Methane and ethane activation without adding oxygen: promotional effect of W in Mo–W/HZSM-5

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The conversions of methane and ethane over Mo/HZSM-5 and W/HZSM-5 catalysts are compared. A reaction model for hydrocarbon formation over Mo/HZSM-5 catalysts is proposed, which involves heterolytic splitting of methane and a molybdenum–carbene intermediate. Ethene is shown to be the initial product of methane conversion, and it undergoes further reaction to form aromatics in a solid acid environment. The promotional effect of addition of tungsten in the Mo–W/HZSM-5 catalyst in methane conversion reaction suggests the formation of Mo–W mixed oxide. The product selectivity patterns of Mo/HZSM-5 and W/HZSM-5 catalysts in ethane conversion reaction are consistent with a dual-path model involving dehydrogenation and cracking (or hydrogenolysis) of ethane. The rates of both these reactions over Mo/HZSM-5 are higher than over W/HZSM-5.

Keywords: acid-assisted heterolytic splitting of methane; Mo/HZSM-5; W/HZSM-5; Mo–W/HZSM-5; promotional effect of tungsten

1. Introduction

The chemistry of converting C_1 sources into higher molecular weight hydrocarbons has always been the focal point of catalytic research. In the past 15 years, the oxidative coupling of methane has received wide attention. Recently, we have reported an alternative route for methane activation using Mo/HZSM-5 catalysts and without adding oxygen [1–3]. This process requires the presence of Mo oxide and acid sites and was thought to occur via acid-assisted heterolytic splitting of methane to CH_3^+ and H^-. A carbene mechanism has been proposed for the transformation of CH_3^+ to ethene in which the formation of a molybdenum–carbene-like complex intermediate is of significance [3]. In a solid acid environment, oligomerization of ethene occurs and finally leads to the formation of aromatics.

Our previous study on this subject implies that the polarization of a C–H bond in CH_4 and the formation of C_2^+ hydrocarbon products over HZSM-5 is much more difficult. However, the formation of these products can be promoted very much over Mo/HZSM-5 zeolite catalysts. Therefore, transition metal cations, such as Mo species in high oxidation state, will be more favorable for the polarization of the C–H bond. In addition, the $Mo{=}CH_2$ metallocarbene species, if they exist, are more stable than free carbene. In fact, the formation of CH_2 over supported Mo catalysts was also proposed by Lunsford for methanol conversion [4].

In this paper, we further examine the catalytic properties of Mo/HZSM-5 and W/HZSM-5 in the methane conversion reaction. Besides, these two catalysts are also compared in the ethane conversion reaction. Preliminary studies on the promotional effect of W in Mo–W/HZSM-5 catalysts are presented. The results of methane conversion over Mo/HSAPO-34 catalysts are reported in order to reinforce our proposal that ethene is the intermediate for aromatic formation. HSAPO-34, which has the framework topology of the natural zeolite chabazite, has been shown to convert methanol selectively to C_1–C_3 hydrocarbon products, due mainly to the shape-selective effect of its framework structure [5]. The framework structure of HSAPO-34 contains a three-dimensional channel system consisting of large ellipsoidal cages 1.1 nm long and 0.65 nm wide. Each of these cages can be entered through the eight-member ring windows with a diameter of about 0.38 nm.

2. Experimental

ZSM-5 with SiO_2/Al_2O_3 ratio of 50 was used in this work. The Mo/HZSM-5 catalyst was prepared as described previously [1–3]. This method was also used for the preparation of the Mo/HSAPO-34 catalyst. The W/HZSM-5 catalyst was prepared by impregnating NH_4ZSM-5 with ammonium tungstate aqueous solution, prepared by mixing tungstenic acid and aqua ammonia. The impregnated sample was dried at 383 K for 4 h, and then calcined at 773 K for 4 h. The Mo–W/HZSM-5 catalyst was prepared by the co-impregnation method.

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XPS measurements were performed on a VG Escalab 210 spectrometer, using Mg K_α radiation ($h\nu = 1253.6$ eV). The charging effect of the samples was corrected by using Si 2p (BE = 102.7 eV) as the internal standard. The recorded spectra were processed by the attached computer so that multi-valence states of Mo species could be identified.

For HZSM-5 supported catalysts, catalytic reactions were carried out with 2 g of catalyst placed in a fixed-bed continuous-flow reactor at a gas space velocity (F/W) of 1440 ml/(g h), and under a reaction pressure of 200 kPa. The products were withdrawn periodically from the outlet of the reactor and analyzed by gas chromatography with a 4 m long squalane column and a hydrogen flame ionization detector. For HSAPO-34 supported catalysts, catalytic reactions were performed with 200 mg of catalyst in a continuous-flow fixed-bed microreactor operating at a reactor pressure of about 15 kPa. The hourly space velocity of methane used was 1500 ml/(g h). The reactor effluent was analyzed on-line with a Shimadzu GC-9AM gas chromatograph. Methane conversion (see below) and product selectivity were both calculated on the carbon number basis, i.e. $\%\text{conversion} = 100 \sum C(\text{product}) / \sum C(\text{product} + \text{unreacted methane})$.

The amounts of coke deposited on the catalyst during the reaction were determined by the TG-DTA method.

3. Results

3.1. XPS study on Mo/HZSM-5

The XPS spectra of 3% Mo/HZSM-5 catalysts after various treatments are shown in table 1. From the binding energies of the Mo $3d_{5/2}$ level, it was shown that Mo ions in the fresh catalyst are mainly in the Mo^{6+} oxidation state. The binding energies of the Mo $3d_{5/2}$ levels of Mo^{6+}, Mo^{5+} and Mo^{4+} were reported to be 233.0, ~ 232 and 229.2 eV [6,7]. During the methane conversion reaction, reduction of Mo^{6+} to Mo^{5+} and Mo^{4+} occurs. The binding energies of the Mo $3d_{5/2}$ level of Mo species after methane reaction at 973 K for 40 min were 233.3 and 229.3 eV. Only when the catalyst was reduced in pure H_2 is the metallic Mo with binding energy at 227.6 eV prominent [8].

3.2. Conversion of methane and ethane over Mo/HZSM-5 and W/HZSM-5

The data for the catalytic conversion of methane and ethane over 2% Mo/HZSM-5 and W/HZSM-5 catalysts are summarized in table 2. In both reactions, Mo/HZSM-5 exhibits much higher activity than W/HZSM-5. W/HZSM-5 is completely inactive for methane conversion. It is noticed that in the case of ethane conversion over the less active blank HZSM-5 support, methane and aromatics (mainly benzene) distributed evenly in the product. However, Mo/HZSM-5 catalyst shows higher methane selectivity, but the reverse is observed over W/HZSM-5.

3.3. Conversion of methane over Mo–W/HZSM-5

The activity and stability of Mo/HZSM-5 catalyst for methane conversion after incorporating W additive are shown in tables 3 and 4. Even though a higher CH_4 conversion is observed on the Mo–W/HZSM-5 catalyst, it is interesting to note that its coking rate is smaller than that of Mo/HZSM-5. The possibility of converting CH_4 at relatively low temperatures is also reported in table 5. The fresh Mo/HZSM-5 catalyst shows no activity for CH_4 conversion at 773 and 873 K. However, after the Mo/HZSM-5 catalyst was partially "treated" in CH_4 stream at 973 K, it exhibits evident activity for CH_4 conversion at 873 K. A much better activity can be obtained with partially treated Mo–W/HZSM-5 catalyst, with a CH_4 conversion of 6.8% at 873 K.

Table 1
XPS spectra of Mo/HZSM-5 catalyst under various treatments

Sample and pretreatment	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Si 2p
(a) fresh cat. calcined at 873 K	233.2	236.5	103.0
(b) fresh cat. calcined at 1023 K	233.0	236.5	103.3
(c) after CH_4 reaction at 973 K for 40 min	233.3	236.5	
	229.3	232.5	103.5
(d) (c) under UHV at 673 K for 30 min	232.7	235.9	
	228.7	231.9	103.2
(e) TPR of (a) in H_2 to 973 K	233.3	236.4	
	231.7	234.9	
	228.7	231.9	103.3
(e) reduced (d) in H_2 at 973 K for 1 h	231.3	234.4	
	227.7	231.0	103.2
MoO_3	233.0	236.1	
HZSM-5			103.1

Table 2
Catalytic conversion of methane and ethane over W/HZSM-5 and Mo/HZSM-5

Catalyst	Feed	Temp. (K)	Conv. (%)	Selectivity (%)	
				aromatics	CH_4
HZSM-5	C_2H_6	923	5.9	51.8	48.2
W/HZSM-5	CH_4	973	0	0	
	C_2H_6	923	24.7	80.2	19.8
Mo/HZSM-5	CH_4	973	8.2	100	
	C_2H_6	923	92.8	33.1	66.9

3.4. Conversion of methane over Mo/HSAPO-34

Table 6 shows the typical catalytic data for methane conversion over Mo/HSAPO-34 catalysts at 973 K. The activity and aromatic selectivity are the highest at the initial stages of the reaction, but decrease with increasing time on stream. As this happens, the selectivity of ethene increases sharply and is > 70% after 2 h on stream. The selectivities of C_2 and C_3 hydrocarbons amount to > 90%. In addition, shortly after the sharp decrease in the yield of benzene as the catalyst deactivates, ethene yield increases and reaches a maximum. Furthermore, increasing the contact time during the reaction leads to an increase in total activity and aromatic (and also ethane) selectivity, while the selectivity to ethene decreases. The deactivated catalyst can be regenerated by simply calcining in air flow at 873 K for about 1 h.

4. Discussion

4.1. Mo active sites in methane conversion

The first and most crucial step in direct methane conversion to higher hydrocarbons is the dissociation of its C–H bonds. Until now, only supported molybdenum oxide with high Mo oxidation state has shown significant activity. In fact, catalyst samples pre-calcined at 773 K were found to be most active. XPS study on fresh Mo/HZSM-5 catalyst revealed that Mo is mainly in a 6+ oxidation state. Therefore, dissociation of these bonds may require the presence of a high electric gradient at the active sites. It is thus natural to suggest that the first step of methane conversion involves heterolytic dissociation of the C–H bond. The generation of a "$^+CH_3$ pool" via this process is represented in reaction scheme (1).

Table 3
Improvement of Mo/HZSM-5 catalyst by W addition [a]

Catalyst	CH_4 conv. (%)	Coking rate (g/(g h))
Mo/HZSM-5	8.2	1.4×10^{-2}
Mo–W/HZSM-5	11.0	9.3×10^{-3}
W/HZSM-5	0	–

[a] Reaction temperature: 973 K, CH_4 purity is 98%.

Table 4
Activity maintenance of Mo–W/HZSM-5 catalyst [a]

Time on stream (h)	1	3	5	6	7	8	11
CH_4 conv. (%)	5.4	10.3	9.5	13.3	13.9	10.5	8.7

[a] Reaction temperature: 973 K, CH_4 purity is 98%.

$$\mathrm{Mo^{VI}(=O)_3 + {}^{\delta-}H{-}C^{\delta+}{-}H_3}$$
$$\rightarrow \mathrm{Mo^{VI}(=O)_3 + H^- + {}^+CH_3} \qquad (1)$$

Considering the constraints imposed by the pore dimension of the catalyst supports (both HSAPO-34 and HZSM-5), and the structural arrangement of MoO_3, the active species of MoO_3 involved in C–H bond dissociation will be either in the form of monomer or dimer [9,10]. This suggestion is also consistent with previous XRD observations for high dispersion of MoO_3 [3].

Reduction of Mo^{6+} occurred during the reaction as demonstrated by XPS measurement. In that case, hydrocarbon chain initiation should involve Mo active sites in either 4+ or 5+ oxidation states. Since the Mo^{4+} concentration is higher than that of Mo^{5+}, the model for ethene formation, as shown in reaction scheme (2) is proposed.

$$\mathrm{2H^- + Mo^{VI}(=O)_3 \rightarrow Mo^{IV}(=O)(-O^-)_2 + H_2\uparrow}$$
$$\mathrm{Mo^{IV}(=O)(-O^-)_2 + {}^+CH_3}$$
$$\rightarrow \mathrm{Mo^{IV}(=O)(-O^-)(-OH)(=\mathbf{CH_2})}$$
$$\mathrm{Mo^{IV}(=O)(-O^-)(-OH)(=\mathbf{CH_2}) + {}^+CH_3}$$
$$\rightarrow \mathrm{Mo^{V}(=O)_2(-OH)(-\mathbf{C_2H_5})}$$
$$\mathrm{Mo^{V}(=O)_2(-OH)(-\mathbf{C_2H_5})}$$
$$\rightarrow \mathrm{Mo^{IV}(=O)(-OH)_2 + C_2H_4\uparrow} \qquad (2)$$

A molybdenum–carbene intermediate is formed by the interaction between a Mo^{4+} site and $^+CH_3$ and most importantly, Mo^{4+} can be regenerated through the desorption of ethene. It should be mentioned here that the direct methane conversion reaction is quite different from the methane decomposition reaction on reduced transition metals, whereby carbide, CH_x and graphite are formed [11,12]. In the absence of an external hydrogen supply, carbide is unlikely the main species involved in hydrocarbon chain initiation and growth. The initiation and growth of a hydrocarbon chain can of course

Table 5
CH_4 conversion at low temperatures [a]

Catalyst	React. temp. (K)	CH_4 conv. (%)
fresh Mo/HZSM-5	773	0
	873	0
partially treated Mo/HZSM-5	773	trace
	873	3.0
partially treated Mo–W/HZSM-5	773	trace
	873	6.8

[a] CH_4 purity is 99.995%.

Table 6
Methane conversion over Mo/HSAPO-34 catalysts

Catalyst[a]	CH_4 conv. (%)	Selectivity (%)				
		$C_2^=$	C_2	$C_3^=$	benz.	tol.
HSAPO-34	0.01	31.0	69.0	–	–	–
MoO_3	0.01	50.9	49.1	–	–	–
Mo/HSAPO-34-A	0.60	40.2	17.5	1.8	36.4	4.1
Mo/HSAPO-34-B	0.40	71.1	17.1	3.6	8.1	–
Mo/HSAPO-34-C	0.61	33.1	16.2	1.4	45.0	4.2

[a] The metal loading of HSAPO-34 supported catalysts is 4%. A: 40 min on stream. B: 2 h on stream. C: after regeneration at 873 K in air for 1 h.

involve different CH_x species formed by further transformation of $^+CH_3$.

The reversible transformation between Mo^{5+} and Mo^{4+} is not only consistent with the XPS results, but also explains the good catalytic stability of Mo/HZSM-5. These findings show that hydrocarbon products in this study are very unlikely to be produced through oxidative coupling of methane, where MoO_3 itself is the source of oxygen. Therefore, the direct methane conversion reaction studied here is an example of non-oxidative reaction. Schemes (1) and (2) are also applicable to dimeric MoO_3, where one of the Mo=O groups is replaced by two bridging Mo–O– groups.

4.2. Conversion of methane over Mo/HSAPO-34

Unlike the case of methanol conversion over HSAPO-34 where the reaction temperatures were 673 K, the formation of aromatics becomes favorable in the cages at 973 K [5]. However, free diffusion of aromatics out of the cages is restricted by the eight-membered ring windows. The filling up of the cages with coke (aromatic compounds) deactivates the catalyst, and the catalytic activity thus decreases with increasing time on stream. The observed relationship of benzene–ethene yield as the Mo/HSAPO-34 catalyst decayed showed clearly that ethene is the intermediate for the formation of aromatics (scheme (3))

$$\begin{aligned} &C_2H_4 + H^+{-}^-OZ \rightarrow C_2H_5^+ \rightarrow \text{oligomer} \\ &\quad \rightarrow \text{aromatic} \quad (Z = \text{zeolite}) \qquad (3) \end{aligned}$$

This suggestion is also supported by a space velocity study.

4.3. Conversion of methane and ethane over Mo/HZSM-5 and W/HZSM-5

It is interesting to note that alkane reacts differently over Mo/HZSM-5 and W/HZSM-5 catalysts despite of the chemical similarities between molybdenum and tungsten. Firstly, the catalytic activity of Mo/HZSM-5 is much higher than that of W/HZSM-5 catalysts. Therefore, Mo/HZSM-5 is a more efficient dehydrogenation catalyst than W/HZSM-5. Secondly, both types of catalyst have different product selectivity. In the case of ethane conversion over HZSM-5, both methane and aromatics constitute equally to the hydrocarbon product. With reference to the works on propane by Kwak et al. [13], this implies that the catalytic reaction of ethane over HZSM-5 can proceed via two different routes: either acid-catalyzed cracking to methane or dehydrogenation to ethene. The introduction of transition metal onto HZSM-5 provides an additional dehydrogenation site, but does not affect significantly the rate of the acid-catalyzed cracking reaction.

Taking into consideration the high reaction temperature and the product selectivity of both catalysts, a dual-path process, as shown in reaction scheme (4), is proposed for the ethane conversion reaction over Mo/HZSM-5 and W/HZSM-5 catalysts.

$$\begin{aligned} &\text{aromatic formation} \quad 3C_2H_6 \rightleftharpoons 3C_2H_4 + 3H_2 \\ &\qquad\qquad\qquad\qquad \rightarrow C_6H_6 + 6H_2 \\ &\text{methane formation} \quad nH_2 + nC_2H_6 \rightarrow 2nCH_4 \qquad (4) \end{aligned}$$

Since the reaction occurred at high temperature, it is fair to consider the formation of methane from a cracking (or hydrogenolysis) side reaction process, utilizing the hydrogen produced from the first process which involved dehydrogenation. For simplicity, the hydrogen species involved in these reactions are collectively represented as H_2.

From the selectivity ratio of aromatics (mainly benzene) to methane, the value of n can be determined. n is found to be about 6 for Mo/HZSM-5 catalyst. This means that all the hydrogen produced in the reaction forming aromatic products is involved in the side reaction. Taking into account the methane produced from the acid-catalyzed reaction does not affect significantly this value of n. For W/HZSM-5, n is between 1/3 and 3/4. The lower limit is obtained by taking into consideration the methane produced from acid-catalyzed cracking of ethane on the same concentration of acid sites as HZSM-5. The small n value indicates that only a small fraction of hydrogen produced is involved in the side reaction over W/HZSM-5 catalysts. Therefore, besides dehydrogenation, the cracking (or hydrogenation) power of Mo/HZSM-5 catalyst is also higher than that of W/HZSM-5. From scheme (4) and the results of ethane conversion, it can be shown that the intrinsic rate of dehydrogenation of ethane over Mo/HZSM-5 is about 1.6 times that of W/HZSM-5. For the side reaction, the observed rate over Mo/HZSM-5 is about 22.0 times that of W/HZSM-5. However, since the initial concentration of hydrogen is higher in Mo/HZSM-5 than in W/HZSM-5, the relative intrinsic rate should be less than 22.0.

4.4. The promotion effect of W species for methane conversion over Mo/HZSM-5

The activity and stability of Mo/HZSM-5 catalyst for methane conversion can be improved by incorporating tungsten as an additive. As has been described previously, W/HZSM-5 is not active for methane conversion at this temperature. Even though the reactant feed contained 2% of C_2 impurity, the participation of tungsten active sites can only account for a small fraction of the increment in activity, since most C_2 will react with the major and more active molybdenum active sites. The promotional effects of tungsten on the catalytic activity and stability leads us to consider the formation of mixed Mo–W oxide, either bimetallic or closely interacted. The presence of tungsten oxide (or tungsten) in the molybdenum oxide matrix probably leads to the so-called ensemble effect, which may restrict the formation of graphite or sintering of molybdenum active species. The formation of graphite not only causes the blocking of active sites, but hydrogenation of graphite leads mainly to the formation of non-productive methane [14]. On the other hand, surface C_1 species present in the form of $^+CH_3$, CH_x and carbide are useful for the formation of C_{2+} hydrocarbon products.

The study of methane conversion over partially treated catalysts provides further confirmation on the promotional effect of tungsten. In this case, high purity methane was used. Furthermore, the results of this study show that surface carbon species formed during the induction period may play some role for methane conversion. However, more works are required on this area for better understanding of the mechanism of interaction between methane and surface carbon species.

The value of methane conversion of 13.9% (table 3) is slightly higher than that of 11.6%, estimated from thermodynamic consideration. Part of this difference can be accounted for by the total conversion of 2% ethane impurity. In addition, some methane may be lost through coking reaction. Disregarding this factor in the calculation of methane conversion (see experimental) will lead to a slightly higher conversion value.

5. Conclusion

Mo/HZSM-5 catalysts are active and selective for the conversion of methane to aromatics without using oxygen. The activity and stability of the catalyst can be improved by addition of tungsten. W/HZSM-5 catalyst exhibits excellent selectivity for ethane aromatization and thus, it may be a potential catalyst to be developed for industrial ethane aromatization process. The promotional effect of tungsten in Mo–W/HZSM-5 catalyst is correlated to the formation of Mo–W mixed oxide. Surface carbon species deposited on the catalyst may take part in the conversion of methane. Meanwhile, Mo/HSAPO-34 is a good catalyst for selective formation of ethene and other low hydrocarbons.

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