Methane activation without using oxidants over Mo/HZSM-5 zeolite catalysts

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The effect of Mo loading, calcination temperature, reaction temperature and space velocity on the catalytic performance of methane dehydrogenation and aromatization without using oxidants over Mo/HZSM-5 has been studied. The XRD and BET measurements show that Mo species are highly dispersed in the channels of the HZSM-5 zeolite, resulting from the interaction between the Mo species and the zeolite, which also leads to a decrease in its crystallinity. The Brønsted acidity, the channel structure and the state and location of Mo species in the zeolite seem to be crucial factors for its catalytic performance. It was found that 2% Mo/HZSM-5 calcined at 773 K showed the best aromatization activity among the tested catalysts, the methane conversion being 9% at 1013 K with the selectivity to aromatics higher than 90%. The experimental results obtained from the variation of space velocity gave evidence that ethylene is an initial product. On the basis of these results a possible mechanism for methane dehydrogenation and aromatization has been proposed in which both the heterolytic splitting of methane in a solid acid environment and a molybdenum carbene-like complex as an intermediate are of significance.

Keywords: methane activation; without using oxidants; heterolytic splitting of methane; molybdenum carbene-like complex

1. Introduction

The catalytic conversion of methane to desired chemical products or liquid fuel is a great challenge to and a long-term project in catalysis science. In as early as the seventies, it was reported that methane can be activated and proceeds via the homologation reaction in ultra-strong acid medium [1,2]. A CH_5^+ intermediate was supposed to be formed first, which then decomposed into CH_3^+ and H_2. As a unique

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example, the H–D exchange reaction of methane also has been extensively studied in acid medium in the presence of a transition metal salt such as $PtCl_2$ [3]. Most researchers recognized the platinum carbene-like compound as an active intermediate for the reaction. Unfortunately, the H–D exchange reaction seems to have a very distinct feature and until now no other reagents could be found as replacements in order to follow the same reaction as in the H–D exchange of methane. Anyway, it seems that a strong acid medium and a transition metal carbene-like complex intermediate are crucial for the methane activation in homogeneous catalysis. For clarity, we term it acid-assisted heterolytic splitting of methane. The acid-assisted heterolytic splitting of methane will give CH_3^+ and H^-.

In recent years, the activation of methane has been actively studied, using dioxygen or other oxidants, in heterogeneous catalysis. The most extensive study has been the oxidative coupling of methane (OCM) in the co-feed mode with oxygen, since 1982. As Lunsford suggested, methane can be activated via homolytic splitting on the catalyst surface to form methyl radicals which result from the interaction between methane and oxygen species that most possibly are in the form of O^- on the catalyst surface [4]. The catalyst basicity is of significance for the OCM since most of the catalysts active for the reaction are composed of or modified with alkali and alkali earth metal compounds. Yet, there is no direct correlation between the reactivity of the OCM and the basicity of a catalyst [5,6]. Focusing on the catalyst basicity, a few researchers put forward an alternative proposal for the mechanism of the activation of methane [6,7]. Here, methane is first heterolytically split into CH_3^- and H^+ under the assistance of basic sites on the catalyst surface. We term it basicity-assisted heterolytic splitting to differentiate from the above mentioned acid-assisted heterolytic splitting. Usually the CH_3^- species, once formed, will transform quickly to methyl radicals by giving up an electron. In this case, the oxygen species and methyl radicals still play key roles in the OCM, as suggested by Lunsford [4]. Although until now there is no direct experimental evidence for either homolytic or heterolytic splitting of one C–H bond in methane, it is interesting to notice that the acidity is an important factor in the activation of methane in homogeneous catalysis, while the basicity plays a key role in the activation of methane in heterogeneous catalysis, even if we accept the concept of heterolytic splitting in both heterogeneous and homogeneous catalysis.

Because of the difficulty in meeting the conditions required by industrial application of the OCM (till now no catalyst could reach a C_2 yield beyond 30–40% while the selectivity to C_2 was higher than 80%), most catalytic chemists now move their attention from the OCM to other reactions. Among these is the partial oxidation of methane, either for the production of synthesis gas [8] or for the production of higher hydrocarbons and oxygenates. The direct transformation of methane to higher hydrocarbons and aromatic products has been reported, using dioxygen and nitrous oxide as oxidants, over ZSM-5 zeolite catalysts [9–11]. Like in the OCM, using N_2O as an oxidant in the partial oxidation has been more successful. Han and coworkers [12,13] reported the direct partial oxidation of CH_4 with O_2 to higher hydrocarbons, and in particular C_{5+} liquids, over HZSM-5 (in the presence of a C_3 additive) and metal containing ZSM-5 catalysts at 713–733 K. The authors believed that CH_3OH is a key product and that it is crucial that two metal functions of the catalyst, dehydrogenation and oxidation, are in balance. The conversion of methane to benzene over high silica zeolite based catalysts in a pulse-reactor was briefly reported [14], but only very limited information was provided. Lately, Claridge et al. reported their studies of the conversion of methane–oxygen mixtures to aromatics over metal oxides and supported metal catalysts [15]. They claimed that over $K/BaCO_3$ and/or $NaCl/MnO_2$ catalysts the conversion was about 13% with the selectivity to aromatics of 18–23% at 1223 K. The authors suggested that the formation of aromatics possibly proceeds via an ethylene intermediate.

Comparing the methane activation in homogeneous and heterogeneous catalysis, the distinct feature is that oxidants are not necessary in the former case, but are necessary in the latter case. It is very interesting and of significance to explore the possibility of the activation of methane without using oxidants in heterogeneous catalysis. In 1993, Wang, Xu et al. [16] reported on the dehydrogenation and aromatization of methane without using oxidants on transition metal ion modified HZSM-5 zeolite catalysts. Among the tested catalysts Mo/HZSM-5 is the best. The activation of methane on Mo/HZSM-5 zeolite catalysts was discussed in terms of a carbenium ion mechanism. In this paper, we further reported the dependence of reaction temperature and space velocity, Mo loading and calcination temperature on the catalytic performance of methane dehydrogenation and aromatization over Mo/HZSM-5 catalysts. The XRD and BET measurements show that Mo species are highly dispersed in the channels of HZSM-5 zeolite, resulting from the interaction between the Mo species and the zeolite, which also leads to a decrease in the crystallinity. The Brønsted acidity, the channel structure and the state and location of Mo species in the zeolite seem to be crucial factors for its catalytic performance. Considering the HZSM-5 zeolite with an acidic solution-like environment in solid form, a mechanism of the methane activation without using oxidants over Mo/HZSM-5 catalysts is discussed in more detail along with a combined line containing the concept of a molybdenum carbene-like complex as in homogeneous catalysis and the polarization of one C–H bond in methane as in the reaction of light paraffin aromatization in heterogeneous catalysis.

2. Experimental

2.1. MATERIALS

The ZSM-5 zeolite, supplied by Nankai University, with SiO_2/Al_2O_3 ratio of 50 was first converted into its ammonium form (NH_4ZSM-5) by repeated ion exchange (four times, each lasted about 2 h) with a 1 N NH_4NO_3 aqueous solution at about 368 K. The sample was then dried at 383 K overnight and calcined at a designated temperature for 6 h. Me/HZSM-5 (Me = Mo, Zn and so on) catalysts were prepared by impregnating NH_4ZSM-5 with ammonium heptamolybdate or an aqueous solution of corresponding metal nitrates, then drying at 383 K overnight and calcining at a designated temperature for 6 h. The Mo loading nominally was 1, 2, 3, 4.5, 6, 8, 10% in weight. Finally, the catalysts were pressed, crushed and sorted into sizes of 40–60 mesh. For comparison, Al_2O_3 and SiO_2 produced by Degussa were used to prepare 2% Mo/Al_2O_3 and 2% Mo/SiO_2 catalysts.

2.2. CATALYTIC TESTS

The catalytic test was performed in a fixed bed continuous-flow quartz reactor with 8 mm i.d. The catalyst charge was 0.2 g. It was covered with quartz sand of 10 mm high as a preheater. The catalyst zone was heated under an air stream (15 ml/min) to 973 K and maintained at 973 K for 40 min. After the pretreatment, methane was introduced into the reactor through a Brooks mass flowmeter. The hourly space velocity of methane was 1500 ml/g h, the pressure of the reactor system was 115 kPa and the reaction temperature was 973 K in a standard test. The tail gas was sampled after 40 min running from the reactor outlet and analyzed by a Shimadzu GC-9AM gas chromatograph. Aliphatic and aromatic hydrocarbons were separated in temperature programmed mode on a 4 mm × 3 m long column filled with Porapak Q and detected with a hydrogen flame ionization detector. The conversion of methane and selectivity of the products were calculated on the basis of carbon number balance.

In the regeneration test, 2% Mo/HZSM-5 was used as the catalyst and the reaction conditions were the same as mentioned above. The regeneration procedure was as follows: after running the catalyst for several hours, the methane feed was switched to air stream (15 ml/min) at 973 K for 1 h and then switched back to the methane feed for its reaction test after regeneration. In the life test, the reaction temperature was 1013 K.

Methane was 99.95% pure. Analysis of the air and helium used in the experiment showed the absence of any H_2 and hydrocarbons.

2.3. XRD AND BET MEASUREMENTS

Specific surface areas and average pore diameters of the samples were obtained by the BET method from the adsorption isotherm at liquid nitrogen temperature, 78 K, and taking a value of 0.162 nm^2 for the cross-section area of N_2. The measurement was performed with a Micromeritics ASAP-2000 equipment and data were proceeded and analyzed by an IBM computer.

X-ray powder diffraction patterns were obtained on a Rigaku diffractometer using Cu K_α radiation at room temperature. The instrumental conditions were selected as 40 kV and 100 mA at the scanning rate of 8°/min. Powder diffractograms of samples were recorded over a range of 2θ values from 5° to 40°. All XRD spectra were recorded, stored and processed using a computer system attached to the instrument.

3. Results

3.1. DEHYDROGENATION AND AROMATIZATION OF METHANE WITHOUT USING OXIDANTS OVER Mo/HZSM-5 ZEOLITE CATALYSTS

The reaction results of methane on various catalysts are summarized in table 1. The conversions of methane over HZSM-5 and Mo/NaZSM-5 were almost the same as, but the selectivities to ethylene and aromatics were much higher than the blank. This means that either the non-modified HZSM-5 or the Mo/NaZSM-5 zeolite catalyst exhibits little activity for the dehydrogenation and aromatization of methane. 2% Mo/Al_2O_3 and 2% Mo/SiO_2 catalysts showed only little activities and the conversions of methane were less than 1%, but the selectivity to aromatics on both samples were much higher than those on HZSM-5 and Mo/NaZSM-5, as shown in table 1. The methane conversion greatly increased by loading Mo species on and/or in the zeolite with a remarkable change in the selectivities to C_2 and aromatics (mainly benzene and toluene). The selectivity to C_2 was less than 10% and the selectivity to aromatics is higher than 90% at 973 K over 2% Mo/HZSM-5 zeolite catalyst. Among the tested transition metal modified HZSM-5 catalysts, Mo/HZSM-5 exhibited the best activity for the methane dehydrogenation and aromatization.

The methane conversion and the selectivity to aromatics increased, while the selectivity to C_2 decreased with increasing reaction temperature (see fig. 1). Thermodynamically it is reasonable that the high reaction temperature is favorable for

Table 1
Methane aromatization over various catalysts [a]

Samples	Conv. CH_4 (%)	Selectivity (%)				
		$C_2^=$	C_2	C_3	benz.	tol.
blank	0.1	17.8	82.2	0.0	0.0	0.0
HZSM-5	0.1	32.1	56.1	0.0	11.8	0.0
MoO_3/Al_2O_3	0.7	19.0	9.7	0.0	61.4	9.2
MoO_3/SiO_2	0.8	7.8	4.6	0.0	85.5	2.1
MoO_3/NaZSM-5	0.1	44.2	38.5	0.0	17.3	0.0
MoO_3/HZSM-5	5.6	3.0	2.2	0.1	90.4	4.4
Zn/HZSM-5	1.0	16.1	3.5	1.3	69.9	9.2
Cu/HZSM-5	0.6	34.0	12.1	1.3	50.1	2.4
Pt/HZSM-5	0.03	31.4	68.6	0.0	0.0	0.0
Ni/HZSM-5	0.01	60.0	40.0	0.0	0.0	0.0

[a] $T = 973$ K, HSV = 1500 h^{-1} g^{-1}, metal loading: 2%.

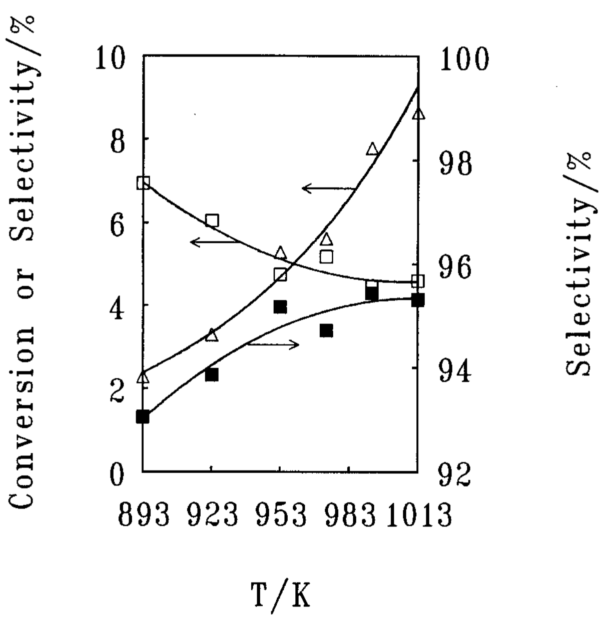


Fig. 1. Effect of reaction temperature on the aromatization of methane over 2% Mo/HZSM-5 calcined at 773 K for 6 h. (△) Methane conversion; (□) selectivity of C_2; (■) selectivity for aromatics.

the aromatization of methane. The conversion of methane and the selectivity to aromatics over 2% Mo/HZSM-5 decreased with increasing space velocity of methane as shown in table 2. The selectivity to C_2 and the ratio of ethylene to ethane increased with increasing space velocity. This implies that ethylene is an initial product of the reaction and aromatics come in succession from the further transformation of ethylene produced, which is in agreement with the TPAR results reported in our previous paper [16].

3.2. DEPENDENCES OF Mo LOADING AND THE CALCINATION TEMPERATURE ON THE CATALYTIC PERFORMANCE OF Mo/HZSM-5 ZEOLITE CATALYSTS

Fig. 2 shows the reaction results on Mo/HZSM-5 zeolite catalysts with different

Table 2
Effect of space velocity on the reaction results on 2% Mo/HZSM-5 zeolite catalysts calcined at 773 K for 6 h

SV	Conv. CH_4 (%)	Selectivity (%)					$C_2^=/C_2$
		$C_2^=$	C_2	C_3	benz.	tol.	
1500	5.6	3.0	2.2	0.1	90.4	4.4	1.4
3000	4.3	5.6	2.8	0.3	86.0	5.5	2.0
4500	2.3	12.2	3.1	0.8	78.1	5.9	3.9

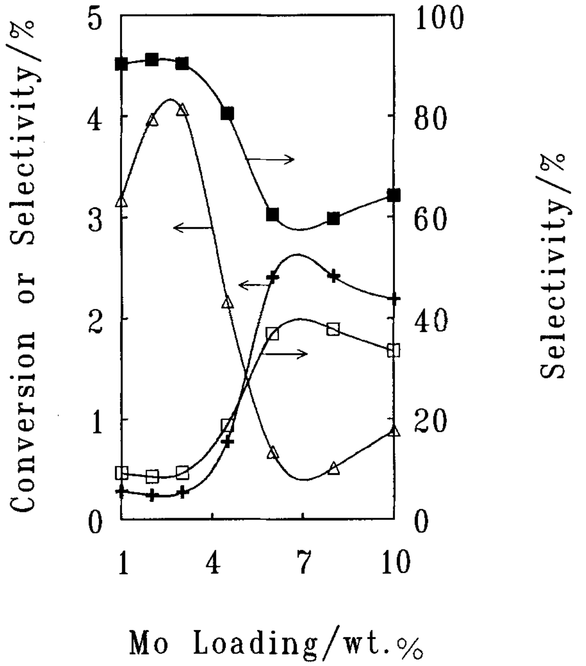


Fig. 2. Effect of Mo loading on the aromatization of methane over Mo/HZSM-5 calcined at 973 K for 6 h (reaction temperature: 973 K). (△) Methane conversion; (□) selectivity of C_2; (■) selectivity for aromatics; (+) selectivity of C_3.

Mo loading. The methane conversion appears a maximum at about 2–3% Mo loading. After that, it decreases substantially with increasing Mo loading and reaches its lowest level at 6% Mo loading. When the Mo loading is higher than 6%, the CH_4 conversion does not change very much. But the selectivity to C_2 hydrocarbons increases with increasing Mo loading and reaches a maximum at 6%. The variation of the selectivity to aromatics with Mo loading is reverse to that of the selectivity to C_2 hydrocarbons. Again, it gives us a clue that ethylene is an initial product and high Mo loading is not compatible with further transformation of ethylene. Meanwhile, the CH_4 conversion and selectivities of the products are all varied abruptly at a Mo loading of 6%. It implies that, if the Mo loading is higher than 6%, some of the Brønsted acidity will be destroyed and the zeolite channels may be blocked up by the deposition of Mo species.

Fig. 3 shows the reaction results on 2% Mo/HZSM-5 catalysts calcined at different temperatures. The CH_4 conversion and aromatics selectivity decrease, and the C_2 selectivity increases with increasing calcination temperature. It seems that the effect of calcination temperature is similar to that of Mo loading on the catalytic performance over Mo/HZSM-5 catalysts. This means that both high calcination temperatures and high Mo loading are factors in the catalyst preparation that cause a remarkable aggregation of the Mo species in the channels. The channels will be blocked up and the catalyst will lose its reactivity.

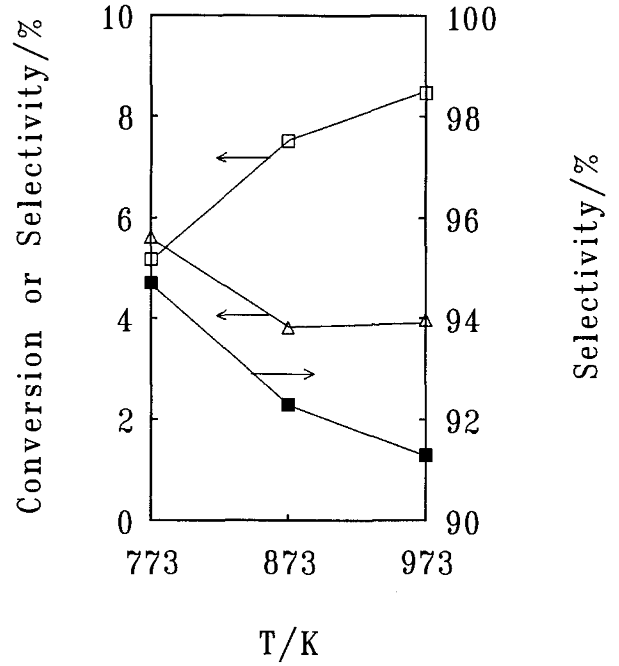


Fig. 3. Effect of calcination temperature on the aromatization of methane over 2% Mo/HZSM-5 (reaction temperature: 973 K). (△) Methane conversion; (□) selectivity of C_2; (■) selectivity for aromatics.

The variation of CH_4 conversion with time on stream and its repeatability after regeneration are shown in figs. 4 and 5. After 3 h running at 1013 K, the CH_4 conversion did not change very much. The CH_4 conversion even increased a little after the first regeneration of the catalyst. This implies that the structure of the zeolite catalyst did not change remarkably during the reaction and regeneration.

3.3. CATALYST CHARACTERIZATION BY XRD AND BET

The XRD patterns of Mo/HZSM-5 catalysts with different Mo loading calcined at 973 K for 6 h are shown in fig. 6. For comparison, in fig. 6 are also included some XRD patterns obtained from the samples of pure MoO_3, the mechanical mixture of MoO_3 and HZSM-5 zeolite. It is clear that the crystallinity of HZSM-5 zeolite decreases with increasing Mo loading, as shown in fig. 6. Again the crystallinity of HZSM-5 zeolite reaches its lowest level at the Mo loading of 6%. Meanwhile the Mo species are highly dispersed on the zeolite surface and/or in its channels since not any MoO_3 crystallite pattern could be detected if Mo loading is less than 10%. The XRD measurements give evidence that there is some kind of interaction between Mo species and the HZSM-5 zeolite, which leads to the destruction of the zeolite skeleton in some extent.

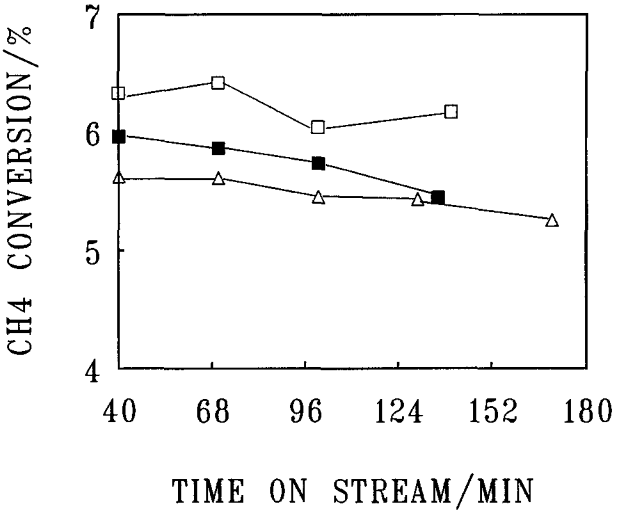


Fig. 4. Effect of regeneration on the conversion of methane over 2% Mo/HZSM-5 calcined at 773 K for 6 h (reaction temperature: 983 K). (△) On the fresh catalyst; (□) on the catalyst after the first regeneration; (■) on the catalyst after the second regeneration.

The surface area (BET) and average pore size and volume measurements are listed in table 3. The surface area obviously decreases, and the average pore diameters increase with increasing Mo loading. The decreasing trend of the surface areas

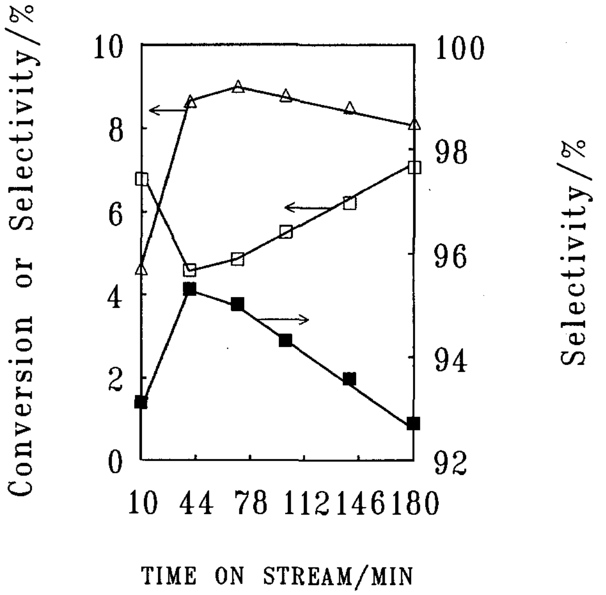
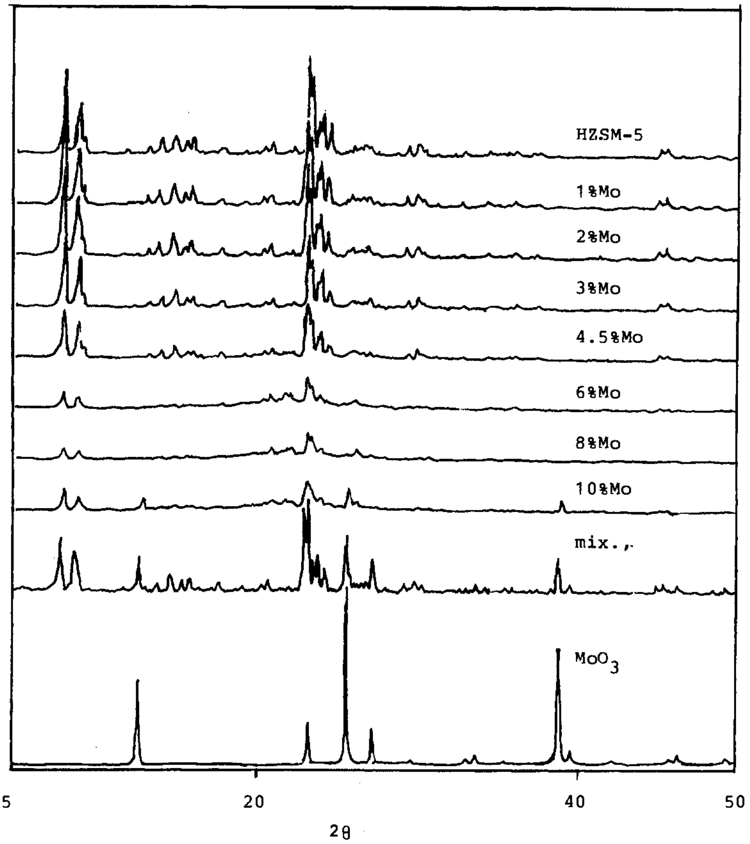


Fig. 5. Effect of time on stream on the aromatization of methane over 2% Mo/HZSM-5 calcined at 773 K for 6 h (reaction temperature: 1013 K). (△) Methane conversion; (□) selectivity of C_2; (■) selectivity for aromatics.



mix., a mechanical mixture of 10%MoO_3 and 90%HZSM-5.

Fig. 6. XRD patterns of Mo/HZSM-5 catalysts with different Mo loading. All the Mo/HZSM-5 zeolite catalysts were calcined at 973 K for 6 h except those specially mentioned.

of the Mo/HZSM-5 zeolite catalysts with Mo loading is in parallel with the XRD measurements. This also implies that high Mo loading will block up the channels of the zeolite, leading to a decrease in surface area and an increase in average pore size.

4. Discussion

4.1. THE DISPERSION OF Mo SPECIES AND ITS INTERACTION WITH HZSM-5 ZEOLITE

The dispersion of Mo species and its interaction with various zeolites recently is a topic which received much attention in chemical catalysis. Three kinds of interaction between zeolite support and metal cations are usually discussed in literature.

Table 3
Surface area and average pore diameter of Mo/HZSM-5 zeolite catalysts. All the Mo/HZSM-5 zeolite catalysts were calcined at 973 K for 6 h except those specially mentioned

Mo loading (%)	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (micro.) (cm^3/g)
1	337.9	1.50	0.095
2	305.7	1.57	0.087
3	276.0	1.65	0.085
4.5	176.9	1.74	0.061
6	78.3	1.85	0.028
8	53.1	1.90	0.015
10	91.3	1.82	0.029
HZSM-5 (773 K)	362.1	1.45	0.123
HZSM-5 (973 K)	363.7	1.49	0.111
2% Mo/HZSM-5 (773 K)	333.3	1.49	0.110
2% Mo/HZSM-5 (873 K)	352.5	1.51	0.115
2% Mo/HZSM-5 (973 K)	305.7	1.57	0.087

These are the cation exchanges with Na^+ and/or H^+, the incorporation of Mo ions into MFI frameworks and the migration of Mo species into the channels during the preparation and reaction. Unfortunately, the results obtained by different authors are quite different and some times even contradictory. Cid et al. [17] have studied the MoO_3/NaY zeolite prepared by impregnating NaY with aqueous solutions of ammonium heptamolybdate. The authors pointed out that the crystallinity and specific surface area decreased almost linearly with increasing Mo loading. But no clear evidence could be found for a complete breakdown of the zeolite structure and for the presence of a MoO_3 phase. Based on the IR spectra and, particularly, the diffuse reflectance spectra, they suggested that at relatively low Mo loading (less than 4.5%), Mo is predominantly present as a tetrahedrally coordinated MoO_4^{2-} species, presumably within the zeolite channels. Khulbe et al. [18] reported that, when MoO_3/NaY zeolite catalyst was prepared by the thermal decomposition of ammonium heptamolybdate adsorbed in the NaY zeolite in aqueous media, at least a few Mo ions can be exchanged with Na ions in NaY zeolite. Based on the comparison of the values for interplanar spacing and 2θ between MoO_3/NaY and NaY, they concluded that the crystallinity of the zeolite did not change on calcining it at 873 K if the Mo loading is less than 4.5%, which is contrary to the conclusion obtained by Cid. Meanwhile, the presence of Mo ions in MoO_3/NaY increased the concentration of the electron-accepting and -donating sites in the sequence $MoO_3/NaY > NH_4Y > NaY$. Anderson et al. [19] prepared Mo/USY zeolites by using various precursors and activation procedures. The authors observed that, with the exception of using $Mo(CO)_6$ which leads to an external loading of MoO_3, the precursors locate a higher quantity in the channels of the zeolite. Dong et al. studied the dispersion and surface state of

MoO_3 on ZSM-5 zeolite [20]. The sample was prepared by the solid reaction between MoO_3 and ZSM-5 at 723 K for 24 h. Due to the strong interaction between MoO_3 and the framework of the zeolite during calcination, MoO_3 can migrate into the channels of ZSM-5 zeolite and disperses in the form of non-crystallite surface species. They proposed that there were two different surface species, one was Mo^{6+} ions in tetrahedral coordination and the other was in octahedral coordination. It seems that a few Mo ions may be exchanged with H^+ and/or Na^+ ions, but most of Mo species will migrate into and well disperse in the channels.

The results obtained from both XRD and BET measurements on Mo/HZSM-5 zeolite catalysts, cannot be explained in terms of a dilution effect when the Mo loading is lower and less than 4.5%. Secondly, due to the big size and charge density difference between Al^{3+} or Si^{4+} and Mo^{n+} ($n = 2$–6), the incorporation of Mo into the MFI framework should be very difficult, if it is possible. Thirdly, cation exchange may be possible: a few Mo ions can behave like that, as reported in ref. [20]. The important thing is that the capacity of cation sites of the zeolite used in this work is rather small compared with the Mo contents used. We think that a more important and reasonable explanation is that the Mo species will migrate into and disperse in the channels of the HZSM-5 zeolite during calcination. The Mo species may exist in tetrahedral coordination and octahedral coordination in HZSM-5 zeolite as suggested in ref. [17]. When the Mo loading is beyond 4.5% or for the catalyst with a Mo loading as high as 6%, the Mo species may migrate into the zeolite channels during its calcination and form a crystallite of MoO_3. If the crystallite grows large enough, it may partly block up the channels and thereby cause a decrease in the surface area and an increase in the average pore diameters as measured. This may be the reason for the substantial change in the catalytic property of MoO_3/HZSM-5 at about 6% Mo loading.

Since the migration of MoO_3 species into the channels of the zeolite will be easier with increasing calcination temperature, the concentration of Mo species located in the channels may be increased and eventually also lead to blocking up of the channels. Both of the effects of Mo loading and the calcination temperature on the dispersion state indicate that the activation of methane on Mo/HZSM-5 is closely related to the channel structure and the location of Mo species as mentioned above. Although the migration of Mo species into the channels is a more reasonable explanation, at the moment, we cannot differentiate the effect caused by cation exchange from that caused by migration and aggregation of Mo species in the channels.

In the OCM, the reaction is described as a surface induced homogeneous reaction. This is not the case for methane dehydrogenation and aromatization over Mo/HZSM-5 catalyst. We notice that the methane conversion is at a minimum when the surface area is close to minimum (see fig. 2 and table 3). This implies that the reaction should be controlled by the reaction that happens on the catalyst surface.

4.2. THE MECHANISM OF METHANE DEHYDROGENATION AND AROMATIZATION OVER Mo/HZSM-5 CATALYSTS

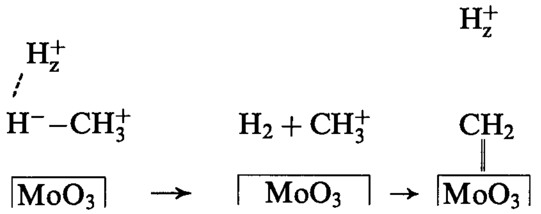
When we think over the mechanism of methane dehydrogenation and aromatization over Mo/HZSM-5 zeolite catalysts, there are two approaches that we can follow. First HZSM-5 zeolites, modified by Zn and Ga ions, are widely used as catalysts for the so-called cycle process for the aromatization of C_2–C_4 light paraffins. The mechanism of this reaction has also been extensively studied. A possible mechanism was proposed by Buckles et al. [21], in which the induction of C–H bond polarization in the light paraffin molecule, caused by the modified Ga and/or Zn ions, and the direct participation of the Brønsted acid sites of the zeolite in the reaction have been emphasized. Secondly, we may follow the line for the methane activation as it occurs in the superacid environment in homogeneous catalysis. This was suggested by Kowalak and Moffat [22]. In their study on the partial oxidation of methane catalyzed by H-mordenite and fluorinated mordenite with nitrous oxide as oxidant, they found that eliminating the oxidant lowers the methane conversion, but produces mainly ethane and ethylene. The authors claimed that the C–H bond cleavage in methane can result from protonation by superacid centers of the mordenites used. According to our results, the reactivity of methane over the HZSM-5 zeolite catalyst is so little that the protonation of methane to directly form a CH_5^+ intermediate can be neglected. It seems more reasonable that the aromatization of methane over Mo/HZSM-5 may follow the same mechanism as light paraffin does over Zn or Ga/HZSM-5 catalysts. Because of the stability of the C–H bond in methane, the induction of its polarization is more difficult so that cations in high valence state (such as Mo^{6+} ion) may be necessary. According to our reaction results listed in table 1, it seems that the existence of Mo ions in the channel, the channel structure and the acidity of ZSM-5 are three important factors for the methane activation. In addition, the effect of space velocity on the reaction leads to the conclusion that ethylene is the initial product of the reaction and the aromatics come from the further reaction of ethylene. This conclusion is in agreement with that drawn from the TPAR experiment reported in ref. [16]. We proposed that methane activation is via the formation of CH_3^+ with the help of the Brønsted acid sites of HZSM-5 zeolite and molybdena in the channel. It means that the heterolytic splitting of methane happens in an environment of "solid acidic solution" of zeolite in the presence of Mo species. The possible mechanism for ethylene formation is as follows:

(1) One of the C–H bonds in methane is polarized via its interaction with the MoO_3 species in the channel of HZSM-5 zeolite,

$$\begin{array}{ccc} CH_4 & & H^- - CH_3^+ \\ \boxed{MoO_3} & \rightarrow & \boxed{MoO_3} \end{array}$$

(2) The polarized molecule of methane reacts with the Brønsted acid site (H_Z^+)

of HZSM-5, thereby forming a catalytic cycle of the formation of carbene intermediates,



$$\begin{array}{ccccc} H_z^+ & & & & H_z^+ \\ / & & & & \\ H^- - CH_3^+ & & H_2 + CH_3^+ & & CH_2 \\ & & & & \| \\ \boxed{MoO_3} & \rightarrow & \boxed{MoO_3} & \rightarrow & \boxed{MoO_3} \end{array}$$

(3) A transformation of molybdenum carbene-like species via $CH_2{=}MoO_3$ dimerization to produce ethylene as primary products of the reaction.

(4) Ethylene aromatization on the HZSM-5 zeolite to produce benzene and methyl benzene.

5. Conclusions

The XRD and BET measurements show the evidence that Mo species are highly dispersed in the cavities and channels of the HZSM-5 zeolite, resulting from the interaction between the Mo species and the zeolite, which also leads to the decrease in its crystallinity. No more dispersion sites are available if the Mo loading is higher than 6%. XRD measurement clearly shows the existence of the crystallite of MoO_3 if the Mo loading is higher than 10%, which may block up the channels.

The concept of heterolytic splitting of methane, via the polarization of a C–H bond, to form CH_3^+ in an environment of "solid acidic solution" of zeolite, gives further evidence that, despite the highest chemical stability of methane among organic molecules, many approaches are still left available for its activation. It seems that Mo carbene-like species, the channels of HZSM-5 zeolite and the Brønsted acid sites play a crucial role in the activation of methane through the acid-assisted heterolytic splitting mode. It is of significance to further study the mechanism and give more direct evidence of the process for the activation of methane and the formation of the transition metal carbene-like species for developing the theory of methane activation and exploring new reactions for the methane conversion.

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References

[1] G.A. Olah, Y. Halpern, J. Shen and Y.K. Mo, J. Am. Chem. Soc. 93 (1971) 1251.
[2] G.A. Olah and J.A. Olah, J. Am. Chem. Soc. 93 (1971) 1256.

[3] D.E. Webster, Adv. Organometall. Chem. 15 (1977) 147.
[4] J.H. Lunsford, *Proc. 10th Int. Congr. on Catalysis*, Part A, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 69.
[5] V.R. Choudhary, V.H. Rane and S.T. Choudhari, Catal. Lett. 6 (1990) 95.
[6] J.A. Lapszewicz and X.-Z. Jiang, Catal. Lett. 13 (1992) 103.
[7] V.D. Sokolovskii and E.A. Mamedov, Catal. Today 14 (1992) 331.
[8] Y.F. Chang and H. Heinemann, Catal. Lett. 21 (1993) 215.
[9] S.A. Shepelev and K.G. Ione, React. Kinet. Catal. Lett. 23 (1983) 323.
[10] J.R. Anderson and P. Tsai, Appl. Catal. 19 (1985) 141.
[11] S.S. Shepelev and K.G. Ione, J. Catal. 117 (1989) 362.
[12] S. Han, D.J. Martenak, R.E. Palermo, J.A. Pearson and D.E. Walsh, J. Catal. 136 (1992) 578.
[13] S. Han, D.J. Martenak, R.E. Palermo, J.A. Pearson and D.E. Walsh, J. Catal. 148 (1994) 134.
[14] O.V. Bragin, T.V. Vasina, A.V. Preobrazhenskii and Kh.M. Minachev, Izv. Ser. Khim. No. 3 (1989) 750.
[15] J.B. Claridge, M.L.H. Green, S.C. Tsang and A.P.E. York, Appl. Catal. A 89 (1992) 103.
[16] L. Wang, J. Huang, L. Tao, Y. Xu, M. Xie and G. Xu, Catal. Lett. 21 (1993) 35.
[17] R. Cid, F.J. Gil Llambias, J.L.G. Fierro, A. Lopez Agudo and J. Villasenor, J. Catal. 89 (1984) 478.
[18] K.C. Khulbe, R.S. Mann and C.D. Ajaka, Zeolites 13 (1993) 572.
[19] J.A. Anderson, B. Pawelec and J.L.G. Fierro, Appl. Catal. A 99 (1993) 37.
[20] Y. Dong, S. Liu, Q. Zhang, J. Liu and K. Yang, Acta Petrolei Sinica (Petroleum Processing Section) 8 (1992) 66.
[21] G. Buckles, G.J. Hutchings and C.D. Williams, Catal. Lett. 11 (1991) 89.
[22] S. Kowalak and J.B. Moffat, Appl. Catal. 36 (1988) 139.