Zeolites

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Selective Petroleum Refining Over a Zeolite Catalyst with Small Intracrystal Mesopores**

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Since the discovery of surfactant-templated mesophases in 1992,[1] there has been persistent interest in their use as petroleum-refining catalysts. Although aluminum-substituted MCM-41 silica is effective for cracking heavy petroleum fractions into more valuable lighter products,[2] the material is not practical owing to low acidity and poor hydrothermal stability that limits longevity.[3] Mesoporous aluminosilicates assembled from protozeolitic nanoclusters[4] are more active in comparison to MCM-41, but the lack of crystallinity precludes catalytic performance equivalent to a zeolite.

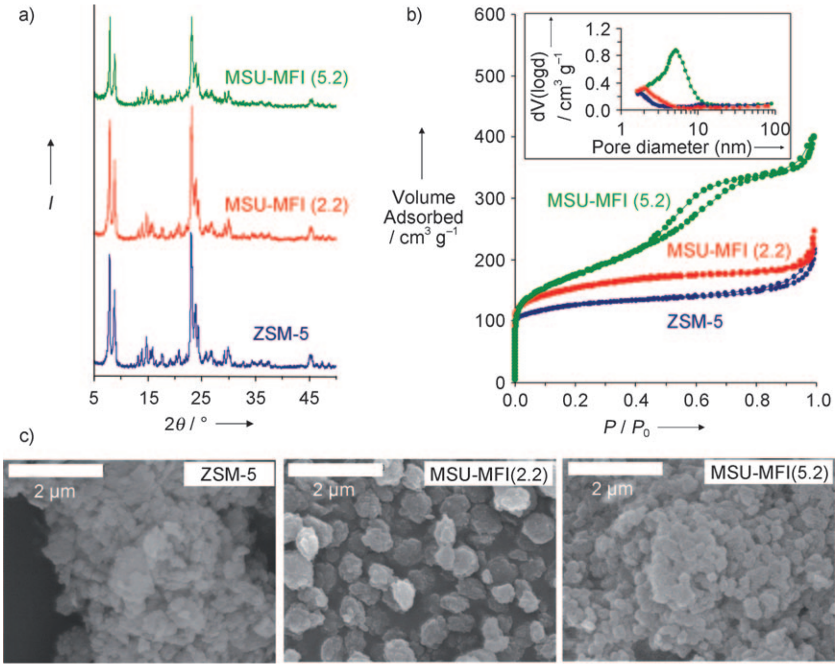

Figure 1. a) XRD powder patterns, b) N_2 isotherms at −196°C; inset: mesopore distributions (color code as in (a) and (b)), and c) SEM images for calcined ZSM-5 and templated MSU-MFI(2.2) and MSU-MFI(5.5) zeolites.

Recent efforts to improve petroleum-refining catalysts focus on mesoporous zeolites to improve accessibility to framework active sites and enhance selectivity through additional cracking within the mesopores.[5] Mesoporous zeolites can be prepared by limiting the size of the crystals, but the resulting intercrystal mesopores exhibit broad pore size distributions with little possibility for the fine control needed for substrate or product selectivity.[6] Intracrystal mesopores are formed through the incorporation of a hard[7] or soft[8,9] template during zeolite crystallization. Hard carbon templates can provide intracrystal mesopores with narrow size distributions,[10] but the occlusion of soft molecular organics into growing zeolite crystals provides greater mesopore size control.[8,9] In parallel with efforts for synthesizing mesoporous zeolites, new zeolites with larger framework pores are being reported.[11] These new zeolites have framework pore sizes up to 1.22 nm, but the pores still are smaller than desired.

Conventional cracking catalysts leave up to 20% of an average barrel of oil unrefined, a result mainly of inadequate accessibility to the zeolite component. This unrefined fraction could be lowered (perhaps to 5–10%) with a zeolite containing small (2–10 nm) mesopores. Moreover, the combination of regular mesoporosity and framework microporosity could provide a new approach to tailoring catalyst reactivity and selectivity towards more valuable products, such as gasoline and light alkenes. Herein we demonstrate for the first time the gas–oil cracking activity and selectivity of mesoporous ZSM-5 zeolite catalysts made by soft templating[8] with 2.2 and 5.2 nm intracrystal mesopores, denoted MSU-MFI(2.2) and MSU-

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MFI(5.2), respectively. The templated derivatives exhibit enhanced reactivity and, more importantly, substantially enhanced product selectivity in comparison to conventional ZSM-5. Although mesoporosity is known to improve the catalytic reactivity of a zeolite,[12] the benefits of small intracrystal mesopores with regard to improved product selectivity have not been demonstrated to date.

The powder X-ray diffraction (XRD) patterns in Figure 1a show that the protonated forms of the MSU-MFI conjugates have the same crystal structure as conventional ZSM-5. Small decreases in peak intensities are observed with increasing intracrystal mesoporosity (see below), which is consistent with the accompanying reduction in the intrinsic density and scattering power of the crystals.

The N_2 isotherms and mesopore size distributions in Figure 1b illustrate the differences in porosity for the MSU-MFI conjugates and ZSM-5. Especially noteworthy is the greater uptake of nitrogen by the MSU-MFI derivatives in comparison to ZSM-5 at $P/P_o \approx 0.10$–0.90 as a result of the filling of the small mesopores. The mesoporosity for the MSU-MFI derivatives originates from the templating effect of the intracrystal porogen, whereas the mesoporosity of the conventional ZSM-5 zeolite arises exclusively from textural pores formed through the aggregation of small crystallites (see the SEM images in Figure 1c). Thus, the mesopore distribution is centered at 2.2 nm for the MSU-MFI(2.2) phase templated by a silylated α,ω-diamine porogen and at 5.2 nm for MSU-MFI(5.2) templated by a silylated polyethylene imine polymer.[8] ZSM-5 has a much broader mesopore distribution and does not show a clear peak in the small mesopore range. As shown by the comparison of textural properties (see Table 1), the mesoporous and external surface areas are much larger for the templated MSU-MFI derivatives. The decrease in microporosity that occurs particularly for the MSU-MFI(5.2) congener is a consequence of intracrystal mesopores formation. Decreasing the crystal size of ZSM-5 or any other zeolite results in an increase in the external surface area at the expense of microporous surface area.[6] Similarly, the formation of intracrystal mesopores also leads to reduced microporosity, because the walls of the mesopores are structurally analogous to external surfaces and do not contribute microporous surface area or pore volume.

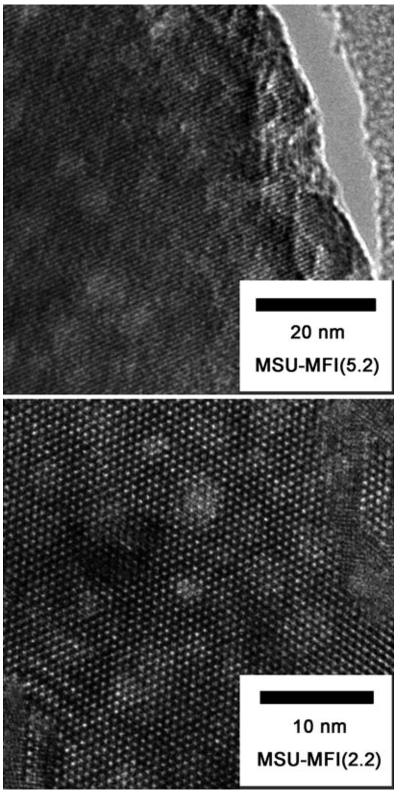

Figure 2. TEM images of thin-sectioned MSU-MFI zeolite derivatives.

Figure 2 provides high resolution TEM images for the MSU-MFI conjugates. The MSU-MFI(5.2) image reveals lattice fringes that extend over the entire particle, indicating the entire particle is crystalline. The larger light contrast areas randomly distributed throughout the crystal indicate the presence of intracrystal mesopores of nearly the same size. The image for MSU-MFI(2.2) also shows the crystallinity of the microporous framework (regular light dots), as well as randomly distributed intracrystal mesoporosity. Conventional ZSM-5 does not show these hierarchical features.

The acidic properties of ZSM-5 are especially important when it is intended for use as a cracking catalysts.[13] The total number of acid sites (ca. 0.40 mmol g^{-1}), as measured by temperature programmed desorption (TPD) of NH_3, is similar for templated MSU-MFI and conventional ZSM-5 derivatives, each with a Si/Al ratio near 50 (see Table 1). ^{27}Al magic-angle spinning (MAS) NMR spectroscopy confirmed the exclusive presence of tetrahedral aluminum centers associated with framework Brönsted acid sites. (see Supporting Information, Figure S1).

As anticipated based on differences in mesoporosity, the gas–oil cracking results in Figure 3 illustrate the superior reactivity and product selectivity of the templated MSU-MFI catalysts. Increasing the catalyst to oil ratio (c/o, w/w) from 1.0 to 1.8 increases the conversion for ZSM-5 from 32 to 44 wt %, whereas the MSU-MFI catalysts provide higher conversions of 48 to 64 wt %. It is clear that the MSU-MFI conjugates are substantially more active in comparison to the conventional ZSM-5 zeolite which lacks small mesoporosity. Moreover, the templated derivatives exhibit similar

Table 1: Textural and acidic properties of MSU-MFI and ZSM-5 catalysts.[a]

Catalyst[a]	Total Surface Area [$m^2 g^{-1}$]	Microporous Surface Area [$m^2 g^{-1}$]	Mesoporous and External Surface Area [$m^2 g^{-1}$]	Micropore Volume [$cm^3 g^{-1}$]	Mesopore Volume[b] [$cm^3 g^{-1}$]	Number of Acid Sites[c] [mmol g^{-1}]
ZSM-5	463	408	55	0.18	0.14	0.40
MSU-MFI(2.2)	547	399	148	0.17	0.16	0.40
MSU-MFI(5.2)	612	153	459	0.07	0.38	0.42

[a] Si/Al = 50. [b] Determined from the N_2 uptake at $P/P_o \approx 0.10$-0.90. [c] Determined by NH_3 TPD.

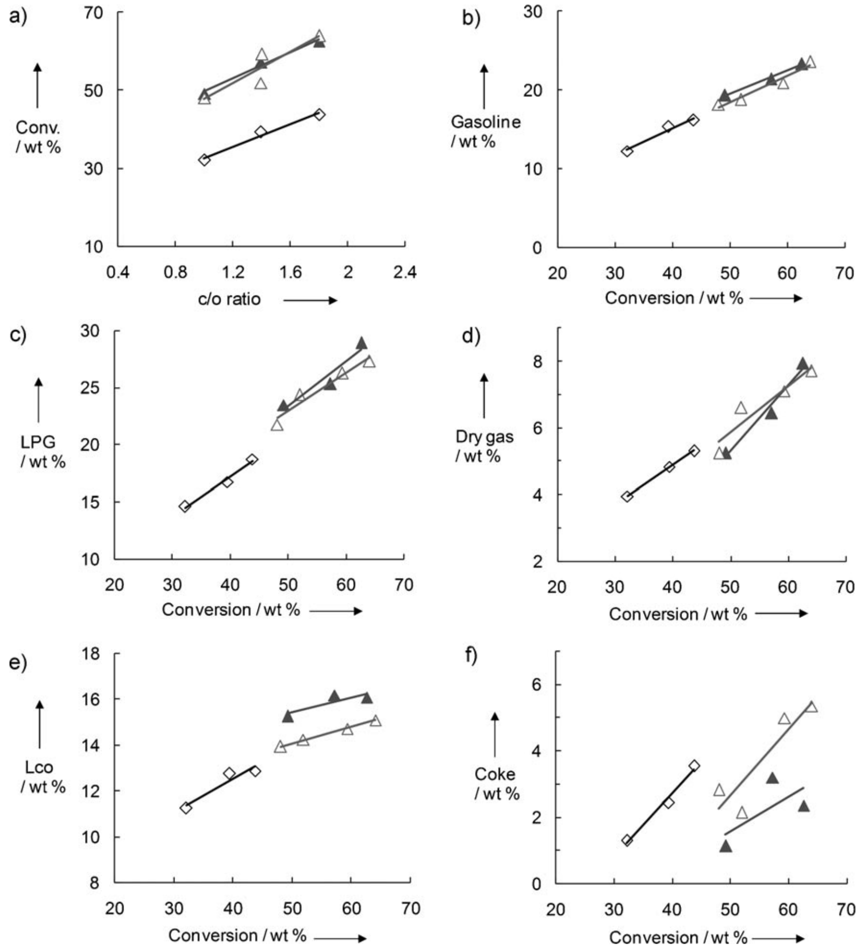

Figure 3. Catalytic properties of conventional ZSM-5 (◇) and templated MSU-MFI(2.2) (△) and MSU-MFI(5.2) (▲)zeolite catalysts for the cracking of gas–oil at 550°C: a) Gas–oil conversion (wt%) versus catalyst to oil (c/o) ratio, and b) gasoline, c) liquefied petroleum gases (LPG; total C_3+C_4), d) dry gas (H_2, C_1+C_2), e) light cycle oil (LCO), and f) coke yields (wt%) versus gas–oil conversion.

conversion activity, indicating that small mesopores with average diameters of 2.2 and 5.2 nm are sufficient to initiate cracking of the large hydrocarbons present in gas–oil by providing improved access to the acid sites of the zeolite framework.

We also see from Figure 3 that the higher conversions for the MSU-MFI conjugates are accompanied by higher yields of gasoline, light cycle oil (LCO) or diesel fuel, liquefied petroleum gases (LPG) or total C_3+C_4 hydrocarbons and dry gas (H_2 and total $C\ +C_2$) in comparison to ZSM-5. The MSU-MFI zeolites clearly exhibit bimodal reactivity for the cracking of large hydrocarbons in intracrystal mesopores leading to increased gasoline and LCO and the cracking of smaller molecules in framework micropores provides increased LPG. With regard to undesired coke formation, MSU-MFI(5.2) provides exceptionally low yields (1.1 wt%) in comparison to ZSM-5 (3.5 wt%) at approximately 45% conversion. The improved product selectivity provided by the MSU-MFI conjugates is unprecedented. ZSM-5 currently is used as a commercial fluid catalytic cracking (FCC) additive to boost octane ratings and LPG yields, but these improvements occur only at the expense of lower gasoline yields.[13,14] A FCC additive analogous to MSU-MFI(5.2) should provide substantially greater processing benefits.

Of high importance in petroleum refining is the production of light olefins as feed stocks. The light olefins yields obtained with the present catalysts are shown in Figure 4. Extrapolating the propylene and butylenes yields to the same conversion levels, we see that the MSU-MFI derivatives are far more selective toward these desired olefins. The improved selectivity is attributed to olefin precursor formation in intracrystal mesopores and subsequent olefin formation in micropores.

Our results clearly indicate the importance of small intracrystal mesopores in boosting not only the reactivity, but more importantly, the product selectivity of a

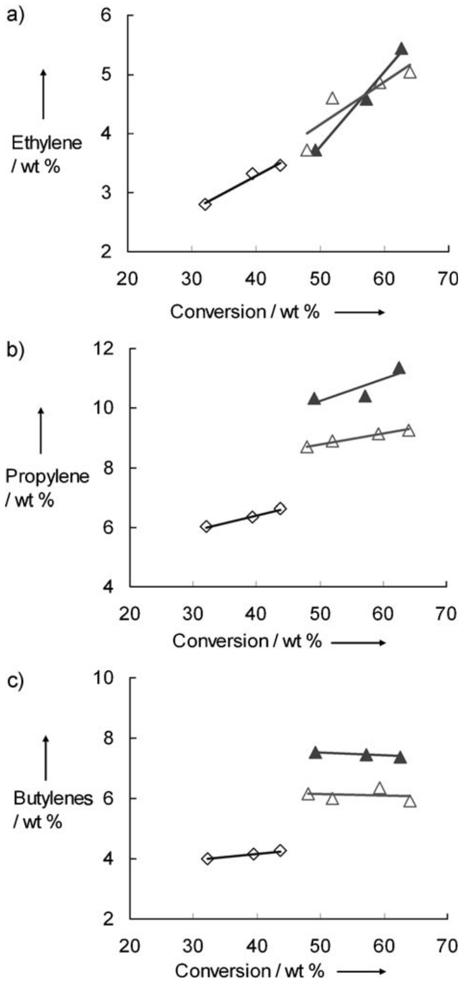

Figure 4. Yields (wt%) of a) ethylene, b) propylene, and c) butylenes versus gas–oil conversion for ZSM-5 (◇), MSU-MFI(2.2) (△), MSU-MFI(5.2) (▲) zeolite catalysts.

gas–oil cracking catalyst. Analogous benefits can be expected for mesoporous zeolites containing higher acidity and larger framework micropores. In particular, zeolite Y catalyst with small intracrystal mesopores would open new perspectives for the design of highly active and selective petroleum cracking catalysts.

Experimental Section

MSU-MFI zeolites with average intracrystal pore sizes of 5.2 and 2.2 nm were prepared using silylated polypropylene oxide diamine (Jeffamine D-4000, Huntsman) and polyethylenimine (PEI, Aldrich) polymers as mesoporogens with molecular weights of 4000 and 25 000 Daltons, respectively.[8] XRD patterns were recorded on a Rigaku Rotaflex Diffractometer using $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.542$ Å). N_2 isotherms at −196 °C were obtained on a Micromeritics ASAP 2000 sorptometer. SEM and TEM images were obtained on Jeol JSM 6400 and 2200 FS instruments, respectively. NH_3 TPD was performed using a commercial apparatus (Altamira AMI-1) and an online mass spectrometer (Baltzers, Omnistar). Vacuum gas–oil cracking was carried out on a Single Receiver Short-Contact-Time Microactivity Test unit operated at 560 °C, a 12 s reaction time and a 1.0–1.8 C/O ratio. Additional materials and methods description is given in Supporting Information.

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