Catalysis Letters 62 (1999) 215–220

Methane aromatization in the absence of an added oxidant and the bench scale reaction test

Yuan Lu [a], Zhusheng Xu [a], Zhijian Tian [a], Tao Zhang [a] and Liwu Lin [b,*]

[a] *Laboratory of Natural Gas Utilization and Applied Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, 456 Zhongshan Road, Dalian 116023, PR China*

[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, 456 Zhongshan Road, Dalian 116023, PR China*

Received 26 June 1999; accepted 12 August 1999

A bench scale reaction test for methane aromatization in the absence of an added oxidant was performed and its reaction result evaluated based on the carbon balance of the system. The result was compared with those obtained from the micro-reaction test to ensure the accuracy of the internal standard analyzing method employed in this paper. The catalytic performances of modified Mo/HZSM-5 catalysts were examined. It was found that pre-treatment by steam on HZSM-5 weakened the serious deposition of coke, and pre-impregnation of n-ethyl silicate on HZSM-5 could improve the conversion of CH_4, but had little effect on coke formation. A low temperature activation procedure including pre-reduction of the catalyst with methane prevents the zeolite lattice from being seriously destroyed by high valence state Mo species when the Mo loading is high. It was suggested that Mo_2C species detected by XRD spectra was the active phase for CH_4 aromatization.

Keywords: methane aromatization, bench scale test, steam treatment, activation procedure, Mo_2C

1. Introduction

The declining of crude oil reserves has led to the considering of natural gas as an alternative supply for petrochemical feedstocks. Novel processes concerning the direct utilization of natural gas, such as methane coupling to ethylene or aromatics, have shown potential commercial interest. Direct conversion of methane–oxygen mixtures to aromatics has been reported, but with poor selectivity for aromatics due to deep oxidation [1]. It was found by Wang et al. [2] that high selectivity to aromatics could be obtained by methane conversion on a Mo/HZSM-5 catalyst without the presence of any oxidant. Many papers concerning the improvement of the catalyst and the mechanism of the reaction have been reported [3–19]. However, little attention has been paid to the bench scale reaction test. Due to the different catalyst preparation procedures and reaction conditions adopted, distinct difference exists among the results reported. The different analyzing method was also one of the crucial factors leading to those differences. The method of internal standard for the analysis of the products of CH_4 aromatization was first employed by Lunsford et al. [13] and Liu et al. [16], respectively, to calculate the CH_4 conversion and product selectivities, with the consideration of coke formation based on the carbon balance of the reaction. According to results reported by Lunsford et al. [13], a CH_4 conversion of 8% with benzene selectivity of 70% and coke selectivity of 15% could be obtained on the Mo/HZSM-5 catalyst at 973 K. Liu et al. [16] also reported that CH_4 could be converted to aromatics on Mo/HZSM-5, including a distinct amount of naphthalene, with a conversion of 8% and coke selectivity of 32%. An internal standard analyzing method similar to those reported by Lunsford et al. and Liu et al. was also used in this work for the investigation of the catalytic performance of Mo/HZSM-5 improved by steam pre-treatment or n-ethyl silicate pre-deposition on HZSM-5. A bench scale reaction test was performed, the condensable products were collected and the weight of the coke was tested by TPO-TG to obtain the catalytic performance of Mo/HZSM-5 according to carbon balance in the reaction procedure. The result was compared with those obtained by the internal standard analyzing method to ensure the accuracy of the analyzing system.

It has been reported, respectively, by Lunsford et al. [13] and Solymosi et al. [10–12] that, according to their XPS results, Mo_2C was the active phase for the title reaction. However, it is difficult to distinguish the characteristic signal of Mo_2C from that of metallic molybdenum, and divergence exists concerning the characteristic C 1s signal of Mo_2C. So XRD determination was employed in this work to ensure the formation of Mo_2C crystallite on the used catalyst.

According to the results reported earlier, the activity of Mo/HZSM-5 with high Mo loading was very low, due to serious decomposition of the zeolite lattice caused by Mo species dispersed into the channel of the zeolite during calcination, activation or reaction procedures at high temperatures [3,7]. The catalyst was generally activated in air at 973 K for about 1 h before CH_4 was introduced into the reactor at the beginning of the reaction test. It was sug-

---

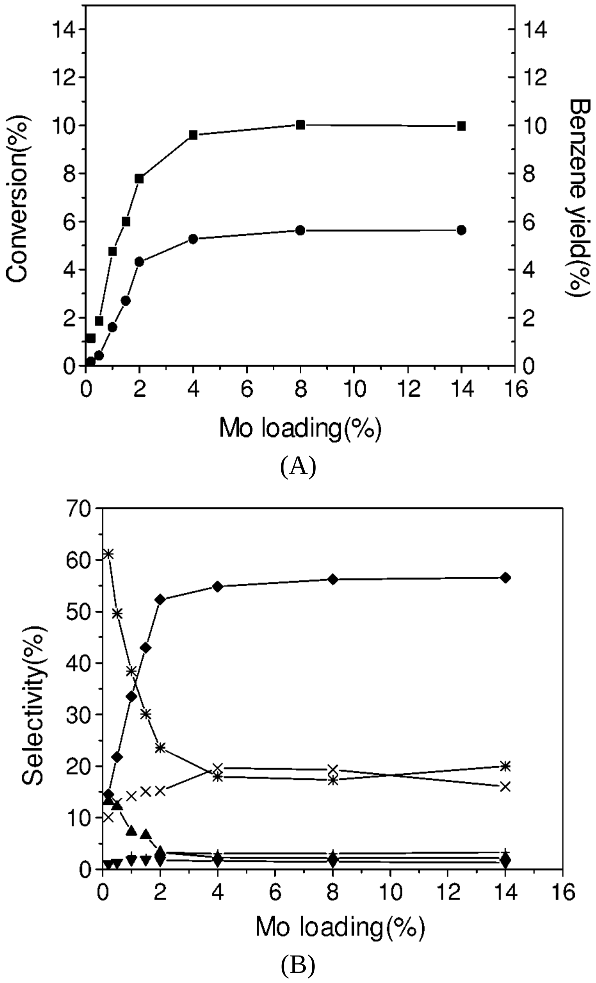
[*] To whom correspondence should be addressed.

gested that the serious decomposition of the zeolite lattice was caused by high Mo loading and high calcination and reaction temperatures [6]. In this work, in order to investigate the crucial factor leading to serious decomposition of the zeolite lattice when the Mo loading was high, the catalyst was pre-reduced by methane at a comparatively low temperature before the running of the reaction test.

2. Experimental

2.1. Catalyst preparation

The Mo-containing catalyst was prepared by incipient wetness impregnation of HZSM-5 or modified HZSM-5 zeolites with an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot H_2O$, Tianjin Fourth Chemical plant). HZSM-5 with Si/Al mole ratio of 25 was supplied by Nankai University. After impregnation, the catalyst was dried at 383 K for 4 h, and then calcined in air at 823 K for 6 h. Mo/HZSM-5 means that HZSM-5 was used as the support directly, while HZSM-5(ST) means HZSM-5 treated by steam. The steam treatment condition was: $T = 823$ K, P (pressure of water) $= 290$ mm Hg, space velocity of $N_2 = 6000$ ml $g^{-1}\,h^{-1}$. After steam treatment the zeolite was washed with 0.5 N HCl at 363 K for 2 h and then dried by air at 383 K for 4 h before being used. Mo–Si/HZSM-5 means that before the impregnation of the Mo species, HZSM-5 was impregnated with cyclohexane solution of n-ethyl silicate (Si (%) $= 0.4\%$), then dried at 383 K for 4 h and calcined in air at 823 K for 6 h.



(A)

(B)

Figure 1. (A) CH_4 conversion (■) and benzene yield (●), (B) selectivities, towards benzene (♦), coke (∗), naphthalene (×), ethene (▲), ethane (▼) and toluene (+) versus Mo loadings on the Mo/HZSM-5 catalyst for CH_4 non-oxidative aromatization at 973 K, 1 atm and space velocity $= 1500$ ml $g^{-1}\,h^{-1}$. Time on stream $= 300$ min.

2.2. Reaction test

The internal standard analyzing system for the methane reaction test was performed on a fixed-bed continuous-flow microreactor system, with a 10 mm i.d. quartz tubular reactor containing 1.5 ml catalyst. The catalyst was activated at 773 K under He flow for 0.5 h and then CH_4 was introduced into the reactor to ensure the catalyst to be partly reduced before the reaction temperature was reached. A feed gas mixture of 97.5% CH_4 (99.995%) with 2.5% Ar (99.99%) as the internal standard for analysis was purified to get rid of trace amount of O_2 and H_2O, and then introduced into the reactor at a flow rate of 1500 ml $g^{-1}\,h^{-1}$ (GHSV $= 600$ h^{-1}). The reaction was conducted either at 973 or at 1023 K under a total pressure of 1 atm. The reaction products were collected by a six-way valve. An online gas chromatograph (Shangfen 103 type) equipped with a thermal conductivity detector (TCD) and two 4 mm × 3 m Porapak-P columns were employed to analyze hydrocarbon products including ethylene, ethane, benzene, toluene and naphthalene. H_2, Ar, CO, CH_4 and CO_2 were analyzed by another on-line GC (Shangfen 102 type) with TCD and a 3 mm × 3 m activated carbon column. An internal standard analyzing method similar to that reported by Liu et al. [16] was used to calculate the methane conversion and the selectivity toward hydrocarbon products according to mass balance for carbon. Then the selectivity of coke, including undetected heavy aromatics, could be obtained.

For the bench scale reaction test (figure 1), a 30 mm diameter quartz tube packed with 20 ml (4 wt%)Mo/HZSM-5 catalyst was used as the reactor. Purified natural gas ($P = 1$ atm, $CH_4 > 99\%$, $C_2H_6 + N_2 < 1\%$) was introduced into the reactor as the feed at a space velocity of 1500 ml $g^{-1}\,h^{-1}$. The reaction temperature was controlled at 973 K. The activation procedure of the catalyst was the same as that used in the internal standard analyzing system. Condensable C_6–C_{10} aromatics were collected by two ethanol-dry ice cooling traps (201 K) connected in series. The collectable yield exceeds 99% of the theoretical evaluated amount based on the saturation pressure of benzene at 200 K and the methane conversion. The tail gas out of the cooling traps was sampled and analyzed with the GC to check whether the aromatics had been fully collected. Collection was conducted starting from TOS (time on stream) of 40 min in order to avoid the initial activity induction period, up to TOS of 280 min. During this period the catalytic activity was relatively stable. The amount of coke formed during the reaction was measured by the TPO-TG method. When evaluating the weight of the coke, the weight of hydrogen contained in the coke was neglected, and it was supposed that the lattice oxygen in MoO_3 was lost due to the reduction of MoO_3 to Mo_2C. So the weight loss during the coke burning plus the weight of lattice oxygen in MoO_3 was taken as the weight of the coke formed during the reaction.

2.3. TG and XRD measurements

The TPO-TG measurements were performed on a P-E TGS-2 type instrument. The oxygen flow rate was controlled at 50 $\mathrm{ml\,min^{-1}}$, with temperature increasing rate of 10 $\mathrm{K\,min^{-1}}$. X-ray diffraction patterns were obtained on a Rigaku D/max-rb diffractometer using Cu Kα radiation at room temperature. The instrumental conditions were selected as 40 kV and 50 mA at a scanning rate of $8^\circ\ \mathrm{min^{-1}}$. Powder diffractograms of samples were recorded over a range of 2θ values from 5 to 65°.

3. Results and discussion

3.1. The bench scale reaction test

A bench scale reaction system was set up in order to ensure the accuracy of the internal standard analyzing system used in this paper. The condensable components in the product were collected and the weight of coke on the used catalyst was tested through coke-burning by the TPO-TG method to obtain the yield of aromatics and coke. Methane conversions and yield of aromatics obtained from the bench scale reaction system and those obtained by the internal standard analyzing method were listed in table 1. It is shown that the results obtained by the internal standard analyzing method are reliable. Thus the method was used for all the reaction tests listed below.

3.2. Catalytic performance of modified Mo/HZSM-5 catalysts

Table 2 shows the results of methane aromatization in the absence of an added oxidant on Mo/HZSM-5, Mo/HZSM-5(ST) and Mo–Si/HZSM-5 catalysts. It is shown that CH_4 aromatization at high temperature was accompanied by serious coke formation, but for the (4 wt%)Mo/HZSM-5(ST) catalyst, the steam treatment weakened the serious coke formation. When we modified the catalyst by pre-impregnation with Si on the zeolite, i.e., (4 wt%)Mo–Si/HZSM-5, the activity of the catalyst became a little higher, but the selectivity to coke was almost unchanged.

3.3. Catalytic performance and XRD spectra of Mo/HZSM-5 with different Mo loading

It has been reported earlier that the activity of Mo/HZSM-5 with high Mo loading was very low, due to serious decomposition of the zeolite lattice caused by Mo species dispersed into the channel of the zeolite during calcination, activation or reaction procedures at high temperatures [3,7]. It is generally accepted that the main factors leading to this phenomenon are high Mo loading and high calcination and reaction temperatures. Liu et al. [6] have reported that when

Table 1
Results of bench scale reaction test and of internal standard analyzing system.[a]

	Results of the internal standard analyzing system				Results of bench scale reaction	
	60 min TOS[b]	120 min TOS	180 min TOS	240 min TOS	Experiment 1 (40–280 min)	Experiment 2 (40–280 min)
Benzene yield	5.35	5.35	5.45	5.36	5.41	5.34
Toluene yield	0.24	0.31	0.36	0.30	0.26	0.24
Naphthalene yield	3.25	2.93	2.30	2.25	2.68	2.51
Total aromatics yield	8.84	8.59	8.11	7.91	8.35	8.09
Coke yield	1.83	2.11	1.79	1.76	1.89	1.92
Conversion	11.09	11.08	10.30	9.77	10.58	10.42

[a] Reaction temperature: 973 K; reaction pressure: 1 atm; GHSV = 600 $\mathrm{h^{-1}}$.
[b] Time on stream.

Table 2
Catalytic performance of (4 wt%)Mo/HZSM-5 and modified catalysts analyzed by internal standard method.[a]

Catalyst (reaction temperature (K))	Methane conversion (%)	Selectivity (%)						Yields of aromatics (%)
		Benzene	Toluene	Naphthalene	C_2	CO	Coke	
(4 wt%)Mo/HZSM-5 (973)	11.08	48.33	2.79	26.42	2.39	1.03	19.04	8.59
(4 wt%)Mo/HZSM-5 (1023)	17.57	40.36	2.45	19.89	2.62	0.94	33.74	11.02
(4 wt%)Mo/HZSM-5(ST) (973)	10.14	60.86	3.67	21.29	4.90	0.37	8.90	8.70
(4 wt%)Mo–Si/HZSM-5 (973)	11.73	52.92	2.24	21.94	2.56	0.70	19.64	9.04

[a] Time on stream = 120 min; reaction pressure: 1 atm; GHSV = 600 $\mathrm{h^{-1}}$.

the catalyst was calcined at high temperatures, or when the Mo loading was high, a large amount of Mo species would move into the channel of the zeolite, leaching out the lattice Al and leading to the decomposition of the zeolite lattice with the formation of $Al_2(MoO_4)_3$, which was not active for the title reaction. It was generally suggested [3,7,11,13] that the acid sites within the channels of ZSM-5 were active sites for the formation of aromatics from ethylene, which was thought to be the initial product of methane conversion on Mo species. Therefore, the ZSM-5 zeolite framework is important for methane aromatization.

According to the results reported earlier [3,7], at the beginning of the reaction test, the catalyst was generally activated in air at 973 K for about 1 h before CH_4 was introduced in the reactor. In this paper, in order to study the main factor that influence the decomposition of the zeolite lattice, and to find a method for effectively preventing the zeolite from being destroyed by Mo species, a new activation procedure different from those reported earlier [3,7] is used. The catalyst was activated at 773 K under He flow for 0.5 h and then CH_4 was introduced into the reactor to ensure the catalyst to be partly reduced before the high reaction temperature was reached. Results different from those reported earlier [3,7] were obtained.

The CH_4 conversion and products selectivity versus Mo loading are shown in figure 1 (A) and (B). It is shown that the activity and aromatics selectivity increase rapidly with increasing Mo loading when the Mo loading is lower than 4%. However, the selectivities toward coke and ethylene are high at low Mo loading and decrease sharply with increasing Mo loading. When the Mo loading exceeds 4%, the activity and products selectivity remained almost the same with increasing Mo loading.

As for the (4 wt%)Mo/HZSM-5, the results are similar with those reported by other authors [13,16] using the same analyzing method. However, results different from those reported earlier [3,7] were obtained when the Mo loading was higher. From figure 1(A) it is worth noting that even with Mo loading as high as 14%, the activity of the catalyst was still very high, almost the same as the activity of the (4 wt%)Mo/HZSM-5 catalyst. But the situation is different if the normal activation procedure such as those reported earlier [3,7] was performed before the reaction, which generally included calcination of the catalyst in air or oxygen at 973 K for about 1 h. If the (4 wt%)Mo/HZSM-5 catalyst was activated by air at 973 K for 1 h before the reaction, a methane conversion of 6%, with benzene yield of 2.5% was obtained, which is much lower than those obtained by the new activation procedure. However, no distinct difference was observed for the (4 wt%)Mo/HZSM-5 catalyst when different procedure of activation were employed.

Compared with the results reported earlier [3,7], it is supposed that the high activity of the high Mo loading catalyst is due to the new activation procedure used in this work. By using this method the Mo species on the catalyst was partly reduced to low valence states before further increasing of temperature. Therefore, it is concluded that the low valence state Mo species, unlike the high valence one (MoO_3), would not lead to serious decomposition of the zeolite lattice even with high Mo loading. This was proved to be true by XRD spectra listed in figures 2–4. It is shown in figures 2(B) and 3 that the coked catalysts as well as the catalyst treated by H_2 at temperature as high as 1173 K for 1 h after coking, maintained high crystallinity even with Mo loading as high as 14%. No $Al_2(MoO_4)_3$ signal was detected. But if the catalyst was calcined in air at 1173 K for 1 h, the signal intensity of the zeolite crystals sharply decreased, accompanied by the distinct appearance of the $Al_2(MoO_4)_3$ signal (figure 4), and no distinct conversion of methane could be observed on it. So it could be concluded that neither the high calcination temperature nor the high Mo loading, but the valence state of the Mo species is the crucial factor for the decomposition of the zeolite lattice. As for catalysts with low Mo loadings such as 4 wt%, Mo is highly enriched on the external surface of ZSM-5 [13], and the amount of Mo within the channels is comparatively

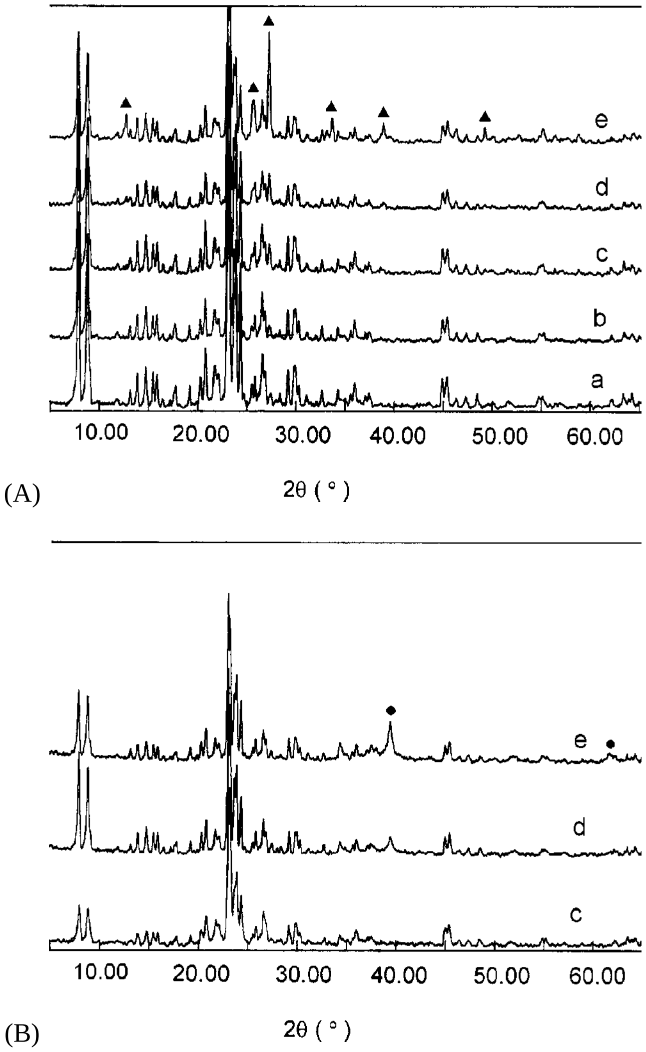


Figure 2. XRD patterns of catalysts with different Mo loadings: (A) fresh Mo/HZSM-5, and (B) samples obtained by treatment of coked Mo/HZSM-5 (time on stream = 360 min) by H_2 at 1173 K for 1 h. (▲) MoO_3, (●) α-Mo_2C: (a) 0, (b) 2, (c) 4, (d) 8 and (e) 14%.

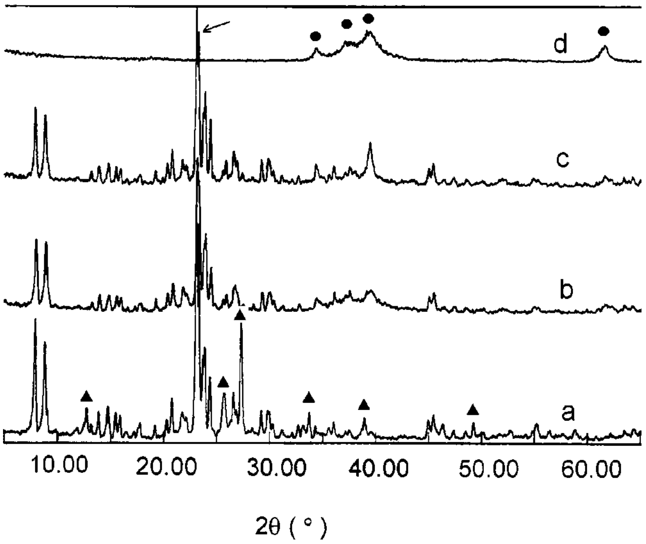


Figure 3. XRD patterns of α-Mo_2C and (14 wt%)Mo/HZSM-5: (a) fresh (14 wt%)Mo/HZSM-5, (b) coked (14 wt%)Mo/HZSM-5 by CH_4 at 973 K for 6 h, (c) regenerated catalyst (b) by H_2 at 1173 K for 1 h and (d) α-Mo_2C obtained by reaction of MoO_3 with CH_4 at 973 K for 6 h.

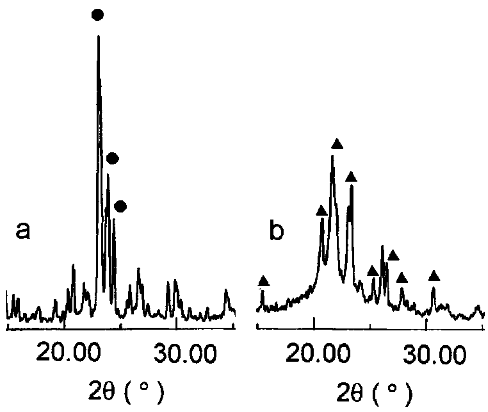


Figure 4. XRD patterns of regenerated (14 wt%)Mo/HZSM-5: (a) regenerated by H_2 at 1173 K for 1 h and (b) calcined in O_2 at 1173 K for 1 h. (▲) $Al_2(MoO_4)_3$, (●) ZSM-5.

small, so that no serious decomposition of the zeolite lattice was observed. However, when Mo loading is high, it is supposed that more Mo species would diffuse into the channel of the zeolite, leading to the serious decomposition of the lattice, especially at high calcination temperature.

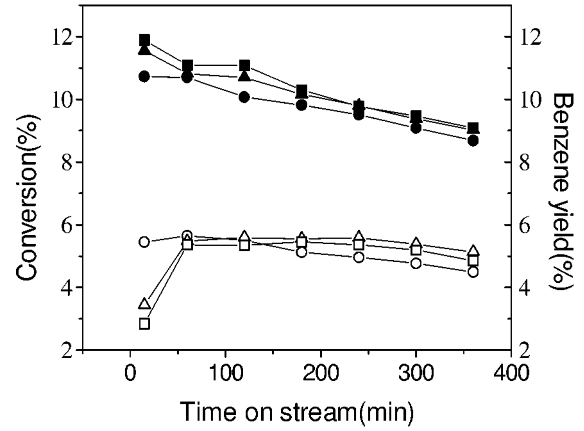


Figure 5. CH_4 conversion (solid) and benzene yield (open) on fresh (4 wt%)Mo/HZSM-5 catalyst (■, □) and coked (4 wt%)Mo/HZSM-5 regenerated by H_2 (●, ○) or by O_2 (▲, △).

It is shown in figure 2 (A) and (B) that a signal of MoO_3 crystals appears when Mo loading exceeds 4% for the fresh catalyst, but it disappeared and was replaced by the signal of Mo_2C crystals for the used catalyst with Mo loading higher than 4%. The signal of Mo_2C on the coked (14 wt%)Mo/HZSM-5 is broad and weak as shown in figure 3, sample (b), which implies that MoO_3 was reduced by CH_4 during the reaction and converted to microcrystals of Mo_2C. After treatment of coked (14 wt%)Mo/HZSM-5 by H_2 at 1173 K for 1 h, the characteristic signal of Mo_2C crystals becomes narrow and sharp (figure 3, sample (c)), which implies that the sintering of the microcrystals of Mo_2C occurred. It has been described earlier [20] that ZSM-5 undergoes a displacive transformation from monoclinic to orthorhombic when it occludes bulky ions, altering the relative peak positions and intensities in the XRD patterns. Lucas et al. [21] reported that coke inside the channel of ZSM-5 produced the same effect as occluded TPA ions. From figure 3 we can see that after a period of reaction the ZSM-5 undergoes the same transformation as denoted by Lucas et al. [21]. However, as pointed out by an arrow in figure 3, it is shown that the transformation is reversible when the coked catalyst was treated in flow H_2 at 1173 K for 1 h. So we can conclude that at least a part of the coke is located in the channel of the coked catalyst and most of the coke was removable during H_2 treatment. The activities of the fresh catalyst and the catalyst regenerated by H_2 at 1173 K and those by O_2 at 823 K are shown in figure 5. It is shown that the activity is almost the same as for the fresh catalyst. But the stability with time on stream of the catalyst regenerated by H_2 was not as good as that regenerated by O_2, which may be caused by the sintering of the Mo_2C microcrystals or little amount of residual coke on the catalyst. On the other hand, it should be noted that the induction period of the initial activity diminished for the H_2 regenerated catalyst when compared with the fresh or O_2 regenerated one, which implies that Mo_2C species formed during reaction and detected by XRD may be the active Mo phase for the title reaction, which is the same as those proposed by Lunsford et al. [13] and Solymosi et al. [12] according to their XPS results.

4. Conclusion

The bench scale reaction test shows that the internal standard analyzing system used in this paper is reliable to examine the activity and product selectivity involving coke formation. Pre-treatment of HZSM-5 by steam could distinctly reduce the formation of coke during the reaction. Pre-deposition of silicate on HZSM-5 before the impregnation of Mo species could improve the performance of the catalyst by increasing the methane conversion, but has little effect on the preventing of coke formation. By changing the activation procedure it has been found that, unlike high valence Mo species (MoO_3), reduced Mo species would not destroy the zeolite lattice. Pre-reduction prevents the zeolite from serious decomposition, and the catalytic performance of the catalyst with high Mo loading (14 wt%) is as good as that with low Mo loading (4 wt%) if the new activation procedure is employed. Regeneration of coked catalyst at high temperature by H_2 can restore the activity, but the stability is not as good as that regenerated by O_2. It is proposed according to the XRD result that microcrystals of Mo_2C sinter to large crystals during the high temperature regeneration by hydrogen. No obvious induction period of initial activity is observed on the H_2 regenerated catalyst during the reaction, which implies that the Mo_2C species detected by XRD is probably the active phase for methane aromatization.

Acknowledgement

This work was sponsored by the National Natural Science Foundation under grant no. 29573137.

References

[1] J.B. Claridge, M.L.H. Green, S.C. Tsang and A.P.E. York, Appl. Catal. A 89 (1992) 103.
[2] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.
[3] Y. Xu, S. Liu, L. Wang, M. Xie and X. Guo, Catal. Lett. 30 (1995) 135.
[4] Y. Xu, W. Liu, S. Wong, L. Wang and X. Guo, Catal. Lett. 40 (1996) 207.
[5] Y. Shu, Y. Xu, S. Wong, L. Wang and X. Guo, J. Catal. 170 (1997) 11.
[6] W. Liu, Y. Xu, S. Wong, L. Wang, J. Qiu and N. Yang, J. Mol. Catal. A 120 (1997) 257.
[7] L. Chen, L. Lin, Z. Xu, X. Li and T. Zhang, J. Catal. 157 (1995) 190.
[8] L. Chen, L. Lin, Q. Xin, P. Ying, M. Cheng, Z. Xu and T. Zhang, React. Kinet. Catal. Lett. 56 (1995) 267.
[9] L. Chen, L. Lin, Z. Xu, T. Zhang and X. Li, Catal. Lett. 39 (1996) 169.
[10] F. Solymosi, A. Erdöhelyi and A. Szöke, Catal. Lett. 32 (1995) 43.
[11] F. Solymosi, A. Szöke and J. Cserényi, Catal. Lett. 39 (1996) 157.
[12] F. Solymosi, J. Cserényi, A. Szöke, T. Bansagi and A. Oszkó, J. Catal. 165 (1997) 150.
[13] D. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.
[14] B.M. Weckhuysen, M.P. Rosynek and J.H. Lunsford, Catal. Lett. 52 (1998) 31.
[15] B.M. Weckhuysen, D. Wang, M.P. Rosynek and J.H. Lunsford, J. Catal. 175 (1998) 338; 175 (1998) 347.
[16] S. Liu, Q. Dong, R. Ohnishi and M. Ichikawa, J. Chem. Soc. Chem. Commun. (1997) 1455.
[17] S. Liu, L. Wang, Q. Dong, R. Ohnishi and M. Ichikawa, Stud. Surf. Sci. Catal. 119 (1998) 241.
[18] Y. Schuurman, T. Decamp, A. Pantazidis, Y. Xu and C. Mirodatos, Stud. Surf. Sci. Catal. 109 (1997) 351.
[19] J. Zhang, M.A. Long and R.F. Howe, Catal. Today 44 (1998) 293.
[20] D.M. Bibby, N.B. Millestone, J.E. Patterson and L.P. Aldridge, J. Catal. 97 (1986) 493.
[21] A. de Lucas, P. Canizares, A. Duran and A. Carrero, Appl. Catal. A 156 (1997) 299.