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Short communication

Preparation and application of Ba/ZSM-5 zeolite for reaction of methyl vinyl ether and methanol

Yang Wang [a], Guixing Jian [a], Zhihong Peng [b], Jiaji Hu [a], Xin Wang [a], Wubiao Duan [a], Bo Liu [a,*]

[a] Department of Chemistry, School of Science, Beijing Jiaotong University, Beijing 100044, PR China
[b] State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materials Academy of Science Research, PR China

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ABSTRACT

The ZSM-5 zeolite is widely used to catalyze the reactions of methanol to olefins. Herein, we have prepared the H-ZSM-5 doped with barium (Ba/ZSM-5) using incipient wetness impregnation method. The Ba modified catalysts were used to catalyze a new reaction of methanol with methyl vinyl ether to improve the selectivity of ethylene and propylene ($C_2^= + C_3^=$). The reaction catalyzed by Ba doped H-ZSM-5 shows higher propylene selectivity over H-ZSM-5. The reaction mechanism is discussed.

1. Introduction

Light olefins such as propylene and ethylene are important basic chemicals and have extensive applications. Currently, light olefins mainly come from steam cracking and catalytic cracking (FCCs). However, the petroleum route is unable to meet the increasing demand of olefins, especially for propylene. Therefore, other ways to prepare light olefins have been studied, including the conversion from methanol to olefin (MTO), the propane dehydrogenation (PDH) and the conversion from methanol to propylene (MTP). Amongst the above methods, turning methanol to $C_2^= + C_3^=$ (MTO) is regarded as the most economical way comparing with the conventional oil-based route [1–5].

MTO technology has focused on the development of the catalyst with high selectivity, especially H-ZSM-5 [6,7]. Research on doping metal atoms to H-ZSM-5 catalyst showed that even a trace amount of the metal atoms in H-ZSM-5 could significantly influence the MTO productions [8]. Sadegh et al. reported the use of the H-ZSM-5 powder modified by iridium through impregnation. Results show that iridium doped H-ZSM-5 leads to a decrease in strong acidic sides and improves the selectivity of propylene [9]. Other groups have adopted a non-metallic doping way to modify the zeolites, such as B and P, leading to an improvement of the catalytic selectivity [10–14]. The same group of alkali metal including Mg, Ca and Sr has been extensively investigated. It is found that the number of strong acid sites can be reduced and the distribution of acid center is improved [15–18]. Therefore, the Ba modified catalysts are expected to inhibit the formation of aromatic hydrocarbons, increase the carbon deposition resistance, and lead to an increase of olefin yield.

Recently, researchers tried to enhance the MTO performance by co-feeding. Mier et al. and others have studied the co-feeding of methanol and *n*-butane or *i*-butane over the H-ZSM-5 catalyst [19–23]. They found that there is an enhancement of the olefin formation selectivity and the lifetime of the catalyst. Methyl vinyl ether is a kind of material with special double bond structure; it is reasonable to expect to produce vinyl fragments in the thermal decomposition. In addition, methoxy fragments, the vital intermediate in the formation progress of olefins [12,24,25], from the pyrolysis of methyl vinyl ether are also possible if we consider the similarity of chemical structure between methyl vinyl ether and vinyl ethyl ether which had confirmed the generation of ethoxy in the pyrolytic reactions [26].

We are trying to combine the metal modification and co-feeding strategies in order to improve the selectivity in MTO conversion. In this paper, we will report the improved selectivity in MTO process when Ba modified zeolites (Ba/ZSM-5) and co-feeding of methyl vinyl ether are employed.

2. Experimental

2.1. Preparation and characterization of Ba/ZSM-5

The Ba/ZSM-5 zeolite was prepared by the incipient wetness impregnation method. Briefly, a certain amount of $Ba(NO_3)_2$ in aqueous solution was added dropwisely into 20 g H-ZSM-5 zeolite (SiO_2/Al_2O_3

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* Corresponding author.
E-mail address: boliu@bjtu.edu.cn (B. Liu).

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ratio = 38) suspended in an equal volume of deionized water. The slurry was stirred at room temperature for 12 h, dried overnight at 110 °C, and then calcined in air at 550 °C for 6 h before being crushed carefully. The content of Ba modified zeolites is calculated by the following formula:

$$X\% = \frac{M_1 n}{m + M_2 n} \times 100\%.$$

In which "X" is the mass fraction of Ba in H-ZSM-5. "M_1" and "M_2" represent the atomic mass of Ba and the relative molecular mass of $Ba(NO_3)_2$, respectively. In addition, "m" is the quantity of H-ZSM-5 and "n" is moles of $Ba(NO_3)_2$. 3Ba/ZSM-5 denotes 3 wt.% content of Ba in the catalysts, 5Ba/ZSM-5 for 5 wt.% of Ba.

XRD patterns of H-ZSM-5 sample data are acquired by Rigaku Ultima IV. Scanning Electron Microscope (SEM) images of the H-ZSM-5 were gotten by Hitachi 3400.

2.2. Catalytic reaction

The apparatus for catalytic reactions is shown in Fig. 1 schematically. The experiments were conducted in a clean and dry quartz tube furnace. Under atmospheric pressure, the reactor was purged with nitrogen before heating. The accurate temperature controller was employed to set temperature. Methanol mixed with methyl vinyl ether was added to the reactor through Liquid inlet pump when the temperature is stable. WHSV (weight hourly space velocity) is controlled by 1.8–2.2 h^{-1}. After the reactions were stable for certain time, the gaseous products were collected with the gas pocket of aluminum foil. The compositions of the products were identified by GC–MS.

3. Results and discussion

3.1. Structure and morphology

XRD patterns of H-ZSM-5 and Ba/ZSM-5 zeolites are shown in Fig. 2. It displays the same peaks as pure H-ZSM-5 zeolite at the range of 2θ = 23–25°, which indicates that the H-ZSM-5 crystal structure was retained after Ba impregnation. Diffraction peak intensity of the samples is almost the same, illustrating that the degree of crystallinity is intact. However, It can be clearly seen that the differences at 2θ = 22.88, 37.37 and 29.77 respectively which represents the $BaO_{1.3}$ (PDF#47-1488) formed in H-ZSM-5.

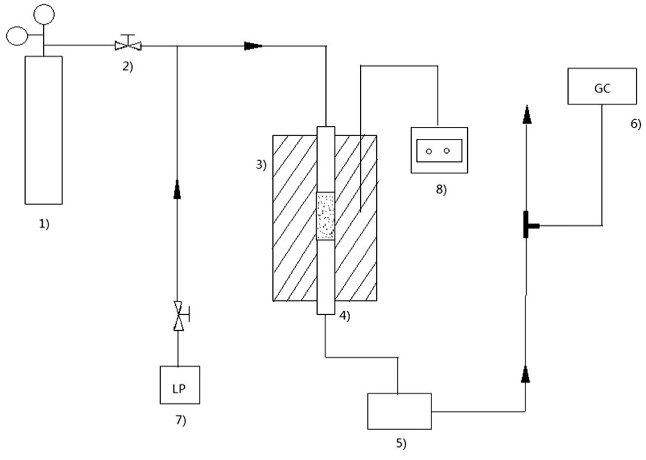

Fig. 1. Apparatus for catalytic reactions. (1) High-purity nitrogen, (2) Shut-off valve, (3) Tubular furnace, (4) Fixed bed reactor, (5) Gas–liquid separator, (6) GC–MS, (7) Liquid inlet pump, (8) Temperature controller.

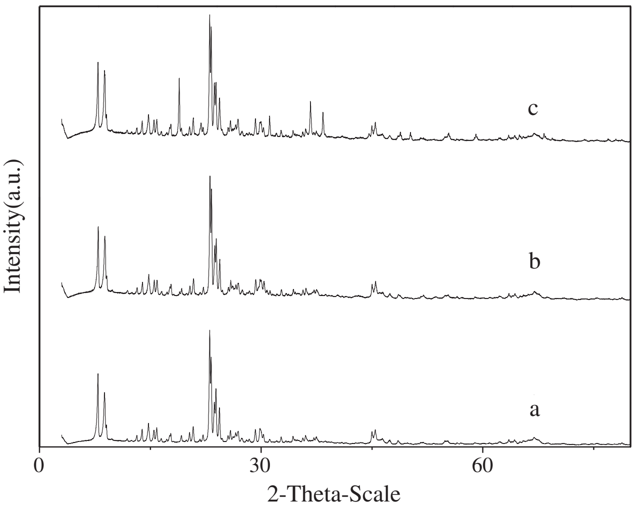

Fig. 2. XRD patterns of H-ZSM-5 (a), 3Ba/ZSM-5 (b) and 5Ba/ZSM-5 (c).

The morphology and structure characteristics of H-ZSM-5 and Ba/ZSM-5 catalysts were shown in Fig. 3. No clear differences on morphology of both the modified catalysts and unmodified one are observed. The absence of conglomeration indicates that $BaO_{1.3}$, converted from the $Ba(NO_3)_2$, disperses well on H-ZSM-5.

3.2. Influence of methyl vinyl ether and content of Ba

In olefin forming process, dimethyl ether as primary product is crucial which is related to superficial methoxy. Generally, methoxy is catalyzed by the Brønsted acid on the surface of the catalyst which is a complex process; therefore, extra methoxy is expected to simplify the previous steps in order to make the reaction efficiently and participate in the circulation of "hydrocarbon pool" to increase the yield of propylene. Using the H-ZSM-5 and Ba modified H-ZSM-5, we studied the effect of the addition of methyl vinyl ether into methanol during the MTO process at 450 °C and at atmospheric pressure. Fig. 4 shows the yield of propylene in the reaction, when using H-ZSM-5, the addition of methyl vinyl ether shows higher light olefin selectivity than methanol feeding only. Moreover, as the reaction proceeds, the mixture of the H-ZSM-5 showed a relatively stable trend compared with methanol.

As seen in Fig. 4, when the mixture is catalyzed by 3Ba/ZSM-5, the yield of propylene reached up to 53%. However, it presents the opposite trends and lower than expected when the contents of Ba are 5 wt.%, the mixture catalyzed by 5Ba/ZSM-5 showed lower selectivity even compared with H-ZSM-5, it is because the selectivity of propylene is affected not only by the acid strength of catalyst, but also by the particle size and the specific surface area, especially the specific surface area [17], we can see that the peak intensity of $BaO_{1.3}$ is strong in Fig. 1, which means the content of Ba in H-ZSM-5 is excessive. The acid sites of the catalyst are occupied by Ba which leads to the decreased specific surface area of catalyst and reduces the number of active center that is negative for the formation of propylene. In addition, the faster inactivation performance illustrates that the activity center of the catalyst is blocked easily and deactivated finally.

3.3. Influence of temperature

As reported [27,28], temperature is an important factor in influencing the performance of MTO catalyst, simultaneously, the degree of thermal decomposition of methyl vinyl ether is also greatly controlled by temperatures. Therefore, the performance of the joint reaction could be different when changing in temperatures. When mixed with 5 wt.% methyl vinyl ether, using Ba/ZSM-5 as the catalyst, Table 1

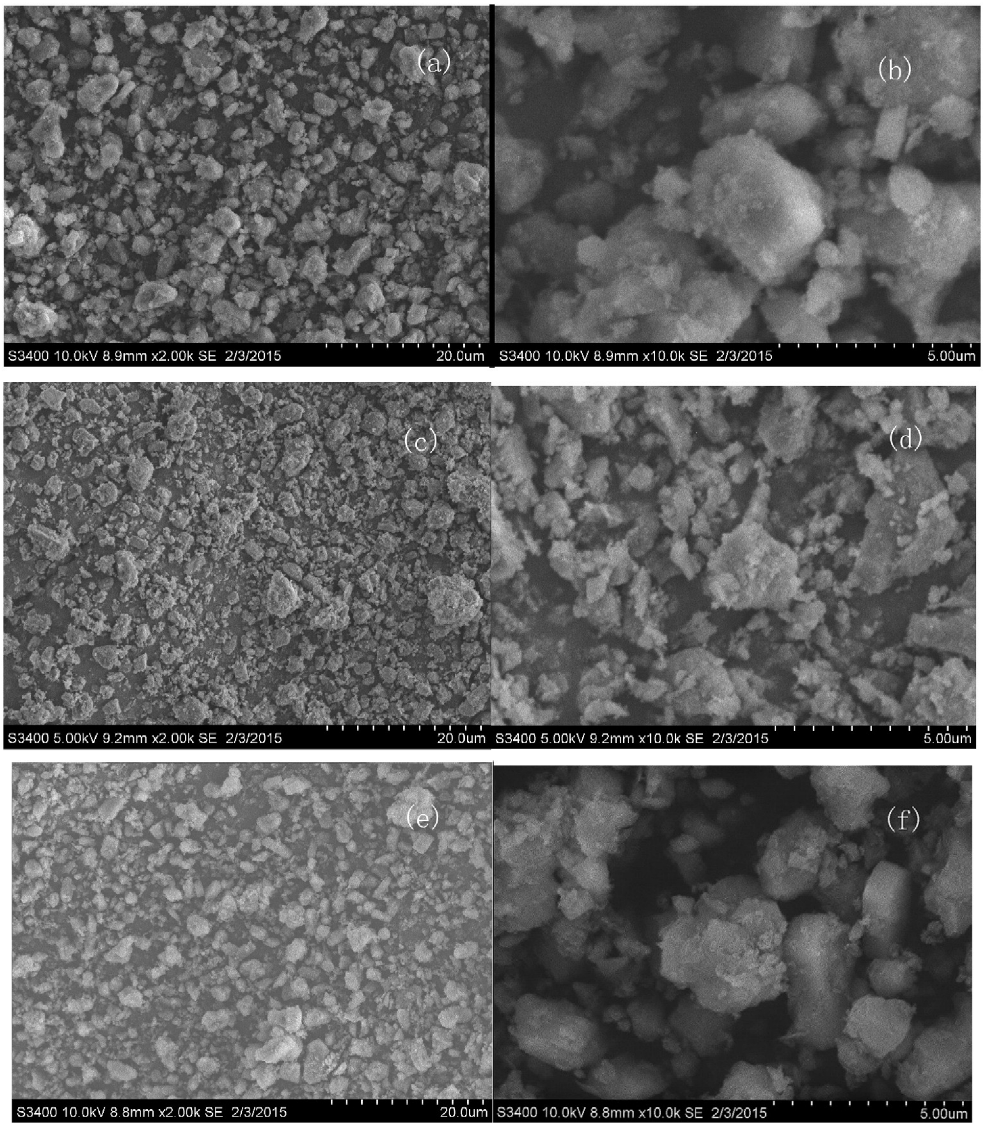

Fig. 3. SEM images of H-ZSM-5 (a, b), 3Ba/ZSM-5 (c, d) and 5Ba/ZSM-5 (e, f) zeolites.

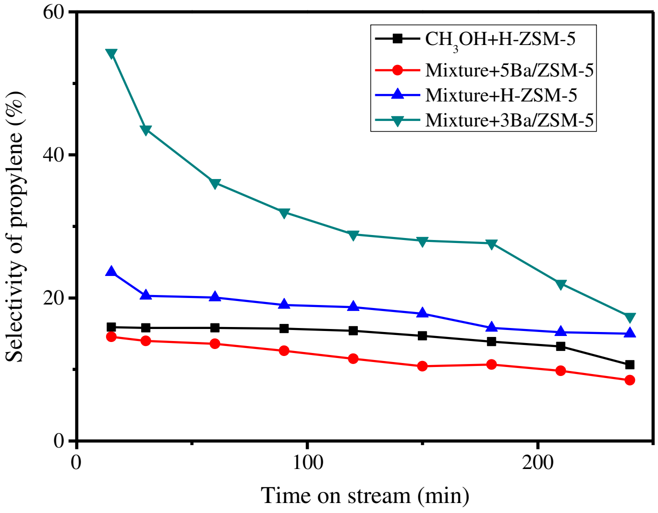

Fig. 4. The evolution of $C_3^=$ yield with time on stream at different conditions.

shows the olefin yield at different temperatures (350 °C, 450 °C and 550 °C) under the conditions of atmospheric pressure and WHSV of 1.8–2.2 h^{-1}. The corresponding changes in selectivity with reaction time have been shown in Fig. 5. The selectivity of propylene and olefins is enhanced as temperature increases, apparently, the yield of olefin is

Table 1
MTO reaction results of different temperatures.

Temperature (°C)	MVE (wt.%)	Time (min)	Selectivity (%)		
			$C_2^=$	$C_3^=$	$C_2^= + C_3^=$
350	5	30	12.46	15.58	28.04
		150	12.11	12.48	24.59
		240	13.10	12.10	25.20
450	5	30	14.29	20.29	34.58
		150	11.40	15.80	27.20
		240	10.56	12.90	23.46
550	5	30	16.28	30.56	46.84
		150	14.11	24.02	38.13
		240	8.31	22.90	31.21

($C_2^=$ and $C_3^=$ mainly represent ethylene and propylene, respectively. MVE represents methyl vinyl ether.)

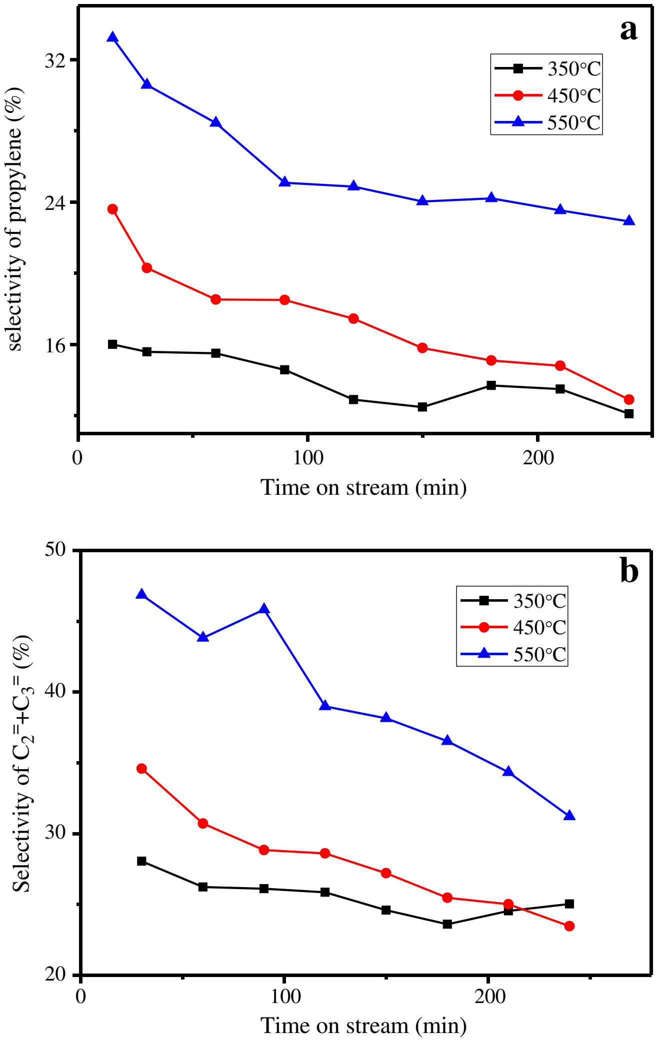

Fig. 5. The evolution of $C_3^{=}$ yield (a) and $C_2^{=} + C_3^{=}$ yield (b) with time on stream at different temperatures.

higher at 550 °C than others because of the high activity in the initial time, subsequently, it can be seen that the tendency of the yield drops faster due to the formation of cokes at high temperature which covers the active sites of the catalyst reducing the number of active centers, thus leading to faster catalyst deactivation. When the temperature is low, the process goes through an incomplete reaction, the catalyst pore unobstructed, however, the catalyst activity is not optimal, most of the active sites have not been used, which turn out to be the weaker catalytic activity.

4. Conclusions

The Ba modified H-ZSM-5 zeolite has been prepared by using the incipient wetness impregnation method. H-ZSM-5 and Ba modified H-ZSM-5 have been used to catalyze reaction of methanol with vinyl methyl ether. It shows that the addition of methyl vinyl ether into methanol can significantly enhance the yield of olefins on 3Ba/ZSM-5, especially for propylene, however, the excess Ba in H-ZSM-5 could reduce the zeolite specific surface area, leading to a decrease for the yield of propylene.

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