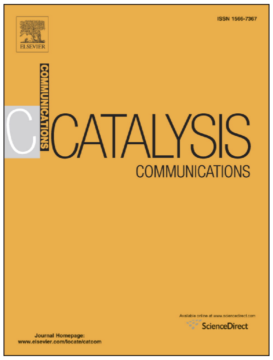

The catalytic performance of Mo-impregnated HZSM-5 zeolite in CH4 aromatization: Strong influence of Mo loading and pretreatment conditions

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The catalytic performance of Mo-impregnated HZSM-5 zeolite in CH_4 aromatization: Strong influence of Mo loading and pretreatment conditions

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Abstract: The catalytic activity and stability of Mo/HZSM-5 solid with Mo loading higher than 10 wt% in methane aromatization are significantly improved after pretreatment with a CH_4/Ar/He (9:1:10, v/v) gas mixture. A 16 wt% Mo loading is found to provide the best catalytic performance for the aromatization of methane and better than previously reported in the literature (similar reaction conditions) over Mo-impregnated HZSM-5 zeolites. After 30 h of continuous reaction at 700 ^{o}C and using a space velocity of 1500 ml g^{-1} h^{-1}, the 16 wt% Mo-based catalyst provides an aromatic yield of 7.8% and a CH_4 conversion of 9.5%.

Keywords: Methane aromatization; Mo/HZSM-5; Optimum Mo loading; Pretreatment with CH_4/Ar/He.

1. Introduction

Much effort has been devoted to enhancing the activity and stability of Mo/HZSM-5 catalysts in the methane dehydroaromatization reaction since the pioneering work of Wang et al. [1]. In various essential catalyst preparation conditions, the calcination temperature of 500 °C, a zeolitic Si/Al ratio between 10 and 25, and the impregnation technique are gradually accepted as the most suitable synthetic conditions of Mo/HZSM-5 for the above stated reaction [2,3]. However, there is a controversy on the optimum loading of Mo, apparently as the most important chemical composition factor for the catalytic performance of this particular Mo-based catalyst prepared by the impregnation method and calcined at 500 °C. It was reported that the catalytic activity increases with Mo loading up to 2-3 wt% [4-6], 4 wt% [3], or 6 wt% [7,8] over Mo/HZSM-5. A further increase of the Mo content resulted in a decrease of both methane conversion and selectivity to aromatics, and an increase in the selectivity to C_2-hydrocarbons. On the other hand, for a practically acceptable activity for the Mo/HZSM-5 catalyst in methane aromatization, the reaction temperature is usually set at least 200 °C higher than the optimum calcination temperature of the catalyst applied. This temperature difference affects the influence of pretreatment method on the catalytic performance of Mo/HZSM-5. Previous activations of Mo/HZSM-5 solids prior to the catalytic aromatization reaction were mostly conducted in He or Ar inert gas [1-8].

Recently, Tempelman et al. [9,10] reported that the effect of pre-reduction of Mo/HZSM-5 in 80 vol% CH_4/He on the catalytic performance was more positive than the pretreatment of Mo catalyst in He or air gas atmosphere. To avoid rapid release of reaction heat due to MoO_3 reduction by CH_4 and an abrupt increase in the concentration of water produced during this activation of catalyst, the present work has developed a pretreatment method of Mo/HZSM-5 with a diluted CH_4 gas mixture (55 vol% inert gas). After the application of this new pretreatment method, the catalytic activity and stability of Mo/HZSM-5, especially that with Mo loadings higher than 10 wt%, were significantly enhanced. Among these catalysts, HZSM-5 zeolite loaded with 16 wt% Mo exhibited the best catalytic performance for the methane aromatization reaction.

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolite (Si/Al = 25, particle size distribution as shown in Fig. S1) was supplied by Nankai University, People's Republic of China. All the Mo/HZSM-5 catalyst samples were prepared via the wet impregnation method. A 3-g portion of HZSM-5 zeolite was impregnated with 50 ml of aqueous solution of ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Sigma-Aldrich) containing the required amount of molybdenum (x wt% loading) at room temperature for 24 h. The resulting material was dried in a Binder oven at 120 ^oC and then calcined in a Nabertherm furnace at 500 ^oC in static air for 6 h. The freshly prepared Mo/HZSM-5 samples were then pressed, crushed and sieved to 20-40 mesh for catalytic evaluation. In the following Sections, a Mo/HZSM-5 catalyst with different Mo loading is denoted as M-x (M=Mo/HZSM-5; x=Mo loading value).

2.2. Catalyst evaluation

Catalytic tests were carried out in a continuous fixed-bed flow quartz reactor (i.d.= 7 mm) system at 700 ^oC and atmospheric pressure. The gases used in this work were all UHP grade. Typically, 0.5-g of catalyst sample was first heated in the reactor to 700 oC at the ramp rate of ~22^oC min^{-1} under a gas mixture containing 45 vol% CH_4, 5 vol% Ar and 50 vol% He at the flow rate of 25 ml min^{-1} in order to reduce the catalyst and remove adsorbed/produced water. When the temperature reached 700 ^oC, another gas mixture consisting of 90 vol% CH_4 and 10 vol% Ar (12.5 ml min^{-1}) was introduced into the reactor in place of the pretreatment gas mixture and the catalyst test was then started. For comparison, the effects of typical pretreatment methods (Fig. S2) reported in the literature [7,8,11-13] on the catalytic performance of Mo/HZSM-5 were also investigated. All reactants and products were analyzed using two Agilent 5820 online gas chromatographs equipped with flame ionization and thermal conductivity detectors, where Ar in CH_4 was used as an internal standard. To prevent product condensation the reactor outlet gas lines and gas sampling valves were kept above 160 ^oC. CH_4 and higher hydrocarbon products (e.g. C_2H_4, C_2H_6, C_6H_6, C_7H_8, and $C_{10}H_8$) were separated by a Porapak-P packed column and then analyzed using the FID detector. H_2, Ar, CO, CH_4, and CO_2 were separated by an activated carbon packed column and then analyzed using the TCD detector. CH_4 conversion and selectivities/yields of carbon-containing products were calculated on a carbon number basis.

2.3. Catalyst characterization

Nitrogen physical adsorption measurements of the parent and Mo-modified HZSM-5 zeolites at -196 ^oC were carried out on a Micromeritics automatic surface area and pore size analyzer (TriStar II 3020). All the samples were outgassed under vacuum at 350 ^oC for 5 h prior to analysis. The micropores volume was determined according to the t-plot method.

The Mo content was determined by ICP-AES (Optima 7300DV). The various solutions for analysis were prepared by digesting ca. 0.25 g of the dried sample (120 ^oC for 6 h) in a 10-ml concentrated nitric acid solution, followed by adding 15 ml concentrated HF solution at 0 ^oC and then some deionized water up to 50 ml. The spent sample was treated at 600 ^oC for 2 h under air for coke removal before digesting. Mo content analysis (Table 1) showed that most of Mo loaded was remained on the fresh Mo/HZSM-5 catalyst after calcination at 500 ^oC in air for 6 h. After treatment of the 16 wt% Mo-impregnated HZSM-5 zeolite with CH_4/Ar/He (9:1:10, v/v) at 700 ^oC

and space velocity of 1500 ml g^{-1} h^{-1} for 3 min, there was a slight decrease in the Mo loading of the catalyst, ca. from 14.2 to 13.6 wt%.

3. Results and discussion

This work first investigated the effects of typical pretreatment methods developed in the present work and those reported in the literature [7,8,11-13] on the catalytic performance of 6 wt% Mo/HZSM-5, the most widely studied catalyst for methane aromatization. As shown in Figs. 1a and S3a, although activation of the catalyst at 600 ^{o}C under inert helium before reaction could enhance the activity of Mo/HZSM-5, this Mo-based catalyst exhibits better catalytic activity and stability after pretreatment with a reductive gas than an inert one. Furthermore, compared with H_2 gas pretreatmentat 350 ^{o}C for 6 h, pretreatment with CH_4/Ar/He (9:1:10, v/v) is a very simple but highly efficient method for improving the catalytic performance of the Mo/HZSM-5 solid. On the other hand, with increasing Mo loading from 6 to 16 wt%, differences in the effects of various pretreatment methods on the catalytic performance of Mo/HZSM-5 become obvious (Figs. 1b and S3b).

Activities and aromatic yields at 700 ^{o}C and a space velocity of 1500 ml g^{-1} h^{-1} over the 2-28 wt% Mo/HZSM-5 zeolites after pretreatment in CH_4/Ar/He (9:1:10, v/v) mixture are given in Figs. 2 and S4, and Table 1. In all cases, benzene is found to be the major aromatic product, accompanied by other heavier aromatic molecules that include mainly naphthalene and a small amount of toluene; C_2-hydrocarbon products include ethylene and ethane (yield ratio of $C_2H_4/C_2H_6 > 1$). After reaction for 10 h, a methane conversion of 5.5%, an aromatic yield of 3.2% and a C_2-hydrocarbon yield of 0.8% are observed over the 2 wt% Mo loaded catalyst. The ratio of aromatic yield to methane conversion ($Y_{aromatics}/C_{CH4}$) is 0.58.

Methane conversion, aromatic yield, and $Y_{aromatics}/C_{CH4}$ increase with increasing Mo loading and reach maximum values of 11.4%, 9.8%, and 0.86, respectively, at the Mo loading of 16 wt%. Meanwhile, C_2-hydrocarbon yield slightly decreases to 0.5%. By further increasing the Mo loading, a decrease of methane conversion and aromatics yield and a slight increase of selectivity to aromatics and C_2-hydrocarbon yield are obtained. When the Mo loading reaches 28 wt%, the Mo/HZSM-5 gives an aromatic yield of 8.4% and a methane conversion of 9.6% ($Y_{aromatics}/C_{CH4} = 0.87$), both values being higher than those obtained over the 6 wt% Mo-based catalyst. It is interesting to note that HZSM-5 loaded with a Mo content of 50 wt% is still active for the methane aromatization reaction under the same pretreatment and reaction conditions reported for the other Mo loadings; an aromatic yield of 5.7% at a methane conversion of 12.4% is obtained after 2 h of reaction.

On the other hand, with increasing Mo loading the evolution of catalytic stability is similar to that observed for the catalytic activity of the Mo/HZSM-5 sample in the dehydro-aromatization of methane, although the selectivity to coke decreases with increasing Mo loading from 2 to 28 wt%. Of those catalysts investigated, the 16 wt% Mo-impregnated HZSM-5 zeolite exhibits the most stable catalytic performance. After 30 h of continuous reaction at 700 ^{o}C and a space velocity of 1500 ml g^{-1} h^{-1}, an aromatic yield of 7.8% at a methane conversion of 9.5% is still able to be obtained (Fig. 2d). In addition, the induction time of the Mo/HZSM-5 becomes slightly longer at higher Mo loadings.

The above results are different from those reported in the literature [3-8], in which Mo/HZSM-5 with Mo loading higher than 10 wt% exhibits poorer or much poorer catalytic performance for methane aromatization than the Mo/HZSM-5 catalyst with Mo loadings of 6 wt% or lower (Fig. S5). For the HZSM-5 zeolite, the adsorption of perfluorotributyl amine showed that most of its Brønsted acid sites (>96%) were located inside the zeolitic channels [7]. After impregnation of the zeolite with ammonium heptamolybdate tetrahydrate aqueous solution, Wang et al. [14] reported that even after the Mo-impregnated HZSM-5 zeolite was treated at 400 ^{o}C, zeolitic acidity was not modified, and relatively little Mo was present in the channels of ZSM-5. It is well known [6-8,14] that calcination temperature of 500 ^{o}C could drive in part of Mo species loaded into the zeolitic channels, where the cationic Mo-oxo complexes could replace the protons and anchor on the internal surface of the zeolite. This Mo diffusion is enhanced with increasing Mo loading from 6 to 28 wt%, as reflected in the reduction of the specific volume of micropores [Fig. S6]. Since those Mo species dispersed inside the zeolite pores are reported to be the precursors of active phases responsible for the activation of methane [15,16], this can reasonably explain the enhanced catalytic activity of Mo/HZSM-5 with suitably increasing Mo loading. On the other hand, it is reported that methane is activated on Mo sites via heterolytic splitting of C-H bonds assisted by the Brønsted acid sites of HZSM-5, and synergy between the Mo_2C clusters and the acid sites plays an important role in this activation [4]. Excessive Mo loading, such as 28 wt%, leads to the formation of inadequate synergistic sites between active Mo and Brønsted acid sites for methane activation. Thus, the observed reduction in the catalytic activity of Mo/HZSM-5 appears reasonable. Moreover, insufficient acidic sites due to Mo overload would promote dehydrogenation of reaction intermediates to carbonaceous materials, which would deposit on the active sites, thus causing deactivation of Mo/HZSM-5. As a result, the 16 wt% Mo loading is found to be the optimum one for the catalytic performance of Mo/HZSM-5 in CH_4 transformation to aromatic hydrocarbons at the examined experimental conditions.

4. Conclusions

Mo/HZSM-5 with Mo loading larger than 10 wt% shows significantly enhanced catalytic activity and stability in the non-oxidative conversion of methane to aromatic hydrocarbons after pretreatment with a diluted CH_4 gas mixture (55 vol% Ar/He). Among these Mo loadings, 16 wt% is the most suitable for the catalytic performance of Mo-impregnated HZSM-5 zeolites in this aromatization reaction. After 30 h of continuous reaction at 700 ^{o}C and 1500 ml g^{-1} h^{-1}, this 16 wt% Mo-based catalyst can give rise to an aromatic yield of 7.8% at a CH_4 conversion of 9.5%. Hitherto, the most widely studied catalysts for methane aromatization are those based on Mo/HZSM-5 with Mo loading of 6 wt% or lower. This work presents novel results about the catalytic aromatization of methane over Mo/HZSM-5 zeolite impregnated with high Mo loadings (e.g. ≥10 wt%).

Acknowledgements

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Captions to Figures

Figure 1. The effect of pretreatment method on the catalytic activity of Mo/HZSM-5 in methane aromatization at 700 ^{o}C and 1500 ml g^{-1} h^{-1}: (a, top) Mo/HZSM-5 catalyst with Mo loading of 6 wt%, pretreatment methods 1-5; (b, bottom) Mo/HZSM-5 catalysts with Mo loadings of 6, 10 and 16 wt%, pretreatment methods 3 and 5.
Note: the activity data were recorded after 10 h of reaction; Methods 1, 2, and 3: pretreatment in helium at 500 ^{o}C, 600 ^{o}C and 700 ^{o}C, respectively, for 0.5 h; Method 4: pretreatment in hydrogen at 350 ^{o}C for 6 h; Method 5: pretreatment in CH_4/Ar/He (9:1:10, volume).

Figure 2. Catalytic dehydroaromatization of methane at 700 ^{o}C and 1500 ml g^{-1} h^{-1} over Mo/HZSM-5 catalyst: (a), (b) and (c) report catalytic performance (CH_4 conversion and various hydrocarbon yields) of the Mo/HZSM-5 with various Mo loadings (2-28 wt%) after a 10-h test; (d) catalytic performance of Mo/HZSM-5 with a Mo loading of 16 wt%.
Note: A CH_4 conversion of 47.1% and traces of C_2-hydrocarbon products were observed on the M-28 catalyst after 0.5 h on stream.

Figure 1

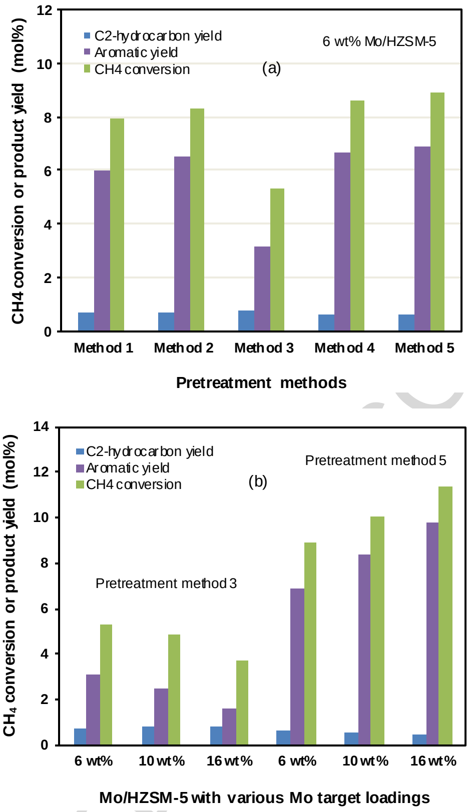

(a)
6 wt% Mo/HZSM-5
C2-hydrocarbon yield
Aromatic yield
CH4 conversion
CH4 conversion or product yield (mol%)
0
2
4
6
8
10
12
Method 1
Method 2
Method 3
Method 4
Method 5
Pretreatment methods
(b)
Pretreatment method 5
Pretreatment method 3
C2-hydrocarbon yield
Aromatic yield
CH4 conversion
CH₄ conversion or product yield (mol%)
0
2
4
6
8
10
12
14
6 wt%
10 wt%
16 wt%
6 wt%
10 wt%
16 wt%
Mo/HZSM-5 with various Mo target loadings

Figure 2

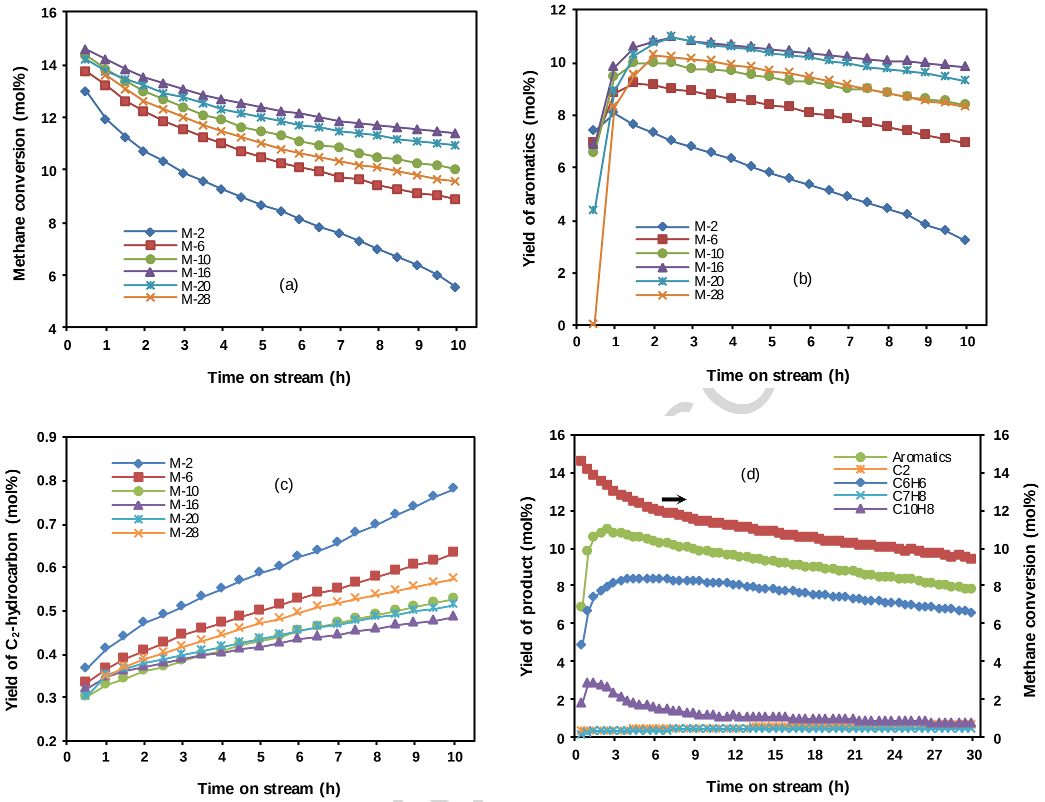

Methane conversion (mol%)
16
14
12
10
8
6
4
0
1
2
3
4
5
6
7
8
9
10
Time on stream (h)
M-2
M-6
M-10
M-16
M-20
M-28
(a)
Yield of aromatics (mol%)
12
10
8
6
4
2
0
Time on stream (h)
(b)
Yield of C_2-hydrocarbon (mol%)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
Time on stream (h)
(c)
Yield of product (mol%)
Methane conversion (mol%)
0
3
6
9
12
15
18
21
24
27
30
Time on stream (h)
(d)
Aromatics
C2
C6H6
C7H8
C10H8

Table 1 Catalytic activity of Mo/HZSM-5 materials with different Mo loadings in methane aromatization at 700 °C and 1500 ml g^{-1} h^{-1} [a]

Nominal Mo loading (wt%)[b]	Analyzed Mo loading (wt%)[b]	Methane conversion (mol%)	Selectivity (%)				
			C_2[c]	C_6H_6	C_7H_8	$C_{10}H_8$	Coke[d]
2	1.9	5.5	14.1	44.1	3.2	10.8	27.8
6	5.4	8.9	7.1	62.1	3.9	11.7	15.2
10	8.9	10.1	5.3	67.4	3.9	12.1	11.3
12	10.7	11.2	4.5	70.8	3.6	11.2	9.9
16	14.2	11.4	4.3	71.9	3.7	10.5	9.6
20	17.7	10.8	4.7	74.2	3.9	8.1	9.1
24	21.1	10.3	5.3	74.2	4.0	8.5	8.0
28	24.4	9.6	5.9	73.8	4.3	9.0	7.0

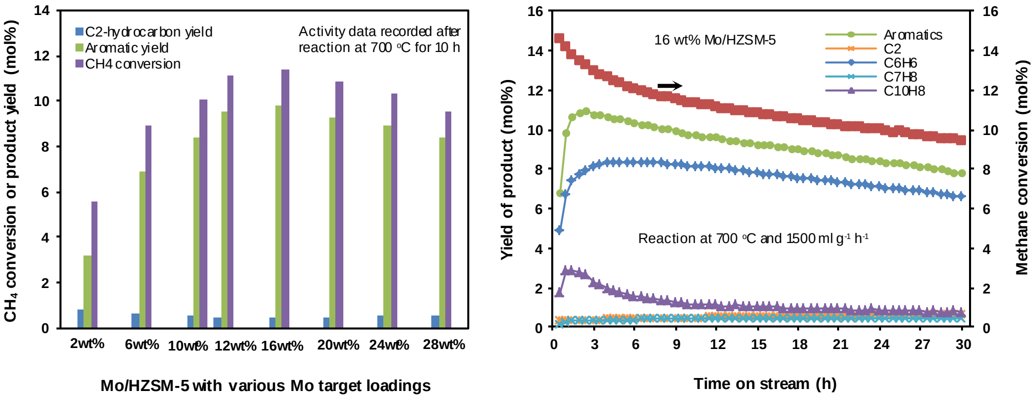
[a] Data were recorded after 10 h of reaction time

[b] Mo content of fresh Mo/HZSM-5 catalysts

[c] $S_{C2} = S_{C2H4} + S_{C2H6}$

[d] $S_{Coke} = 100\% – (S_{C2} + S_{C6H6} + S_{C7H8} + S_{10H8})$

Graphical abstract



Highlights

- The catalytic performance of >10 wt% Mo/HZSM-5 was significantly improved
- 16 wt% Mo-doped HZSM-5 shows the best behavior in catalytic aromatization of CH_4
- Prereduction with 45 vol% CH_4/Ar/He is a highly efficient pretreatment method