Promotional effect of Pt on non-oxidative methane transformation over Mo-HZSM-5 catalyst

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Received 5 September 1995; accepted 6 March 1996

The influence of modification of Mo-HZSM-5 catalyst by Pt on methane non-oxidative transformation to ethylene and aromatics is investigated. Carbon accumulation on the catalyst is studied by means of DTA and TG methods. It is demonstrated that the addition of Pt to Mo-HZSM-5 considerably enhances the catalyst stability and reduces the carbon deposition on the catalyst. In the meanwhile, Mo-HZSM-5 is shown not to be a good catalyst for methane non-oxidative conversion because the total efficiency for methane conversion to useful products is even lower than it is in the oxidative coupling process.

Keywords: methane; non-oxidative conversion; platinum/molybdenum/HZSM-5 zeolite

1. Introduction

The vast reserves of natural gas (of which the predominant component is methane) have been driving chemists to pursuit more economic processes for the chemical utilization of this resource. However, the direct catalytic conversion of methane to more valuable chemicals still remains an unsolved problem in both catalytic science and industry. The recent reports on the non-oxidative oligomerization of methane to benzene and ethylene seem to open a practical route [1–4]. It has been shown that an optimal methane conversion of about 6.7%, an ethylene selectivity of 14.7%, and a benzene selectivity of about 80.8% were achieved over a 2% Mo-HZSM-5 catalyst under the conditions of 700°C, 1 atm and GHSV of methane of 1400 ml/(g cat h) in a continuous flow reactor [3]. However, the existing problems in this route now are the low methane conversion and the poor stability of the catalyst.

In an attempt to search for more effective catalysts for this interesting reaction, the influence of the modification of Mo-HZSM-5 catalyst by Pt on the reaction performance in the methane non-oxidative transformation to ethylene and aromatics is investigated. It is surprising to find from the study of carbon deposition on the catalyst that the use of the Mo-HZSM-5 catalyst, which was formerly demonstrated to be an effective catalyst for methane non-oxidative conversion, showed no advantage over the oxidative processes, while the Pt–Mo-HZSM-5 composite was an excellent catalyst.

2. Experimental

2.1. Preparation of catalysts

The Mo-HZSM-5 catalyst was prepared by the impregnation method. HZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 38 was obtained by repeated ion exchange of NaZSM-5 with an aqueous solution of ammonium nitrate (1 N) for four times and then calcined in air at 500°C for 6 h. The HZSM-5 powder was impregnated with an aqueous solution of ammonium heptamolybdate (0.025 gMo/ml). Finally the sample was dried at 120°C overnight and calcined at 720°C for 8 h.

Modification of the 2% Mo-HZSM-5 catalyst by Pt was carried out by impregnating the calcined 2% Mo-HZSM-5 catalyst with an aqueous H_2PtCl_6 solution. Then it was dried and calcined under the same conditions as above.

2.2. Catalytic tests

Methane conversion tests were performed at 700°C and atmospheric pressure in a quartz tubular flow micro-reactor (the dimensions of the reaction zone of the reactor were: i.d. = 8 mm, length = 25 mm, other parts were filled with quartz) containing about 0.6 g catalyst (30–60 mesh) in each run. The space velocity of methane was about 1400 ml/(g cat h) and the flow rate ratio was $CH_4 : He = 1 : 1$. An on-line gas chromatograph equipped with Porapak QS columns which were controlled in a temperature-programmed mode (from RT to 200°C) and a TC detector was used. The methane conversion and the product selectivity were calculated on a carbon number base. The purity of methane was higher

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than 99.95% and the purity of helium was higher than 99.99%.

2.3. Carbon deposition study

The carbon accumulation on the catalysts was studied by means of DTA and TG. DTA spectra were recorded using a Perkin-Elmer 1700 model instrument in an oxygen flow, with a temperature ramp of 8°C/min. TG spectra were obtained using a Perkin-Elmer TGS-2 instrument in an oxygen flow at a heating rate of 10°C/min.

3. Results and discussion

3.1. Effect of Pt on the reaction performance of Mo-HZSM-5

As we already know, the major problems in non-oxidative methane conversion are the low methane conversion and the poor stability of the catalyst [3]. In an attempt to promote the 2% Mo-HZSM-5 catalyst, we tried to modify the catalyst by introducing platinum metal. The Pt-HZSM-5 catalyst exhibited very little activity to the aromatization of methane and it deactivated quickly. However, if platinum was added into the Mo-HZSM-5 catalyst, significant results were obtained. Table 1 gives the catalytic results over various platinum modified 2% Mo-HZSM-5 catalysts. We can see that the procedure for the introduction of Pt and Mo to HZSM-5 did not significantly influence the catalytic performances. By comparing the methane conversions and the selectivities for benzene over the modified and the unmodified 2% Mo-HZSM-5 catalysts [3], it is easy to find that the activity of the catalyst has not been improved significantly with the addition of Pt to Mo-HZSM-5. However, the greatest advantage of the modification by platinum is that the catalyst stability was prolonged. Fig. 1 shows such a comparison of the catalyst stability. It can be seen that after 150 min of operation, the Pt modified catalyst maintains the methane conversion above 6% while the unmodified catalyst deactivated rapidly. It is worthy to pay more attention to this result, as it overcomes the notorious problem of quick deactivation of the catalyst in the aromatization of light hydrocarbons. This result indicates the possibility of the continuous transformation of methane into benzene under non-oxidative conditions, which foresees a possibility of the commercialization of this process if the catalyst activity can be further enhanced. This improvement of catalyst stability by platinum most probably originates from the alleviation of coke deposition by platinum atoms. This suggestion will be further substantiated by the DTA-TG results and BET surface areas of the deactivated catalysts.

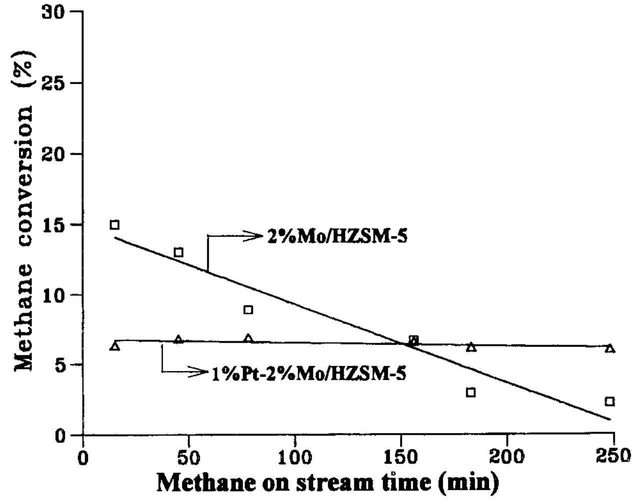

Fig. 1. Comparison of the catalyst stability of the platinum modified and the unmodified 2% Mo-HZSM-5 catalysts.

3.2. Study on carbon deposition by DTA and TG methods

Serious carbon deposition on HZSM-5 zeolite during the reaction cannot be prevented at such a high temperature (700°C). The most apparent influence of coke deposition on the catalyst surface might be the coverage of the active sites and the blockage of the zeolite pores. In fact, both the BET surface area and the micropore volume decrease after coke deposition. Some of these data of several catalysts after methane on stream for 4 h are given in table 2. It can easily be noticed that both the surface area and the micropore volume decrease drastically after reaction, irrespective of the Mo content in the catalyst. The deposited carbon could block the molybde-

Table 1
Reaction performances of various Pt–Mo-HZSM-5 catalysts at 700°C, 1 atm and methane space velocity of 1400 ml/(g cat h)

Catalyst[a]	CH_4 conversion (%)	product selectivity (%)		
		CO	C_2	C_6H_6
0.5% Pt–2% Mo (c)	5.9	16.3	4.7	79.1
1% Pt–2% Mo (c)	6.4	13.2	4.6	82.2
1% Pt–2% Mo (Pt)	6.9	14.8	3.9	81.3
1% Pt–2% Mo (Mo)	5.9	11.4	6.7	81.2

[a] The characters in parentheses indicate the preparation methods. c refers to coimpregnation, Pt or Mo means platinum or molybdenum was first impregnated, followed by the introduction of another metal.

Table 2
BET surface areas and the micropore volumes of some coked catalysts [a]

Catalyst	BET surface area [b] (m^2/g)	Micropore volume [b] (cm^3/g)
HZSM-5	281.9 (359.2)	0.107 (0.112)
1% Mo-HZSM-5	134.5 (311.5)	0.056 (0.109)
5% Mo-HZSM-5	197.4 (240.5)	0.065 (0.084)
1% Pt–2% Mo-HZSM-5	224.1 (301.6)	0.090 (0.107)

[a] After methane on stream for 4 h at 700°C.
[b] The number in parentheses is the value of the fresh catalyst.

num surface and the channels of the HZSM-5 zeolite, thus impede the interaction of molybdenum species with the incoming methane molecules. It could also cover the acidic sites of the catalyst. The coverage of the active sites, both the molybdenum oxide species and the Brønsted acid centers, will undoubtedly result in the deactivation of the catalyst [3].

The TG profiles of the various coked catalysts recorded in an oxygen atmosphere are shown in fig. 2. Analyses of the TG data of the coked catalysts showed that the percentages of deposited coke in total amount of the catalysts were: HZSM-5: 0.8%, 1% Mo-HZSM-5: 8.2%, 5% Mo-HZSM-5: 2.7% and 1% Pt–2% Mo-HZSM-5: 3.8%, after 4 h of methane on stream under the similar reaction conditions. Attention should be paid to the fact that the more active the catalyst, the higher the amount of deposited carbon. Take the 1% Mo-HZSM-5 for example, the total amount of deposited carbon corresponds to a methane conversion of about 1.6%, while the methane conversion to higher hydrocarbons is 4.2%. This means that about 21.6% of the total converted methane became deposited carbon. This figure is very discouraging to this route of methane conversion because there will be about 21.6% of methane wasted. It is thus suggested that this process using Mo-HZSM-5 as a catalyst does not show any advantage over the oxidative process (in which also about 20% of converted methane became CO and CO_2 [5]). However, the modification of Mo-HZSM-5 by platinum greatly suppresses the carbon deposition on the catalyst. The result of a calculation based on the 1% Pt–2% Mo-HZSM-5 catalyst demonstrates that about 11% of converted methane became deposited carbon. The use of the Pt–Mo-HZSM-5 catalyst clearly manifests the advantages of the non-oxidative path over the oxidative processes by improving the catalyst stability and reducing the carbon deposition.

Fig. 3 shows the DTA curves of the coked catalysts under an oxygen flow. It is suggested that the nature of the deposited carbon possibly was different over different catalysts. Possibly two kinds of coke were present on

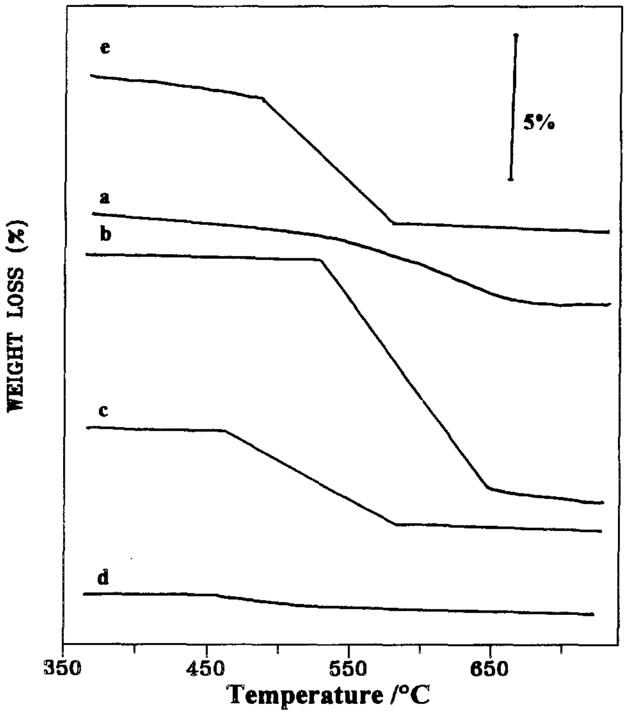

Fig. 2. TG profiles of the coked catalysts. (a) HZSM-5, (b) 1% Mo-HZSM-5, (c) 5% Mo-HZSM-5, (d) 10% Mo-HZSM-5, (e) 1% Pt–2% Mo-HZSM-5. All the catalysts were coked for 4 h.

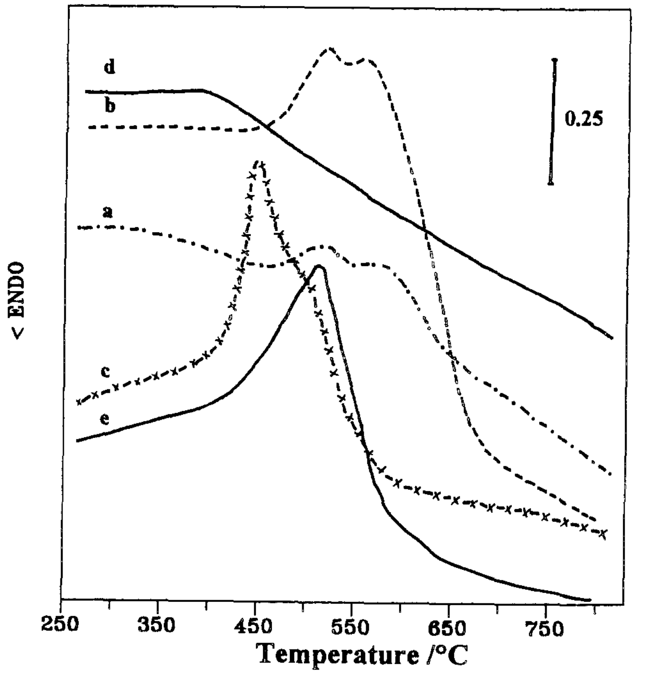

Fig. 3. DTA curves of the coked catalysts. (a) HZSM-5, (b) 1% Mo-HZSM-5, (c) 5% Mo-HZSM-5, (d) 10% Mo-HZSM-5, (e) 1% Pt–2% Mo-HZSM-5. All the catalysts were coked for 4 h.

the deactivated catalysts because always two peaks were exhibited during the oxidation process. With the increase of Mo loading, the peaks which represent the oxidation of the accumulated coke on the catalyst shifted to lower temperatures. When the Mo content was 10%, no well defined peak was observed. The coke on the Mo-HZSM-5 catalyst with a high Mo content can easily be oxidized. This possibly means that the deposited carbon on the catalyst with a high Mo-loading is less strongly held than that on the Mo-HZSM-5 catalyst with a lower Mo content.

Previously it was found that modification of Mo-HZSM-5 by platinum greatly improves the catalyst stability. The reason possibly can be attributed to the suppression of coke formation on the catalyst by the platinum. Furthermore, the DTA and TG results demonstrate that the nature of the deposited coke is different from that on the unmodified catalyst. The coke on the Pt–Mo-HZSM-5 catalyst can easily be oxidized (at a much lower temperature) as compared to that on the unmodified Mo-HZSM-5 catalyst. The part of the coke that was strongly held on the catalyst was eliminated by the presence of platinum. Accordingly there was only one peak in its DTA curve. It is therefore concluded that the improvement of the catalyst stability by addition of platinum is originated from the impedance of the formation of the strongly held coke, possibly is that part on the acidic sites of the catalyst.

Work on the investigation of other factors which might influence the catalyst stability and activity, including the conversion of methane by platinum metal, the interactions of Pt, Mo and HZSM-5 zeolite, and so on, is in progress. Studies on the reaction mechanism are also under way.

4. Conclusions

The incorporation of Pt into Mo-HZSM-5 greatly enhances the catalyst stability. This enhancement is largely due to the suppression of carbon accumulation on the catalyst, especially strongly held carbon. It is demonstrated that the unmodified Mo-HZSM-5 catalyst does not show any advantage over the oxidative processes in methane utilization while the Pt–Mo-HZSM-5 catalyst seems to be a more promising catalyst for the non-oxidative methane conversion process.

References

[1] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.

[2] L.Y. Chen, L.W. Lin, Z.S. Xu, J.L. Zang and T. Zhang, Paper presented at the *Methane and Alkanes Conversion Symposium,* San Diego, 13–18 March 1994 (Plenum Press, New York, 1996), in press.

[3] L.Y. Chen, L.W. Lin, Z.S. Xu., T. Zhang and X.S. Li, J. Catal. 157 (1995) 190.

[4] K. Murata and H. Ushijima, J. Chem. Soc. Chem. Commun. (1994) 1157.

[5] J.R. Rostrup-Nielsen, Catal. Today 18 (1993) 125.