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Promotional role of water added to methane feed on catalytic performance in the methane dehydroaromatization reaction on Mo/HZSM-5 catalyst

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Abstract

The addition of a few percent of water to methane feed significantly improved catalytic performance in the methane dehydroaromatization reaction on 6 wt% Mo/HZSM-5 catalysts at 0.3 MPa and 998–1073 K. Exactly three times as much hydrogen as CO was produced from H_2O and methane, suggesting that the reforming reaction was accompanied with the dehyrocondensation reaction of methane. However, addition of water above 2.6% resulted in a sudden drop of catalytic activity after several hours of time on stream. Coke, a main inhibitor of the reaction, produced a lesser amount with increasing water concentration in methane feed. The HZSM-5 structure of Mo/HZSM-5 examined by XRD and ^{27}Al-MAS-NMR techniques remains intact even after the reaction at 1073 K in the presence of water except for a high water concentration of 2.6%, where framework aluminum migrates to extraframework positions, which may be responsible for the sudden drop of the catalytic activity. Small Mo_2C clusters, an active species of the reaction, were always observed on used catalysts by EXAFS analysis. Stabilities of Mo_2C and C in a water atmosphere were estimated from equilibrium calculations and discussed in conjunction with the reactivity of coke formed on the catalyst during the methane dehydroaromatization reaction. Based on the above results, the sudden drop of catalytic activity at an excess addition of water may be explained by the two consecutive reactions of $CH_4 = C + 2H_2$ and $C + H_2O = CO + H_2$ (reforming reaction as a whole). These two consecutive reactions proceed whenever coke is present on the catalyst but not on the catalyst having no coke. Therefore, water can pass through on the catalyst having no coke and eventually almost all aluminum atoms in the lattice position move out by the action of water. Then, the catalyst can not promote the reforming reaction and also the dehydrocondensation reaction of methane.

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Keywords: Methane dehydroaromatization; Water addition; Mo/HZSM-5 catalyst; ^{27}Al-MAS-NMR; Thermodynamic calculation

1. Introduction

The conversion of methane to petrochemical feedstocks and fuels remains a formidable challenge. The direct catalytic dehydroaromatization of methane to benzene, naphthalene, and hydrogen is important because of industrial interest in the effective utilization of natural gas and hydrogen production for fuel cells. Since the initial discovery [1] in 1993, there has been a general agreement [2–9] that Mo, Re, or W loaded on such zeolites as HZSM-5, HMCM-22, and HZSM-11 having a 10-member ring uniquely promotes the selective dehydroaromatization reaction of methane to aromatics such as benzene and naphthalene.

Although much research work has been conducted, some problems remain concerning this reaction, not only from the standpoint of academic research but also from the need for potential industrial utilization of natural gas. The formation of serious carbonaceous deposits in the dehydrocondensation reaction of methane is one of the major obstacles in its development. It has been reported that coke formation can be reduced by means of adding some second metals [5,10] and of weakening the acidity of HZSM-5 or HMCM-22 [11–14] of Mo/HZSM-5 or Mo/HMCM-22 catalysts. The small amount of O_2 added in methane feed may partly remove the coke deposition on the active sites and result in an improvement of the catalytic performance of the Mo/HZSM-5 catalyst [15,16]. We 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], and alternative feed flow between methane and H_2 or CO_2 on Mo/HZSM-5 [20–22], leads to a remarkable enhancement of the catalyst

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stability owing to the efficient suppression of coke formation. Analogous to CO_2 and H_2, H_2O may also be a good reagent that removes coke accumulation on Mo/HZSM-5 by the reforming reaction ($H_2O + CH_x$ $(x = 0–4) \rightarrow CO + H_2$). However, water may destroy the structure of HZSM-5 zeolite at high temperatures [23]. Here, we study the additive effect of water in the dehydrocondensation of methane on Mo/HZSM-5 in terms of catalytic performance toward hydrogen and benzene, and catalytic stability associated with coke formation. In addition, we use XRD and ^{27}Al-MAS-NMR techniques to determine the structure of HZSM-5 zeolites before and after the reactions. Active Mo phase during the reaction was examined by EXAFS analysis of the catalyst used. Further, thermodynamic stabilities of Mo–carbide and carbon toward water, CO_2, and hydrogen are calculated and compared with the reaction results.

2. Experimentals

A 6 wt% Mo-loaded HZSM-5 ($Si/Al_2 = 40$) catalyst was prepared by the incipient impregnation method with an aqueous ammonium molybdate solution. The resulting materials were dried at 393 K and calcined at 773 K for 5 h as reported previously [7]. Mo/HZSM-5 was precarburized with methane at 973 K for 1 h prior to the dehydroaromatization reaction. The reaction of methane with or without H_2O was carried out at 0.3 MPa and at 998–1073 K by a fixed-bed continuous-flow system with a quartz reactor of 8 mm i.d., in which 0.9 g of catalyst for the reaction at 1023 K and 0.2 g at 998 and 1073 K were charged. A mixture gas of 90% methane and 10% Ar was fed to the reactor. The methane flow rate was set to 30 $ml\,min^{-1}$. If necessary, methane/Ar was passed through a water bubbler and fed into the reactor. The bubbler was thermostated at 300, 318, and 336 K, which will give 1, 3.2, and 7.2% of water vapor, respectively, if thermally equilibrated. As will be explained in Section 3.1, however, the real concentration of water was estimated to be 1.7, 2.2, and 2.6% when temperatures of the bubbler were kept at 300, 318, and 336 K, respectively. Even methane/Ar was contaminated by 0.6% water. Hereafter, the estimated water percentage will be used throughout the text. The products were analyzed by two GCs equipped with FID and TCD detectors and by one micro GC for analyzing hydrogen, similarly as reported elsewhere [7]. Using an internal standard analyzing method with 10% Ar in the feed gas, methane conversion, selectivities of hydrocarbon products and coke formation formed on the catalysts were evaluated according to the mass balance of carbon. Formation rates of hydrocarbon products, and coke formed were calculated as well and were expressed in carbon base. The formation rate of hydrogen was expressed in mole base.

The amount of coke formed on the catalysts was measured by the temperature-programmed oxidation (TPO) method. The TPO spectra were obtained by using a TG-DTA 2000S (Mac Science Ltd.) combined with a Thermolab Mass spectrometer on 30 mg of catalyst under flowing 115 $ml\,min^{-1}$ of an O_2/He (15/100) gas mixture at temperature raising rate of 10 $K\,min^{-1}$, as previously described [19]. The catalysts before and after the reactions were characterized by X-ray powder diffraction (XRD) in order to confirm the reservation of the crystallinity of the zeolite. XRD patterns were obtained on a MiniFlex X-ray diffractometer (Mac Science Ltd.) using Cu-K_α radiation at room temperature and instrumental settings of 30 KV and 15 mA. The powder diffractograms of the various samples were recorded from 5 to 50° with a scanning rate of $4°/min$. The stability of Al in a zeolite framework was determined by ^{27}Al-MAS-NMR analysis. ^{27}Al-MAS-NMR spectra were obtained on a Bruker DRX-400 spectrometer at 9.4 T using a ZrO_2 rotor, which was spun at 8 kHz, and recorded at 104.3 MHz using a 0.75-μs ($\pi/12$) pulse with a 3-s recycle decay. An aqueous Al solution was used as the reference of the chemical shift. Mo K-edge XAFS (X-ray absorption fine structure) measurements were conducted on Mo/HZSM-5 samples in cells (in situ) at the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF, Tsukuba, Japan) to characterize the Mo catalyst after the reaction with methane plus water flow at 1023 K. The energy and current of the electrons (or positions) were 2.5 GeV and 250 mA, respectively, and a Si(311) channel-cut monochromator was used.

3. Results and discussion

3.1. *Effect of water addition in methane feed on the catalytic performance in the methane dehydrocondensation reaction*

Figs. 1 and 2 show that the addition of water to methane feed gas induces a significant effect on the formation rates of benzene, hydrogen, and CO and improves catalysts stability in the methane dehydroaromatization reaction over Mo/HZSM-5 catalysts at 993 or 1073 K and at 0.3 MPa. The other minor products such as naphthalene, toluene, ethene, and ethane, had a catalytic performance similar to that of benzene. At 993 K, the formation rate of benzene (Fig. 1A) decreased to a half of the initial stage of reaction after 6 h of time on stream in CH_4/Ar as the feed gas, while by the addition of 1.7% water in methane feed (Fig. 1A), the decrease in the formation rate of benzene was substantially moderated. However, the further addition of water does not have a positive effect in the activity. In particular, 2.6% water in the methane feed is detrimental to the activity. By increasing the reaction temperature, however, water added in methane feed plays a more vital role in promoting the stability of the reaction. As shown in Fig. 1B, the formation rate of benzene at 1073 K after 3 h of time on stream increased with increasing water concentration in the methane feed. The low profile of water addition in methane feed at low temperatures may be a reason why Li and co-workers [17] could not find a promotional effect by the water addition and the suppression of

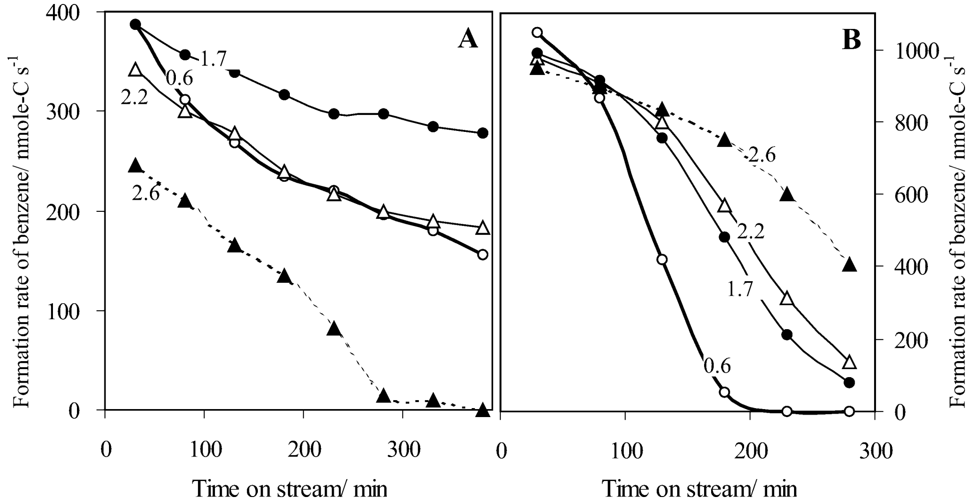

Fig. 1. Formation rate of benzene in methane dehydroaromatization on a 6 wt% Mo/HZSM-5 under flowing methane with 0.6–2.6% water as shown at 0.3 MPa and at (A) 998 or (B) 1073 K.

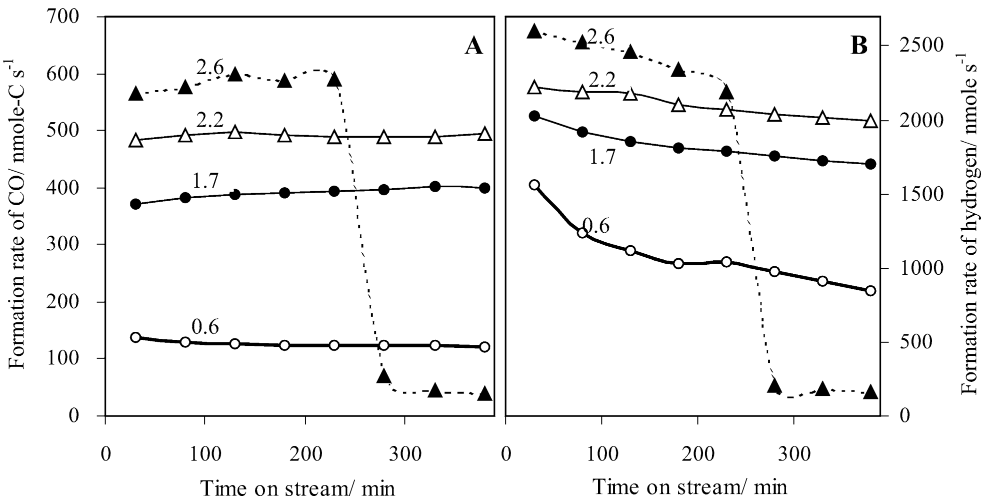

Fig. 2. Formation rates of CO (A) and hydrogen (B) in methane dehydroaromatization on a 6 wt% Mo/HZSM-5 under flowing methane with 0.6–2.6% water as shown at 0.3 MPa and at 998 K.

coke deposition on catalysts in the methane dehydroaromatization reaction at 973 K, 0.1 MPa, and methane space velocity of 1000 h^{-1}.

Fig. 2 shows that the formation rates of CO and hydrogen were higher in the presence of water than in the absence of water in the methane feed, suggesting that extra H_2 and CO were formed from the reforming reaction ($H_2O + CH_4 = CO + 3H_2$). Hydrogen forms not only from the reforming reaction but also from the dehydrocondensation and the decomposition reactions of methane to produce aromatics and carbon, respectively. If the dehydrocondensation and the decomposition reactions of methane proceed to the same extent irrespective of water concentration, the amount of hydrogen or CO formed via the reforming reaction may be calculated from the difference in the hydrogen or CO formation rate measured under flowing methane with and without water vapor. In Fig. 3 are shown plots of ratios of hydrogen to CO calculated as above against time on stream. Evidently, the reforming reaction ($CH_4 + H_2O = CO + 3H_2$) is really proceeding since the average ratio falls into a stoichiometric ratio of 3. This result does not exclude consecutive reactions such as [$CH_4 = CH_x(x = 0\text{–}4) + (2 - x/2)H_2$, $H_2O + CH_x = CO + (1 + x/2)H_2$], if the stoichiometry of the reforming reaction is satisfied as a whole. From Fig. 2A, the average rate of CO formation was calculated to be 128, 385, 491, and 584 nmol s^{-1} under flowing methane and under flowing methane bubbled through water thermostated at 300, 318, and 336 K, respectively. Considering that 1 mol of CO reacts with 1 mol of water in the reforming reaction, the concentration of water in methane feed was estimated as 0.6, 1.7, 2.2, and 2.6%, respectively. It should be noted here that methane/Ar is contaminated by 0.6% water and the water concentrations estimated are very much less than that expected from the equilibrated values, showing low efficiency of the bubbler for supplying water vapor.

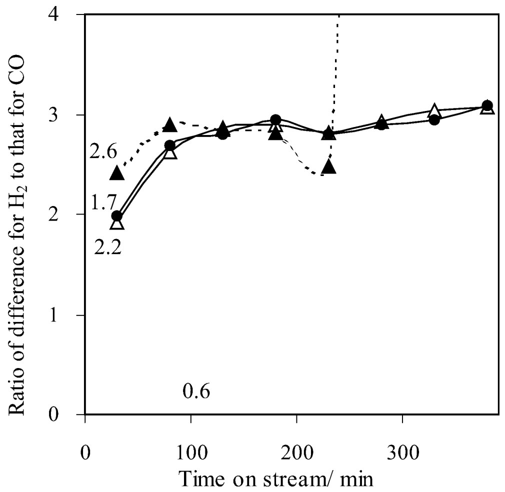

Fig. 3. Ratio of the gap between formation rates of hydrogen under flowing methane with 1.7–2.6% water as shown and under flowing methane with 0.6% water to that between CO formation rates in methane dehydroaromatization on a 6 wt% Mo/HZSM-5 at 0.3 MPa and at 998 K.

A long period of experiments was conducted at 1023 K and 0.3 MPa to demonstrate the usefulness of water for stabilizing the activity as shown in Fig. 4. As were the cases at 998 and 1073 K, the activity under flowing methane/Ar mixture decreased drastically and reached zero in 19 h of time on stream. The additions of 1.7 and 2.2% water in methane substantially moderated the formation rate of benzene, which remained at high levels of 600–700 nmol C s^{-1} over a period of 22 h. The exact same stabilization was observed when 3.2% CO_2 was added into methane feed, as has been similarly reported [18–20]. It is apparent that the formation rates of benzene and other hydrocarbons decrease either slowly as in the case of methane/Ar flow or suddenly as in the case of methane with 2.6% water. The slow decrease in rate of formation of the hydrocarbons does not accompany the decrease in the rate of reforming reaction while after the sudden drop of benzene formation, all the reactions ceased to proceed.

3.2. TPO studies of coke formed on Mo/HZSM-5 during the methane conversion reaction

The character of coke formed during the reaction on the Mo/HZSM-5 catalyst surface was evaluated by TPO studies. Fig. 5 shows the TPO spectra as a function of CO_2 formation on the used Mo/HZSM-5 for the methane dehydroaromatization reaction in the reactant flow of methane with various amounts of water. As shown in Fig. 5A, the TPO studies of Mo/HZSM-5 after the reaction at 1023 K for a long period of 22 h demonstrate that the total amounts of coke deposited on Mo/HZSM-5 catalysts were greatly reduced with the addition of water to the methane feed. And the peak position moved ca. 40 K to the lower temperature with increasing water concentration in methane feed from 0.6 to 2.6%. This is probably due to the difference in coke characteristics and/or the amount of coke formed at different water concentrations. Querini and Fung [24] discussed shifts in peak temperature in relation to the amount of coke formed on the surface. The decreasing amount of coke formation by water addition to methane feed is analogous to that of CO_2, owing to the effective removal of surface carbon to stabilize the catalytic performance under the prevailing conditions [6,7,18]. As presented in the previous section, the stability of the catalytic performance increases with increasing water concentration up to 2.2% in the feed at 1023 K, as expected from the decrease of amount of coke, suggesting that the slow decrease in the activity is due to coke accumulation. With 2.6% water in the feed, the amount of coke formation further decreased. However, the activity drops suddenly after several hours of time on stream. These results imply that the amount of coke is not a sole factor governing the stability of the reaction.

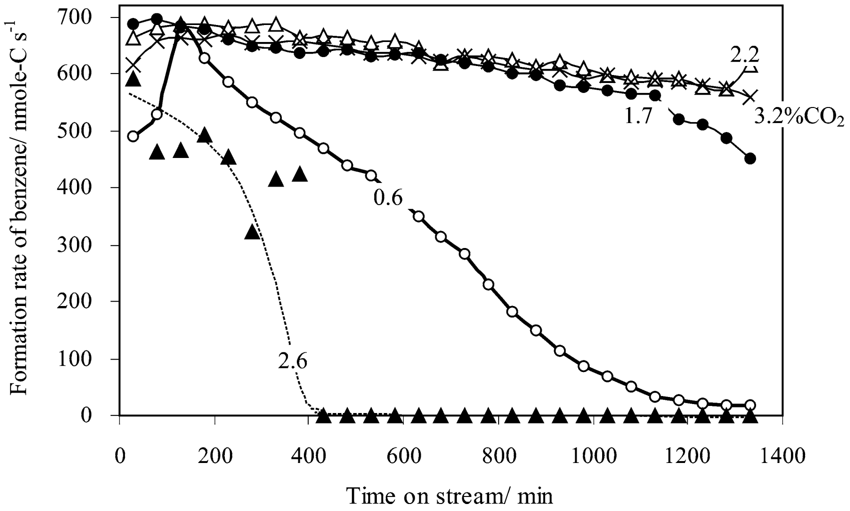

Fig. 4. Long-term experiment for the formation rate of benzene in methane dehydroaromatization on a 6 wt% Mo/HZSM-5 under a flowing gas mixture of methane with 0.6–2.6% H_2O as shown or 3.2% CO_2 (x) at 0.3 MPa and 1023 K.

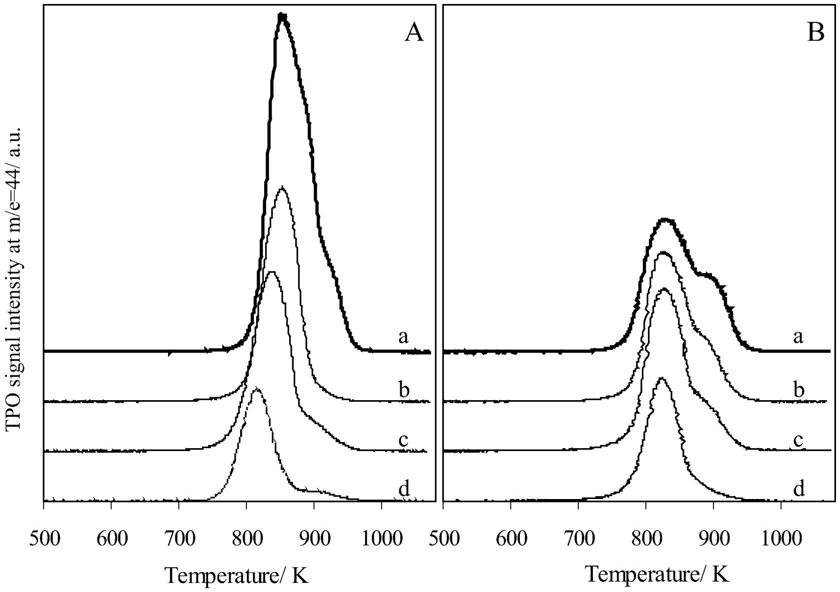

Fig. 5. TPO mass spectra at $m/e = 44$ of 6 wt% Mo/HZSM-5 catalysts after the reaction (A) for 22 h at 1023 K, and (B) for 6 h at 1073 K, respectively, under a flowing gas mixture of methane with (a) 0.6, (b) 1.7, (c) 2.2, and (d) 2.6% of steam. Same scales of y-axes for A and B are used.

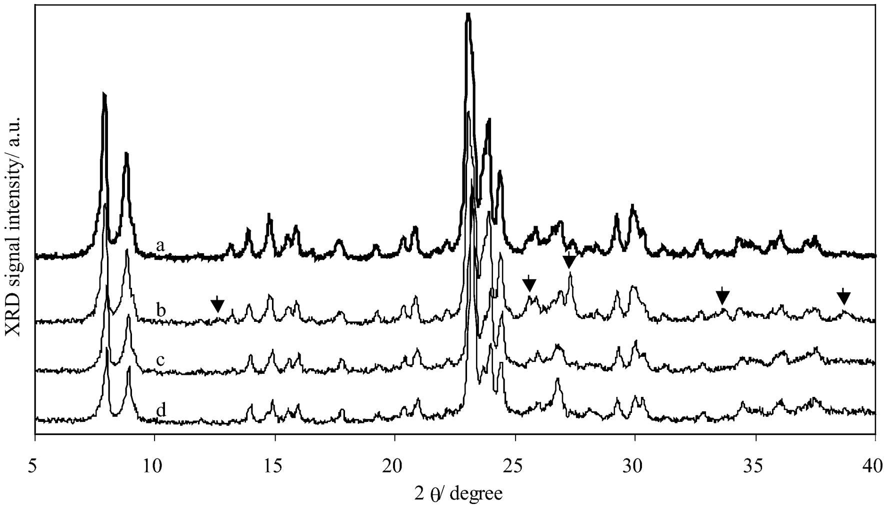

Fig. 6. XRD spectra of various samples; (a) HZSM-5, (b) fresh 6 wt% Mo/HZSM-5 dried at 373 K, (c) 6 wt% Mo/HZSM-5 after the reaction for 22 h at 1023 K, and (d) 6 wt% Mo/HZSM-5 after the reaction for 6 h at 1073 K, under flowing methane. Arrows refer to peaks of MoO_3, PDF 05-0508.

In contrast to the reaction at 1023 K, the TPO spectra of Mo/HZSM-5 after the reaction at 1073 K for a period of 6 h show that the peak temperature did not move with the addition of water to the methane feed, as presented in Fig. 5B. Further, the peak was clearly separable into two peaks at 825 and 900 K, which were attributed to carbon associated with molybdenum and carbonaceous deposits on the Brønsted acid sites of the zeolite, respectively [14]. The height of a peak at 825 K did not change appreciably while that at 900 K decreased with increasing water concentration in the feed. Coke oxidized at 900 K in TPO spectra may be responsible for the slow deactivation of catalytic activity in the methane dehydroaromatization reaction at 1073 K.

3.3. *XRD studies on crystallinity of Mo/HZSM-5 used in the methane dehydroaromatization reaction*

Fig. 6 shows XRD patterns of pure HZSM-5 and various Mo/HZSM-5 samples. All peaks in a XRD pattern of Mo/HZSM-5 dried at 373 K coincide in position with those of parent HZSM-5 except for small peaks marked by arrows, which can be assigned to MoO_3. According to PDF file 05-0508, MoO_3 will give peaks at $2\theta = 27.3$, 23.2, 25.7, 33.7, 12.8, and 39.0° in decreasing order of intensity. Although the second largest peak of $2\theta = 23.2°$ could not be detected due to overlapping with intense peaks of HZSM-5 at $2\theta = 23.1$ and 23.3° [25], all other peaks were clearly identified. After

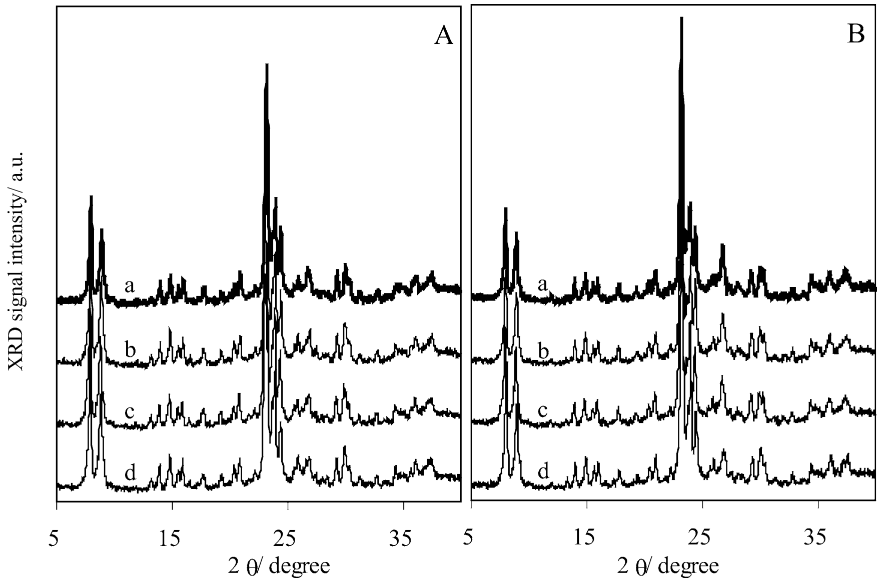

Fig. 7. XRD spectra of 6 wt% Mo/HZSM-5 after the reaction (A) for 22 h at 1023 K and (B) for 6 h at 1073, under a flowing gas mixture of methane with (a) 0.6, (b) 1.7, (c) 2.2, and (d) 2.6% of steam. Same scales of y-axes for A and B are used.

the calcination at 773 K and the methane dehydroaromatization reaction at 1023 or 1073 K (c and d), all peaks originated from Mo species disappeared and all peaks from HZSM-5 were reserved, suggesting that the Mo species highly dispersed on the support HZSM-5. Fig. 7 shows XRD spectra of 6 wt% Mo/HZSM-5 after the methane dehydroaromatization reaction with or without water in methane feed. After the reaction at 1023 K for 22 h of time on stream (A) and at 1073 K for 6 h (B), the XRD patterns of all Mo/HZSM-5 samples were very similar to each other in the peak positions and in the peak heights, regardless of concentrations of water (0.6–2.6%) in the feed. These results strongly suggest that the support HZSM-5 structure of Mo/HZSM-5 is not destroyed even under such serious conditions as the presence of water at elevated temperatures. As presented in the previous section, the catalytic activity suddenly dropped to zero under flowing methane with 2.6% H_2O at 998 and 1023 K. This result could not be explained by the destruction of the zeolite framework.

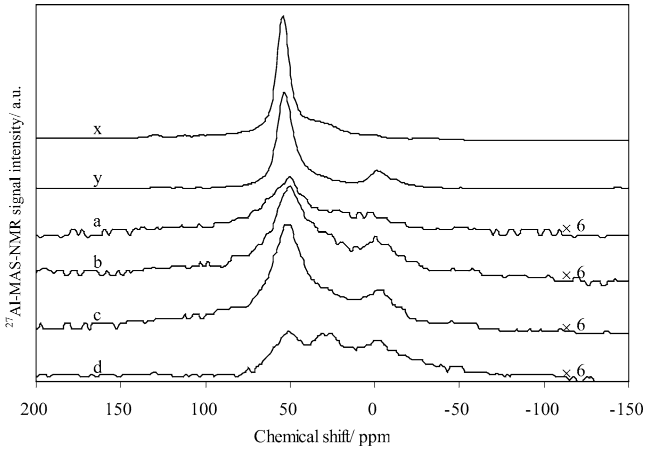

Fig. 8. ^{27}Al-MAS-NMR spectra of (x) HZSM-5, (y) fresh 6 wt% Mo/HZSM-5 calcined at 773 K, and used 6 wt% Mo/HZSM-5 for the reaction under a flowing gas mixture of methane with (a) 0.6, (b) 1.7, (c) 2.2, and (d) 2.6% steam at 1023 K for 22 h. Signal intensities of a, b, c, and d lines were expanded 6 times.

3.4. ^{27}Al-MAS-NMR studies on the Al environment of Mo/HZSM-5 used in the methane dehydroaromatization reaction

In order to obtain the information on the aluminum environment on the HZSM-5 support of molybdenum, ^{27}Al-MAS-NMR experiments were conducted on a parent HZSM-5 and the Mo/HZSM-5 samples treated under various conditions. According to Ma et al. [26], ^{27}Al-MAS-NMR spectra of Mo-loaded zeolites are characterized by four peaks at 53, 14, 0, and -14 ppm, which are ascribed to tetrahedral framework aluminum, hydrated aluminum molybdate, hexahedral extraframework aluminum, and aluminum molybdate. As seen in lines x and y of Fig. 8, a minor part of the aluminum framework is extracted by molybdenum in forming aluminum molybdate during the preparation procedures of Mo/HZSM-5. After the methane dehydrocondensation reaction, the intensity of ^{27}Al-MAS-NMR spectra on the Mo catalysts decreased drastically as shown in lines a–d of Fig. 8, implying that a large part of aluminum becomes invisible due to large quadrupolar interactions [27]. The spectra nevertheless revealed the change in aluminum environment by the action of water. A large part of aluminum stays in similar positions as the fresh Mo/HZSM-5 at water concentrations lower than 2.2% (lines a–c) while they migrate from framework to extraframework positions at 2.6% water in methane feed (line d). Removal of coke with burning in air at 837 K results not only in the inten-

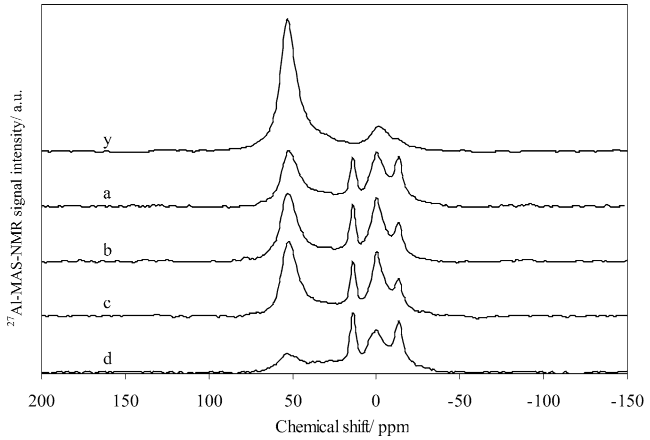

Fig. 9. ^{27}Al-MAS-NMR spectra of (y) fresh 6 wt% Mo/HZSM-5 calcined at 773 K, and 6 wt% Mo/HZSM-5 used for the reaction under a flowing gas mixture of methane with (a) 0.6, (b) 1.7, (c) 2.2, and (d) 2.6% steam at 1023 K for 22 h and then calcined at 823 K for 2 h.

sity recovery of the NMR spectra but also the migration of aluminum from framework to extraframework positions as shown in Fig. 9. Further migration of aluminum with water was clearly demonstrated from the comparison of lines a–c, which are very similar each other, with line d. It is then concluded from Figs. 8 and 9 that the sudden drop of the activity under flowing methane with 2.6% H_2O at 998 and 1023 K is induced from the migration of aluminum from framework to extraframework positions but not from the destruction of zeolite framework.

3.5. XAFS studies on the Mo environment of Mo/HZSM-5 used in the methane dehydroaromatization reaction

The active phase formed on the Mo/HZSM-5 catalyst was characterized by using in situ Mo *K*-edge XAFS studies as shown in Fig. 10. The radial distribution functions of the Mo samples reacted under flowing methane with 2.6% water at 1023 K for different times on stream shared the same main peak at 0.26 nm with Mo_2C but not with Mo metal foil, which gives two peaks at 0.24 and 0.28 nm. The peak at 0.26 nm comes from the Mo–Mo distance of Mo_2C. Distance and coordination number of the Mo–Mo bond of Mo_2C in the Mo/HZSM-5 after reaction for different times on stream were abstracted by the curve-fitting of their radial distribution functions and were obtained as 0.298 nm and 4.95 for 1 h, 0.299 nm and 4.12 for 3 h, and 0.298 nm and 3.10 for 6 h of time on stream at 1023 K, respectively. Although the distances of all samples are practically the same as that of the parent Mo_2C (0.298 nm), the coordination numbers (3.10–4.95), which have a strong relation to the peak height, are much smaller than that of Mo_2C (12), suggesting the formation of small Mo_2C clusters for the active species of the methane dehydrocondensation reaction. With increase of time on stream, the peak height at 0.26 nm decreases while that at 0.15–0.17 nm increases as if they are compensating each other. The peak at 0.15–0.17 nm can be assigned to a Mo–O bond. It may be then concluded that a part of the Mo–Mo bonds in small Mo_2C clusters is converted to Mo–O bonds by the reaction with water during the reaction. However, the conversion of Mo–Mo to Mo–O bonds with water could not be responsible for the sudden drop of activity observed in Figs. 1A, 2A, and 4 but may be the reason for the slow decrease in the activity.

3.6. Stability of Mo_2C and C in a H_2O, CO_2, or H_2 atmosphere under thermodynamic equilibrium conditions

As stated in the Introduction, the decline of the catalytic activity due to the accumulation of carbonaceous deposit is

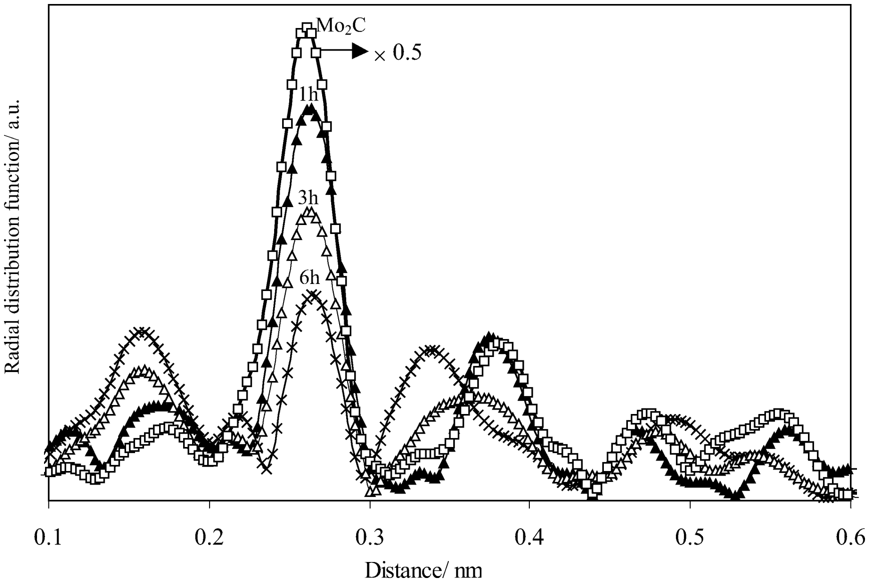

Fig. 10. Mo *K*-edge EXAFS radial distribution function of Mo_2C as a reference (signals were divided by 2) and 6 wt% Mo/HZSM-5 used for the reaction under a flowing gas mixture of methane with 2.6% steam for 1, 3, and 6 h at 1023 K.

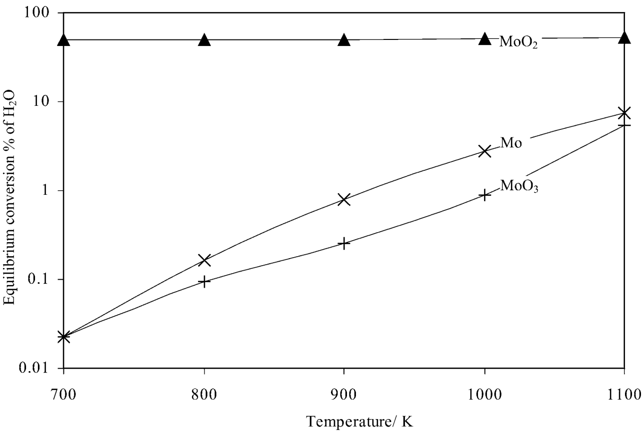

Fig. 11. Equilibrium conversion percentage of H_2O in the reaction with Mo_2C to produce Mo, MoO_2, and MoO_3 at 0.3 MPa.

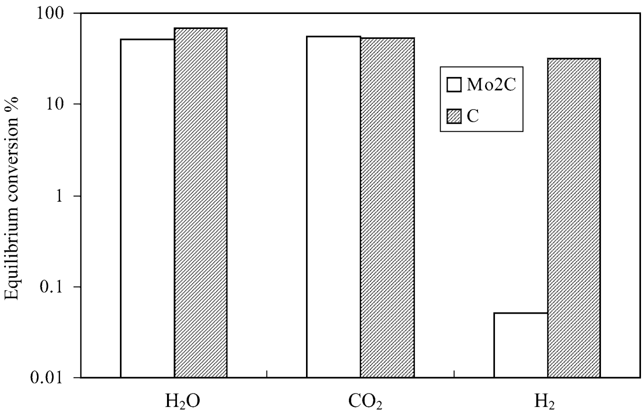

Fig. 12. Equilibrium conversions percentage of H_2O, CO_2, and H_2 in the reaction with Mo_2C (blank) and C (shaded) to produce MoO_2 and CO at 1000 K and 0.3 MPa, respectively.

one of the major obstacles in the development of the methane dehydrocondensation reaction. CO_2 and H_2 have been reported to effectively remove carbonaceous deposit [18–22]. It was found in this report that water was similarly reactive with coke as CO_2 and H_2. Stabilities of carbon in H_2O, CO_2, and H_2 atmospheres were estimated from equilibrium calculations of such reactions as $C + H_2O = CO + H_2$, $C + CO_2 = 2CO + H_2$ and $C + H_2 = CH_4$ by use of thermodynamic tables [28] and were compared with that of Mo_2C. Reaction of Mo_2C with H_2O or CO_2 may produce Mo, MoO_2, MoO_3, or others. Fig. 11 shows the equilibrium conversion percentage of water in Mo, MoO_2-, and MoO_3-forming reactions from Mo_2C and water such as $Mo_2C + H_2O = 2Mo + CO + H_2$, $Mo_2C + 5H_2O = 2MoO_2 + CO + 5H_2$, and $Mo_2C + 7H_2O = 2MoO_3 + CO + 7H_2$. The equilibrium conversion percentage shows how much water is transformed to the products under equilibrium conditions and at a set temperature and pressure. Clearly the MoO_2-forming reaction is the most favorable in the reactions of Mo_2C with water. MoO_2 is also the most favorable product in the reactions of Mo_2C with CO_2. Then, stabilities of carbon in H_2O, CO_2, and H_2 atmospheres were compared with that of Mo_2C at 1000 K and 0.3 MPa when MoO_2 is the product for reactions of Mo_2C with water and CO_2. The results are shown in Fig. 12. Evidently, C and Mo_2C are equally unstable in H_2O and CO_2 atmospheres while C is 1000 times less stable and more reactive in H_2 than Mo_2C. Care must be taken that these calculations are based on the thermodynamic value of the compound at the most stable state. It is expected during the methane dehydrocondensation reaction that subatomic carbon clusters are constantly supplied from the methane decomposition reaction ($CH_4 = C + 2H_2$) and transform to large carbon ensembles and eventually to the most stable carbon, graphite, at high temperatures if carbon is not removed from the system. The small carbon ensembles should be less stable and more reactive than graphite. As shown in Fig. 3, the peak at high temperatures in the TPO spectra, which was attributed to carbonaceous deposits on the Brønsted acid sites, was preferentially removed with water, suggesting that the small carbon ensembles react with water before growing to large carbon ensembles. Exactly the same results were reported on the Mo/HZSM-5 and Re/HZS-5 catalysts under flowing methane with CO_2 in the methane dehydrocondensation reaction [17,19]. It may then be concluded that all the water fed into methane stream is used up by the facile reaction with small carbon ensembles ($C + H_2O = CO + H_2$) and hence, HZSM-5 preserves its structure when the water concentration is low. With an excess amount of water, the framework aluminum in HZSM-5 starts to migrate out as demonstrated in ^{27}Al-MAS-NMR and XRD studies.

4. Conclusions

This work can be summarized as follows.

1. A small amount of water addition to methane feed promotes benzene and hydrogen production, and significantly improves the stability of the Mo/HZSM-5 catalyst at 998–1073 K and 0.3 MPa. The reforming type of reaction ($CH_4 = CH_x (x = 0\text{–}4) + (2 - x/2)H_2$, $H_2O + CH_x = CO + (1 + x/2)H_2$) is really proceeding to remove coke and to form extra CO and H_2, which, in turn, reacts with coke. The amount of coke decreases with increasing water concentration by these reactions. Unfortunately, a sudden drop of catalytic activity after several hours of time on stream is observed in the presence of an excess amount of water (2.6%) in the methane feed at 998–1023 K.

2. TPO experiments demonstrate that the amount of coke on Mo/HZSM-5 catalysts monotonously decreases with increasing water concentration added to the methane feed. It seems that the coke appearing at high temperatures in TPO is more labile than that at low temperatures. The peaks appearing at high and low temperatures have been attributed to carbonaceous deposits on the Brønsted acid sites of the zeolite and carbon associated with molybdenum, respectively.

3. XRD shows that the HZSM-5 structure of the catalyst used does not change under the reaction conditions of 993–1073 K and methane feed with water vapor of 0.6–2.6%.

4. ^{27}Al-MAS-NMR studies of catalysts used reveal that aluminum stays in a framework position up to a 2.2% water concentration at 1023 K. At a 2.6% water concentration at 1023 K, and for a long time on stream, a large part of aluminum migrates out from framework to extraframework positions, which may be responsible for the sudden drop of the catalytic activity under the reaction conditions.

5. EXAFS experiments reveal that small Mo_2C clusters are formed on the catalyst used for the reaction at 1023 K and 0.3 MPa with or without the presence of water and are the active species of the methane dehydrocondensation reaction. A part of the Mo–Mo bond in Mo_2C is converted to a Mo–O bond by the reaction with H_2O.

6. Thermodynamic calculations suggest that C and Mo_2C are equally unstable or reactive in a H_2O atmosphere if C and Mo_2C are in their most stable states. In contrast, TPO results appear to show a higher activity of water with carbonaceous deposits or carbon than that with carbon associated with molybdenum or Mo_2C. These results may be rationalized by the facile reaction of small carbon ensembles formed from the methane decomposition before their transformation to stable carbon, graphite. Because of the complete consumption of water by the facile reaction with carbon clusters, HZSM-5 preserves its structure in the presence of water and at high temperatures.

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