



Designing MFI-based catalysts with improved catalyst life for C_3 and C_5 oligomerization to high-quality liquid fuels

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ABSTRACT

Light olefin oligomerization is an important alternative for the production of clean liquid automotive fuels and can be performed in the presence of solid acid catalysts. Among these, medium-pore zeolites, and especially ZSM-5, have been widely described in the open literature. In this work, the relative importance of intracrystalline diffusion path lengths for the product molecules (depending on the zeolite crystal size and the presence of mesopores in the crystallites) and Brønsted acid site density are discussed for two different olefins, propene and 1-pentene. Thus, ZSM-5 samples with (a) the same crystallite size and different acid site density, (b) the same density of acid sites and different crystallite size, (c) postsynthesis generation of mesopores by different desilication severities, and (d) samples with similar crystal size, mesoporosity, and acid site density, but with a different ratio of external to internal acid sites have been prepared and studied for oligomerization of propene and 1-pentene. The results obtained suggest that the properties required for a best-performing catalyst (maximum conversion and lowest deactivation rate) are different for these two alkenes. Whereas Brønsted acid site density is determinant for propene oligomerization when intracrystalline diffusion path lengths are below a certain critical value, the presence of a large number of Brønsted acid sites is not sufficient in the case of 1-pentene, and additional mesoporosity becomes crucial. Thus, mesoporous ZSM-5 samples prepared by postsynthesis desilication treatments present a greater improvement in initial conversion and catalyst life for 1-pentene oligomerization than for conversion of propene.

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1. Introduction

Oligomerization of light alkenes, such as propene and butenes, represents an important route to the production of environmentally friendly synthetic liquid fuels, free of sulfur and aromatics [1–6]. The process allows production of olefinic mixtures in the range of gasoline and diesel. Thus, depending on the operating conditions and catalyst used, the ratio of diesel to gasoline can be modified [2–4]. In fact, high temperatures (>300 °C) and low pressures (≤30 bar) increase gasoline yield, whereas lower temperatures and higher pressures favor the formation of heavier oligomers within the diesel fraction. Concerning the catalysts, different solid acids have been described as catalysts for the oligomerization of olefins in the open [2,3,7–20] and in the patent literature [1,21–32]. Among them, medium-pore zeolites with either mono- or tridirectional pore systems have been the most successful, mainly for vapor-phase oligomerization processes [2,3,20,21]. Other structures, such as monodirectional 10-R ZSM-22 [33], ZSM-57 [34], with 10R-channels provided with wide lobes,

or large-pore ZSM-12 [35] and USY [36] zeolites, have also been described for oligomerization of C_3 – C_6 in the supercritical or liquid phase and are commercially applied [6]. If one considers a carbocation mechanism for olefin oligomerization, it is clear that in the absence of geometrical constraint, highly branched high-molecular-weight products would be formed. Thus, from the point of view of the fuel product quality (especially diesel) and catalyst life, it is desirable to obtain less branched molecules while avoiding the formation of heavier products, which will remain adsorbed within the catalyst pores, leading to relatively fast deactivation, at least when the reaction is carried out in the gas phase. Therefore, in this specific case, medium-pore zeolites (and especially ZSM-5) have been the preferred catalysts for C_3 and C_4 oligomerization to produce gasoline and diesel, while larger pore zeolites are rapidly deactivated [13,14,17]. Nevertheless, for oligomerization reactions that produce larger molecules with higher boiling points and higher heats of adsorption than the reactants, it will be mandatory to design a medium-pore zeolite catalyst with optimum acid site density and textural properties. These parameters should be even more critical when larger olefins (C_5) have to be oligomerized [12,16,18].

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In this work, we have studied how the different catalyst parameters influence activity, selectivity, and catalyst life and the optimization of a ZSM-5-based catalyst for oligomerization of propene and 1-pentene on the bases of its physicochemical properties. ZSM-5 samples with (a) the same crystallite size and different acid site densities, (b) the same density of acid sites and different crystallite sizes, (c) postsynthesis generation of mesopores by different desilication severities, and (d) samples with similar crystal size, mesoporosity, and acid site density but with different ratios of external to internal acid sites have been prepared and studied as catalysts for oligomerization of propene and 1-pentene. The role played by the different catalyst parameters in their catalytic behavior will be shown, as well as the fact that the key variable determining activity and selectivity for ZSM-5 is different when the objective is C_3^- oligomerization and when the olefin to be oligomerized is C_5^- .

2. Experimental

2.1. Catalyst preparation

The starting ZSM-5 samples were supplied by Zeolyst (CBV3020, CBV5020, and CBV8020) and TRICAT (TZP322, TZP302A, and TZP302H) in their ammonium form. Desilication treatment was performed by contacting the as-supplied zeolites with a basic solution of NaOH heated at the desired treatment temperature, under vigorous stirring. The liquid-to-solid ratio used was 33 by weight. After the desired time, the solid was separated by filtration and washed with deionized water until the pH was lowered to a value of 7.0. The Na-zeolite was then washed with a 0.8 M oxalic acid solution for 2 h, at 70 °C, for selective dealumination of the external surface. The dealuminated zeolite was separated from the solution by filtration, washed, and finally calcined at 375 °C for 3 h. The samples were named *M-MFI-T-t-OX*, where *M* is the NaOH solution concentration, *MFI* is the parent ZSM-5 zeolite, for example, TZP322 or CBV5020, *T* is the treatment temperature, *t* the duration of the desilication, and *-OX* stands for the oxalic acid treatment. Exceptionally, the Na-zeolite obtained after the basic desilication was ion-exchanged with a 2.5 M NH_4Cl solution (*L/S* = 10, *T* = 80 °C, *t* = 1 h, refluxed under vigorous stirring), washed with deionized water until chloride-free, and dried overnight at 100 °C. This ion exchange treatment was repeated twice before calcination in a muffle for 3 h at 500 °C. The ammonium-exchanged samples were labeled *M-MFI-T-t-A*. For comparison purposes, sample TZP322 was calcined (HTZP322) and then, in the acid form, it was treated with a 0.5 M alkaline solution for 90 min at 85 °C, and finally selectively dealuminated by means of an oxalic acid treatment, as described above. This sample was named 0.5-HTZP322-85-90-OX.

2.2. Catalyst characterization

The chemical composition of the catalysts was determined in a Varian-715-ES Inductivity-Coupled Plasma Analyzer (ICP). X-ray diffraction (XRD) was used to assess the purity and relative crystallinity of the different MFI zeolite samples. XRD patterns were ob-

tained at room temperature in a Philips X'pert diffractometer using monochromatized Cu $K\alpha$ radiation. Textural properties were obtained from nitrogen adsorption isotherms, measured at 77 K (–196 °C) using an ASAP 2000 Micromeritics instrument. The micropore volume of the products was calculated by the *t*-plot method, and the mesopore volume according to the BJH correlation. The acidity of the zeolites was determined by infrared spectroscopy combined with adsorption–desorption of pyridine at different temperatures. Infrared spectra were measured with a Nicolet 710 FT-IR spectrometer. Pyridine adsorption–desorption experiments were carried out on self-supported wafers (10 mg cm^{-2}) of original samples previously activated at 400 °C and 10^{-2} Pa for 2 h. After wafer activation, the base spectrum was recorded and pyridine vapor (6.5×10^2 Pa) was admitted into the vacuum IR cell and adsorbed onto the zeolite. Desorption of pyridine was performed under vacuum over three consecutive 1-h periods of heating at 150, 250, and 350 °C, each followed by IR measurement at room temperature. All the spectra were scaled according to the sample weight. The numbers of Brønsted and Lewis acid sites were determined from the intensities of the bands at ca. 1545 and 1450 cm^{-1} , respectively, using the molar extinction coefficients given by Emeis [37].

Scanning electron microscopy (SEM) was performed using a Jeol JSM 6399 microscope (20 kV) equipped with a secondary electron images detector using gold-coated powder specimens. Transmission electron microscopy (TEM) characterization was carried out in a Philips CM10 (100 kV) microscope. Before TEM observation, the samples were prepared by suspending the solid in isopropanol, ultrasonication for 1 min, and placing one drop on a carbon-coated copper grid (300 mesh).

Solid-state ^{27}Al MAS NMR spectra were recorded in a Varian Unity VXR-400WB spectrometer, at 104.2 MHz with a spinning rate of 7 kHz and a 9° pulse length of 0.5 μs with a 0.5-s repetition time. Chemical shifts were reported relative to $[Al^{3+}(H_2O)_6]$.

X-ray photoemission spectra (XPS) were recorded in a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a nonmonochromatic Al X-ray source operating at 200 W. The samples were pressed into a small disk and evacuated in the pre-chamber of the spectrometer at 1×10^{-9} mbar. Quantitative data were calculated from the Al2p and Si2p peak intensities after non-linear Shirley-type background subtraction and corrected by the transmission function of the spectrometer. The CasaXPS software was used for spectra processing.

2.3. Catalytic tests

The catalytic experiments were performed in a 10-mm internal diameter downflow stainless-steel fixed-bed reactor at 200 °C, 4.0 MPa, and contact times ranging from 0.08 to 0.17 h. Under these conditions, the reaction occurs in the gas phase. The catalyst (particle sizes 0.25 mm and 0.42 mm) was diluted in all cases with SiC (0.64–0.25 mm) to obtain a bed volume of 4.0 cm^3 . Under these conditions, a plug flow pattern was ensured [38]. The temperature in the catalyst bed was controlled by two independent heating zones, with the corresponding thermocouples properly placed inside the catalytic bed. Before reaction, the catalysts were activated

Table 1
Physicochemical properties of as-supplied commercial MFI samples.

Sample	Average crystal size (nm)	(Si/Al) _{Supplier}	(Si/Al) _{ICP}	BET (m^2/g)	$V_{\text{micropore}}$ (cm^3/g)	V_{mesopore} (cm^3/g)
CBV3020	200	15	15	397	0.160	0.110
CBV5020	163	25	20	375	0.154	0.085
CBV8020	580	40	31	389	0.168	0.072
TZP-322	173	15	11	391	0.168	0.112
TZP-302A	912	15	10	364	0.171	0.058
TZP-302H	1805	15	10	373	0.173	0.046

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