Dehydrogenation and aromatization of methane under non-oxidizing conditions

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The dehydrogenation and aromatization of methane on modified ZSM-5 zeolite catalysts has been studied under non-oxidizing conditions with a fixed bed continuous-flow reactor and with a temperature programmed reactor. The results show that benzene is the only hydrocarbon product of the catalytic conversion of methane at high temperature (973 K). The catalytic activity of ZSM-5 is greatly improved by incorporating a metal cation (Mo or Zn). H_2 and ethene have been directly detected in the products with a mass spectrometer during TPAR. A carbenium ion mechanism for the activation of methane is suggested.

Keywords: Dehydrogenation and aromatization; methane; MoHZSM-5; ZnHZSM-5; ZSM-5 zeolites

1. Introduction

The catalytic conversion of methane to desired chemical products or liquid fuel is not only a promising approach for the utilization of natural gas resource but also a great challenge to catalysis science. Recently the partial oxidation and oxidative coupling of methane have been extensively studied, but many problems are still left. Meanwhile, the fact that aromatic products can be formed by the oxidation of methane over ZSM-5 zeolite catalysts has been reported [1,2], but little success was achieved in obtaining a useful selectivity or yield of aromatics. A few results for the conversion of methane to benzene over high silica zeolite based catalysts in a pulse-reactor had been briefly reported [3], but only very limited information was provided from which it is not possible to assess the course of the reaction or its main mechanistic features. Lately Claridge et al. reported their studies of the conversion of methane : oxygen mixtures to aromatics over metal oxides and supported metal catalysts [4]. 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% under the reaction temperature of 1223 K. The authors also suggested that the formation of aromatics possibly proceeds via an ethene intermediate. The present paper reports on the dehydrogenation and aromatization of methane under non-oxidizing conditions on modified ZSM-5 catalysts. The activation of methane on bifunctional catalysts is discussed in terms of a carbenium ion mechanism.

2. Experimental

2.1. MATERIALS

The ZSM-5 zeolites were supplied by Nankai University and are commercially available ($SiO_2/Al_2O_3 = 25, 50$). Firstly, the ZSM-5 zeolites were converted into ammonium forms (NH_4ZSM-5) by repeated ion exchange (four times) with a 1 N NH_4NO_3 aqueous solution at around 368 K for 1 h. These were then dried at 383 K for 4 h. HZSM-5 catalysts were prepared by calcining NH_4ZSM-5 at 773 K for 4 h. MHZSM-5 (M = Mo, Zn) catalysts were prepared by impregnating NH_4ZSM-5 with ammonium molybdate or zinc nitrate aqueous solution, then drying at 383 K for 4 h and calcining at 773 K for 4 h. The metal loading was 2% in weight. Finally, the catalysts were pressed, crushed and sorted into sizes of 10–30 mesh.

Methane was 99.995% pure. Analysis of the air and helium used showed the absence of any H_2 and hydrocarbons.

2.2. CATALYTIC TESTS

The catalytic tests were carried out with about 2.0 g catalyst placed in a fixed bed continuous-flow stainless steel reactor. The catalyst zone was heated under an air stream to 973 K and held at 973 K for 30 min. After pretreatment, methane was introduced into the catalyst bed through a flowmeter. The hourly space velocity of methane is around 1440 ml/g h. The products were withdrawn periodically from the outlet of the reactor and analyzed by gas chromatography. Aliphatic and aromatic hydrocarbons were separated on a 4 m long squalane column and detected with a hydrogen flame ionization detector. The conversion and selectivity were calculated on the carbon number basis.

2.3. TEMPERATURE PROGRAMMED AROMATIZATION REACTION (TPAR)

Fig. 1 shows a scheme of the setup used in this work for TPAR experiments. TPAR were carried out in a quartz tubular microflow reactor containing 0.2 g catalyst. Firstly, the catalysts were heated to 973 K at 32 K/min in a He stream and

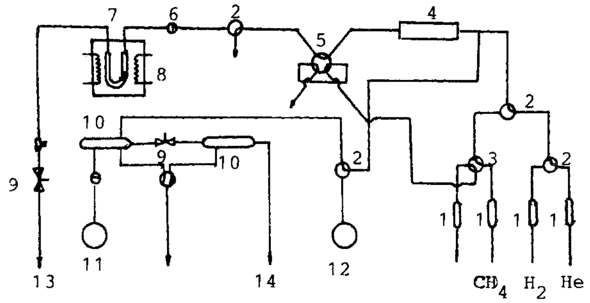

Fig. 1. Schematic diagram of the setup for TPAR experiments. 1, purifier; 2, three-way valve; 3, four-way valve; 4, mass flow controller; 5, six-way valve; 6, injection hole; 7, reactor; 8, heater; 9, valve; 10, buffer; 11, vacuum gauge; 12, gauge; 13, mass spectrometer; 14, mechanical pump.

held at 973 K for 30 min. Then, the reactor was brought to room temperature. At room temperature the stream was switched from 50 ml/min He to 30 ml/min of methane. Finally, TPAR was started by programming the temperature increase from room temperature to 1073 K at 16 K/min. The signals corresponding to H_2 ($m/e = 2$), $C_2^=$ ($m/e = 26$), C_2^0 ($m/e = 30$), and C_6H_6 ($m/e = 78$) as a function of temperature (time) were recorded with a TE-150 mass spectrometer. The reaction system pressure was kept at 40 kPa.

3. Results

The reaction results of methane on various ZSM-5 zeolite catalysts are summarized in table 1. The HZSM-5 catalyst shows a little activity for the conversion of methane at 973 K with a selectivity to benzene of 100%. The conversion of methane was greatly increased by loading Mo or Zn ion in the zeolites without any loss in the selectivity to benzene. MoHZSM-5 exhibited the best activity, while neither

Table 1
The conversion of methane over various ZSM-5 zeolites [a]

Catalyst	Ratio of SiO_2/Al_2O_3	CH_4 conv. (%)	Selectivity of benzene (%)
HZSM-5	25	1.4	100
	50	1.0	100
ZnHZSM-5	25	3.0	100
	50	2.3	100
MoHZSM-5	50	7.2	100
	25	4.4	100
MoNaZSM-5	0	0	0
MoO_3	0	0	0

[a] Reaction temperature: 973 K; pressure: 200 kPa; $F/W = 1440$ ml/g h.

MoNaZSM-5 nor MoO_3 has any activity for the reaction. The MoHZSM-5 catalyst was quite stable for the reaction under the given condition as shown in fig. 2. The conversion of methane over MoHZSM-5 increased with increasing the partial pressure of methane as shown in table 2. The selectivity to benzene of 100% under non-oxidizing conditions is of significance. It obviously depends on the nature of the catalyst used.

A study by TPAR over HZSM-5, ZnHZSM-5 and MoHZSM-5 zeolites gave further evidence as shown in figs. 3–5. Two important observations can be made from the results: (1) The starting temperature for the dehydro-aromatization of methane over MoHZSM-5 is about 973 K, which is about 50 K lower than that over ZnHZSM-5. HZSM-5 zeolites did not exhibit any activity for the aromatization under the given experimental conditions. (2) Ethene and H_2 can be directly detected from TPAR and both evolved over MoHZSM-5 at about 973 K, which is the same temperature at which benzene evolved.

4. Discussion and conclusion

The comparison between the catalytic behavior of HZSM-5 and MHZSM-5 (M = Mo, Zn) showed that the activity for the dehydro-aromatization of methane is enhanced by loading Mo or Zn in HZSM-5 zeolite. With respect to the role of Zn in the conversion of propane into aromatics over ZnHZSM-5, Mole and Anderson [5] suggested the zinc cation acts as a hydride acceptor to give a transient species such as $[Zn–H]^+$. In an analogous manner, we suggest that the activation of methane over HZSM-5 and MHZSM-5 zeolite catalysts is via the carbenium ion

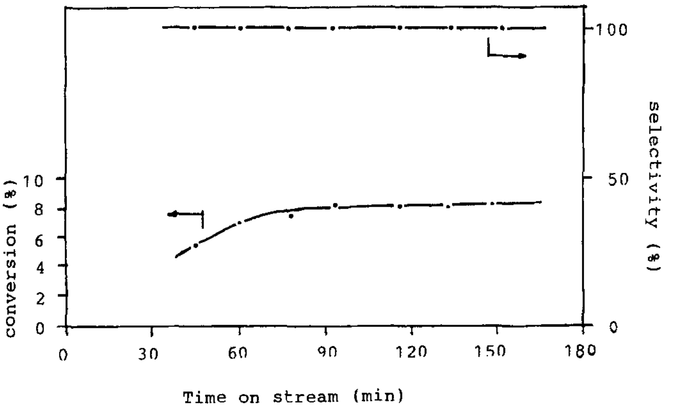

Fig. 2. The change in activity with time of the MoHZSM-5 catalyst for the aromatization of methane.

Table 2
Pressure dependence of the aromatization activity of methane over MoHZSM-5 [a]

Reac. pressure (kPa)	Partial pressure of CH_4 (kPa)	CH_4 conv. (%)	Diluting gas
200	200	4.4	–
100	100	2.9	–
200	100	2.9	N_2

[a] Reaction temperature: 973 K; $F/W = 1440$ ml/g h.

mechanism. In the case of ZnHZSM-5 catalyst, Zn^{2+} cations act as a hybride acceptor to give $[Zn\text{–}H]^+$,

$$CH_4 + Zn^{2+}(s) \rightarrow CH_3^+(s) + [Zn\text{–}H]^+ , \qquad (1)$$

Cid et al. reported the physicochemical characterization of MoO_3–NaY zeolite catalysts prepared by impregnation of NaY zeolite with aqueous solutions of ammonium heptamolybdate [6]. They found that the preparation procedure results in a substantial loss in crystallinity and surface area with Mo loadings beyond 7% MoO_3. At relatively low Mo loadings, Mo species appear to be well dispersed on the zeolite, and mostly within the zeolite cavities as strongly attached tetrahedrally coordinated MoO_4^{2-}. Dong et al. studied the dispersion and surface state of MoO_3 on ZSM-5 zeolite [7]. 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 zeolite during calcination, MoO_3 migrates into the cavities of ZSM-5 zeolite and disperses as a non-crystalline surface species. Based on the

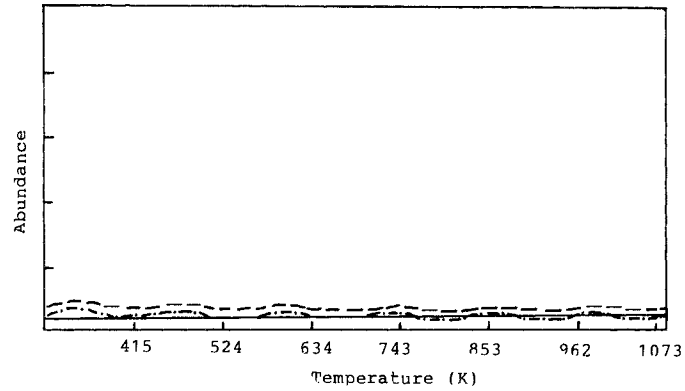

Fig. 3. TPAR profiles of methane conversion over HZSM-5 ($SiO_2/Al_2O_3 = 25$). $F/W = 9000$ ml/g h, $P = 40$ kPa. (· · ·) $m/e = 78$ (C_6H_6); (———) $m/e = 2$ (H_2); (– – –) $m/e = 26$ (C_2H_4); (– · –) $m/e = 30$ (C_2H_6).

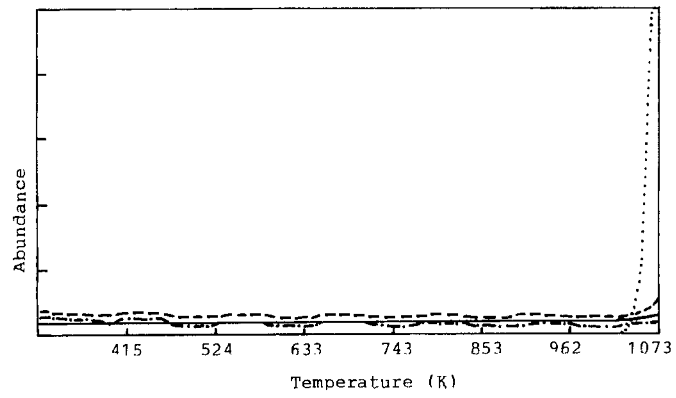

Fig. 4. TPAR profiles of methane conversion over ZnHZSM-5 ($SiO_2/Al_2O_3 = 25$). $F/W = 9000$ ml/g h, $P = 40$ kPa. (· · ·) $m/e = 78$ (C_6H_6); (———) $m/e = 2$ (H_2); (– – –) $m/e = 26$ (C_2H_4); (–·–) $m/e = 30$ (C_2H_6).

results, they proposed that there are two different surface species. One is Mo^{6+} ions in tetrahedral coordination and another in octahedral coordination. By reference to the above-mentioned publications, in the case of MoHZSM-5 catalyst, Mo^{6+} species in ZSM-5 zeolite may act as hybride acceptor to give $[Mo–H]^{5+}$,

$$CH_4 + Mo^{6+}(s) \rightarrow CH_3^+ + [Mo–H]^{5+} . \qquad (2)$$

In the case of the HZSM-5 catalyst, a protonic site may act as a hydride acceptor (to give hydrogen directly),

$$CH_4 + H^+(s) \rightarrow CH_3^+(s) + H_2 . \qquad (3)$$

Methane undergoes conversion over ZSM-5 by a carbenium ion mechanism to

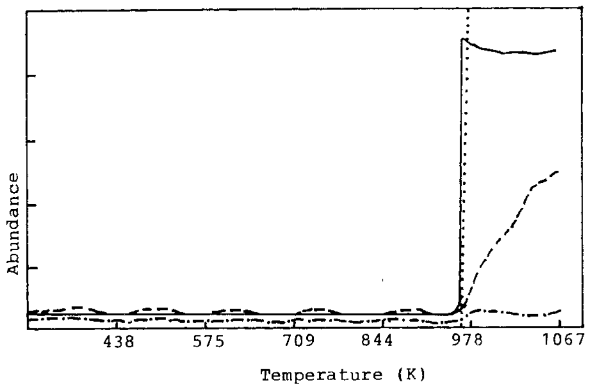

Fig. 5. TPAR profiles of methane conversion over MoHZSM-5 ($SiO_2/Al_2O_3 = 25$). $F/W = 9000$ ml/g h, $P = 40$ kPa. (· · ·) $m/e = 78$ (C_6H_6); (———) $m/e = 2$ (H_2); (– – –) $m/e = 26$ (C_2H_4); (–·–) $m/e = 30$ (C_2H_6).

Table 3
Thermodynamics of the conversion of alkane to aromatics and alkene [a]

Alkane	Temperature (K) required for $\Delta G_r^0 = 0$ [b]	
	to benzene	to ethene
CH_4	1348	1623
C_2H_6	848	1047

[a] Thermodynamic data taken from ref. [8].
[b] The free energies of the reaction.

aromatics or C_2 products under non-oxidizing conditions. Thermodynamically, dehydro-aromatization of methane is a more favorable reaction than dehydrodimerization. The thermodynamic data are shown in table 3. Thus, the high selectivity to benzene is achieved at higher temperatures, but at lower temperature, benzene is not obtained.

The Mo modified ZSM-5 catalysts exhibited excellent catalytic activity and selectivity to benzene for the conversion of methane at 973 K under non-oxidizing conditions. The Mo or Zn loaded in the ZSM-5 played a significant role in methane activation. The aromatization reaction of methane with a conversion of 7–8% and the selectivity to benzene of 100% is quite stable over MoHZSM-5 catalyst under the given conditions. H_2 and ethene may be the primary products in the conversion of methane to benzene. The yield of benzene increased with increasing partial pressure of methane.

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