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# Crystal-plane effects of MFI zeolite in catalytic conversion of methanol to hydrocarbons

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ABSTRACT

We report the direct characterization of coke information in the clearly resolved (0 1 0) and (1 0 0) planes of various anisotropic MFI zeolites using EELS techniques, in a model reaction of methanol to hydrocarbons. For the first time, we found that the main coke species varied between different planes and depended on the crystal structure. The coke species was graphite carbon and polyaromatic hydrocarbon over MFI nanosheets and MFI with *b*-axis length 60 nm, respectively. The diffusion of aromatics out of conventional MFI zeolites was found only through the straight channels, while small molecules randomly diffused through both channels, resulting in different coke deposition on the (0 1 0) plane and the (1 0 0) plane from different precursors. As all product molecules diffused only through the straight channels, the MFI nanosheet showed a distinct crystal-plane selective effect of coke deposition, in contrast to nearly uniform coke distribution throughout the entire external surface for conventional zeolites. This anisotropic diffusion behavior influenced the gaseous and liquid products significantly, providing deep insight into the MFI catalyst for the selective control of products via crystal structure.

## 1. Introduction

Zeolites are the most commonly used catalysts for the methanol-to-hydrocarbons (MTH) process [1] (olefins [2], gasoline [3], or aromatics [4,5]). The small pore sizes of zeolites (0.3–1 nm) endow catalysis with unique size and shape selectivity [6,7], but give rise to constraints on molecular diffusion within zeolite crystals [8]. Consequently, zeolite-catalyzed reactions are often limited by slow diffusion.

The provision of a secondary network of meso- and/or macropores has been evaluated in MTH processes. For example, Aramburo et al. [9] reported that mesoporous ZSM-5 prepared by a steaming treatment exhibited higher resistance to deactivation and MTH selectivity than conventional ZSM-5, because he reduced formation of polyaromatic compounds together with the generation of mesoporosity reasonably preserved the diffusion properties of the reacting and generated molecules. We developed a hierarchical zeolite hollow fiber, a hollow bayberry sphere, and an ordered nanowire array with trimodel interconnect pores [4,5,10]. These unique structures with abundant intercrystalline voids can effectively enhance the mass transfer of guest molecules and exhibit higher aromatics selectivity than their conventional analogue, which set a new record in hierarchical zeolite research.

Macroscopic variables such as the crystallite size in one or more dimensions also affect the product selectivity of MTH. Improved resistance to coking with increasing external (mesopore) surface area can be envisaged due to the facilitated escape of coke precursors and the larger area that needs to be covered to block access to the micropores [11–13]. Ryoo et al. [14] synthesized MFI nanosheets with only one unit cell thickness that exhibited a five-fold longer lifetime than the conventional ZSM-5 catalyst when used for MTH conversion. This conclusion is consistent with our report, in which nanosized ZSM-5 showed enhanced selectivity of aromatic products in comparison with conventional ZSM-5 in the MTA process. In addition, we synthesized nanosized MFI zeolite with a short *b*-axis and fully opened straight channels [15]. This structure exhibited 98% ultrahigh aromatic selectivity, more than 300 h lifetime, and high antihydrothermal ability.

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The properties of the materials and their catalytic performance are significantly influenced by the nature of the exposed facets. Since Li et al. found the shape-dependent catalytic behavior of ceria ($CeO_2$) for CO oxidation in the early 2000 s [16], numerous studies have focused on facet-controlled synthesis and catalytic properties of low-dimensional nanocrystals (NCs), including oxides, metals, and supported catalysts [17–20]. However, the crystal-plane effect of zeolites on the catalytic performance has not been reported until now. For the zeolite catalyst, not only the acidic sties (Al distribution) on the external surface are probably different [21], but also the different surfaces are assigned to different pore mouths (such as TNU-9 [22], IM-5 [23], ITQ-43 [24], and MFI [6,25,26]), linked with the product selectivity inside the channel. Besides the complicated chemistry, another challenge comes from the preparation of zeolites with a desirable defined plane and associated characterization techniques at the nanoscale [7,10,27,28]. These three factors result in less understanding of the catalytic nature produced by or reflected on the crystalline plane.

Here, taking the MFI zeolite (slightly elliptical ($5.6 \times 5.4$ Å in diameter), with straight channels perpendicular to the (0 1 0) plane and cross-linked by nearly circular ($5.4 \times 5.1$ Å in diameter) sinusoidal channels perpendicular to the (1 0 0) plane) [29], as an example, we aimed to clarify the crystal-plane selective effects in the zeolite on its catalytic performance and product distributions. For this purpose, a series of MFI zeolite catalysts with comparable absolute porosity, acidity, and *a*-axis lengths, but distinct *b*-axis lengths, were prepared and tested. The samples were denoted as MFI ($x$) with $x$ the *b*-axis length. We used high-resolution EELS (energy resolution of $\sim$0.3 eV with a small focal depth of <10 nm) to clearly characterize the chemical nature of coke species at different surfaces of single crystalline MFI zeolites with clearly defined (1 0 0) and (0 1 0) planes. We found coke significantly differing in density on different planes for the first time, providing sufficient information to show that the diffusion of various intermediate products was through specific paths inside zeolite channels in catalytic reactions. It allowed us to link the dynamic coke deposition information with the selectivity variation of the gaseous C1–C4 hydrocarbon and C6–C9 aromatic products, providing a powerful tool for deep understanding of zeolite-related catalysis.

## 2. Experimental

### 2.1. Synthesis of surfactants

#### 2.1.1. Synthesis of surfactants $[C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}]Br_2$ (denoted as $C_{22-6-6}Br_2$)

For synthesis of $C_{22-6-6}Br_2$, we followed the procedures described in the literature [30]. A quantity of 39.0 g (0.10 mol) of 1-bromodocosane (TCI, 98%) was dissolved in 500 mL toluene and added dropwise into a mixture of 500 mL acetonitrile and 172 g (1.0 mol) N,N,N′,N′-tetramethyl-1,6-diaminohexane (Aldrich). The reaction was refluxed in an oil bath at 70 °C for 10 h. After cooling to room temperature, the white solid ((N-(6-(dimethylamino)hexyl)-N,N-dimethyldocosan-1-aminium bromide; $C_{22-6}Br$) was filtered, washed with diethyl ether, and dried in a vacuum oven at 50 °C. A quantity of 56.2 g (0.10 mol) of $C_{22-6}Br$ and 34 g of 1-bromohexane (Aldrich, 98%) were dissolved in 500 mL acetonitrile and refluxed at 70 °C for 10 h. After cooling to room temperature, the white solid was filtered, washed with diethyl ether, and dried in a vacuum oven at 50 °C.

#### 2.1.2. Synthesis of surfactants $[C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}](OH)_2$ (denoted as $C_{22-6-6}(OH)_2$)

$C_{22-6-6}Br_2$ was converted to $C_{22-6-6}(OH)_2$ through reaction with $Ag_2O$ in distilled water. The solution containing $C_{22-6-6}Br_2$, $Ag_2O$, and water was stirred for 24 h at an $Ag_2O/C_{22-6-6}Br_2$ molar ratio of 1.2 at room temperature. The remaining $Ag_2O$ powder and the AgBr precipitate formed were removed by filtration. The resultant solution contained 13 wt% $C_{22-6-6}(OH)_2$.

### 2.2. Synthesis of MFI zeolites with different *b*-axis lengths

MFI zeolite nanosheets were prepared according to a procedure from the literature [31]. In a typical synthesis of MFI zeolite with *b*-axis length of 2 nm, water glass (an aqueous solution of sodium silicate, $SiO_2/Na = 1.75$, 29 wt.%$SiO_2$), $Al_2(SO_4)_3$ $18H_2O$ (Aldrich), NaOH, $C_{22-6-6}Br_2$ ($C_{22-6-3}Br_2$ for zeolite with Si/Al = 25), $H_2SO_4$, and distilled water were mixed to obtain a gel composition of 30 $Na_2O$:1 $Al_2O_3$:100 $SiO_2$:10 $C_{22-6-6}Br_2$:18 $H_2SO_4$:4000 $H_2O$. The resultant gel was transferred to a Teflon-coated stainless steel autoclave and heated at 150 °C for 5 days with the autoclave set to tumbling at 60 rpm. After crystallization, the zeolite product was filtered, washed with distilled water, and dried at 120 °C. The product was calcined at 550 °C for 4 h under flowing air.

For synthesis of MFI zeolite with *b*-axis length 10 nm, tetraethylorthosilicate (TEOS, from TCI), $Al_2(SO_4)_3$ $18H_2O$, $C_{22-6-6}(OH)_2$, and distilled water were mixed to obtain a gel composition of 100 $SiO_2$:1 $Al_2O_3$:15 $C_{22-6-6}(OH)_2$:3 $H_2SO_4$:6000 $H_2O$. The mixture was transferred to a Teflon-coated stainless steel autoclave and heated at 150 °C for 9 d with the autoclave set to tumbling at 60 rpm.

For catalytic reactions, the $H^+$ forms of the MFI zeolite nanosheets were obtained by $NH_4^+$-ion exchange of the calcined zeolites with a 1 M $NH_4NO_3$ solution at 80 °C for 2 h three times followed by intermediate calcination in air at 550 °C for 4 h.

MFI zeolites with *b*-axis lengths 60 and 220 nm were synthesized by the clear solution method. TEOS, aluminum isopropoxide, tetrapropylammonium hydroxide (TPAOH), and distilled water were mixed to obtain a gel composition of 100 TEOS:1 $Al_2O_3$:$x$ TPAOH:3700 $H_2O$ ($x$ = 0.30 and 0.15). After being stirred for 3 h at 35 °C, the resultant solution was heated at 80 °C in order to remove the ethanol generated during the hydrolysis of TEOS and then water was added to maintain a constant volume. After crystallization at 170 °C for 3 d, the product was recovered by centrifugation and dried overnight at 100 °C. Finally, the template was removed by calcination in static air at 550 °C for 4 h.

MFI zeolite was impregnated with a solution of the $Zn(NO_3)_2$ $6H_2O$ precursor. The mixture was stirred at room temperature for 8 h and dried overnight in an oven at 100 °C. The dried powder was calcined in flowing air at 550 °C. The samples were denoted as MFI ($x$), in which $x$ stands for the *b*-axis length. The MFI (2) and MFI (60) zeolites without Zn modification were denoted as MFI (2)-WZ and MFI (60)-WZ, respectively.

### 2.3. Catalytic performance testing

The MTH reaction were performed under conditions of 1 atm, 475 °C, and WHSV = 0.8 $h^{-1}$ under $N_2$ flow (40 mL $min^{-1}$) in a conventional fixed-bed stainless steel reactor (i.d. 13.0 mm) equipped with a thermocouple in the middle of the catalyst bed. A quantity of 0.5 g of catalyst was placed in the fixed-bed reactor. The flow rates of pure methanol and $N_2$ were controlled using a dual micro-plunger pump and mass flow controllers, respectively. A gas chromatograph (Shimadzu GC-2014) with two flame ionization detectors (FID) was used to detected $C_1-C_4$ and $C_{5+}$ aliphatics and aromatics, respectively.

The detailed procedures for characterization are presented in the Supplementary Information.