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Structural and physicochemical effects of MFI zeolite nanosheets for the selective synthesis of propylene from methanol

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ABSTRACT

MFI zeolite nanosheets (NS-MFI) with two different thicknesses (2.5 nm and 7.5 nm) and various Si/Al_2 ratios (100–700) were prepared and their catalytic activities for propylene production from methanol were investigated. According to analyses of X-ray diffraction patterns as well as scanning electron microscopy, transmission electron microscopy, and N_2 adsorption results, all NS-MFI catalysts had a well-developed nanosheet structure with a high specific surface area and a large mesopore volume. In the methanol-to-propylene (MTP) reaction, they showed greater activity and selectivity to propylene and longer lifetimes than commercial ZSM-5. Among these NS-MFI zeolites, thinner NS-MFI had better catalytic activity in MTP reactions than thicker NS-MFI at the same Si/Al_2 ratio, and superior catalytic performance for MTP reactions was observed at a Si/Al_2 ratio of 500. These results can be attributed to the appropriate acid density and the facile diffusion of molecules in the NS-MFI catalysts.

1. Introduction

Light olefins such as ethylene and propylene are the most important commodity petrochemicals. They are conventionally produced by the thermal cracking of naphtha [1]. However, with the continued high price of crude oil, the depletion of petroleum reserves, the global warming problem, and the increasing demand for light olefins, the development of alternative routes for light olefin production from renewable or non-petroleum resources such as biomass, natural gas, and coal is highly desirable [2,3]. The methanol-to-olefin and the methanol-to-propylene (MTP) routes are the most promising alternatives for light olefin production [4–8]. At the same time, America's recent shale gas revolution has increased the production of natural gas, leading to great interest in the MTP process for on-purpose propylene production due to the sharply increased demand for propylene [6]. Therefore, the MTP process, when coupled with the transformation of natural gas to methanol, is a promising alternative pathway with which to produce propylene from nonpetroleum resources [6–9].

ZSM-5, with its 10-membered-ring MFI structure, is a well-known MTP catalyst due to its high propylene selectivity resulting from its optimum pore size for MTP reactions. One of the main drawbacks of MTP catalysts is the deactivation of the catalyst by coke formation [10], which limits the diffusion of reactants/products within zeolite catalysts. This requires periodic catalyst regeneration, and is one of the main factors lowering the efficiency of the MTP process. Therefore, improving the coke tolerance of MTP catalysts is an important way to increase their performance levels. The deactivation of MTP catalysts by coking can be controlled by optimizing the acidity and pore structure of the catalysts. The Si/Al_2 ratio of the zeolite catalyst influences the coke formation process due to the strong interaction between carbonaceous materials and acid sites [9,11,12]. For this reason, high-silica MFI zeolites are preferred [9,13]. Other ways to improve the coke resistance have been studied, including the use of nano-sized MFI and mesoporous MFI zeolites with faster diffusion rates [14–16,31]. In fact, the

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higher resistance to coke formation and shorter diffusion path of mesoporous zeolites are important advantages responsible for their successful applications to catalytic reaction processes.

Recently, MFI zeolite nanosheets (NS-MFI) with a thickness of 2.5 nm along the *b*-axis were introduced by Choi et al. [17]. NS-MFI zeolites have since been studied for application to various reactions, such as *n*-heptane hydroisomerization [18], *n*-decane isomerization and hydrocracking [19], decalin cracking [20], and the Friedel–Crafts alkylation of benzene [21]. NS-MFI zeolites have a special form of micro-meso-porosity induced by nanosheets with a unilamellar structure. This mesoporous structure can enhance the coke tolerance of the catalyst for MTP applications [6]. Very recently, Kim and Ryoo reported that external acid sites on NS-MFI zeolite revealed no catalytic activity for methanol-to-hydrocarbon conversion [22]. Thus, the determination of the optimum structural and physicochemical properties in the MTP reaction is necessary because a decrease in the crystal size causes an increase in the diffusivity of molecules in catalyst and a decrease in the internal acid site concentration simultaneously. In this work, we prepared a series of NS-MFI zeolites with two different nanosheet thicknesses and various Si/Al_2 ratios synthesized with multi-ammonium surfactants [23]. The prepared NS-MFI catalysts were systematically examined to find the optimum NS-MFI catalyst and the reaction conditions for MTP reactions.

2. Experimental

2.1. Synthesis of NS-MFI

The MFI zeolite nanosheets were synthesized with multi-ammonium surfactant structure-directing agents (SDA) by a process described in the literature [18]. A series of nanosheet MFI zeolites with different Si/Al_2 ratios ranging from 100 to 700 and different nanosheet thicknesses of 2.5 nm and 7.5 nm were prepared. The 2.5 nm thick MFI zeolite nanosheets were synthesized using $C_{22}H_{45}{-}N^+(CH_3)_2{-}C_6H_{12}{-}N^+(CH_3)_2{-}C_6H_{13}(Br^-)_2$ [$C_{22\text{-}6\text{-}6}(Br)_2$] as a SDA. In brief, a sodium silicate solution (Si/Na = 1.75, 15 wt% SiO_2) was used as a silica source, and sodium aluminate (53 wt%, Sigma–Aldrich) was used as the alumina source. The various gel compositions of the starting mixture were 100 SiO_2:*a* Al_2O_3:7.5 $C_{22-6-6}(Br)_2$:30 Na_2O:24 H_2SO_4:4000 H_2O with *a* ranging from 0.142 to approximately 1 depending on the Si/Al_2 ratio, which ranged from 100 to 700. For the 7.5-nm-thick MFI zeolite nanosheets, the SDA was $C_{22}H_{45}{-}N^+(CH_3)_2{-}C_6H_{12}{-}N^+(CH_3)_2{-}C_6H_{12}{-}N^+(CH_3)_2{-}C_6H_{12}{-}N^+(CH_3)_2{-}C_6H_{13}(Br^-)_4$ [$C_{22\text{-}6\text{-}6\text{-}6\text{-}6}(Br)_4$] [23]. The molar composition of the starting mixture was 100 SiO_2:0.1 Al_2O_3:2.5 $C_{22-6-6-6-6}(Br)_4$:30 Na_2O:20 H_2SO_4:4000 H_2O. The mixtures were heated in a Teflon-lined autoclave while tumbling in an oven at 150 °C for 5 d. The zeolite products were collected after filtration, washing with water, and dried at 100 °C. The zeolites thus obtained were calcined at 550 °C in air. The zeolites were ion-exchanged three times with 1 M of a NH_4NO_3 solution and subsequently calcined again at 550 °C for full conversion to the H^+ form. These samples are denoted “NS-MFI-*n*,” meaning *nanosheets of MFI zeolite* with a Si/Al_2 ratio of *n* in the text. A commercial MFI zeolite in the NH_4^+ form was purchased from Zeolyst (CBV28014, $Si/Al_2 = 280$) and calcined at 550 °C before use. The zeolite was composed of aggregated nano-sized crystals with a wide distribution of thicknesses ranging from 20 to 50 nm. This sample is designated as “H-ZSM-5” in the text.

2.2. Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex instrument using Cu Kα radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 40 mA (1.6 kW). Scanning electron micrograph (SEM) images were obtained with a FEI Nova 230 instrument operating at 2 kV. Transmission electron microscopy (TEM) images were taken from the thin edges of particles supported on a porous carbon grid using Tecnai G2 F30 equipment operated at 300 kV. Nitrogen adsorption isotherms were measured at −196 °C on a Micromeritics TriStar 3000 volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 300 °C in a degassing station. The Brunauer–Emmett–Teller (BET) equation was used to calculate the apparent surface area from adsorption data obtained at P/P_0 values between 0.05 and 0.2. The total volume of micro- and mesopores was calculated from the amount of nitrogen adsorbed when P/P_0 was equal to 0.95, assuming that adsorption on the external surface was negligible compared to adsorption in the pores. The pore size distributions (PSD) were calculated by analyzing the adsorption branch of the N_2 sorption isotherm using the Barrett–Joyner–Halenda (BJH) method. Si/Al_2 molar ratios of all samples were determined by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) using an OPTIMA 4300 DV (Perkin Elmer). The surface acidity of the catalysts was measured by means of the temperature-programmed desorption of ammonia (NH_3-TPD) using a BEL-CAT TPD analyzer with a TCD detector. For the identification of the acid site type, the Fourier transform infrared (FT-IR) spectra of pyridine adsorption were observed using a Thermo Nicolet Nexus spectrometer equipped with a liquid-nitrogen-cooled MCT detector. Wafers of the samples were pretreated at 300 °C for 2 h in a vacuum. After cooling, the samples were treated with pyridine at 100 °C and the spectra were recorded after evacuation at 250 °C. Coke depositions of the catalyst were investigated by recording weight changes on a thermogravimetric analyzer (TA Instruments TGA Q500). Runs under air were carried out at a heating rate of 10.0 °C/min to 900 °C.

2.3. Catalytic test

The MTP reaction was carried out with a fixed-bed reactor at atmospheric pressure. 0.2 g of powder catalyst was loaded into the reactor. The catalyst was then pretreated under a flow of N_2 at 500 °C for 1 h before the reaction, after which methanol was pumped into the reactor through an evaporator, where the concentration of the methanol was held in a range of 10–40 vol.% under a N_2 balance. The weight-hourly space velocity (WHSV) and the reaction temperature used were 2.5 h^{-1} and 500 °C, respectively, as a standard reaction condition in this work without further notation. In addition, to compare the effects of the reaction conditions, the WHSV was 10 h^{-1} and reaction temperatures of 450 and 550 °C were used, with a denotation. The products were analyzed using an on-line gas chromatograph (Varian GC3800) equipped with a FID detector, a CP-Volamine capillary column, and a Porapak Q packed column.

3. Results and discussion

3.1. Crystal structure and physicochemical properties of NS-MFI catalysts

Fig. 1 shows typical SEM and TEM images taken of the commercial H-ZSM-5 and the NS-MFI samples with different thicknesses synthesized using a multi-ammonium surfactant as SDAs. The SEM and TEM images of the NS-MFI samples indicate that the samples were composed of ultrathin MFI zeolite nanolayers. The zeolitic nanolayers had very uniform thicknesses of 2.5 nm (a) and 7.5 nm (b) along the crystal *b*-axis, as clearly shown in the TEM images. These zeolite nanolayers were interconnected to form a