Catalysis Letters Vol. 90, Nos. 3–4, October 2003 (© 2003)

Shape selectivity in methane dehydroaromatization over Mo/MCM-22 catalysts during a lifetime experiment

J. Bai, Shenglin Liu, Sujuan Xie, Longya Xu*, and Liwu Lin*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian P.O. Box 110, 116023, P.R. China

Received 14 April 2003; accepted 10 July 2003

Dehydroaromatization of CH_4 with 2% CO_2 on 6Mo/MCM-22 in a 100-h lifetime test was carried out at 993 K, atmospheric pressure and 1500 mL/gh. The duration of the lifetime test can be divided into an induction stage, stable stage and deactivation stage on the basis of the selectivities of hydrocarbons and coke. The characteristics of deposited coke with different time onstream were studied using TPO and TG techniques. There were two peaks corresponding to two kinds of coke recorded in TPO profiles, and the oxidation temperature of coke shifted to higher values with less hydrogen content with the increase of coke deposits. BET and Benzene-TPD techniques were employed to study the variation of specific surface area of the external and micropore surface versus time onstream. With the accumulation of coke deposits, although the pores became partially blocked and the internal surface decreased, methane could still enter the channel and was converted to benzene with shape selectivity until a critical value of coke deposition was reached.

KEY WORDS: CH_4; dehydroaromatization; Mo/MCM-22; coke formation; shape selectivity; specific surface area.

1. Introduction

Currently, a great challenge and an intriguing problem in heterogeneous catalysis is the catalytic conversion of methane to higher hydrocarbons and aromatic compounds as alternative feedstocks for the petrochemical industry. Since the nonoxidative conversion of methane to benzene on Mo/ZSM-5 reported in 1993 [1], many papers have been reported considering the catalytic performance, reaction mechanism and catalyst characterization [2–7]. Another interesting catalyst, Mo/MCM-22 reported by Bao *et al.*, features a higher benzene ratio and a lower naphthalene yield in comparison with Mo/ZSM-5 [8]. The fatal drawback of this reaction is that the methane conversion was drastically suppressed and the catalyst deactivated in a few hours due to serious coke formation. To prolong the life of the MDA (methane dehydroaromatization) catalyst, Ichikawa *et al.* reported that adding several percent CO or CO_2 to the CH_4 flow resulted in a higher stability of catalytic methane conversion to benzene in the prolonged time onstream on Co- and Fe-modified Mo/ZSM-5 catalyst due to the substantial suppression of coke [9].

Many researchers have investigated coke deposition of the Mo/ZSM-5 catalyst [10–13], and the main data was about the weight of coke deposition. For the Mo/MCM-22 catalyst, Bao *et al.* studied the character of coke deposited on catalyst reacted for 3 h through TPH, $TPCO_2$ and TPO methods [14]; but the operation and observation of long lifetime tests of the steady state are still in infancy. In order to approach the steady state of MDA catalysts under acceptable industrial conditions, it is important to pursue long-duration operation in a whole regenerated cycle and to make certain the proper regeneration time. In this paper, we use nitrogen adsorption, Benzene-TPD, thermogravity (TG) and temperature-programmed oxidation (TPO) techniques to investigate deposited coke and the changes in Mo/MCM-22 catalyst as a function of time onstream for 100 h, and bring forward that there is a critical value for coke capacity based on the shape selectivity of benzene.

2. Experimental

2.1. Synthesis of the MCM-22 zeolite

The MCM-22 zeolite was synthesized by using an organic mixture solution (denoted by OMS) as a template. The OMS was produced by catalytic hydrogenation of caprolactam and was composed of hexamethyleneimine and caprolactam. A certain amount of aluminium sulfate, sodium hydroxide, OMS, silica, and deionized water were added into a vessel in that order under vigorous stirring for 20 min. Then, the reaction mixtures were introduced into a stainless-steel autoclave, heated to 423 K and kept for a given time until crystallization was completed. After the autoclave was quenched in cold water, the crystalline products were filtered, washed with water and dried at 383 K overnight

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* To whom correspondence should be addressed.
E-mail: lyxu@dicp.ac.cn

[15]. The XRD pattern of a representative sample agreed with that of pure MCM-22 given in reference [16]. The HMCM-22 zeolite was obtained by ion exchange of the MCM-22 zeolite with an aqueous solution of ammonium nitrate (1 mol/L) for four times and then by calcination at 803 K for 6 h.

2.2. Catalyst preparation and evaluation

The 6Mo/MCM-22 catalyst was prepared by the conventional impregnation (incipient wetness) of HMCM-22 ($SiO_2/Al_2O_3 = 32$) zeolite powder with $(NH_4)_6(Mo_7O_{24})4H_2O$ aqueous solution. After the impregnation, the sample was dried at 383 K and calcined at 773 K in air for 6 h. On the basis of the weight ratio of impregnating Mo in $(NH_4)_6(Mo_7O_{24})4H_2O$ to zeolite powder, the catalyst was denoted as 6Mo/MCM-22. The catalytic test was carried out under atmospheric pressure of CH_4 with CO_2 in a continuous flow microreactor system equipped with a quartz tube (i.d. 8 mm) packed with 0.4 g of catalyst pellets of 16 ~ 32 mesh. After flushing with helium at 993 K for 30 min, a feed gas mixture of 90% CH_4, 2% CO_2 and 8% Ar, used as an internal standard for analysis, was introduced into the fixed-bed reactor at a flow rate of 11.2 mL/min (space velocity = 1500 mL/(g cat h^{-1})) through a mass flow controller.

Hydrocarbons including alkanes (and/or alkenes) such as CH_4, C_2H_4, C_2H_6 and aromatics such as benzene, toluene, xylene and naphthalene in the tail-gas were analyzed by an on-line gas chromatograph (Varian CP 3800) equipped with a column of SE-30 and a flame ionization detector (FID). A Hayesepe-D column, a 13X column and a thermal conducting detector (TCD) were also placed on the same chromatograph for the on-line analysis of H_2, Ar, CO, CH_4, CO_2, C_2H_4, C_2H_6, etc. Conversion of methane, selectivity of hydrocarbons, CO and coke formation on the catalyst were calculated according to the mass balance of hydrocarbons [17], and the CO originating from CO_2 was excluded because CO_2 was completely consumed on the catalyst.

2.3. TPO and TG measurement

The characterization of the coke deposited on the catalyst was measured by the TPO method. Each catalyst sample (100 mg) was loaded to a U-type quartz microreactor. After purging in a helium flow (30 mL/min) at 423 K for 1 h, the temperature of the sample was lowered to 313 K and the helium flow switched to a flow composed of 2% O_2 and 98% He at a flow rate of 20 mL/min. The total oxidation products were detected by an on-line gas chromatograph equipped with a TCD and the temperature increasing at 4 K/min. The main oxidation products (CO_2, CO, H_2O, etc.) were monitored by an on-line mass spectrometer (MS).

The TG measurements were carried out on a Perkin–Elmer TGA instrument by heating the sample from room temperature to 1073 K at a heating rate of 4 K/min under O_2 stream with a flow rate of 40 mL/min.

2.4. TPD measurement

Benzene-TPD (temperature-programmed desorption) measurements were performed on a conventional set-up equipped with a thermal conductivity detector. The sample (100 mg) was first flushed with a helium flow (20 mL/min) at 773 K for 30 min and then cooled to 373 K. After that, it was saturated with benzene until equilibrium. When the integrator's baseline was stable throughout, being flushed with a helium flow, benzene-TPD was promptly started at a heating rate of 10 K/min. The amount of benzene desorpted from the sample was detected on-line by TCD.

2.5. Specific surface area and micropore area measurements

The specific surface area and micropore area of the samples were determined by the BET method on the basis of the nitrogen adsorption isotherm at liquid nitrogen temperatures, and a value of 0.162 nm^2 for the cross-sectional area of N_2. The measurements were performed with ASAP 2010 Micromeritics equipment.

3. Results

3.1. Steady manufacturing of benzene from CH_4 with CO_2 on the 6Mo/MCM-22 catalyst

Many researchers have been encouraged to enhance the activity of catalysts for steady manufacturing of benzene from methane. Various methods such as the addition of promoters to Mo-based catalyst, the addition of several percent CO, CO_2 or O_2 to the CH_4 feed and optimizing reaction conditions are all effective in stabilizing the catalytic activity within a short operation period for the 6Mo/ZSM-5 catalyst [9,18,19]. It was proposed by Ichikawa *et al.* [9] that the addition of CO_2 in CH_4 feed resulted in improved catalyst stability due to efficient suppression of coke formation on the catalyst. In our experiment, the same merit of CO_2 was also found over 6Mo/MCM-22. Here, we introduce a complete reaction period with a 100-h lifetime test of the 6Mo/MCM-22 catalyst for the dehydroaromatization of CH_4 with the addition of 2% CO_2 to the feed. The results shown in figure 1(b) demonstrated that in most of the time onstream, the selectivity of benzene (about 88%) and naphthalene (less than ~8%) in the hydrocarbons was steadily main-

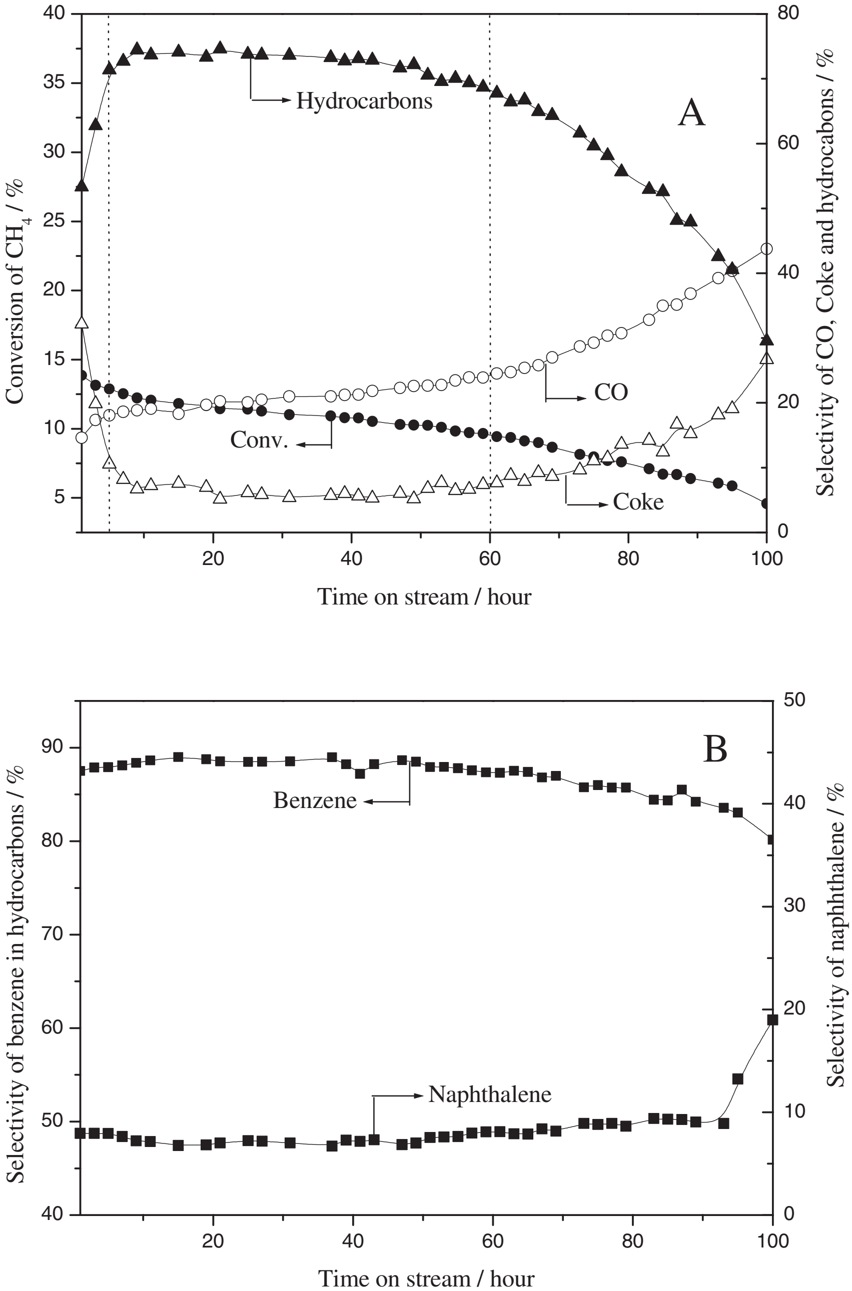

Figure 1. The reaction performance of 6Mo/MCM-22 catalyst as function of time onstream. (A) The conversion of CH_4 and the selectivity of CO, coke and hydrocarbons in CH_4 conversion, (B) the selectivity of benzene and naphthalene in hydrocarbons. Reaction conditions: $T = 993\,K$, $P = 1\,atm$, $SV = 1500\,mL/gh$, $CO_2 = 2\%$.

tained. According to the changes in selectivity of hydrocarbons and coke (see figure 1(a)), the whole period can be divided into three stages. The first stage is the induction period (0–5 h), where the hydrocarbons selectivity increased from 53.3 to 71.4% while the coke selectivity decreased. The second stage is the steady period (5–60 h), where the selectivity of hydrocarbons, CO and coke was maintained at ~70, ~20, and less than 10%, respectively. During this period, the conversion of methane, as shown in figure 1(a), only moderately decreased from 12.7 to 9.5%. The third is the deactivation period (60–100 h), where the selectivity of CO and coke increased remarkably at the expense of the decreasing of hydrocarbons selectivity.

3.2. *Characterization of coke deposited on 6Mo/MCM-22 catalyst by TPO and TG techniques*

Because of the importance of coke formation in the dehydroaromatization of methane, researchers have investigated coke deposition on the catalyst (mainly zeolite ZSM-5 as the support), but most of the data were obtained on a catalyst reacted for less than 10 h. In our

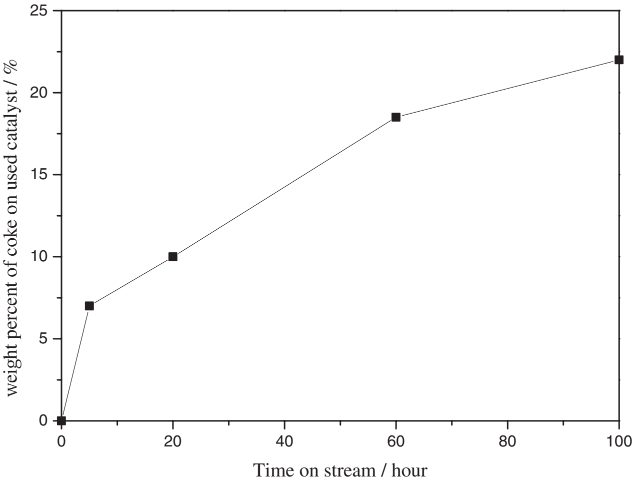

Figure 2. The coke deposition on catalysts reacted for different lengths of time onstream.

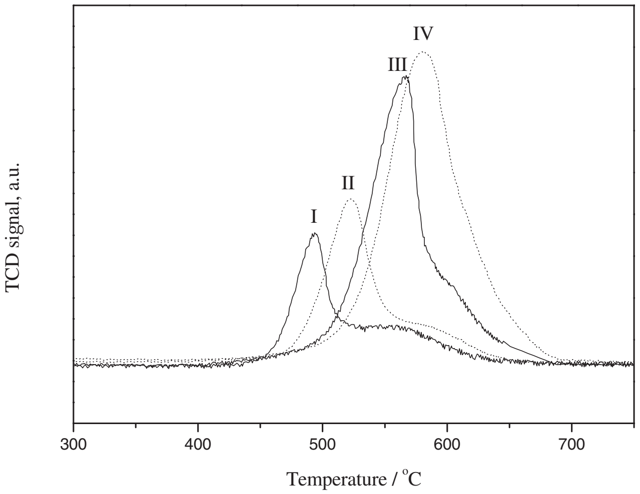

Figure 3. Temperature-programmed oxidation (TPO) of deposited coke on the catalysts reacted for different lengths of time onstream.

work, the character of the coke deposited on 6Mo/MCM-22 with different times onstream from 5 to 100 h in the dehydroaromatization of CH_4 was studied by TPO and TG methods.

Figure 2 shows the TG data of the catalysts reacted for different times onstream. It is reasonable that the coke deposition on catalyst increased with prolonged reaction times. In the first few hours (0–5 h), the increasing rate of coke formation was remarkable, it maybe because, in the induction period, MoO_3 was reduced and carburized by methane to active molybdenum species as Lunsford and Solymosi suggested [13,20–23]. The rate of carbon accumulation (calculated on the amount %wt. of TG/reaction time onstream (hour)) was linear in the time onstream from 5 to 60 h, implying that the reaction was running in a steady state. While during the period of 60–100 h, the amount of coke deposited on catalyst changed to a lower rate due to the deactivation of catalyst.

The TPO experiments were conducted to evaluate the coke deposited on catalysts after being reacted with a mixture of CH_4 and 2% CO_2 for 5 h, 20 h, 60 h, and 100 h, respectively. During the TPO process of coked 6Mo/MCM-22 from 300 to 750 °C, the carbonous materials existed in reacted 6Mo/MCM-22 after the reaction was all oxidized, and the results are shown in figure 3 (TCD signal). Each curve shown in figure 3 can be divided into a sharp peak at low temperature and a broad peak at high temperature. This kind of TPO profile is typical of a bifunctional catalyst, especially of the zeolite-supported metal catalyst reported by Sachtler *et al.* [12], i.e., the first peak is attributed to more reactive coke probably associated with Mo species, and the broad one is irreversible or inert coke associated with acid sites [9]. It is interesting to note that the area of the low-temperature peak of each curve increases more obviously than that of the high-temperature peak as the reaction progresses. Furthermore, the peak area of the low-temperature peak is much larger than that of the high-temperature peak, suggesting that there is more reactive coke than inert coke on reacted catalyst [9].

The peak temperature of each curve is different. The peak temperatures of the low- and high-temperature peaks (deconvoluted by the Gauss curve fitting method, not shown) are denoted as (a,b). The values of curve I, II, III, and IV are (496 °C, 565 °C), (519 °C, 585 °C), (565 °C, 625 °C), and (585 °C, 650 °C), respectively, i.e., the oxidation temperature of the coke deposited on the catalyst shifts to higher values with time onstream.

The MS results (synchronously obtained with a TCD detector) of the representative samples (catalyst reacted for 20 and 100 h, respectively) are shown in figure 4. For the catalyst reacted for 20 h (figure 4(a)), the oxidation products of the low-temperature peak (from the initial to inflexion between two peaks as shown in figure 3) are CO_2, CO, and H_2O, with CO_2 being the dominating oxidation product. However, there is almost no H_2O detected by the MS in the high-temperature peak, and the preferential oxidation product is CO rather than CO_2. As for the catalyst reacted for 100 h (figure 4(b)), the same phenomenon can be observed except that the areas of the oxidation products increased. This suggests that there are two types of coke corresponding to the C/H molar ratio of carbonaceous materials on the used catalyst. One is coke such as CHx ($x > 0$), another is graphitic carbon, which is comprised of almost no hydrogen. Ichikawa *et al.* [9] also reported that after the MDA reaction, the catalyst deposited two types of coke, but they did not report whether the coke contained hydrogen or the product distribution of the coke combustion.

Relating the results of TG and TPO, it seems that the character and accumulation of the coke deposition has a significant influence on the oxidation temperature of the carbonaceous material on the used catalysts, which is of

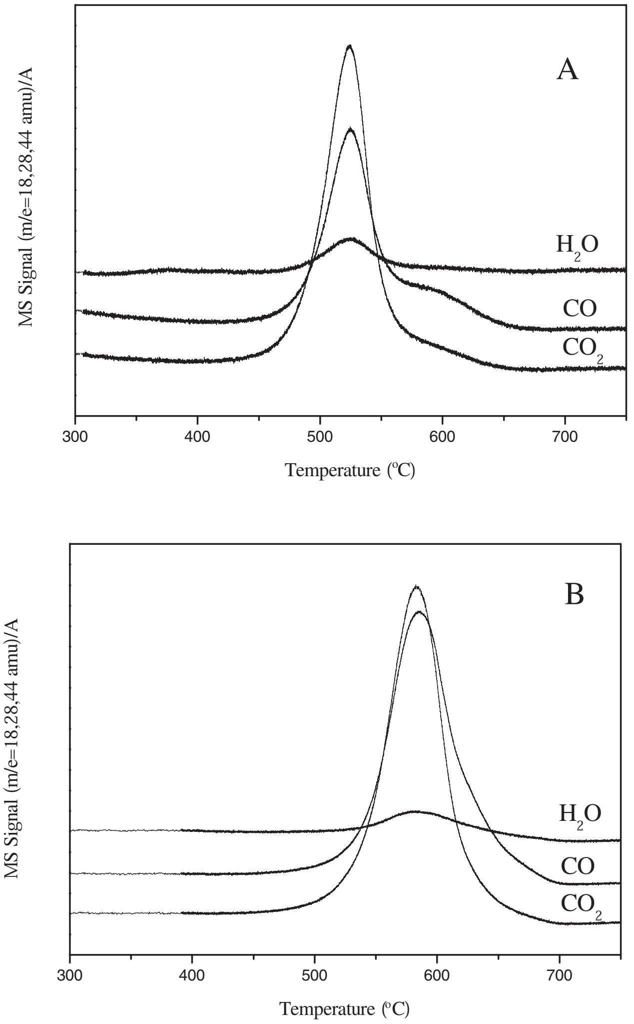

Figure 4. Temperature-programmed oxidation (TPO) of deposited coke on the catalyst reacted for (A) 20 h and (B) 100 h.

importance for the regeneration of deactivated catalysts. In other words, the oxidation temperature of coke shifts to a higher value because of coke accumulation. As for the catalyst reacted for different times on stream, the deposition of coke increased with reaction time, i.e., the blockage of the catalyst became gradually more serious with prolonged time onstream. For the catalysts reacted for 5 and 20 h, the coke deposition was relatively slight, the diameter of channel was large enough for the O_2 molecule to move inside the channel freely to react with coke, thus the oxidation temperature of coke was relatively low. While for the catalysts reacted for 60 and 100 h, the coke deposition was relatively heavy, the diameter of the channel was not as large as the former two catalysts, so the O_2 molecule could not freely move into the channel. The interior coke cannot be oxidized until the outer coke oxidizes completely, resulting in the oxidation temperature of coke being relatively high. The shifting of the oxidation temperature of coke to higher value with time onstream is a result of the accumulation of coke deposits.

3.3. Characterization of reacted 6Mo/MCM-22 catalysts by nitrogen adsorption and benzene-TPD methods

In Section 3.2, the character of coke itself was discussed, but the influence that coke introduced to the catalyst was not covered. The results in the characterization of catalysts taken from the lifetime test after 5, 20, 60, and 100 h are given as follows.

The micropore area and the external surface area determined by the BET method (nitrogen adsorption) of reacted 6Mo/MCM-22 catalysts after different times onstream in methane dehydroaromatization with 2% CO_2 are shown in table 1 and figure 5. The results indicate that during the first stage (0–5 h), coke deposited rapidly as shown in figure 2, the amount of fresh catalyst on the external surface area decreased from 100 to about 90% and the micropore area was significantly reduced to 60%. The rapid decrease in micropore area in comparison to the external surface area, determined by the BET method with N_2 molecule where the shape selectivity is not obvious, is attributed to the complete blockage of a portion of the micropores by coke that will continue until the end of the induction stage. During the steady stage (5–60 h), the internal surface plays an important role in the MDA reaction because of its higher surface area in comparison to the external surface as shown in table 1. In this stage, the micropore area decreased linearly in relation to the amount of carbon deposits while the external surface area decreased very slowly. This result suggests that the dehydroaromatization of methane occurred mainly in the channels. In the deactivation stage (60–100 h), these two areas were both very small, and all reactions slowed down due to the heavy carbonaceous deposits.

In the dehydroaromatization of CH_4 with 2% CO_2, the main product (like benzene) is thought to be formed in the channels with an aperture of 5–6 Å [9], so benzene-TPD was employed to characterize the catalysts before and after certain times onstream. To prevent the cohesion of benzene in the samples, the absorption and the starting desorption temperatures were set at 100 °C. The benzene-TPD profiles are shown in figure 6.

Figure 7 shows the changes in the volume of benzene desorption versus time onstream on the 6Mo/MCM-22 catalyst. The volume of benzene desorption dropped very fast in the first 5 h, i.e., it decreased by almost 74%, while the micropore area determined by N_2 adsorption decreased by only 40%. These results indicate that the benzene adsorption and formation must be limited by the size and structure of the micropores that are changed dynamically by the accumulation of coke deposits. From 60 to 100 h, the volume of benzene desorption decreased from about 10% to almost zero, and then the selectivity for benzene sharply decreased because of the blockage of the pores.

Table 1
The BET data of fresh 6Mo/MCM-22 and reacted catalysts for 5, 20, 60, and 100 h, respectively

Catalyst	Data of BET surface area (m^2/g)	Micropore area (m^2/g)	External surface area (m^2/g)	Maximum pore volume (cm^3/g)
6Mo/MCM-22	362.2	280.3	81.8	0.1535
6Mo/MCM-22-5	243.0	167.5	75.5	0.09885
6Mo/MCM-22-20	193.4	146.4	47.0	0.08238
6Mo/MCM-22-60	95.9	56.2	39.8	0.03835
6Mo/MCM-22-100	65.4	29.3	36.1	0.02455

Note: BET surface area = micropore area + external surface area; BET data was obtained by *t*-Plot method; maximum pore volume and median pore diameter data was obtained by Horvath–Kawazoe method considering the pore with diameter less than 17 Å.

4. Discussion

Shape selectivity is always an interesting topic in heterogeneous catalysis, especially for zeolite-based catalysts used in the laboratory and industry. Lin *et al.* [24] studied the reaction performance of Mo catalysts supported on different zeolites and postulated that a proper size of 5–6 Å (the size of a benzene molecule) is an important factor to produce benzene from methane by dehydroaromatization.

Until now, the two effective catalysts reported in the MDA process were Mo/MCM-22 and Mo/ZSM-5, and the specialty of these two catalysts is the structure of the support. The thoroughly studied zeolite, ZSM-5 [25], contains a zigzag channel system (5.3 × 5.6 Å) intersecting a straight 10-ring channel (5.1 × 5.7 Å) to produce the three-dimensional system. As for the newly manufactured zeolite MCM-22 [26], it crystallizes in thin sheets or platelets and its framework topology is comprised of two independent pore systems which are accessible through 10-membered rings. One of these pore systems is defined by two-dimensional sinusoidal channels, which maintain an effective 10-ring diameter throughout the structure while the other consists of large supercages whose inner free diameter, 7.1 Å, is defined by 12 rings with an inner height of 18.2 Å. This indicates that the pore aperture of these two catalysts is equal to or slightly larger than the size of benzene, so they both show good catalytic performance in the MDA process compared to other zeolites that suggested the importance of shape selectivity in the formation of benzene.

Relating the results of TG, TPO, Benzene-TPD, BET and the catalytic performance of Mo/MCM-22 in the 100-h lifetime test, it can be suggested that the shape selectivity of the catalyst is dynamic in the MDA process. With the accumulation of coke, the diameter of the pores becomes smaller and smaller, and the transportation of benzene becomes more and more difficult. However, the formation of benzene can run

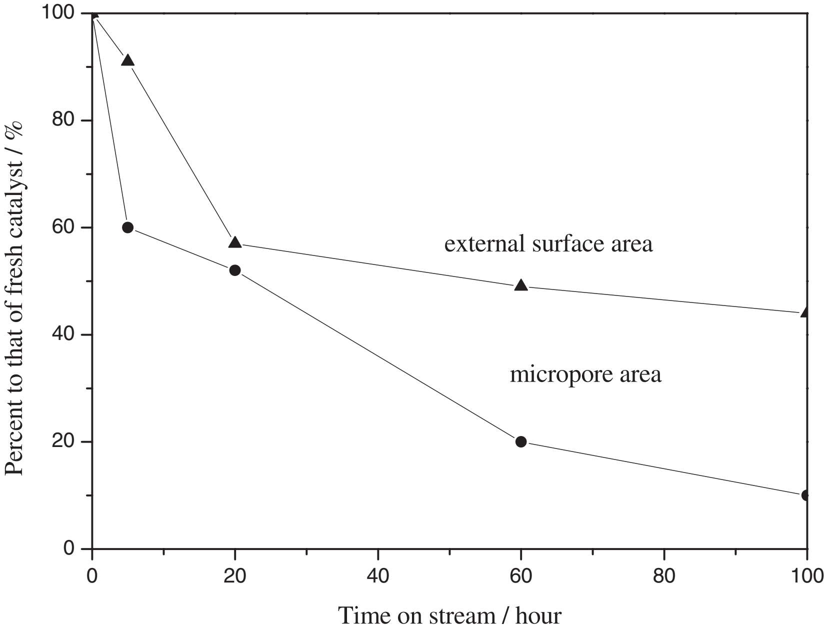

Figure 5. Changes in the BET data of catalysts reacted for 5, 20, 60, and 100 h, respectively, compared with a fresh one.

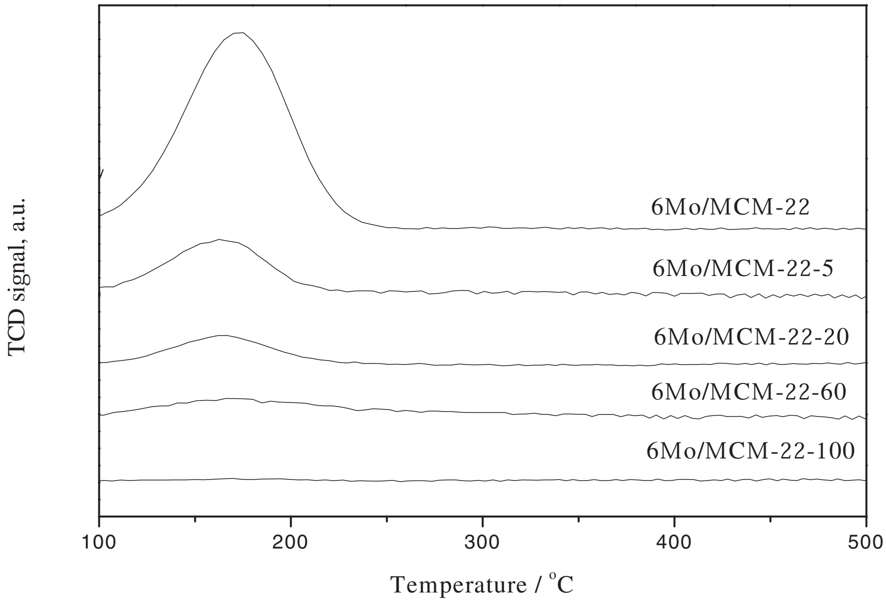

Figure 6. Temperature-programmed desorption (TPD) of benzene on catalysts reacted for 0, 5, 20, 60, and 100 h.

smoothly if the aperture of the pore is large enough to let benzene continually exit the aperture, i.e., the shape selectivity of the catalyst was still effective in the production of benzene even when the pore size was smaller than the fresh catalyst at that time. When the pore was seriously blocked by coke, while benzene could not exit the aperture freely, the shape selectivity of the catalyst was gradually lost due to coke accumulation. This indicates that there is a critical value for coke capacity considering the shape selectivity for benzene during the lifetime test. This critical value may be located at the point where the selectivity for benzene in methane conversion begins to decrease. For the Mo/MCM-22 catalyst, the selectivity of benzene in methane conversion decreased at about 60 h onstream (as shown in figure 2). The coke deposits were determined to be 17 wt% at this point. It is apparent that the critical point of coke capacity of Mo/MCM-22 is this value.

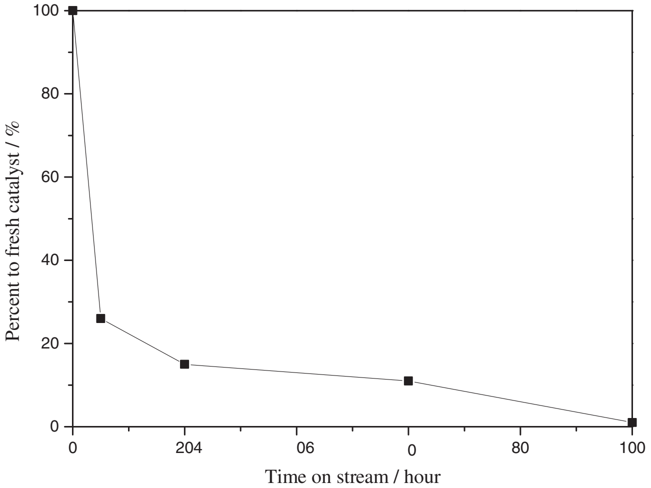

Figure 7. The area percent of benzene-TPD (TCD signal) of the used catalyst to a fresh one.

Considering the above discussion, it can be seen that the duration of the regeneration cycle of a catalyst used in the MDA process is determined by two factors. The first is the rate of coke accumulation, and the other is the coke's capacity to maintain the shape selectivity. In order to get a long life out of the catalyst in the production of benzene from methane, one method is to optimize the reaction conditions and modify the existing catalysts to decrease the rate of coke deposition, and the other method is to develop new types of supports that have bigger coke capacities.

5. Conclusion

During the MDA process, the shape selectivity of the catalyst is a dynamic process due to coke accumulation. Structural differences in the catalyst exhibit different effects on the coke capacity, so the life of a catalyst is determined by both coking rate and coke capacity.

References

[1] L.S. Wang, L.X. Tao, M.S. Xie, G. Xu, J.S. Huang and Y.D. Xu, Catal. Lett. 21 (1993) 35.
[2] L.Y. Chen, L.W. Lin, Z.S. Xu, X.S. Li and T. Zhang, J. Catal. 157 (1995) 190.
[3] L.Y. Chen, L.W. Lin, Z.S. Xu, T. Zhang and D.B. Liang, Catal. Lett. 35 (1995) 245.
[4] Y.D. Xu, S.T. Liu, L.S. Wang, M.S. Xie and X.X. Guo, Catal. Lett. 30 (1995) 135.
[5] F. Solymosi, A. Szoke and J. Cserényi, Catal. Lett. 39 (1996) 157.
[6] S.T. Wong, Y.D. Xu, L.S. Wang, S.T. Liu, G.J. Li, M.S. Xie and X.X. Guo, Catal. Lett. 38 (1996) 39.

[7] Y.D. Xu, Y.Y. Shu, S.T. Liu, J.S. Huang and X.X. Guo, Catal. Lett. 35 (1995) 233.

[8] Y.Y. Shu, D. Ma, L.Y. Xu, Y.D. Xu and X.H. Bao, Catal. Lett. 70 (2000) 67.

[9] R. Ohnishi, S.T. Liu, D. Dong, L.S. Wang and M. Ichikawa, J. Catal. 182 (1999) 92.

[10] R.W. Borry III, Y.-H. Kim, A. Hunffdmith, J.A. Renmer and E. Iglesia, J. Phys. Chem. B 103 (1999) 5787.

[11] W. Li, G.D. Meitzner, R.W. Borry III and E. Iglesia, J. Catal. 191 (2000) 373.

[12] B.A. Lerner, Z.C. Zhang and W.M.H. Sachtler, J. Chem. Soc., Faraday Trans. 89 (1993) 1799.

[13] F. Solymosi, A. Erdohelyi and A. Szöke, Catal. Lett. 32 (1995) 43.

[14] H.M. Liu, L.L. Su, H.X. Wang, W.J. Shen, X.H. Bao and Y.D. Xu, Appl. Catal., A: Gen. 236 (2002) 263.

[15] S.J. Xie, Q.X. Wang, L.Y. Xu, W. Chen, J. Bai and L.W. Lin, Chin. J. Catal. 6 (1999) 583.

[16] M.K. Rubin and P. Chu, U.S. Patent 4,954,325 (1990) to Mobil Oil Corporation.

[17] Y. Lu, Z.S. Xu, L.W. Lin, L.F. Zang, Y.M. Gao, Z.J Tian and T. Zhang, Chin. J. Catal. 3 (1999) 273.

[18] S.D. Yuan, C. Li, Z.X. Hao, Z.C. Feng and Q. Xin, Catal. Lett. 63 (1999) 73.

[19] S. Li, C.L. Zhang, Q.B. Kan, D.Y. Wang and T.H. Wu, Appl. Catal. A 187 (1999) 199.

[20] D.J. Wang, J.H. Lunsford and M.P. Rosynek, Top. Catal. 3 (1996) 289.

[21] D.J. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.

[22] F. Solymosi, J. Cserényi, A. Szöke, T. Bánsági and A. Oszkó, J. Catal. 165 (1997) 150.

[23] F. Solymosi, A. Szöke and J. Cserényi, Catal. Lett. 39 (1996) 157.

[24] C.L. Zhang, S. Li, Y. Yuan, W.X. Zhang, T.H. Wu and L.W. Lin, Catal. Lett. 56 (1998) 207.

[25] E.G. Derouane and Z. Gabelica, J. Catal. 65 (1980) 486.

[26] G.J. Kennedy, S.L. Lawton, A.S. Fung, M.K. Rubin and S. Steuernagel, Catal. Today. 49 (1999) 385.