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Improvement of catalytic performance of MCM-22 in the cracking of *n*-hexane by controlling the acidic property

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ABSTRACT

The catalytic cracking of *n*-hexane to selectively produce propylene on the MCM-22 catalysts dealuminated by nitric acid treatment was carried out as a model reaction of naphtha cracking. The nitric acid treatment of MCM-22 precursors under severe conditions followed by calcination at 823 K has been proven to be an effective dealumination method for MCM-22 zeolite. At a high *n*-hexane conversion of 90%, the dealuminated MCM-22 (D-MCM-22) catalyst with Si/Al = 34 showed a higher propylene selectivity (41 C-%) than H-ZSM-5 and H-Beta catalysts with similar acid amounts. Moreover, D-MCM-22 showed a stability comparable to H-ZSM-5 and much higher than H-Beta catalyst. This would be due to the selective removal of acid sites within supercages, suppressing coke formation and the resultant deactivation.

1. Introduction

Light alkenes, especially propylene that is mainly supplied as a by-product of ethylene production through thermal cracking of naphtha, are acquiring more and more significance in the chemical industry. It is well known that the thermal cracking process requires a high reaction temperature (>1073 K), and moreover, that the product distribution, especially the propylene/ethylene ratio, is difficult to control. Therefore, catalytic cracking of naphtha has been drawing increasing attention. Compared to the thermal cracking, the catalytic cracking of naphtha is carried out at low temperatures and thus is energy-saving [1]. In addition, the catalytic cracking of alkanes over acidic zeolite catalysts gives a high propylene/ethylene ratio, since the transformation of long-chain alkanes to short-chain alkenes occurs at least partly *via* the carbenium ion/β-scission mechanism, *i.e.* by classical bimolecular cracking [2,3].

There are numerous reports of alkane cracking at relatively low temperatures; the reaction mechanism and the effect of zeolite structure have been extensively investigated [3–13]. However, there are only a few papers on cracking at high temperatures above 873 K that is necessary to obtain high alkene yields. Among various zeolite catalysts, ZSM-5 in the acidic form (H-ZSM-5) has been recognized as a prime candidate for practical catalytic cracking because of its high thermal and hydrothermal stabilities and its considerable resistance to deactivation caused by coking as well as its strong acidity [1]. Yoshimura et al. investigated the cracking of light naphtha in the presence of steam at 923 K and found that the addition of lanthanum (10 wt.%) into H-ZSM-5 (Si/Al = 100) increased the yields of ethylene and propylene to 61 C-% and the ethylene/propylene ratio in the product was approximately 0.7; a higher proportion of propylene was achieved compared to the current thermal cracking in the presence of steam. Moreover, the addition of phosphorus (2 wt.%) improved the catalytic life [1].

Recently, we have carried out the catalytic cracking of *n*-hexane and found that small particle H-ZSM-5 (Si/Al = 50) catalyst showed a longer catalytic life than the medium and large particle H-ZSM-5 catalysts [14]. However, the propylene selectivity was still not satisfactory. More recently, we have found that a combination of alkali and acid treatments of H-ZSM-5 leads to a high propylene yield and a long lifetime [15]. This is attributed to the formation of mesopores inside the zeolite particles by alkali treatment, that increases the density of pore openings and also shortens the diffusion path length in the micropores. In addition, acid treatment after alkali treatment can remove the Lewis acid sites on the alkali-treated H-ZSM-5, leading to an increased propylene selectivity and a decreased amount of coke.

The **MWW**-type zeolite, a kind of layered MCM-22 zeolite that was invented by Mobil in 1990 [16], possesses two independent pore systems. One consists of two-dimensional sinusoidal channels composed of slightly elliptical 10-MR, and the other is characteristic of 12-MR supercages accessible through 10-MR windows [17]. MCM-22 zeolite has also proved to be a good cracking zeolite additive for the FCC process in petrochemical industry [18,19]. Meloni et al. investigated *n*-heptane cracking at 723 K over H-MCM-22 zeolite and suggested that *n*-heptane cracking occurs

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through the classical carbenium ion chain mechanism in the supercages, but *n*-heptane cracking occurs through protolysis in the sinusoidal channels, the bimolecular reaction of hydride transfer being impossible in the narrow space available near the protonic sites [20].

In our recent work, we found that H-MCM-22 catalysts with higher Si/Al ratios showed higher propylene selectivities in catalytic cracking of *n*-hexane [21]. By dealumination with ammonium hexafluorosilicate (AHFS), the catalytic life and the propylene selectivity were improved at high *n*-hexane conversions. The AHFS treatment causes a decrease in the amount of Lewis acid sites that accelerate the bimolecular reaction of hydride transfer and resultant coke formation. However, AHFS is a highly toxic, corrosive chemical and not environmentally friendly. Therefore, the development of an alternative method for the dealumination such as acid treatment, hydrothermal treatment, and a combination of steaming and acid treatment is desirable [22–26]. Matias et al. suggested that acid sites in the outer cups of the H-MCM-22 zeolite can be completely deactivated by dealumination through nitric acid treatment, while the acid treatment simultaneously damaged the supercage system. However, only 20% of the aluminum was extracted from the zeolite by this acid treatment [23]. Wu et al. reported that the dealumination of MCM-22 proceeded relatively easily by the combination of calcination or steaming and the subsequent acid treatment under reflux conditions. Moreover, they proposed that these dealumination treatments selectively removed the Brønsted acid sites within 10-MR channels and on the external surface [24]. Because of the high stability against acid of the framework Al atoms in the **MWW**-type zeolite, it is very difficult to dealuminate, being quite resistant to acid treatment even with 14.5 M HNO_3 under reflux conditions [27].

Although the dealumination of calcined MCM-22 has been widely investigated, the dealumination of MCM-22 lamellar precursor before calcination was rarely investigated. Actually, the MCM-22 precursor is less stable compared with the calcined MCM-22 zeolite. Hence, the acid treatment of the MCM-22 precursor could lead to a relatively easy dealumination. Wu et al. reported that a considerable decrease in the framework Al content occurred in the synthesis of interlayer-expanded MCM-22 zeolite through post-synthesis alkoxysilylation of the MCM-22 precursor with diethoxydimethylsilane in nitric acid under reflux conditions [28]. More recently, we further found that the Al atoms located at the specific T site (*i.e.*, T2) in the hexagonal model could be less resistant to the strongly acidic conditions than those at other sites based on ^{27}Al MQMAS NMR results [29]. In addition, we have proved that nitric acid treatment of the MCM-22 precursor leads to the formation of Lewis acid sites in the interlayer 10-MR micropores from the observation of IR using hexamethyleneimine (HMI), pivalonitrile (PN) and CO as probe molecules [30].

In this study, dealuminated MCM-22 zeolites (D-MCM-22) were prepared via dealumination of the MCM-22 precursor by a combination of nitric acid treatment and calcination. The catalytic performance of the dealuminated MCM-22 catalysts has been examined for the catalytic cracking of *n*-hexane as a model reaction of naphtha cracking to selectively produce propylene. Finally, the relationship between the catalytic performance and the acid properties (including the acid amount, acid strength, and acid type) and the distribution of Al in the resulting catalysts, will be discussed.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of MCM-22

The borosilicate **MWW** (B-**MWW**) lamellar precursor was hydrothermal synthesized with fumed silica (Cab-O-Sil M5, Cabot), boric acid (99.5%, Wako), piperidine (PI) (98%, Wako), and deionized water according to the literature with slight modifications [31]. Firstly, 68.4 g of deionized water was added to 23.842 g PI and stirred for 10 min. Then, 18.549 g H_3BO_3 was added and stirred for 1 h. Finally, 12 g fumed silica was added and further stirred for 1 h to obtain a gel with a molar composition of 1 SiO_2:0.75 B_2O_3:1.4 PI:19 H_2O. The hydrothermal treatment was carried out in a Teflon-lined stainless steel autoclave at 443 K for 5 d under tumbling conditions (20 rpm). The sample was filtered, washed, and dried at 373 K. The prepared B-**MWW** precursor was deboronated by calcination at 873 K for 10 h in air followed by acid treatment using 6 M HNO_3 aq. at 393 K for 20 h. Thus obtained deboronated MWW (DeB-**MWW**) was used as seed to speed up the crystallization of MCM-22 zeolite.

The aluminosilicate **MWW** (MCM-22) lamellar precursor was hydrothermal synthesized with fumed silica (Cab-O-Sil M5, Cabot), sodium aluminate (53.1% Al_2O_3, 32.3% Na_2O, Koso Chemical Co., Ltd.), NaOH (97%, Wako), hexamethyleneimine (HMI) (99%, Acros Organics), and deionized water according to the literature [24]. Firstly, 0.6406 g $NaAlO_2$ and 0.9333 g NaOH were dissolved in 81 g deionized water and stirred for 10 min. Then, 8.91 g HMI was added and stirred for 1 h. Finally, 6 g fumed silica and 0.3 g DeB-MWW zeolite (5% weight based on the weight of SiO_2) were added and further stirred for 1 h to obtain a gel with a molar composition of 1 SiO_2:0.15 Na_2O:0.033 Al_2O_3:0.9 HMI:45 H_2O. The hydrothermal treatment was carried out in a Teflon-lined stainless steel autoclave at 423 K for 5 d under tumbling conditions (20 rpm). The sample was filtered, washed, and dried at 373 K to produce the MCM-22 precursor. Direct calcination of the sample in air at 823 K for 10 h resulted in the products with the 3D MWW structure. Thus obtained Na-type sample was converted to the H-type one by treating it with 1 M NH_4NO_3 twice at 353 K for 2 h followed by calcination at 773 K for 2 h in air. Thus prepared H-form MCM-22 was denoted by H-MCM-22(12), where the number in the parentheses means the Si/Al ratio determined by ICP analysis.

2.1.2. Dealumination of MCM-22

Dealuminated MCM-22 (D-MCM-22) zeolites were obtained from the MCM-22 lamellar precursor *via* two routes: (1) The MCM-22 precursor was first calcined and then treated by nitric acid under mild or severe conditions; (2) The MCM-22 precursor was first treated by nitric acid under mild or severe conditions and then calcined. The mild acid treatment was carried out by using 2 M HNO_3 under reflux condition at 393 K for 20 h in a flask with stirring, while the severe acid treatment was provided by using 2 M HNO_3 at 423 K for 20 h in an autoclave without stirring. The solid to liquid weight ratio was 1:50. Calcination was performed in air at 823 K for 10 h. Thus, four different D-MCM-22 zeolite catalysts were obtained (Table 1). The dealuminated MCM-22 zeolites were denoted by D-MCM-22(*x*), where *x* means the Si/Al ratio determined by ICP analysis. As a control, a small particle H-ZSM-5 catalyst with Si/Al = 46 was synthesized according to the literature [14]. An H-Beta catalyst with Si/Al = 45 was obtained by 0.2 M HNO_3 treatment of H-Beta with Si/Al = 12 (JRC-Z-HB25, from the Catalysis Society of Japan) under reflux condition at 393 K for 1 h. The solid to liquid weight ratio was 1:30.

2.2. Catalyst characterizations

The catalysts were characterized by various techniques. The Si/Al ratios were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) Shimadzu ICPE-9000. The X-ray diffraction (XRD) patterns were recorded on a Rint-Ultima III (Rigaku) diffractometer using a Cu Kα X-ray source.