

# METHANE ACTIVATION AND AROMATIZATION WITHOUT USING OXIDANTS OVER Mo/H-ZSM-11 CATALYSTS

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## Introduction

With the development of natural gas exploration, the catalytic conversion of methane has become one of the focal subjects of extensive research in heterogeneous catalysis. Methane aromatization without using oxidants, which produces high value and easily separated liquid aromatic hydrocarbons as well as effectively controls deep oxidation of methane, has intrigued many researchers recent years<sup>[1-6]</sup>. As regards the supports of catalysts for this reaction, only H-ZSM-5, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SAPO-34 *et al* have been used up to now, and the last two have relatively low activity and selectivity<sup>[4,5,6]</sup>. In our previous work<sup>[7]</sup>, the catalytic performance of various zeolites supported Mo-based catalysts, such as H-ZSM-11, H-ZSM-8, and H- $\beta$  were studied for methane non-oxidative aromatization, and possible structural rules of fine supports for this reaction were proposed. A new zeolite supported catalyst — Mo/H-ZSM-11 — was found for this reaction, which exhibits even better catalytic behavior than Mo/H-ZSM-5. In the present paper, some detailed information about Mo/H-ZSM-11 catalysts, such as the dependence of reaction temperature, space velocity of methane and MoO<sub>3</sub> loading on the catalytic performance of Mo/H-ZSM-11 catalysts have been studied and the optimization of the Mo/H-ZSM-11 catalyst was carried out.

## Experimental

**Synthesis of H-ZSM-11 zeolite and preparation of Mo/H-ZSM-11 catalysts.** H-ZSM-11 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25, 50, 100, 200) was synthesized following the method in ref [8] using TBA<sup>+</sup> as template by hydrothermal method.

A mixture of MoO<sub>3</sub> and zeolite was made by grinding. A prescribed amount of MoO<sub>3</sub> with the above-prepared H-ZSM-11 zeolites was thoroughly ground, then calcined at 773K for 4h in air. So the Mo/H-ZSM-11 catalyst was obtained.

**Catalytic Test.** Methane non-oxidative aromatization reactions were carried out in a fixed-bed continuous-flow 8-mm i.d. quartz microreactor. The catalyst charge was 1.0 g (40 ~ 60 mesh). The reaction temperature is 973K. After pretreatment, pure methane was introduced into the reactor at a space velocity of 800h<sup>-1</sup>. The reaction mixture was analyzed by a on-line shimadzu GC-8A gas chromatograph in temperature programmed mode using a 3.5m Porapak P column and detected with TC detector. The methane conversion and product selectivity were calculated on a carbon number base without accounting for coking.

## Results and Discussion

**The effect of MoO<sub>3</sub> loading on the activity of Mo/H-ZSM-11 catalysts.** Variations of the activity of Mo/H-ZSM-11 catalysts with different MoO<sub>3</sub> loadings are shown in Table 1. It can be seen that a maximum of methane conversion and benzene selectivity is observed at MoO<sub>3</sub> loading of 5wt%. Further increasing MoO<sub>3</sub> loading causes the decrease in methane conversion and aromatics selectivity notably. Therefore, the MoO<sub>3</sub> loading on H-ZSM-11 of about 3~5wt% is optimal, which is about the same as that on H-ZSM-5. The XRD patterns of Mo/H-ZSM-11 with different MoO<sub>3</sub> loadings show that the MoO<sub>3</sub> crystallite pattern could not be detected if the MoO<sub>3</sub> loading is less than 10%. It indicates that the Mo species are highly dispersed on the H-ZSM-11 zeolite in the as-prepared Mo/H-ZSM-11 catalyst.

**The effect of reaction temperature on the activity of Mo/H-ZSM-11 catalysts.** As shown in Fig. 1, the activity of Mo/H-ZSM-11 catalyst increases with rising temperature. It is similar to the phenomenon observed over Mo/H-ZSM-5 catalyst. This result is in correspondence with the thermodynamic calculation, that is, methane aromatization under non-oxidative condition is an endothermic reaction, therefore high temperature is more favorable to methane conversion. At different temperatures methane conversion all decrease with increasing time on stream, and the speeds of the decrease of methane conversion are in order of: 923K < 973K < 1023K < 1073K(Fig.1), that is, the higher the reaction temperature is, the faster the methane conversion decreases. This is probably due to the increase of the carbon depositing rate over Mo/H-ZSM-11 catalysts with increasing reaction temperature. By comparison, the Mo/H-ZSM-11 catalyst shows relatively higher activity and stability at 973K, and the selectivity to aromatics is also somewhat higher. So the optimal reaction temperature on Mo/H-ZSM-11 is ~ 973K. XRD patterns of reacted catalysts at various temperatures illustrate that the structure of H-ZSM-11 zeolite is not destroyed.

**The effect of methane space velocity on the catalytic performance of Mo/H-ZSM-11.** The effect of space velocity of methane on the catalytic performance of Mo/H-ZSM-11 is shown in Fig.2. Evidently, the activity of catalysts increase in order of 1500, 800, 250h<sup>-1</sup> space velocity

of methane, that is, the lower the space velocity of methane, the higher the conversion of methane, and the higher the selectivity to aromatics. Clearly, lower space velocity of methane is favorable to the conversion of methane and aromatics production. This phenomenon is similar to that obtained over the Mo/H-ZSM-5 catalyst, which indicates that on the Mo/H-ZSM-11 catalyst ethylene could also be supposed to be the intermediate of methane non-oxidative aromatization. That is, the lower the space velocity, the longer the contact time between methane and the surface of the catalyst, and the larger amount of intermediate ethylene converted to aromatics, favorable to the conversion of methane and aromatics production. This phenomenon is similar to that obtained over the Mo/H-ZSM-5 catalyst, which indicates that on the Mo/H-ZSM-11 catalyst ethylene could also be supposed to be the intermediate of methane non-oxidative aromatization. That is, the lower the space velocity, the longer the contact time between methane and the surface of the catalyst, and the larger amount of intermediate ethylene converted to aromatics.

**The effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio on the activity of Mo/H-ZSM-11 catalysts.** The effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio on the activity of Mo/H-ZSM-11 is shown in Table 2. It can be seen that with decreasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, the activity of Mo/H-ZSM-11 increases. That is, the higher the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is, the lower the methane conversion and selectivity to aromatics are. As is well known, the lower the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is, the more AlO<sub>4</sub> tetrahedral in zeolite framework there is, as a result, the stronger the acidity of H-ZSM-11. the more AlO<sub>4</sub> tetrahedral in zeolite framework there is, as a result, the stronger the acidity of H-ZSM-11. Therefore, the changes of catalyst activity with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios reflect the effect of zeolite acidity on the reaction.

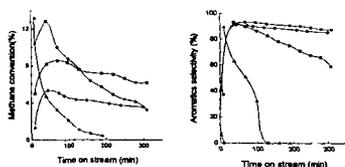
**Table 1 The effect of MoO<sub>3</sub> loading on activity of MoO<sub>3</sub>/H-ZSM-11 catalysts<sup>a</sup>**

MoO <sub>3</sub> loading (%)	Methane conversion (%)	Selectivity (%)		
		Aromatics (C <sub>6</sub> +C <sub>7</sub> )	C <sub>2</sub>	CO
1	4.79	86.0	8.90	5.10
3	8.18	91.5	5.10	3.40
5	8.59	93.1	4.94	1.99
6	7.77	87.7	7.10	5.20
10	5.65	86.2	9.88	3.90

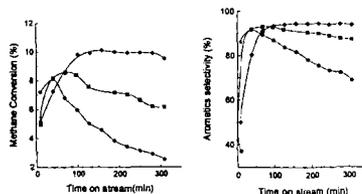
a. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=25, reaction temperature 973K.

**Table 2 The effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio on activity of 3%wt MoO<sub>3</sub>/H-ZSM-11 catalysts at 973K**

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio	Methane Conversion (%)	Selectivity (%)		
		Aromatics (C <sub>6</sub> +C <sub>7</sub> )	C <sub>2</sub>	CO
25	8.18	91.5	5.10	3.40
50	7.87	92.2	4.89	2.89
100	7.11	91.3	5.15	3.55
200	5.06	84.1	6.72	9.18



**Fig.1 Methane conversion and aromatics selectivity over 5%MoO<sub>3</sub>/H-ZSM-11 catalysts with time on stream at different temperatures: 923K, ♦; 973K, ■; 1023K, ●; 1073K, ▲.**



**Fig.2 Methane conversion and aromatics selectivity over 5%MoO<sub>3</sub>/H-ZSM-11 at different space velocity (♦, 250h<sup>-1</sup>; ■, 800h<sup>-1</sup>; ●, 1500h<sup>-1</sup>).**

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