Journal of Catalysis **206,** 134–142 (2002)
doi:10.1006/jcat.2001.3481, available online at http://www.idealibrary.com on IDEAL®

Pressurized Dehydrocondensation of Methane toward Benzene and Naphthalene on Mo/HZSM-5 Catalyst: Optimization of Reaction Parameters and Promotion by CO_2 Addition

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Received September 10, 2001; revised November 21, 2001; accepted November 21, 2001; published online January 14, 2002

The rate of benzene formation with time on stream is remarkably stabilized under pressurized condition in the dehydrocondensation reaction of methane. Under a methane pressure of more than 0.2 MPa and a suitable CO_2 concentration in methane feed, the high activity and stability were achieved at elevated reaction temperatures of more than 1023 K and methane space velocities of more than 5400 ml/(g · h) due to minimized coke formation on the Mo/HZSM-5 catalyst. A high and stable benzene formation rate of 4000 nmol/(g-cat · s) was obtained on the 6% Mo/HZSM-5 catalyst under the optimized reaction conditions, e.g., 1073 K, 0.3 MPa, and 7200 ml/(g · h), and with 5% CO_2 addition. A temperature-programmed oxidation study demonstrated that both addition of CO_2 to the methane feed and increasing of the methane pressure greatly suppressed the deposition of coke on the Mo/HZSM-5 catalyst. Moreover, the H/C ratio of the coke on the catalyst increased due to CO_2 addition and methane pressure increment, implying that the surface carbon had relatively high hydrogen content at the prevailing reaction conditions. It suggests that the added CO_2 reacted with coke before its transformation to inactive graphitic carbon blocking the microporous channels of HZSM-5 zeolite, which is more detrimental for methane dehydrocondensation reaction. © 2002 Elsevier Science (USA)

Key Words: **dehydrocondensation of methane; pressurized condition; CO_2 addition; reaction parameters; Mo/HZSM-5 catalyst; coke; temperature-programmed oxidation.**

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1. INTRODUCTION

The catalytic dehydroaromatization of methane to petrochemical feedstocks such as benzene and naphthalene is of current importance and industrial interest in conjunction with the effective utilization of natural gas (1). Since the earliest report on aromatic compound formation in the dehydroaromatization of methane over Mo/HZSM-5 by Wang *et al.* (2), Solymosi *et al.* (3–5) studied benzene formation on Mo-supported catalysts using different Mo precursors and oxide supports. Lunsford and coworkers (6, 7) and Ichikawa and coworkers (8) analyzed the production of naphthalene and online calculated coke formation by using internal standards of N_2 and Ar, respectively. Ichikawa and coworkers (9) also made a complete analysis of all the condensable products and lower C_2–C_5 hydrocarbons in the effluent gas. Lunsford and coworkers (6) and Solymosi *et al.* (4, 5) found that there is an induction period during which the MoO_3 is reduced by methane and suggested that the formed Mo_2C is possibly responsible for the methane aromatization. Ichikawa and coworkers (10, 11) confirmed the formation of Mo_2C using the extended X-ray absorption fine structure technique and coupling with thermogravimetric analysis/differential thermal analysis/magic-angle sample spinning. More recently, Iglesia and coworkers (12–14) found that the reduction and carburization of $(Mo_2O_5)^{2+}$ species on Mo/HZSM-5 during CH_4 reaction are responsible for the formation of MoC_x particles and the concurrent regeneration of the bridging OH groups initially displaced by the Mo oxo dimers during catalyst exchange.

Although a lot of research work has been conducted, some problems remain to be solved concerning this reaction, not only from the standpoint of academic research, but also from the need of potential industrial utilization of natural gas. The formation of serious carbonaceous deposits in methane dehydrocondensation is one of the major obstacles in its development. However, only a few studies on the suppression of coke by means of adding some second metals (8, 15) and of weakening the acidity of HZSM-5 (16) on Mo/HZSM-5 catalyst have been reported. Recently, Ichikawa and coworkers demonstrated that the addition of a few percent CO and CO_2 to the methane feed over Mo/HZSM-5 (17) and Re/HZSM-5 (18, 19) at 973 K resulted in a remarkable enhancement of the catalyst stability owing to the efficient suppression of coke formation. Therefore, it is relevant to further this study in order to achieve methane conversions of greater than 20% toward benzene and naphthalene, together with stable catalytic performances suitable for potential industrial applications. On the other hand, in most of the previous

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0021-9517/02 $35.00

studies the methane aromatization reaction proceeded at 1-atm methane pressure, with narrow variations in the reaction temperature around 973 K and in the methane space velocity around 1440 ml/(g · h). Accordingly, it is necessary to investigate methane dehydrocondensation by applying a wide range of methane pressure and optimizing other reaction parameters, such as temperature, space velocity, and CO_2 concentration. Moreover, the effective regeneration of the coked catalyst by O_2 and H_2 was studied. After the reaction at various reaction conditions, catalysts were investigated by temperature-programmed oxidation (TPO) to examine the nature of the coke.

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

The Mo/HZSM-5 catalysts were prepared by the wet impregnation technique from NH_4ZSM-5 zeolite ($SiO_2/Al_2O_3 = 40$, gifted by Tosoh Co., Japan) with aqueous solutions of ammonium heptamolybdate (Kanto Chem. Co., Japan, analytical grade). The impregnated catalysts were first dried at 343 K, then heated up to 393 K, and finally calcined at 773 K for 5 h, as described in previous studies (20, 21). Thereafter, the Mo/HZSM-5 catalysts were denoted as x% Mo/HZSM-5, where x is the Mo content in weight percent.

2.2. *Reaction Test and Catalyst Regeneration*

The reaction was carried out in a fixed-bed continuous-flow system at 973–1073 K, at feed flow rates of 7.5–50 ml/min, and under pressures of 0.028–0.5 MPa, with or without CO_2 addition. Briefly, 0.3 g of the catalyst was charged into a 6-mm I.D. quartz tubular reactor. The catalyst was first heated under a He stream (15 ml/min) to 873 K and maintained at 873 K for 30 min, and then a 10% Ar/CH_4 gas mixture as the feed was introduced and the temperature was increased to the reaction temperature. The effluent gases were analyzed with two gas chromatographs. Hydrocarbon products including C_2 and condensable C_6–C_{12} aromatics such as benzene, toluene, xylene, and naphthalene were analyzed with an online FID gas chromatograph using a six-way sampling valve heated at 533 K on a Porapak-P column, while H_2, Ar, CO, CH_4, and CO_2 were analyzed with an online thermal conductivity detector (TCD) GC on an activated carbon column, similarly to that reported elsewhere (17–19). By using 10% Ar as an internal standard, methane conversion, selectivity of hydrocarbon products, and coke formation were evaluated according to the carbon mass balance. All reaction rates were based on the carbon base and expressed in nanomoles per gram of catalyst per second.

The used catalyst was regenerated in O_2 and H_2 streams at the conditions described below. Briefly, the regeneration was conducted separately at 823 and 1123 K, both at a flow rate of 20 ml/min. The regenerated catalyst was used for the reaction as described.

2.3. *Temperature-Programmed Oxidation and Pulse Calibration Experiment*

The temperature-programmed oxidation (TPO) study was conducted on an AMI1 (Altamira Co.) instrument. In a typical TPO experiment, 15 ml/min of 10% O_2/He was fed into the sample cell under ambient conditions. Just after the sample cell, a U-shaped trap cooled at liquid nitrogen was placed to remove the oxidized products, such as CO_2 and H_2O. The temperature was increased linearly at 10 K/min from ambient temperature to 1023 K, at which all carbonaceous deposits were completely oxidized. After the complete oxidation of all carbonaceous deposits, the CO_2 and H_2O caught in the trap were liberated separately by a slow increase in the trap temperature. All these signals were monitored with the TCD. The absolute sensitivity factor of oxygen and water were determined from pulse injection of a set amount of oxygen and water into the detector. All the gases were UHP grade and used without further purification. The hydrogen to carbon ratio (H/C) and the moles of the coke were calculated from the amounts of oxygen and H_2O, on the assumption that the coke can be formulated as CH_h and the reaction of the coke with oxygen takes place according to the following equation:

$$CH_h + (1 + h/4)O_2 \rightarrow CO_2 + h/2H_2O.$$

Then, the moles of water formed is equal to (moles of coke) × (h/2) and the moles of oxygen consumed is (moles of coke) × $(1 + h/4)$. From these equations, the ratio of H/C (h) and moles of coke can be calculated.

2.4. *BET and XRD Measurements*

Surface areas of the samples were obtained using the BET method based on adsorption isotherms at liquid nitrogen temperature, and using a value of 0.162 nm^2 for the cross-sectional area of the N_2 molecule. The measurements were performed with OMNISORP 100CX (Beckman Coulter Co.) equipment and the data were processed and analyzed by a computer.

X-ray diffraction (XRD) patterns were obtained on an MPX3 X-ray diffractometer (Mac Sci. Ltd.) using Cu $K\alpha$ radiation at room temperature and instrumental settings of 40 kV and 100 mA. The powder diffractograms of the various samples were recorded from 5 to 50° with a scanning rate of 5°/min. All XRD patterns were recorded, stored, and processed by a computer system.

3. RESULTS AND DISCUSSION

3.1. Effect of Pressure on the Methane Dehydrocondensation Reaction

The benzene formation rate with time on stream at 973 K and 1350 ml/(g · h) without CO_2 addition on 6% Mo/HZSM-5 catalyst and with varying methane pressure is shown in Fig. 1. At lower pressures of 0.028 and 0.1 MPa, the benzene formation rates declined abruptly with time on stream, possibly due to the poisoning of the catalyst by coke, although the initial rates of benzene formation increased with a decrease in partial pressure of methane. At pressures greater than 0.2 MPa, the benzene formation rates decreased at the initial stage, then reached stable values. However, at relatively high pressures, exceeding 0.5 MPa, the formation rate was relatively suppressed, although a stable rate of benzene formation was obtained. It was found that a stable and high rate of benzene formation was achieved with an optimum methane pressure of around 0.3 MPa.

Further improvement of the catalyst stability with the increase in methane pressure was observed with the presence of CO_2 in the methane feed, as shown in Fig. 2a. Optimum methane pressure was also found to be 0.3 MPa, similar to the case without CO_2 addition. On the other hand, the methane conversion, selectivity of coke, and formation rates of benzene and naphthalene decreased with an increase in methane pressure from 0.1 to 0.4 MPa, as shown in Fig. 2b. The maximum methane conversion of 20% was obtained on Mo/HZSM-5 at 0.1 MPa of methane pressure. The main transformation reactions of methane toward benzene, naphthalene, and coke are represented as $6CH_4 = C_6H_6 + 9H_2$, $10CH_4 = C_{10}H_{10} + 15H_2$, and $CH_4 = C + 2H_2$, respectively, as depicted in Scheme 1. It is obvious that all of these reactions can be classified as molecule-increasing reactions. Then, the results of Fig. 2b can be easily understood from Le Chatelier–Braun's law, that the reactions forming benzene, naphthalene, and coke from methane will shift to the reactant (methane) side, but not to the product side, when the reaction pressure increases. Meanwhile, the improvement in the stability of benzene formation with the increase in the reaction pressure can be explained from the reaction orders to the total pressure, 1.5 for benzene formation and 2 for coke formation. Therefore, at higher pressures, less coke formation on the catalyst and better catalytic stability can be expected.

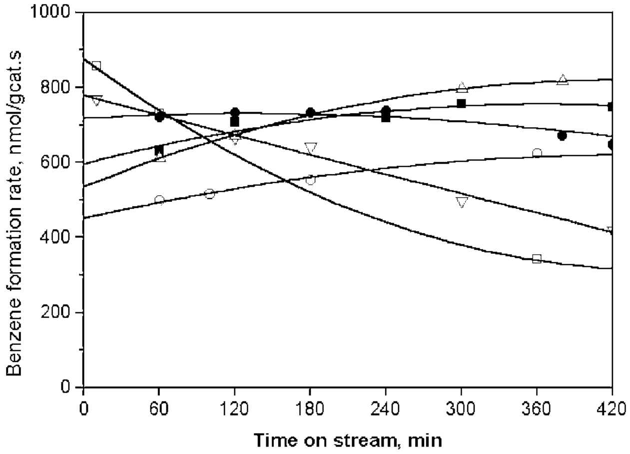


FIG. 1. Changes in benzene formation rate on 6% Mo/HZSM-5 catalyst in methane dehydrocondensation with variations in methane pressure from 0.028 to 0.5 MPa at 973 K and 1350 ml/(g · h) without CO_2 addition; □, ▽, ●, ■, △, and ○ for 0.028, 0.05, 0.1, 0.2, 0.3, and 0.5 MPa, respectively.

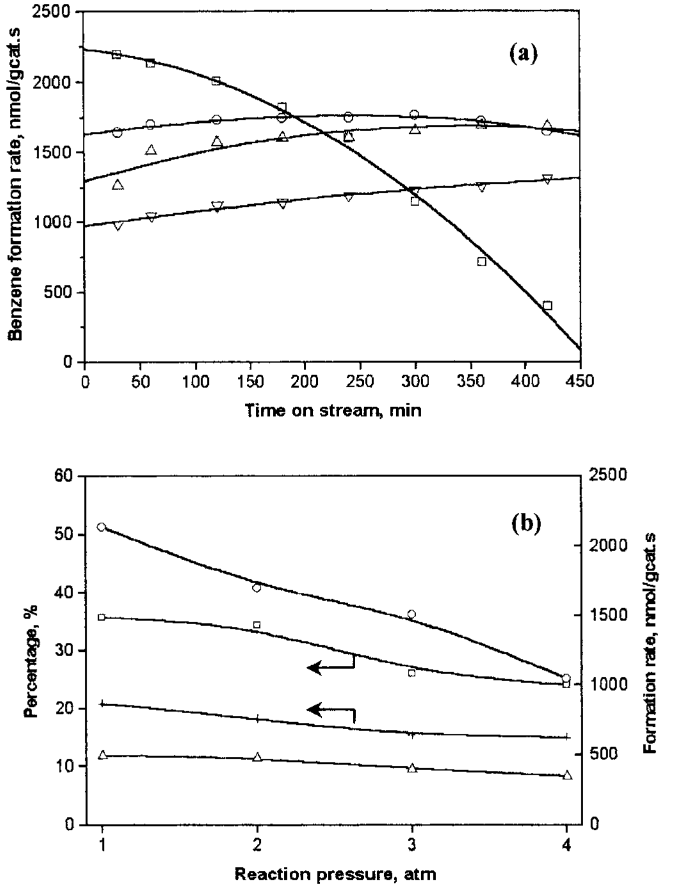
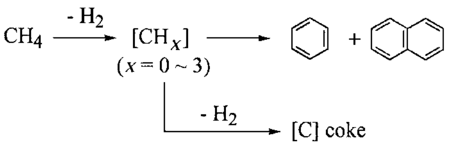


FIG. 2. (a) Effect of methane pressure on benzene formation rate at 1073 K and 2700 ml/(g · h) with 5% CO_2 addition; □, ○, △, and ▽ for 0.1, 0.2, 0.3, and 0.4 MPa, respectively. (b) Effect of pressure on methane conversion (+), coke selectivity (□), and formation rate of benzene (○) and naphthalene (△) on 6% Mo/HZSM-5 catalyst after 60 min time on stream.



SCHEME 1

3.2. Optimizing of Other Reaction Parameters

3.2.1. Reaction temperature. It has been known from thermodynamic consideration that a high reaction temperature is favorable for the methane dehydrocondensation reaction. However, it is difficult to realize stable and high methane conversion at reaction temperatures higher than 1023 K because of serious coke deposition on the catalyst. Table 1 lists the catalytic performance of the 6% Mo/HZSM-5 catalyst at different reaction temperatures. As seen, the initial rate of benzene formation increased from 1000 to 1990 nmol/(g-cat · s) when increasing the reaction temperature from 973 to 1073 K. However, higher reaction temperatures brought about a faster decrease in the catalytic activity due to serious coke deposition. Specifically, at 1073 K, the benzene formation rate declined from 1990 nmol/(g-cat · s) to zero only after 180 min of time on stream.

To get stable catalytic activity, CO_2 was added to the methane feed. It was reported by Ichikawa and coworkers that stable catalytic activity was realized at 973 K, 0.1 MPa, and 1350 ml/(g · h) when 2–3% CO_2 was added to the methane feed (10, 17). Figure 3 shows the time course of benzene formation rates at various reaction temperatures with 2700 ml/(g · h), 0.3 MPa, and 3% CO_2 addition. The initial formation rate of benzene increased from 500 to 1500 nmol/(g-cat · s) when the reaction temperature increased from 973 to 1073 K. Notably, the benzene formation rate was stable during the prolonged reaction time. In particular, at reaction temperatures between 973 and 1048 K, no change in the rate was observed with time on stream. When the reaction temperature was further increased to 1073 K, the benzene formation rate declined at the prolonged reaction time. This implies that the addition of 3% CO_2 to the methane feed may not be enough for the suppression of coke formation at a reaction temperature as high as 1073 K and more CO_2 may be needed. The benzene formation rate at 1073 K, 0.3 MPa, and 2700 ml/(g · h) as a function of CO_2 concentration is depicted in Fig. 4. It is clear that the CO_2 concentration in the reactant gas exerted great influence on the catalytic performance. A higher initial rate of benzene formation was obtained at lower CO_2 percentages in the methane feed. However, the benzene formation rate decreased dramatically without CO_2 and mildly with lower CO_2 addition. Considering both the activity and stability of the catalyst, 5% CO_2 is the optimum concentration for reaction at 1073 K, 0.3 MPa, and 2700 ml/(g · h).

TABLE 1

Effect of Reaction Temperature on Catalytic Performance of 6% Mo/HZSM-5 in Methane Dehydrocondensation Reactions without CO_2 Addition[a]

Reaction temp. (K)	Conv. of methane (%)	Rate of product formation (nmol/(g-cat · s))[b]			
		C_2	Ben	Naph	Coke
973	7.1 (6.5)	120 (150)	1000 (910)	300 (250)	850 (770)
1023	12.2 (10.2)	140 (210)	1350 (920)	430 (130)	2040 (1080)
1073	16.9 (7.2)[c]	180 (80)[c]	1990 (0)[c]	600 (0)[c]	2800 (2290)[c]

[a] Catalyst amount, 0.3 g; methane space velocity, 2700 ml/(g · h); reaction pressure, 0.3 MPa; reaction time, 60 (420) min.

[b] C_2, ethane + ethylene; Ben, benzene; Naph, naphthalene.

[c] Reaction time, 60 (180) min.

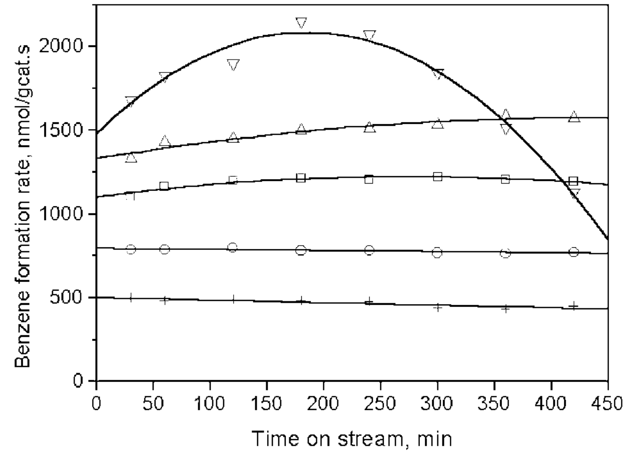


FIG. 3. Changes in benzene formation rate on 6% Mo/HZSM-5 catalyst in methane dehydrocondensation with variations in reaction temperature at 0.3 MPa and 2700 ml/(g · h) with 3% CO_2 addition; +, ○, □, △, and ▽ for 973, 998, 1023, 1048, and 1073 K, respectively.

3.2.2. Methane space velocity. Figure 5a shows the effect of methane space velocity on benzene formation rate at 1073 K, 0.3 MPa, and 3% CO_2 in methane flow. The initial rate of benzene formation increased linearly with an increase in methane space velocity from 1350 to 9000 ml/(g · h), although the last two points deviate a little from the linear line. However, the benzene formation rate declined

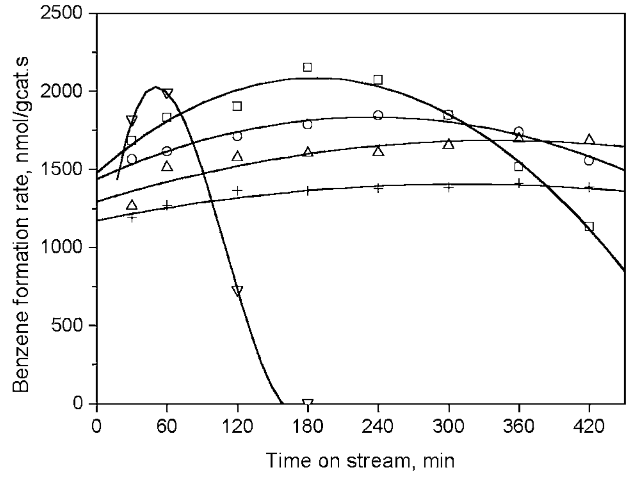


FIG. 4. Effect of CO_2 concentration on benzene formation rate on 6% Mo/HZSM-5 catalyst at 1073 K, 0.3 MPa, and 2700 ml/(g · h); ▽, □, ○, △, and + for 0, 3, 4, 5, and 6% CO_2, respectively.

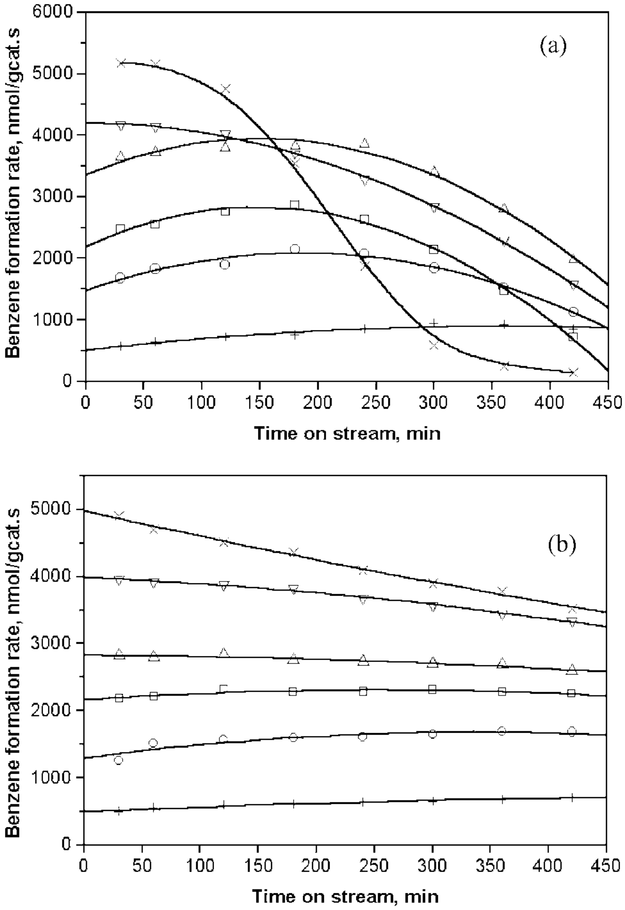


FIG. 5. Changes in benzene formation rate on 6% Mo/HZSM-5 catalyst in methane dehydrocondensation with variations in space velocity at 1073 K and 0.3 MPa with 3% CO_2 (a) and 5% CO_2 (b); +, ○, □, △, ▽, and × for 1350, 2700, 4050, 5400, 7200, and 9000 ml/(g · h), respectively.

with time on stream except in the case of 1350 ml/(g · h). Especially, the rate decreased drastically at a 9000 ml/(g · h) methane space velocity. To ease the decrease in activity with reaction time, the concentration of CO_2 added to the methane feed was increased to 5%. The results are shown in Fig. 5b. As seen, the stability of the catalyst improved greatly. A stable and high benzene formation rate of 4000 nmol/(g-cat · s) was achieved on the 6% Mo/HZSM-5 catalyst at 0.3 MPa, 1073 K, 7200 ml/(g · h), and 5% CO_2 addition.

3.3. Coke Characterization by Temperature-Programmed Oxidation Reaction

3.3.1. TPO spectra of the various Mo/HZSM-5 samples. Figure 6A shows the TPO spectra of the HZSM-5 samples loaded with Mo of 2, 6, and 10% and reacted at 0.3 MPa, 1073 K, and 2700 ml/(g · h) without CO_2 addition. It is apparent from the figure that two peaks were observed which were burned off at 860 and 900 K. With the increase in Mo loading, peak heights that appeared at the high temperature did not change while the ones at the low temperature increased. This implies that the peak that appeared at low temperature may come from the coke that is associated with the Mo species. According to TPO measurements by Iglesia and coworkers (14), the peak at the low temperature was assigned to a carbonaceous species within zeolite channels near the Mo species and the peak at the high temperature to a carbonaceous deposit distant from these Mo species. Referring to a study reported by Xu and coworkers (22), the peak at the high temperature can be assigned to a kind of coke which is related to the Brønsted acidic sites of the zeolite support. Similar trends in TPO profiles were also observed on the samples coked under methane plus 3% CO_2, as shown in Fig. 6B. However, the peak intensities of the coked samples decreased sharply while the TPO peak shifted downward to a lower temperature. This means that the coke formed in the case of methane plus CO_2 has different characteristics from that formed in pure methane feed.

3.3.2. Effect of reaction parameters on coke formation. Figure 7 shows the TPO spectra of the Mo/HZSM-5 samples coked at different methane pressures. As presented, two

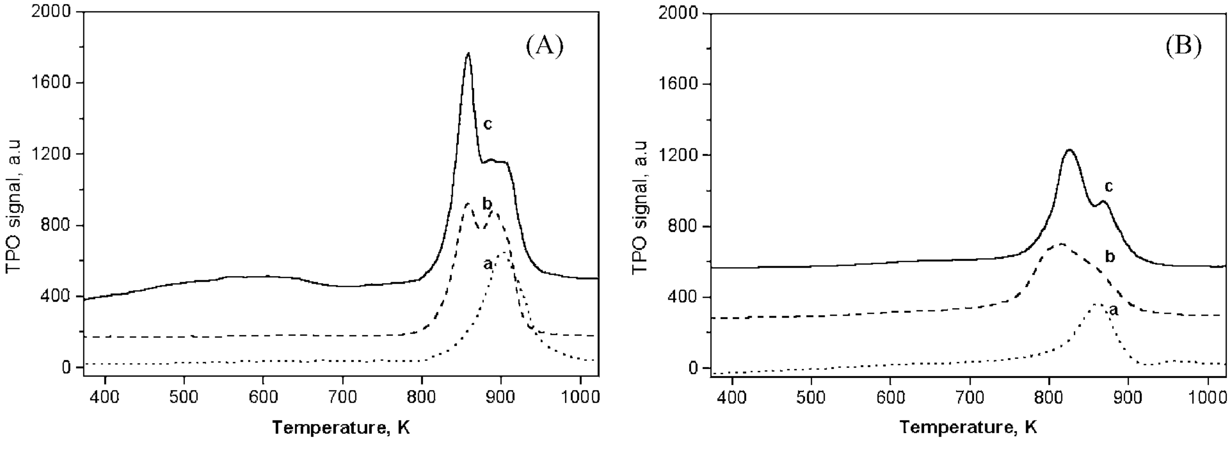


FIG. 6. TPO profiles of the 2 (a), 6 (b), and 10% (c) Mo-loaded HZSM-5 catalysts reacted at 1073 K, 0.3 MPa, and 2700 ml/(g · h) for 7 h without CO_2 (A) and with 3% CO_2 addition (B). Base lines were shifted for the sake of clarity.

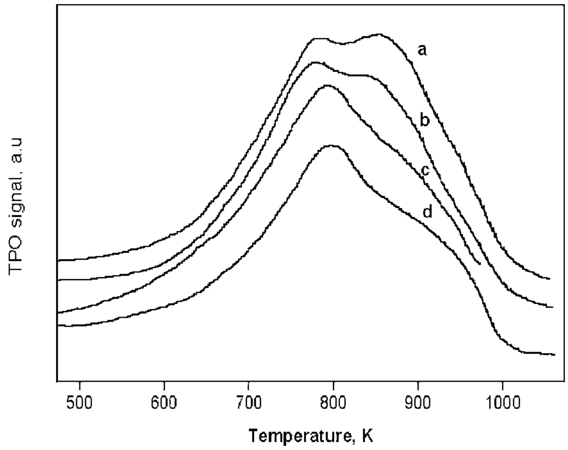


FIG. 7. TPO profiles of the 6% Mo/HZSM-5 samples reacted under various pressurized conditions in methane dehydrocondensation at 973 K and 1350 ml/(g · h) for 7 h. (a) 0.028, (b) 0.05, (c) 0.2, and (d) 0.4 MPa.

distinct coke species corresponding to different oxidation temperatures were identified. With an increase in methane pressure from 0.028 to 0.2 MPa, the peak height at the high temperature decreased greatly and was less pronounced, demonstrating that high pressure in methane aromatization is unfavorable for formation of coke deposits on acid sites. On the other hand, the coke species, which is associated with the Mo species, changed slightly with an increase in the methane pressure. The TPO results, which confirmed a notable improvement in catalyst stability under pressurized conditions in methane dehydrocondensation, were really due to the efficient suppression of coke formation, particularly to the effective reduction of coke deposited on the acid sites of the zeolite support.

Figure 8A shows the TPO spectra of the 6% Mo/HZSM-5 reacted at 973, 1023, and 1073 K. The peak intensity increased almost three times and peak temperature moved ca. 90 K to the higher temperature with the increase in reaction temperature from 973 to 1073 K. This is probably due to the difference in coke characteristics and/or the amount of coke formed at different reaction temperatures. Querini and Fung (23) discussed shifts in peak temperature in relation to the amount of coke formed on the surface. The similar trend of an increase in peak intensity with an increase in reaction temperature was also detected when 3% CO_2 was added to the methane feed, as shown in Fig. 8B. On the other hand, with the addition of CO_2, the peak intensities of the coke decreased sharply, especially at the high temperature. In addition, the TPO peak shifted ca. 70 K to the lower temperature. This again demonstrated the obvious suppression of the coke formation with CO_2 addition in the feed, as previously reported (17).

The TPO data of the 6% Mo/HZSM-5 samples coked at various reaction conditions are summarized in Table 2. It is clear that various reaction conditions, such as reaction temperature (Reac. temp.), the percentage of CO_2 added to the methane feed, total pressure (P), and methane space velocity (SV), all exerted notable influence on the TPO results. The reaction temperature affects the TPO results obviously, as can be seen in entries 1–3, in the case of methane, and as seen in entries 4–6, in the case of methane plus CO_2. The H/C ratios of the samples decreased with the increase in reaction temperature, indicating a loss of hydrogen in the coke at high reaction temperatures. The change in the H/C ratio under pure methane feed was larger (0.37–0.12) than that under methane with 3% CO_2 (0.42–0.36). Furthermore, the hydrogen content in the coke increased with CO_2 addition. The effect of CO_2 on hydrogen content in the coke became more evident with variations in the percentage added, as can be seen in entries 3 and 6–8. The H/C ratio of the coke increased from 0.12 to 0.48 with an increase in percentage of CO_2 from 0 to 6%. All

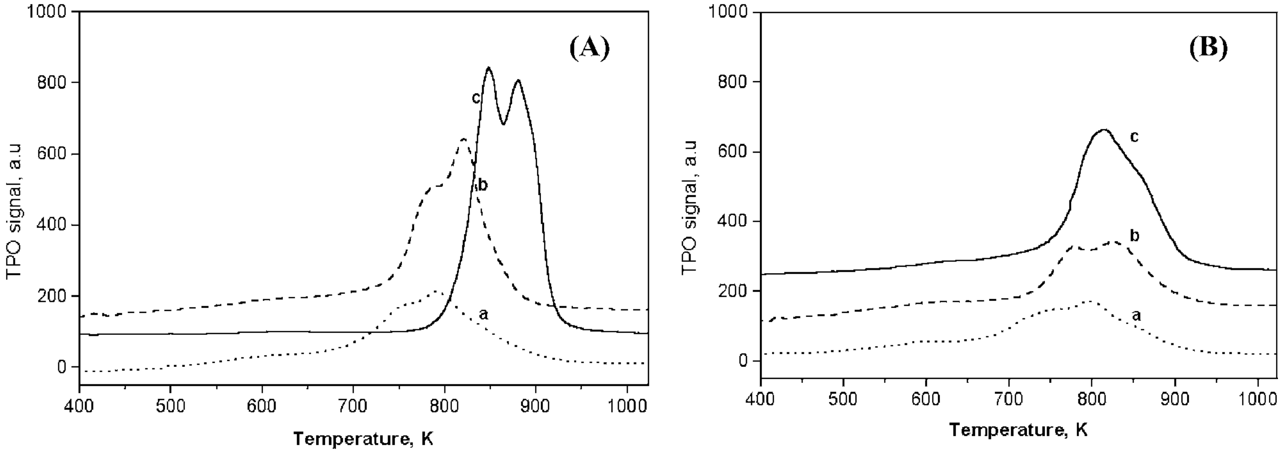


FIG. 8. TPO profiles of the 6% Mo/HZSM-5 samples reacted at 973 (a), 1023 (b), and 1073 K (c) for 7 h without CO_2 (A) and with 3% CO_2 addition (B). Base lines were shifted for the sake of clarity.

TABLE 2

Numerical Results of TPO Experiments on the 6% Mo/HZSM-5 Samples Reacted under Various Conditions[a]

Entry	Reac. temp. (K)	CO_2 (%)	SV (ml/(g · h))	P (MPa)	O_2 area (a.u)	H_2O area (a.u.)	Coke (mol/g-cat)	H/C
1	973	0	2700	0.3	13240	2280	0.00139	0.37
2	1023	0	2700	0.3	21000	2930	0.00224	0.30
3	1073	0	2700	0.3	35850	2088	0.00400	0.12
4	973	3	2700	0.3	11070	2104	0.00115	0.42
5	1023	3	2700	0.3	12370	2198	0.00129	0.39
6	1073	3	2700	0.3	21860	3610	0.00230	0.36
3	1073	0	2700	0.3	35850	2088	0.00400	0.12
6	1073	3	2700	0.3	21860	3610	0.00230	0.36
7	1073	5	2700	0.3	19010	3768	0.00196	0.44
8	1073	6	2700	0.3	16400	3514	0.00168	0.48
9	1073	5	2700	0.1	24950	3909	0.00264	0.34
10	1073	5	2700	0.2	20060	3481	0.00210	0.38
7	1073	5	2700	0.3	19010	3768	0.00196	0.44
11	1073	5	2700	0.4	18720	4086	0.00191	0.49
12	1073	5	1440	0.3	17080	3796	0.00174	0.50
7	1073	5	2700	0.3	19010	3768	0.00196	0.44
13	1073	5	5400	0.3	19950	3294	0.00210	0.36
14	1073	5	9000	0.3	20320	3184	0.00215	0.34

Note. See the experimental section for the calculation of H/C ratio and moles of coke.

[a] All samples were taken after 7 h of time on stream.

these TPO results demonstrate that the beneficial role of CO_2 in coke formation has two aspects. One suppresses the coke amount and the other increases the hydrogen content in coke, which implies that inactive coke can not be formed in the presence of CO_2. In other words, CO_2 may react with the coke before its transformation to the inactive coke. Correlating the TPO data (Fig. 8 and Table 2) and reaction results (Table 1 and Figs. 3 and 4), the severe deactivation of the catalyst at high temperatures without CO_2 addition and the remarkable improvement of the catalyst stability with CO_2 addition can be clearly understood.

It can be observed from the reaction results that the catalytic activity was stabilized with the increase in total pressure (Figs. 1 and 2) and destabilized with the increase in methane space velocity (Fig. 5). Data in Table 2, entries 9, 10, 7, and 11, show the effect of total pressure on coke amount as well as on hydrogen content of the coke. With the increase in reaction pressure, the moles of coke decreased while the hydrogen content in the coke increased. The same trend was also observed with a decrease in methane space velocity, as shown in Table 2, entries 12, 7, 13, and 14. Therefore, it was observed in all series of the experiments that the hydrogen content in coke decreased when the moles of coke increased. This means that, as is usually found (24), the aromaticity of coke increases with an increase in coke content.

3.4. Catalyst Regeneration by Removal of Coke

Figure 9 illustrates the reaction results of various regenerated 6% Mo/HZSM-5 catalysts at 1073 K, 0.3 MPa, 2700 ml/(g · h), and addition of methane plus 4% CO_2. Compared with fresh catalyst, the catalyst regenerated at 823 K by O_2 showed a slightly higher benzene formation rate whereas the catalyst regenerated by H_2 exhibited a lower activity. This implies that the deposited coke was removed by oxidative combustion at 823 K but was not cleared by H_2 treatment at the same temperature. Oyama and coworkers (25) had reported from temperature-programmed surface reactions with hydrogen that three kinds of carbon existed on the aluminum-supported molybdenum carbide. They indicated that the peak at 763 K could be assigned to the reduction of carbidic carbon, and the peaks at 963 and 1083 K were assigned to pyrolytic and graphitic carbon, respectively. Referring to their study, it can be suggested that the coke formed in methane conversion receives less

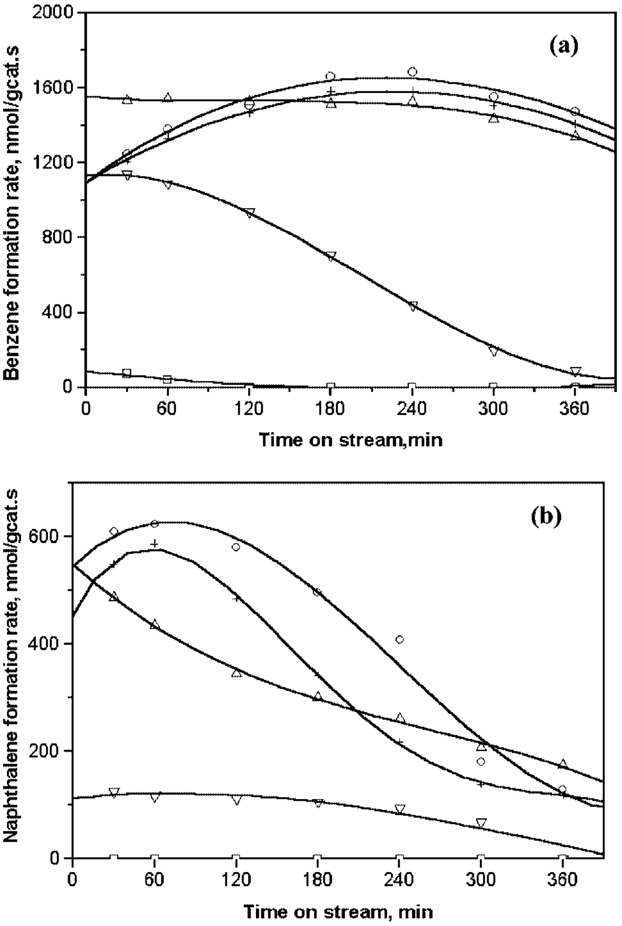


FIG. 9. Formation rates of benzene (a) and naphthalene (b) on fresh 6% Mo/HZSM-5 (+) and on catalysts regenerated by O_2 at 823 K (○), by 3% O_2/He at 1123 K (□), by H_2 at 823 K (▽), and by H_2 at 1123 K (△). Reaction conditions: 1073 K, 0.3 MPa, 2700 ml/(g · h), and 4% CO_2 addition.

of a contribution from carbidic carbon than from pyrolytic and/or graphitic carbon and this kind of coke is difficult to remove with H_2 at 823 K. In addition, it also implies that the coke in pyrolytic and/or graphitic form is more responsible for deactivation of the catalysts for methane conversion, as previously reported by Lunsford and coworkers (26). Regeneration of coked catalyst with H_2 at 1123 K strongly supports this argument of different kinds of coke formed during the reaction. As shown, the activity of the catalyst regenerated by H_2 at 1123 K was completely restored and without an induction period. The disappearance of the induction period for benzene and naphthalene formation suggests that the active molybdenum species was retained in the reductive H_2 atmosphere. In contrast, the regenerated catalyst with O_2 obviously showed the induction period for the formation of benzene and naphthalene which is well-known (4–6). High-temperature regeneration of coked catalyst as 1123 K in 3% O_2/He resulted in a lower benzene formation rate due to the sublimation of molybdenum oxide. Similar regeneration modes for the deactivated Mo/HZSM-5 catalysts after reactions at 950 K for 2 h have been reported by Iglesia and coworkers (27, 28). They demonstrated two regeneration processes: one was treating the used catalyst with 20% H_2/He at 950 K, and the other was using 20% O_2/Ar and raising the temperature from 300 to 950 K.

The rate of naphthalene formation on the catalyst regenerated by O_2 at 823 K was slightly higher than that on the fresh catalyst. Lunsford and coworkers (7) demonstrated that naphthalene was formed in the channels of the zeolite and that its formation decreased obviously with an increase in reaction time due to narrowing of the channel space. Thus, the fact that more naphthalene was formed on the regenerated catalyst implies that the channel space of the zeolite was restored completely after the regeneration process. This conclusion was verified by the following BET results.

Table 3 lists the surface areas of the various Mo/HZSM-5 samples. Reactions with the methane feed over the catalysts led to an obvious decrease in BET surface areas, especially for the reaction without CO_2 addition. The BET surface area of the reacted sample at 1073 K without CO_2 decreased to 2.4 m^2/g, indicating a complete blockage of the zeolite channels by coke deposition. In contrast, with the addition of 4% CO_2, the BET surface area of the reacted 6% Mo/HZSM-5 catalyst at 1073 K retained a surface area of 226 m^2/g, demonstrating that the blockage of the zeolite channels by coke formation was mostly eliminated. On the other hand, the BET surface area of the catalyst regenerated by O_2 was restored to 298 m^2/g, which suggests that pore blockage of the zeolite channels is cleared through the oxidation reaction.

The XRD measurements of the fresh and reacted 6% Mo/HZSM-5 catalysts were also studied. It was noted that the crystallinity of HZSM-5 zeolite decreased slightly after a 7-h reaction at 1073 K. The XRD measurements give evidence that the framework of the reacted zeolite was retained intact and the deactivation of the catalyst was not due to the framework destruction. Thus, it is concluded that blockage of the zeolite channel with coke is one main reason for the deactivation of the catalyst, as previously reported in Ref. (24).

TABLE 3

BET Surface Areas of HZSM-5 Zeolite and Mo/HZSM-5 Catalyst under Different Conditions

Samples	BET surface areas (m^2/g)
HZSM-5	421
Fresh 6% Mo/HZSM-5	312
6% Mo/HZSM-5 (reacted with CO_2)[a]	226
Regenerated 6% Mo/HZSM-5[b]	298
6% Mo/HZSM-5 (reacted without CO_2)[c]	2.4

[a] This sample was taken after a 7-h reaction at 1073 K, 0.3 MPa, and 2700 ml/(g · h) and with addition of 4% CO_2.

[b] This sample was taken after the reaction in footnote *a* and was regenerated by O_2 at 823 K for 2 h.

[c] This sample was taken after a 7-h reaction at 1073 K, 0.3 MPa, and 2700 ml/(g · h) and without CO_2.

4. CONCLUSIONS

1. The remarkable improvement in stability on the 6% Mo/HZSM-5 catalyst occurred under pressurized conditions in the methane dehydrocondensation reaction. At a pressure of greater than 0.2 MPa and, with suitable CO_2 addition in the methane feed, the high activity and stability were achieved even at elevated reaction temperatures and methane space velocities. The stable benzene formation rate of 4000 nmol/(g-cat · s) on the 6% Mo/HZSM-5 catalyst was obtained under the reaction conditions of 1073 K, 0.3 MPa, 7200 ml/(g · h), and 5% CO_2 addition in the feed. In addition, the activity of the regenerated 6% Mo/HZSM-5 catalyst was restored through the effective removal of the deposited coke by O_2 at 823 K or by H_2 at 1123 K.

2. TPO results demonstrated that the addition of CO_2 greatly suppressed the coke formation and at the same time increased hydrogen content in the coke, implying that the CO_2 reacts with coke before its transformation from active to inactive graphitic carbon. It was also demonstrated that both the amount of coke and the H/C ratio are effected by variations in reaction parameters such as methane pressure, reaction temperature, and space velocity.

3. There are mainly two kinds of coke observed. The coke at low temperature is more active and associated with Mo species while the one at high temperature is less active and related to Brønsted acid sites of the zeolite support. The inactive coke blocking the channels of the zeolite support is more deleterious to methane aromatization reactions.

ACKNOWLEDGMENTS

This work was supported by the Proposal-Based New Industry Creative Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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