Journal of Energy Chemistry 26 (2017) 354–358

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Highly selective methanol-to-olefin reaction on pyridine modified H-mordenite

Ting He[a], Guangjin Hou[a,c], Jinjing Li[a], Xianchun Liu[a], Shutao Xu[b], Xiuwen Han[a], Xinhe Bao[a,*]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
[b] *National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
[c] *Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States*

ARTICLE INFO

Article history:
Received 21 November 2016
Revised 13 February 2017
Accepted 14 February 2017
Available online 19 March 2017

Keywords:
Catalysis
Mordenite
Pyridine
MTO
NMR

ABSTRACT

The effects of the acid site in main channels of MOR zeolites on their product selectivity and deactivation in the MTO (methanol to olefin) reactions were investigated. The catalytic analysis demonstrates that the pyridine modified MOR zeolite yielded high selectivity (> 65.3%) of $C_2^=$-$C_4^=$, although the conversion dropped from 100% to 54%. Furthermore, both the catalytic lifetime of MOR and the stability of yielding the lower olefins were increased from less than 30 min to more than 120 min after the modification with pyridine. ^{1}H MAS NMR on MOR and modified MOR shows that the acid sites in main channel do not benefit the productivity of lower olefins and catalysts' lifetime. It can be concluded from ex-situ ^{13}C CP MAS NMR that the deposit species during the MTO reaction depend on the pore sizes, and the formation of large alkyl aromatic species more likely occurs in the 12-ring main channels rather than the 8-ring side pocket.

1. Introduction

As a non-renewable resource, limit reserves of crude oil provides strong driving force for exploring alternative chemical feedstock and developing non-petrochemical processes to meet the rapidly increasing demand for the base chemicals, such as ethene and propene. To date, the MTO (methanol-to-olefin) process was proven to be the most successful non-petrochemical routes for the production of light olefins from abundant resources of natural gas or coal [1–4], which will play an essential role in the global energy chain and chemical industry.

Typically catalysts used in the MTO process are microporous solid acids, including zeolites and zeotype molecular sieves [5–7]. The control of the product distribution in the MTO reaction by varying the catalysts and reaction conditions also provides a powerful way to produce a specific olefin selectively [8,9]. The nature and extent of the reactions of olefins on a microporous solid acid are governed by acid strength, acid site density, catalyst topology, crystallite size, temperature, space velocity, and other process conditions [2,8,10–12]. Many efforts were focused on improving its catalytic performance by various physicochemical modifications. Olsbye et al. reported the influence of acid strength on the stability and product selectivity of microporous catalysts with CHA framework type by using two same topology structure zeolites but with different acid strengths [10]. ZSM-5 zeolites possessing different chemical compositions, acidities and crystal sizes were prepared via the fluoride route, and propylene-to-ethylene ratios could achieve above 5 [13]. Xu et al. investigated the size effect of SAPO-34 on the catalytic performance of MTO reactions, and they found that nanosized catalysts, especially the sheet like SAPO-34 catalyst with 20 nm thickness, exhibited the longest catalyst lifetime and lowest coking rate in MTO reactions [5]. However, during the methanol conversion, zeolite catalyst, such as SAPO-34 with CHA cage and 8-ring pore opening, also accommodates a large amount of organic species as retained materials, which usually cause rapid catalyst deactivation. Mordenite has special features of structure, and exhibits a 12-ring channel structure connected by 8-ring side pockets. The structure of 8-ring pore of SAPO-34 makes it exhibit higher selectivity to lower olefins ($C_2^=$-$C_4^=$), while $C_4^=$-$C_5^=$ olefins are favored over mordenite because of the 12-ring main channels [14]. In our present study, in order to investigate how the acid site distribution in main channel affects

---

* Corresponding author
E-mail address: xhbao@dicp.ac.cn (X. Bao).

http://dx.doi.org/10.1016/j.jechem.2017.02.004
2095-4956/

the selectivity of olefin on MTO reaction, the mordenite zeolite modified by pyridine adsorption was used as the parent catalyst, where the pyridine molecules can only adjust the acid site density in 12-ring channels due to its molecular size. Our results demonstrate that the pyridine modified MOR zeolite has high selectivity to lower olefins, and the catalytic lifetime and the stability can be improved greatly by the modification.

2. Experimental

2.1. Catalysts

H-mordenite was obtained by 4 times ion exchange with 1 M NH_4NO_3 at 353 K for 12 h each time from Na-mordenite (Hongda, Dalian, China). Subsequently, the sample was dried at 393 K for 12 h and denoted as NH_4-mordenite. Then the sample was heated in 1% O_2/Ar flow (60 mL/min) at 773 K for 6 h, and it was put in to a glove box without moisture, denoted as MOR.

Pyridine adsorption experiment was carried out with the following procedure. 0.2 g MOR evacuated to $<10^{-2}$ Pa before pyridine (99.9 %, AR, guoyao) was inducted by pulse injection, and it was heated to 573 K for 12 h. The obtained samples were named as Py-MOR.

2.2. Catalytic testing

MTO reaction was conducted with a continuous flow fixed-bed stainless steel reactor. In the case of MOR, 150 mg catalyst (40–60 mesh) was loaded into the reactor, heated to 573 K at a rate of 3 K/min in a flowing He (20 mL/min) and maintained at this temperature for 2 h, and then methanol was introduced at a weight hourly space velocity (WHSV) of 2 h^{-1}. The effluent gas was analyzed by an online gas chromatograph (Agilent 7890 N) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Methanol conversion and light olefin selectivity are defined in previous literature [13].

2.3. Solid state MAS NMR experiments

All NMR experiments were carried out on a 14.1 T Bruker Avance III wide bore solid-state NMR spectrometer, operating at a Larmor frequency of 600.13 MHz for ^1H, and 150.92 MHz for ^{13}C. A 4.0 mm Bruker MAS double resonance probe was used. ^1H MAS NMR spectra recorded at MAS rate of 12 kHz, using a single pulse sequence with a typical $\pi/4$ pulse length of 2.2 µs and a recycle delay of 10 s. 32 scans were accumulated for each spectrum. The chemical shifts were referred to a KBr-diluted HMB as an external standard. All ^1H NMR spectra were processed and analyzed using the DMFIT software.

The $^1H\rightarrow^{13}C$ CP MAS NMR experiment, a RF field irradiation with constant amplitude was applied on ^{13}C, and a linear ramp of 80%–100% field irradiation applied on ^1H was optimized experimentally to achieve the first-order Hartmann-Hahn matching conditions. The contact time was 5 ms, and the recycle delay was 2 s. A high power ^1H SPINAL-64 decoupling was applied during the acquisition for all ^{13}C NMR spectra. The chemical shifts were referenced to methylene peak in adamantane as an external standard.

3. Results and discussion

3.1. Acidity

The conversion and product distribution of the MTO reaction over zeolites depended on acid site density under reaction conditions. Seo and coworkers investigated the effects of the acid site densities of mordenite zeolites on their product selectivity and deactivation after the dealumination of the parent MOR zeolite [15]. In our work, we modified mordenite zeolites by inducting pyridine molecules. Pyridine molecule has an apropos size of 0.58 nm, which is larger than 8-ring side pocket (0.34 × 0.48 nm) of mordenite but smaller than 12-ring channels (0.74 × 0.65 nm). Therefore, only the acid site density in 12-ring channels can be adjusted by the absorption of pyridine molecules in mordenite zeolites. Fig. 1 shows the ^1H MAS NMR spectra of fresh mordenite (MOR) and pyridine adsorbed mordenite (Py-MOR), respectively. The major signals at 3.5 ppm can be assigned to bridging Si(OH)Al groups (Brønsted acid sites) [16], and the shoulder peak can be assigned to extra-framework Al(OH) species and non-acidic Si(OH) [17]. Upon the adsorption of pyridine, besides the ^1H NMR signals of pyridine itself (6.5 to 8.3 ppm), a signal at low field, 14 ppm, was also observed, which could be assigned to the protonic proton. It can be obviously seen that signal of Bronsted acid site (3.5 ppm), decreased to about 50% after the modification with pyridine. This data is consistent with the previous reports, in which the amount ratio of Bronsted acid site located in 12-ring channels to that in 8-ring side pockets was found to be close to 1:1 [18], and pyridine can only disturb the Bronsted acid site in 12-ring channels of mordenite zeolites [19,20]. It suggests that in our experiment 12-ring channels were occupied fully, and all the residual Bronsted acid sites at 3.5 ppm can be assigned to 8-ring side pocket of mordenite zeolites.

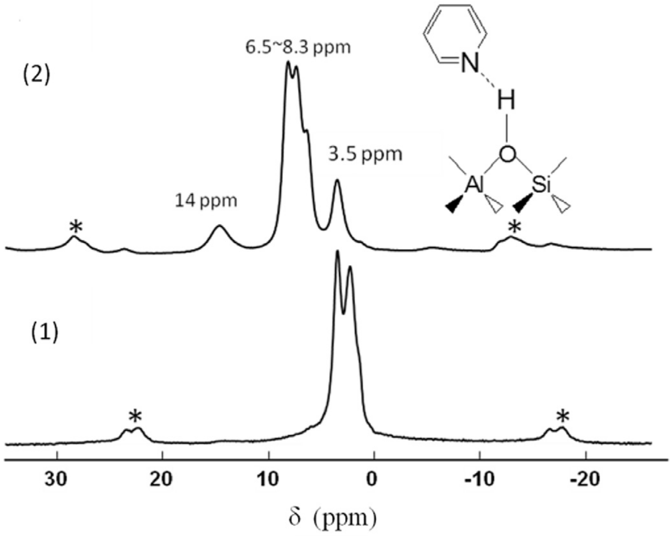

Fig. 1. The ^1H MAS NMR spectra of MOR (1) and Py-MOR (2).

3.2. Catalytic reaction

To further investigate the performance of the modified mordenite in the practical catalysis, MTO reactions were performed on MOR and Py-MOR. Fig. 2(a) shows the conversion of methanol at 573 K over MOR and Py-MOR. It can be expected that the pyridine modified mordenite would give reduced conversion of methanol since the conversion under approximately proportional to the density of Brønsted acid site of zeolites. The conversion of methanol at the same condition decreased from 100% on MOR to 54% on Py-MOR. On the other hand, the catalyst lifetime was prolonged significantly. The product contribution of the third point of conversion curve is plotted in Fig. 2(b). As shown, the proportion of olefin in the product of Py-MOR increases dramatically while the yields of alkane are high on MOR. It suggests that the acid sites in 12-ring channels are more involved in producing alkane than olefin at the current reaction condition, while the acid sites in 8-ring