501), (-501), (-511), (511), (033), (-313), (313); MOR: (330), (150), (202), (350); and FER: (200), (020), (011), (310), (220), (031), (420), (411), (330), (510), (040), (202), (240), (312), (431), according to literature [31–33].

$$\%C = \frac{[\text{peak intensity from sample}]}{[\text{peak intensity from pattern}]} \times 100 \quad (4)$$

The cell parameters were obtained using the EVA Software (release 2006) provided by Bruker.

2.3. Scanning electronic microscopy (SEM)

Powder samples were first dropped onto double-sided carbon tape at the metal stubs. The samples were then coated with platinum using a sputter coater (Leica, model SCD 500). Finally, SEM images were obtained using a scanning microscope (JEOL, model JSM 7001F) under high vacuum.

2.4. Textural analysis

Adsorption isotherms of the parent samples in protonic form were obtained with a surface area and porosimetry analyzer (Micrometrics, ASAP 2020C) based on physisorption of gaseous N₂ at $-196 \text{ }^\circ\text{C}$. Before the analysis, samples were degassed with evacuation (target pressure of 10 $\mu\text{m Hg}$) at 300 °C for 4 h. The equations of BET (Brunauer, Emmet, and Teller), t -Plot, BJH (Barrett, Joyner and Halenda), and MP-Method were used to describe the experimental isotherms.

2.5. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the structural region of calcined samples were obtained with a Thermo Scientific spectrometer (Nicolet, model 6700) from 128 scans and using a spectral resolution of 4 cm⁻¹. The data were analyzed by the OPUS[®] software from Bruker. Each sample was prepared with a mixture of 1:100 wt.% sample/dried KBr (Merck).

2.6. X-ray fluorescence by dispersive energy (XRF-EDX)

An XRF/EDX spectrometer from Shimadzu (model EDX 720) was used to examine the elements in the range from sodium (²³Na) to uranium (⁹²U) in the samples, and its X-ray target was rhodium (Rh). The samples were prepared with polypropylene film and analyzed in vacuum to determine the quantity of elements (silicon and aluminum).

2.7. Atomic absorption spectroscopy (AAS)

Atomic absorption spectrometry (Varian, model AA 240FS) was used to calculate the total Si/Al ratio of the ZSM-5 samples. The use of different techniques for the three studied zeolites was necessary

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