Performance of 3%Mo/ZSM-5 Catalyst in the Presence of Water During Methane Aromatization in Supersonic Jet Expansion

B.S. Liu
Dept. of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China

Dept. of Chemistry, Tianjin University, Tianjin 300072, P.R. China

L. Tian
Dept. of Chemistry, Tianjin University, Tianjin 300072, P.R. China

L. Li
Dept. of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China

C.T. Au
Dept. of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

A.S.-C. Cheung
Dept. of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China

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The influence of water in the CH_4 feed on the performance of 3%Mo/ZSM-5 catalyst during methane direct aromatization under supersonic jet expansion (SJE) condition was investigated. We observed that both surface $Mo_2O_xC_y$ and β-Mo_2C species are catalytically active for methane aromatization under SJE condition. The presence of water can promote the removal of surface carbon before the generation of aromatic-type and/or graphitic carbon. In appropriate amount, water can improve the stability of surface $Mo_2O_xC_y$, and hence resulting in better catalytic performance. The study provided valuable information relevant to the direct utilization of methane hydrate. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 1852–1859, 2011
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Introduction

Methane hydrate (MH) is a form of water ice that contains a large amount of methane. The material has been discovered under sediments of ocean floors as well as in areas of ice-earth. It is estimated that the energy locked up in MH is enormous, more than double the amount of all conventional gas, oil and coal deposits combined.[1] Methane is a clean source of energy and can be converted to useful chemicals.[2–4] According to thermodynamic calculations,[5] the conversion of CH_4 to benzene at equilibrium under nonoxidative conditions is about 12% at 700°C. With cycle processes such as those adopted in chemical industry in mind, one can argue that it is economically feasible to convert methane catalytically to aromatics and hydrogen. However, it is found that catalyst deactivation due to carbon deposition is a major obstacle. In previous works, coke formation on Mo-based catalysts was suppressed during methane dehydroaromatization (MDA) by adding Ga[6] or Ru[7] to the catalysts. We characterized the nature of carbon deposition on Ga-Mo/ZSM-5 and made suggestion on the cause of catalyst deactivation.[8] We reported that

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Correspondence concerning this article should be addressed to A.S.-C. Cheung at hrsccsc@hku.hk.

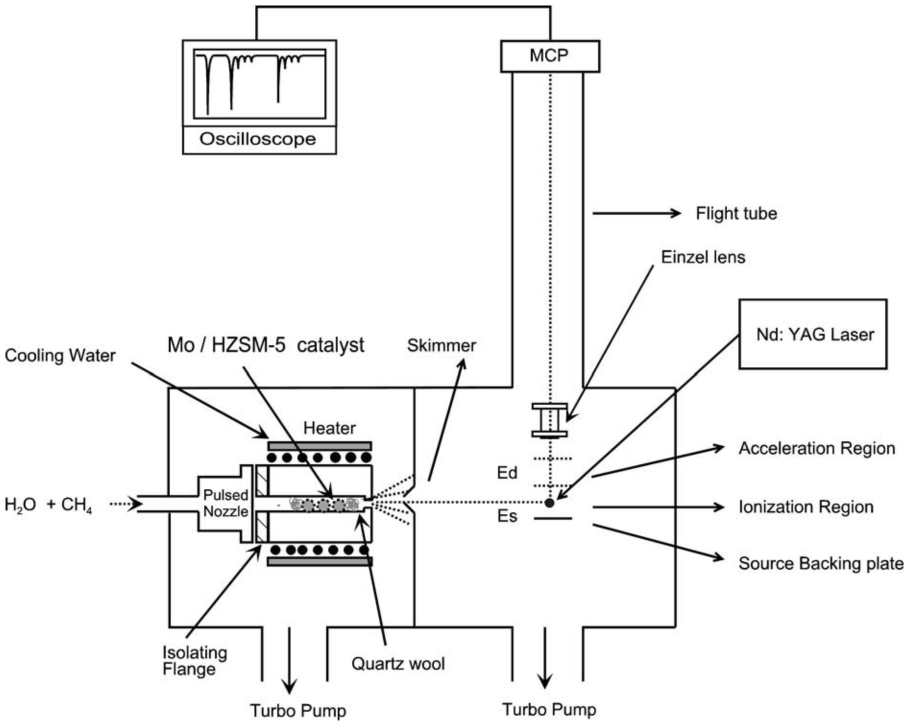

Figure 1. Schematic of TOF-MS apparatus for MDA investigation under SJE condition.

CO_2 can act as a weak oxidizer for coke removal during ethylbenzene dehydrogenation (to styrene) over La_2O_3-V_2O_5/MCM-41[9] and $LaVO_x$/SBA-15[10] catalysts. In view that water is also a weak oxidizer (e.g. in reforming reaction: $H_2O + CH_x$ ($x = 0 \sim 4$) $\rightarrow CO + (1+x/2)\ H_2$), and that HZSM-5 zeolite is hydrothermally stable,[11] we envisage that water can also be used as an agent for coke removal ($C + H_2O = CO + H_2$). For MH utilization, the methane released would inevitably contain a small amount of water, and a technology for methane conversion without the need of removing the water would be of significance.

Later, we reported that under supersonic jet expansion (SJE) condition, the MDA reaction ($6CH_4 = C_6H_6 + 9H_2$; $10CH_4 = C_{10}H_8 + 16H_2$) is over within a short time ($\sim 10^{-3}$ s) before reaching reaction equilibrium.[12,13] With rapid departure of hydrogen and aromatics from catalyst, product/catalyst interaction is limited and coke formation is not serious. In CH_4/CO_2 reforming reactions over La_2NiO_4 and 10%NiO/CeO_2-La_2O_3 catalysts, we found that CO_2 and CH_4 conversions under SJE condition were significantly higher than those at equilibrium.[14] In this article, we report how water can be used as an agent for coke removal in MDA over a 3%Mo/ZSM-5 catalyst under SJE condition. Informative results related to active sites, intermediates and product distribution were collected by time-of-flight mass spectrometry (TOF-MS), X-ray photoelectron spectroscopy (XPS), temperature-programmed oxidation (TPO), and high-resolution transmission electron microscopy (HRTEM) techniques.

Experimental

Preparation and characterization of catalysts

The 3%Mo/ZSM-5 catalyst was prepared by conventional impregnation method described elsewhere.[8] The HZSM-5 zeolite with SiO_2/Al_2O_3 ratio of 25 was supplied by Nankai University (China). The zeolite was stirred in a solution of ammonium heptamolybdate at room temperature (RT) for 24 h, and then dried at 120°C for 3 h, and calcined in air at 500°C for 4 h.

A VGX 900 spectrometer with multichannel detector and Mg K_α radiation (1253.6 eV) was used for XPS investigation. Before introduction to the spectrometer, the sample was pressed onto a piece of double-sided sticking tape and mounted on a sample holder. It was then degassed in the preparation chamber ($\sim 10^{-5}$ Torr) and analyzed in the analyzer chamber ($<7 \times 10^{-9}$ Torr). The effect of surface charging was ratified by means of binding energy (BE) calibration against that of silicon 2p (103.3 eV) as well as making reference to the C 1s BE (284.6 eV) of contaminant carbon.[9]

TPO experiments were carried out on a laboratory-scale GC system.[15] The catalyst (ca. 60 mg) was treated at 150°C in a helium stream for 30 min for removal of adsorbed water. After purging of the entire system with 8%O_2/He flow (60 ml/min) at RT for 30 min, the sample was heated from RT to 800°C at a rate of 10°C/min; the contents of effluent was simultaneously analyzed by a thermal conductivity detector (TCD). The HRTEM images of samples were acquired using a Tecnai G2 F20 electron microscope operated at 200 kV following the procedure described elsewhere.[16]

Apparatus and performance analysis

Shown in Figure 1 is the schematic of the system that consists of a source chamber, an ionization chamber, a TOF detection chamber as well as a fixed-bed reactor attached to a homebuilt TOF mass spectrometer. The feeding device was connected to the reactor and reactant gas was introduced via a pulse valve (diameter: 0.15 mm; backing pressure:

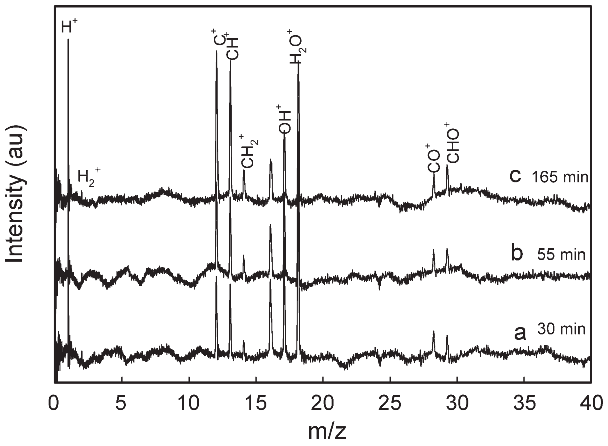

Figure 2. Mass spectra recorded during “induction period” when 3%Mo/ZSM-5 was exposed to CH_4 feed with 1.5% water.

600 kPa) that was electronically controlled. A skimmer with an l-mm-diameter aperture was used to separate the source chamber (5×10^{-6} Torr) and ionization chamber (3×10^{-6} Torr). A two-stage TOF lens assembly (including source backing plate, ionization and acceleration region) and an ion-beam focusing setup of Einzel lens (EL) were housed inside the ionization chamber, where ionization of gases was achieved through a multiphoton ionization process using Nd:YAG laser (266 nm; 10 Hz repetition; 5–6 mJ and pulse width of 5 ns) focused by plano-convex lens of 18 cm focal length. The detection chamber included a flight tube and a microchannel plate (MCP) ion detector.

The MDA reaction was conducted in the quartz reactor (i.d. 4 mm) at a pulsed duration of 300–380 ms and a repetition rate of 10 Hz. The 3%Mo/ZSM-5 catalyst was placed between two quartz-wool plugs inside the reactor. For controlling and measurement of reaction temperature (normally at 730°C), a thermocouple was placed underneath the quartz reactor at the center of the catalyst bed. Typically, about 100 mg of catalyst previously heated to 730°C in a flow of helium was used. The gas effluent after reaction was introduced into the ionization chamber through the skimmer. The ionized species were accelerated through the TOF lens assembly, focused by the Einzel lens, and traversed through a typical TOF field-free region before reaching the MCP detector. Signals from the detector were collected and analyzed by a 300 MHz digital storage oscilloscope.

Results and Discussion

Mechanism of H_2O action and introduction mode of H_2O/CH_4 feed during the induction period

It is known that Mo_2C and $Mo_2O_xC_y$ are active species to catalyze the MDA reaction. In MDA reaction conducted under normal condition (i.e. CH_4 at atmospheric pressure with no water presence), a MoO_x-based catalyst is first exposed to methane (called induction period) for the conversion of MoO_x to $Mo_2O_xC_y$ and/or Mo_2C. Depicted in Figure 2 are the mass spectra collected (at 30, 55, 165 min) when a 3%Mo/ZSM-5 catalyst was exposed to $1.5\%H_2O/CH_4$ at 730°C under SJE condition. Within the “induction period”, H_2^+, C^+, CH_x^+, H_2O^+, OH^+, CHO^+ and CO^+ were detected. As reported by Ding et al.,[2] under normal condition, Mo(VI) species of a MoO_x-based catalyst was subsequently reduced to Mo_2C:

$$3MoO_3 + CH_4 = 3MoO_2 + H_2 + CO_2 + H_2O \quad (1)$$

$$2MoO_2 + 3CH_4 = Mo_2C + CO + 5H_2 + CO_2 + H_2O \quad (2)$$

The authors detected CO, CO_2, H_2, H_2O, C_2H_4, C_2H_6, C_6H_6, and $C_{10}H_8$ during the induction period. Under the SJE condition, we do not detect $C_2H_4^+$, $C_2H_6^+$, and $C_6H_6^+$ but CHO^+ in a span of 165 min (Figure 2c). The identity of CHO^+ was confirmed before through the detection of $^{13}CHO^+$ when $^{13}CH_4$ (rather than $^{12}CH_4$) was introduced to the reactor under SJE condition.[17] As suggested, CHO is formed as a result of CH_x interaction with oxygen on the surface of 3%Mo/HZSM-5, and the decomposition of HCO gives CO and H.[12] Apparently, it is hard to detect the CHO intermediates under normal condition.

We observed that after an “induction period” of 165 min using $1.5\%H_2O/CH_4$, the 3%Mo/ZSM-5 catalyst remained white in color, indicating that the catalyst still remained as molybdenum oxides. According to the thermodynamic data of $Mo_2C + 5H_2O = 2MoO_2 + CO + 5H_2$ and $Mo_2C + 7H_2O = 2MoO_3 + CO + 7H_2$ (at reaction equilibrium),[18] the interaction of Mo_2C with water is highly favorable at 730°C, especially at low pressures (like that of the SJE condition). In other words, the presence of even a small amount of water can result in the conversion of Mo_2C to MoO_x, and it is difficult to form Mo_2C or $Mo_2O_xC_y$ species by exposing the catalyst to $1.5\%H_2O/CH_4$. It is inferred that pure methane has to be used for the formation of Mo_2C or $Mo_2O_xC_y$ before MDA reactions.

Effect of water presence on MDA under SJE condition

All the catalysts were activated in situ before use by exposing to pure methane until $Mo_2O_xC_y$ and Mo_2C were formed on the catalyst surface (as verified by XPS analysis) and C_6H_6 and/or naphthalene detected in the gas phase.

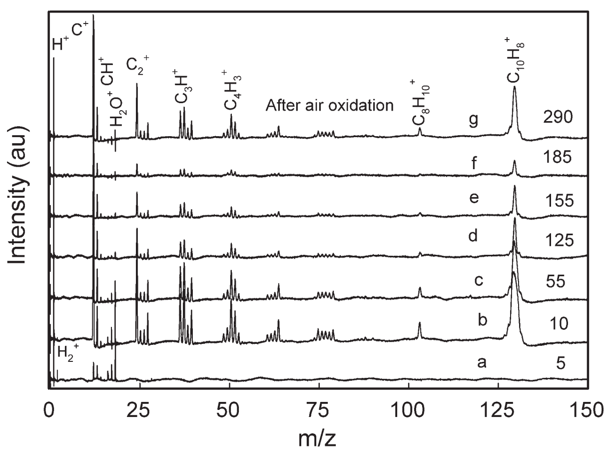

Figure 3. Mass spectra recorded in MDA reaction of pure CH_4 at different on-stream times under SJE condition at 730°C.

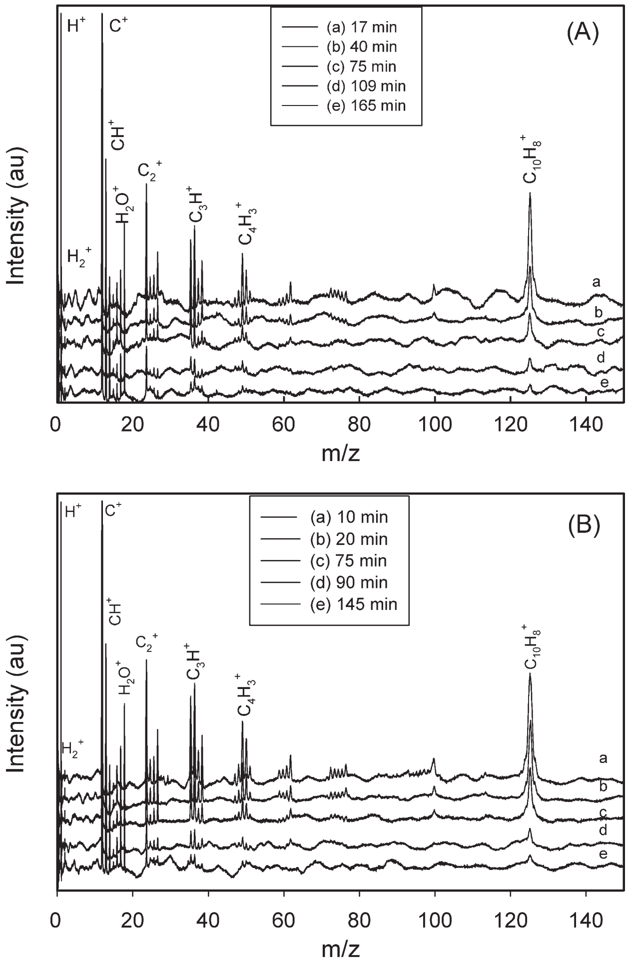

Figure 4. Mass spectra recorded in MDA reaction (A) 1.5% H_2O/CH_4 and (B) 2.0% H_2O/CH_4 at different on-stream times.

Then the reaction starts by introducing a feed of pure CH_4, 1.5% H_2O/CH_4 or 2.0%H_2O/CH_4 to the reactor, with the corresponding mass spectra shown in Figures 3, and 4A,B. In the case of feeding pure CH_4, signals of CH_x^+ radicals are observed together with those of H^+, H_2^+, H_2O^+, OH^+ at 5 min (Figure 3a), indicating the decomposition of CH_4. According to our understanding of methane interaction with 3%Mo/ZSM-5,[6,19,20] CH_4 decomposes on $Mo_2O_xC_y$ to give surface CH_x ($x = 0$–3) species and H_2. With the detection of $C_2H_3^+$ (weak signals) (Figure 3a), one can deduce that there is the occurrence of CH_x dimerization, possibly at the proximity of Mo_2C. At 10 min, intense signals of H_2^+, H_2O^+, C_3H^+, C_4H^+, $C_6H_6^+$ $C_8H_{10}^+$ and $C_{10}H_8^+$ are detected, reflecting the effective generation of aromatic species (Figure 3b). Above 10 min, there is gradual weakening of the $C_8H_{10}^+$ and $C_{10}H_8^+$ signals, implying catalyst deactivation likely to be a result of carbon deposition on Mo_2C.[8,21] The existence of amorphous carbon on the surface of a spent 3%Mo/ZSM-5 catalyst was confirmed in HRTEM study (see description in Figures 7 and 8). By means of heating in situ the spent catalyst in air at 730°C, the catalyst can be reactivated and the $C_8H_{10}^+$ and $C_{10}H_8^+$ signals restored (Figure 3g). The renewal of catalyst activity can be related to the removal of coke through oxidation and gasification of the surface carbon.[12]

As shown in Figure 4, with the addition of 1.5% H_2O (Figure 4A) or 2.0% H_2O (Figure 4B) into the CH_4 feed, $C_8H_{10}^+$ and $C_{10}H_8^+$ signals are detected, and again there is gradual decline of $C_8H_{10}^+$ and $C_{10}H_8^+$ signals with time on stream (Figure 4). It seems that the presence of water is not high enough to give a significant effect on the reaction. According to Ma et al.[22] the action of water in MDA reaction over Mo/ZSM-5 at atmospheric pressure can be rather complex; besides the interaction of H_2O with carbon to form CO and H_2, there is CH_4/H_2O reforming and Mo_2C/H_2O interaction. To have a better insight into the effect of water content on 3%Mo/ZSM-5 performance, we introduce the ''relative naphthalene formation'' factor (%) defined as $C_{10}H_8^+$ signal relative to the initial $C_{10}H_8^+$ signal (taken as 100%) at a particular on-stream time. Plotted in Figure 5 is such a factor against on-stream time (Figure 5). One can see that at water content of 0 or 1.0%, naphthalene formation is relatively low, especially at the initial stage. When water content is 1.4 or 2.0%, there is enhanced production of naphthalene, showing clear improvement of catalyst performance and stability. Note that the content of water vapor in methane originated from MH is generally around 1.8% (at 35°C and <0.3 MPa in total pressure).[23] In other words, the 3%Mo/ZSM-5 catalyst can tolerate such a methane feed with positive effect on the MDA reaction under SJE condition.

Type of deposited carbon on catalyst

The carbon species deposited on a spent 3%Mo/ZSM-5 catalyst were characterized by means of TPO and HRTEM techniques. Figure 6 depicts the TPO profiles of 3%Mo/ZSM-5 catalysts used in MDA reaction at water content of 0.0, 1.0, 1.4, and 2.0%. There are basically two peaks, a small one at about 470°C and a big one in the 580–608°C range. The former is ascribed to the gasification of active carbon species

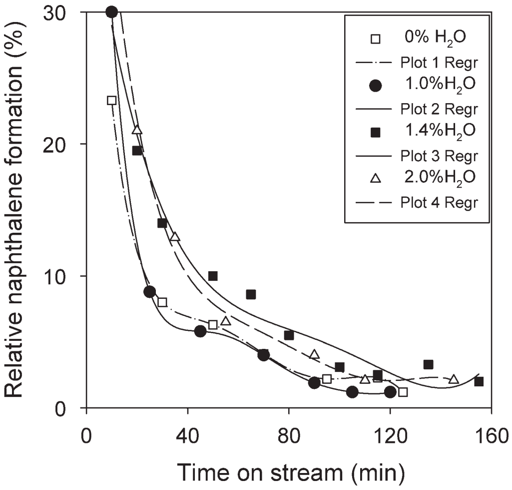

Figure 5. Effect of water content in CH_4 feed on naphthalene formation over 3%Mo/ZSM-5: pure CH_4 (□), 1% H_2O/CH_4 (●), 1.4% H_2O/CH_4 (■), 2.0% H_2O/CH_4 (△).

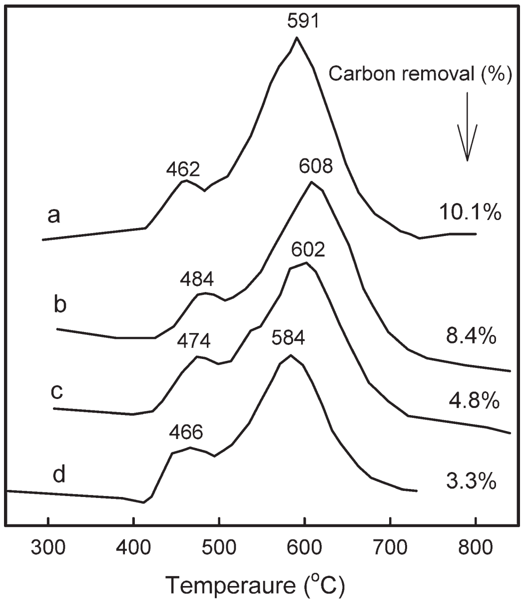

Figure 6. TPO profiles of catalysts used in MDA reaction of different methane feeds: (a) pure CH_4, (b) 1.0% H_2O/CH_4, (c) 1.4% H_2O/CH_4, (d) 2.0% H_2O/CH_4.

(CH_x, $x = 1, 2, 3$) while the latter to the oxidation of amorphous and/or graphitic carbon. The profiles are different from those of MDA reaction conducted under normal condition.[6,8] It was reported that at atmospheric pressure the amount of surface graphitic carbon increased with rise of reaction temperature and/or on-stream time, with the amount of carbon deposition (22–32.8%)[6] significantly higher than those observed under SJE condition (~10%, Figure 6). The small CH_x peaks recorded in the present study indicate that under SJE condition the accumulation of amorphous and graphitic carbon is higher than that of CH_x. It is understandable because due to the rapid departure of H_2, alkene and aromatic products from the catalyst, the surface content of CH_x remains relatively low.

Also shown in Figure 6 are the relative extents of carbon removed from the spent 3%Mo/ZSM-5 catalysts estimated based on the weight loss during TPO experiments. One can see that with a rise of water content, there is a decline in the amount of carbon removal. With increase of water content from 1.0 to 2.0%, both TPO peaks shift to lower temperatures: the CH_x peak from 484 to 466°C, while the high-temperature one from 608 to 584°C. The results suggest that with water acting as a weak oxidizer, surface carbon species are removed ($C + H_2O = CO + H_2$) before being converted to amorphous and/or graphitic carbon. As for the profiles of carbon deposition in the case of pure CH_4 feed (Figure 6a), the successive oxidation of amorphous and graphitic carbon resulted in a lap of TPO peaks. Coke existed mainly in the amorphous form due to relatively short time on stream (ca. 2.5 h), therefore, the temperature required for carbon removal was slightly lower than that at the condition of 1.0% H_2O/CH_4. As shown in Figure 5, the "relative naphthalene formation" factor of 1.4%H_2O/CH_4 is higher than that of pure CH_4 or 1.0%H_2O/CH_4. In other words, coke formation and carbon removal could reach a sort of steady state in MDA reaction under SJE condition. The results

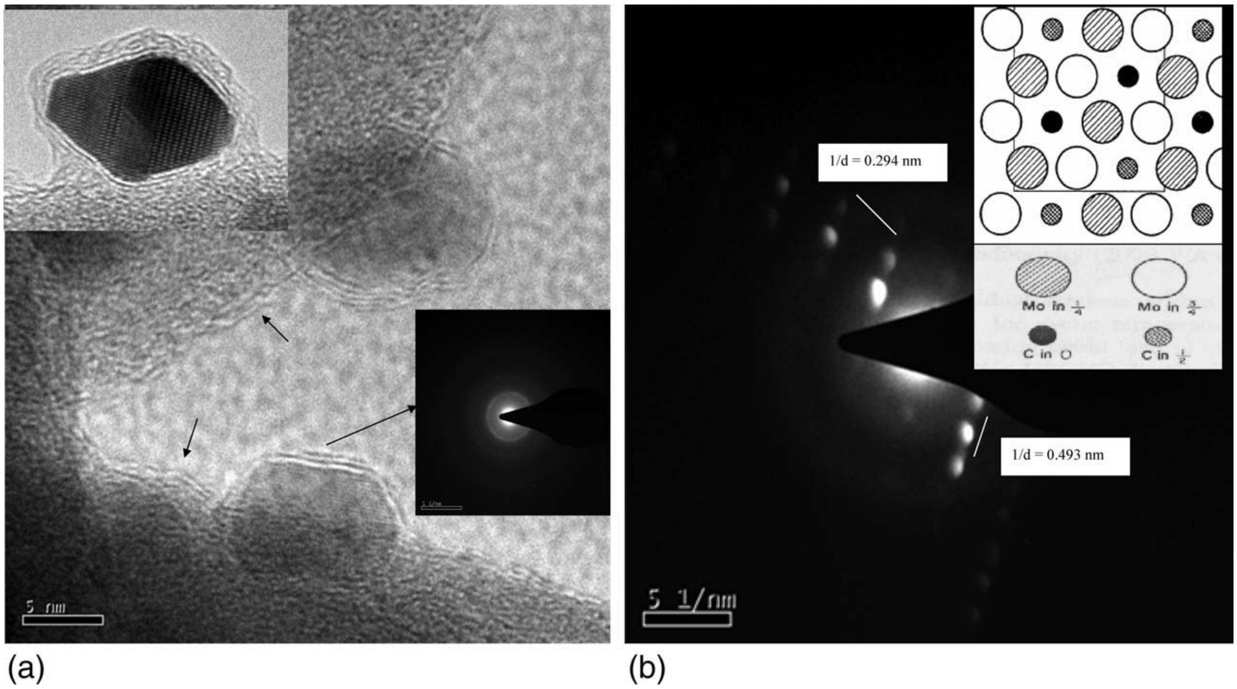

Figure 7. (a) HRTEM images of 3%Mo/ZSM-5 used in methane aromatization for 2.5 h under pure CH_4, the inset in the right is the SAED pattern of amorphous carbon: the inset at the top-left corner is the HRTEM image of a Mo_2C particle; (b) SAED pattern of a Mo_2C particle; the inset is the unit cell of β-Mo_2C depicted by Parthe and Sadagopan in Ref. 24.

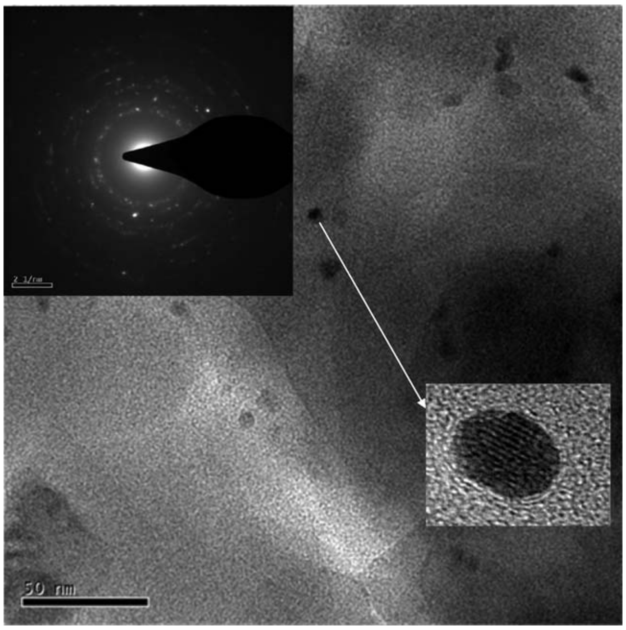

Figure 8. **HRTEM images of 3%Mo/ZSM-5 used in methane aromatization for 2.5 h under 2.0%H_2O/CH_4, the inset is a magnified HRTEM image of a Mo_2C particle; the insert at the top-left corner is a typical SAED pattern of high dispersed Mo_2C nanoparticle located on the surface or inside HZSM-5 channels.**

demonstrated that the methane released from MH can be used directly for MDA reactions with positive effect on catalyst stability and performance.

Figure 7 shows the HRTEM images of 3%Mo/ZSM-5 that was used in MDA reaction where pure CH_4 was used. In the absence of water, Mo_2C particles with grain size of 7–8 nm are detected (Figure 7a). One can see that the particles are wrapped in layers of carbon. The selected area electron diffraction (SAED) pattern (right inset of Figure 7a) in the form of circle indicates that the carbon is amorphous. In addition, graphitic layers in the proximity of the Mo_2C particles can be clearly seen (indicated by small black arrows in Figure 7a). It is deduced that CH_x dimerization occurs at the proximity of the Mo_2C particles. From the HRTEM image of a Mo_2C particle (inset at top-left corner of Figure 7a, one can see hexagonal array of atoms. The SAED pattern of a Mo_2C particle is shown in Figure 7b. Based on the distances between the diffraction spots, we come to interplanar distances of around 0.294 and 0.493 nm, not far away from the lattice parameters ($a = 0.3002$, $c = 0.4724$ nm) of β-Mo_2C unit cell (inset of Figure 7b) reported by Parthe and Sadagopan[24] With the active Mo_2C species enwrapped by amorphous carbon, it is not surprising to see deactivation of catalyst.

Compared to that of pure CH_4 (Figure 7a), the HRTEM image of 3%Mo/ZSM-5 used at a water content of 2.0% (Figure 8) shows less amount of carbon deposition, in agreement with the results of TPO investigation (Figure 6). The Mo_2C particles with size of about 5–8 nm can be recognized clearly (black spots in Figure 8). The Mo_2C particles are not seriously enwrapped by carbon (right inset of Figure 8). The SAED pattern in this region revealed that Mo_2C nanoparticles dispersed highly on the surface or in the channels of ZSM-5 (inset at the top-left corner of Figure 8). One can see four rings with spots that can be indexed (from inner to outer) to (101), (102), (110), and (103) planes of β-Mo_2C. It is worth pointing out that the presence of a small amount of α-Mo_2C is possible.[19,25] The results suggest that rather than richly accumulated with carbon species, the surface of 3%Mo/ZSM-5 is decorated with β-Mo_2C nanoparticles not encapsulated by a large amount of carbon.

Stability of $Mo_2O_xC_y$ and carbon species

The TPO profiles and HRTEM images of used catalysts confirm that a small amount of water in CH_4 can suppress coke formation and improve catalyst stability. Nevertheless, with water presence, there is still a decline in activity with time on stream (Figure 5). According to chemical thermodynamics calculation results, the ability of Mo_2C reacts with H_2O at equilibrium condition is slightly lower than that of carbon reacts with H_2O. Therefore, the coke formed on the brönsted acid sites is companying with the elimination of Mo_2C, the catalyst deactivation with $\geq$2.0%H_2O/CH_4 should be related to the destruction of Mo_2C and/or $Mo_5O_xC_y$ (Figure 5). Figure 9 shows the Mo 3d XPS spectra of various 3%Mo/ZSM-5 samples. For the as-prepared catalyst, the molybdenum species on the surface of HZSM-5 exist mainly as molybdenum oxide. One can see that the Mo $3d_{5/2}$ (B.E = 232.7 eV) and Mo $3d_{3/2}$ (B.E = 235.6 eV) peaks of fresh catalyst can be attributed to Mo^{6+} (MoO_3) species (Figure 9a), a kind similar to that of Mo (VI) reported by Xia et al.[26] The result is in agreement with the picture depicted by Tessonnier et al.[27] that during catalyst synthesis, the MoO_3 crystallites first dispersed on HZSM-5 and then

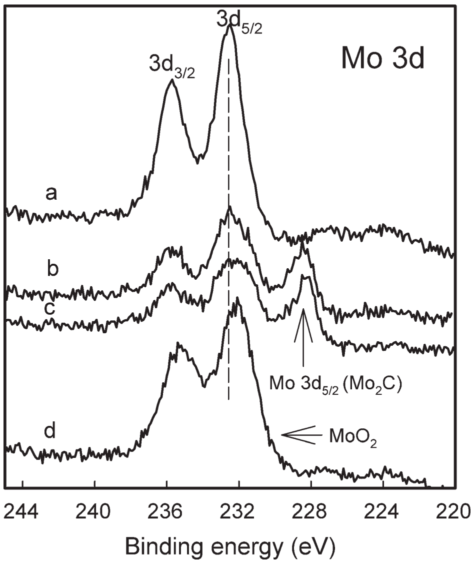

Figure 9. **Mo 3d XPS spectra of 3%Mo/ZSM-5 samples (a) fresh catalyst, (b) exposed to pure CH_4 for 2.5 h, (c) exposed to 2.0% H_2O/CH_4 for 2.5 h, (d) exposure to >3.5%H_2O/ CH_4 for 2 h.**

(Temperature = 730°C).

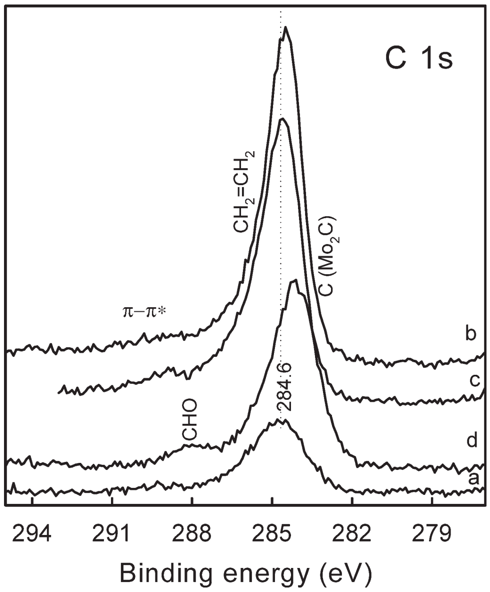

Figure 10. Carbon 1s XPS spectra of 3%Mo/ZSM-5 samples (a) fresh catalyst, (b) exposed to pure CH_4 for 2.5 h, (c) exposed to 2.0% H_2O/CH_4 for 2.5 h, (d) exposure to >3.5%H_2O/CH_4 for 2 h.

(Temperature = 730°C).

migrated as $(MoO_3)_n$ oligomers into the zeolite channels. As for the 3%Mo/ZSM-5 samples collected after 2.5 h of MDA reactions at 730°C using pure CH_4 (Figure 9b) and 2.0%H_2O/CH_4 (Figure 9c) as feed, the Mo 3d XPS profiles show three peaks. The Mo $3d_{5/2}$ peak at BE = 228.5 eV (between that of MoO_2 (229.3 eV)[28] and that of Mo_2C (227.8 eV)[29]) is attributed to $Mo_2O_xC_y$ species originated from the reduction of $(Mo_2O_5)^{2+}$ dimers. Compared to the Mo $3d_{5/2}$ peak at B.E = 232.7 eV of the as-prepared sample, that of the sample exposed to pure CH_4 (Figure 9b) or 2.0%H_2O/CH_4 (Figure 9c) are lower in intensity, indicating that a large portion of MoO_3 and $(Mo_2O_5)^{2+}$ are converted to $Mo_2O_xC_y$ and/or β-Mo_2C. Using the ultra-high field ^{95}Mo NMR technique, Zheng et al.[20] confirmed that there were exchanged Mo species on the zeolite framework. The result of pure CH_4 collected under SJE condition (Figure 9b) differs from those collected under normal condition where MoO_3 species on the surface and/or in the channels of HZSM-5 are completely converted to Mo_2C.[8,30] This is understandable because in the former case, there is a fast diffusion of methane towards the region of low pressure, and the extent of reduction of catalyst by CH_4 is less effective. It is clear that at 2.0%H_2O, the $Mo_2O_xC_y$ is still retained (Figure 9c). However, the Mo $3d_{5/2}$ profile (Figure 9d) of the sample exposed to a CH_4 feed with >3.5% water resembles that of the as-prepared catalyst (Figure 9a). The blue color of the catalyst sample suggests the existence of MoO_2-MoO_3 mixed species.[31] All the results verify that there is complete destruction of Mo_2C and $Mo_2O_xC_y$ species when the water content is >3.5%.

Shown in Figure 10 are the C 1s spectra of the 3%Mo/ZSM-5 samples depicted in Figure 9. Besides the C 1s peaks of amorphous and/or graphitic carbon at 284.6 eV, an asymmetric peak at BE = 286.5 eV attributable to alkene species as well as a weak satellite peak assignable to π–π* transmission (activated by C 1s photoelectrons) appear in the case of exposure to CH_4 and 2.0%H_2O/CH_4 (Figure 10b, c). The results suggest the generation of alkene and aromatic species during MDA reaction. In the case of CH_4 feed with >3.5% water content, C 1s peaks attributable to MoO_3-$Mo_2O_xC_y$-MoO_2[31] and carbonyl species of CHO[12] can be observed (Figure 10d).

Conclusions

The catalytic performance of 3%Mo/ZSM-5 in the presence of water during MDA reaction under SJE condition was investigated. An appropriate amount of water (1.5–2.0%) in methane feed can improve the activity and stability of the 3%Mo/ZSM-5 catalyst in MDA reactions under SJE condition. According to the results of TPO, XPS and HRTEM studies, the improvement of catalytic performance can be related to the removal of surface carbon species before their transformation to surface graphitic or aromatic-type carbon that cause the deactivation of catalyst.

Acknowledgments

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