Promotion effects of Pt and Rh on catalytic performances of Mo/ HZSM-5 and Mo/HMCM-22 in selective methane-to-benzene reaction

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The promotion effects of Pt and Rh on catalytic performances of Mo/HZSM-5 and Mo/HMCM-22 in selective methane-to-benzene reaction were studied in the presence of additive H_2. The selectivity to naphthalene was effectively suppressed and highly selective and stable benzene formation was obtained by the addition of noble metal to the Mo/HZSM-5 and Mo/HMCM-22 catalysts, due to the suppression of carbon deposition on the Brønsted acid sites of zeolite.

KEY WORDS: methane-to-benzene; molybdenum carbides; HZSM-5; HMCM-22; Pt and Rh addition.

1. Introduction

The catalytic conversion of methane-to-benzene (MTB) reaction is of current importance and industrial interest in conjunction with the effective utilization of methane related gases such as natural gas, biogas, and methane hydrate. Since the first report in 1993 by Wang *et al.* [1], Mo_2C/HZSM-5 catalyst was widely studied because of its high activity and selectivity for methane dehydroaromatization towards benzene, toluene and naphthalene [1–25]. As a first step of the reaction, methane should be activated to CH_x species selectively and then it transforms into C2 hydrocarbons. From the previous study, only molybdenum carbide, tungsten carbide, and rhenium metal are active for this selective activation of methane, and the most of other transition metals leads complete methane decomposition. As a second step of the reaction, the activated hydrocarbons are condensed on the Brønsted acid site of HZSM-5 producing benzene. The heavier aromatics such as toluene and naphthalene are formed by successive reaction. Thermodynamically, the productions of benzene, toluene and naphthalene should be equal; however, the selectivity to benzene, toluene, and naphthalene over Mo/HZSM-5 catalyst are 70, 5 and 20%, respectively, due to the molecular shape selective effect of HZSM-5 pore [4–6, 9].

However, there are undesirable reactions, for example, coke formation by complete methane decomposition on molybdenum carbide, or coke formation by heavy aromatics adsorption on the Brønsted acid site of HZSM-5. The problem is that the active sites disappear when the zeolite pore is blocked by coke. In order to improve the stability of the reaction, it is necessary to suppress the coke deposition on the catalyst. From the previous study, there are two sources of coke, one is from methane and another is from heavy aromatics like naphthalene [25], and the latter can be a more critical reason of the deactivation. Thus, not only the stability but also the selectivity to benzene is significant factor to improve this reaction. In any case, the improvement of the catalytic process and the development of highly stable catalysts are strongly required.

We have investigated the additive effects of oxidative gases to the methane feed to stabilize the reaction. As we reported, a small amount of CO, CO_2, or H_2O added into the feed gas can react off the deposited coke during the reaction and significantly enhance the stability of the reaction [15–19]. However, these oxidative gases produce CO and CO_2 as by-products, which make it difficult to separate hydrogen from the reaction mixture. Thus, we have investigated the effects of adding a few percent of H_2 to the methane feed leading to enhanced reaction stability because of the efficient removal of coke under working conditions [20, 21].

Adding a second metal to Mo/HZSM-5 seems to be the most promising way to develop highly stable catalysts for the reaction. Previously, we found that Fe or Co addition to the catalyst is effective to enhance the stability in the presence of CO_2 [16]. However, the effect of second metal addition has not yet been studied in the presence of H_2. Generally, noble metal such as Rh and Pt can promote the hydrogenation of carbon, and the hydrogenolysis of heavier aromatics. Here, we report that the optimum addition of noble metals to Mo/HZSM-5 results in the enhancement of the selectivity to benzene and the effective improvement of the reaction

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stability owing to efficient removal of coke on the Mo/HZSM-5 in the presence of H_2.

2. Experimental

2.1. Catalysts preparation

About 6 wt.% Mo/HZSM-5 (or HMCM-22) was prepared by the impregnation method using NH_4ZSM-5 (or NH_4MCM-22) and an aqueous $(NH_4)_6Mo_7O_{24}$·$4H_2O$ solution. The water solvent was removed by an evaporator, and then the sample was calcined in air at 823 K for 8 h. NH_4ZSM-5 (or NH_4MCM-22) and $(NH_4)_6Mo_7O_{24}$-$4H_2O$ transformed into HZSM-5 (or HMCM-22) and molybdenum oxide, respectively, by the thermal decomposition during the calcination treatment. Iglesia *et al.* reported that $(Mo_2O_5)^{2+}$ dimers were formed in the pore of HZSM-5 due to the sublimation of MoO_3 [25]. Noble metal added catalysts were prepared by co-impregnation method using $RhCl_3$·$3H_2O$ or H_2PtCl_6·$6H_2O$ with the molar ratio (noble metal/Mo) of 0.2.

The molybdenum oxide sample was carburized before the reaction. When molybdenum oxide is carburized by methane directly, β-Mo_2C is formed. The sample was heated under a flowing CH_4 + $4H_2$ mixture up to 973 K using a heating rate of 5 K min^{-1}, and then kept for 2 h at that temperature.

2.2. Methane dehydroaromatization

The catalytic tests were carried out at a pressure of 3 atm in methane with or without H_2 addition in a continuous flow system with a quartz reactor of 8 mm i.d. charged with 0.3 g of catalyst pellets of 20–42 mesh, as has been reported previously [15–21]. The feed gas mixture (99.9% pure, Sumitomo Seika Chem. Co.) of 90 % CH_4 and 10% Ar was introduced into the reactor at 15 ml min^{-1} (space velocity of methane = 2700 ml g-cat.$^{-1}h^{-1}$) through a mass flow controller. Hydrocarbon products including C_2–C_4 alkanes (and/or alkenes) and condensable C_6–C_{12} aromatics such as benzene, toluene, xylene, and naphthalene were analyzed by on-line FID gas chromatography on a Porapak-P column using a six-way sampling valve heated to 533 K and the on-line TCD GC for H_2, Ar, and CH_4 on an activated carbon column. Using an internal standard analyzing method of 10% v/v in the feed gas of methane with or without H_2, the conversion of methane and formation rates of hydrogen and hydrocarbon products were evaluated. Formation rates of hydrocarbon products were calculated as well and were expressed on a carbon basis.

2.3. Characterizations

TG-TPO measurements were conducted in a TG/DTA/MASS system (Mac. Science. Co., TG-DTA2020S). The O_2/He stream consisted of 15 ml min^{-1} O_2 and 100 ml min^{-1} He which was passed over 30 mg of catalyst placed in a fused alumina boat after having been used in the reaction for 50 with H_2 addition. The temperature was increased at a rate of 10 K min^{-1} and H_2O, CO, and CO_2 were continuously monitored by a mass spectrometer (ThermoLab VG Gas) at m/e = 18, 28, and 44, respectively. Relative peak heights of CO + CO_2 were calculated by considering the relative probability of ionization and fragmentation for each compound.

The carbide phases in HZSM-5 were analyzed by X-ray diffraction (XRD), using a Rigaku MiniFlex with a Cu Kα monochromatized radiation source. The powder diffractograms of the various samples were recorded from 20° to 80° with a scanning rate of 2° min^{-1}.

3. Results and discussion

3.1. Effect of hydrogen addition to methane feed

Methane conversion and selectivity to hydrocarbon products over Mo/HZSM-5 and Mo/HMCM-22 catalysts with several amounts of H_2 addition to methane feed are listed in Table 1. Time course of benzene formation rates over Mo/HZSM-5 and Mo/HMCM-22 catalysts are shown in Figure 1. Methane conversion without added H_2 was approximately 9–10%, almost reaching equilibrium (10.5% CH_4 conversion at 1023 K under 0.3 MPa). However, the catalysts were

Table 1
Methane conversion and selectivity to hydrocarbon products over Mo/HZSM-5 and Mo/HMCM-22 catalysts with several amounts of H_2 addition to methane feed

Catalyst	H_2 addition (%)	CH_4 conversion (%)	Hydrocarbon selectivity (%) (carbon base)				
			C_2	C_3	Benzene	Toluene	Naphthalene
Mo/HZSM-5	0	8.9	5.8	0.1	70.0	4.8	19.3
Mo/HZSM-5	6	8.0	6.9	0.8	60.6	5.1	26.6
Mo/HZSM-5	9	7.0	8.0	0.1	67.1	7.4	17.4
Mo/HMCM-22	0	10.0	5.8	0	86.5	7.4	0.3
Mo/HMCM-22	6	8.4	6.9	0	85.4	6.9	0
Mo/HMCM-22	9	7.9	11.1	0	78.5	10.4	0

The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 ml g^{-1} h^{-1} of CH_4 space velocity. The data were taken at 3 h in time on stream.
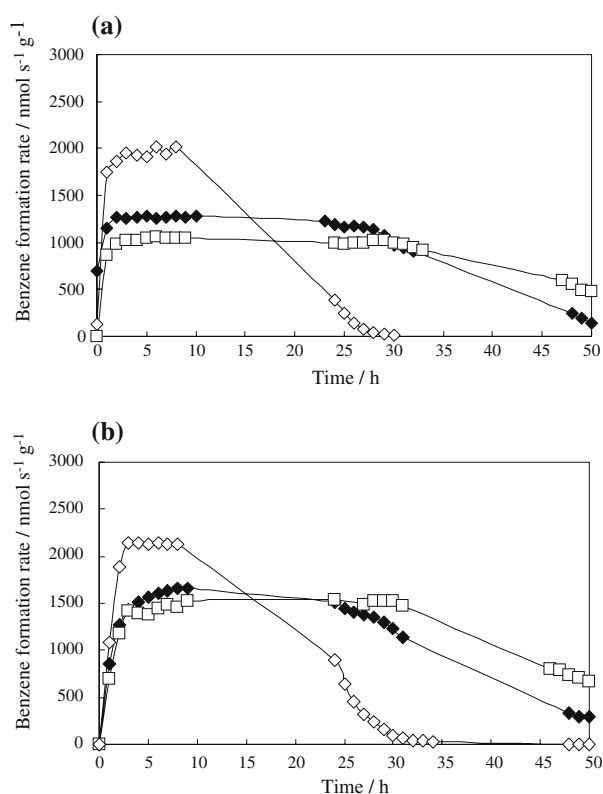
Figure 1. Time course of benzene formation rates over Mo/HHZSM-5 (a) and Mo/HMCM-22 (b) catalysts with several amounts of H_2 addition to methane feed. The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 ml g^{-1} h^{-1} of CH_4 space velocity. $\diamond$: no H_2, $\blacklozenge$: 6% H_2, $\square$: 9% H_2.

deactivated rapidly because of serious carbon deposition. Thus, we had investigated the effects of a few percent of H_2 addition to the methane feed and found that a proper amount of hydrogen (6–9%) promoted remarkably the catalyst stability [20, 21]. When 6 or 9% hydrogen was added into the methane feed gas, methane conversion was lowered to approximately 7 or 8% because of thermodynamic reason, but carbon deposition can be suppressed effectively and longer catalyst life can be obtained. The product selectivity under these conditions was as follows; 70% benzene, 20% naph-

thalene, 5% toluene, 5% C2 hydrocarbons (C_2H_4 and C_2H_6) and a few percent of C3 hydrocarbons (C_3H_6 and C_3H_8) over Mo/HZSM-5, or 85% benzene, 7% toluene, and 7% C2 hydrocarbons (C_2H_4 and C_2H_6) over Mo/HMCM-22. It is known that MCM-22 zeolite has smaller pore size (4.0 × 5.5, 4.1 × 5.1) than ZSM-5 zeolite (5.3 × 5.6, 5.1 × 5.5), and the formation of larger compound became more difficult due to the molecular shape selective effect.

3.2. Effects of noble metal addition on Mo/HZSM-5

Methane conversion and selectivity to hydrocarbon products over noble metal added Mo/HZSM-5 catalysts are listed in Table 2. The reaction was performed at 1023 K, 0.3 MPa, 2700 ml h^{-1} g^{-1} CH_4 SV, and 6–9% H_2 was added to the methane feed. The precursors of these noble metals ($RhCl_3 \cdot 3H_2O$ or $H_2PtCl_6 \cdot 6H_2O$, the molar M/Mo ratio of 0.2) were introduced to the sample together with the molybdenum precursor. By the addition of noble metal, the methane conversion was slightly decreased, since the noble metal can promote the hydrogenation of the reaction products re-forming methane. The selectivity to benzene was increased, and on the contrary, the selectivity to naphthalene was decreased. We discussed that noble metal can catalyze the hydrogenolysis of heavy aromatics such as naphthalene. Under 9% H_2 added condition, the naphthalene formation was effectively suppressed and the selectivity to benzene reached almost 80% over Rh or Pt promoted Mo/HZSM-5 catalysts.

Time course of benzene and naphthalene formation rates over noble metal (Rh or Pt) promoted Mo/HZSM-5 catalysts are shown in Figure 2. Under the reaction condition with added H_2, the initial benzene formation rate did not change so much by the noble metal addition, because the methane conversion was slightly decreased but the selectivity to benzene was increased. This addition was very effective to improve the reaction stability over Mo/HZSM-5 catalyst. Noble metals are known as good catalysts for the activation of hydrogen and for the hydrogenation of carbonaceous species, thus, it can help to remove the deposited coke with

Table 2
Methane conversion and selectivity to hydrocarbon products over noble metal added Mo/HZSM-5 catalysts under 6–9% H_2 addition

Catalyst	H_2 addition (%)	CH_4 conversion (%)	Hydrocarbon selectivity (%) (carbon base)				
			C_2	C_3	Benzene	Toluene	Naphthalene
Mo/HZSM-5	6	8.0	6.9	0.8	60.6	5.1	26.6
Mo/HZSM-5	9	7.0	8.0	0.1	67.1	7.4	17.4
RhMo/HZSM-5	6	7.1	6.7	0.2	68.8	5.7	18.6
RhMo/HZSM-5	9	5.5	13.6	0.4	76.8	8.7	0.5
PtMo/HZSM-5	6	7.2	6.6	0.1	71.6	4.2	17.5
PtMo/HZSM-5	9	5.3	12.3	0.1	79.4	8.2	0

The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 ml g^{-1} h^{-1} of CH_4 space velocity. The data were taken at 3 h in time on stream.
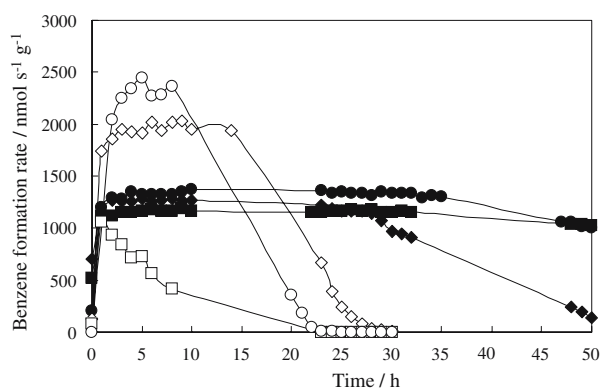
Figure 2. Time course of benzene formation rates over noble metal promoted Mo/HZSM-5 (Rh or Pt/Mo = 0.2). The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 ml g^{-1} h^{-1} of CH_4 space velocity with or without 6% H_2 addition. Solid symbols show the data with 6% H_2 addition, and open symbols show the data without H_2 addition. ◆, ◇: Mo/HZSM-5, ■, □: Rh-Mo/HZSM-5, ●, ○: Pt-Mo/HZSM-5.

added hydrogen and improve the stability. However, under the reaction condition without H_2, they did not give the catalyst any good effects. In the case of Pt addition, the initial benzene formation rate was increased, but deactivated faster. In the case of Rh addition, even the initial rate was lowered. These differences can be due to the different methane decomposition activities of these noble metals. We have investigated the methane conversion over Rh and Pt supported on HZSM-5, and revealed that rhodium showed much higher activity for methane decomposition than platinum, forming no aromatics. These results suggest that methane was presumably decomposed to carbon and hydrogen over noble metal promoters when hydrogen supply was not enough. We discussed that the noble metal addition was effective only under hydrogen-rich condition.

To investigate the ability of Rh and Pt to remove the deposited carbon during the reaction, temperature programmed oxidation experiments (TPO) with the used catalyst (50 h reaction run with 6 % hydrogen addition) were performed. Sum of CO and CO_2 formation profiles during TPO experiments using Mo/HZSM-5, Rh-Mo/HZSM-5, and Pt-Mo/HZSM-5 catalysts are shown in Figure 3. With added H_2 the total amount of the carbon species on the noble metal promoted Mo/HZSM-5 was lower than that on Mo/HZSM-5. The amount of coke on Pt-Mo/HZSM-5 was somewhat lower than that on Rh-Mo/HZSM-5, indicating platinum has higher ability for hydrogenation of carbonaceous species than rhodium. We discussed that platinum which has higher hydrogenation activity and lower methane decomposition activity was more suitable than rhodium as a second metal for Mo/HZSM-5 catalyst. It is accepted that the COx profiles of the Mo/HZSM-5 catalysts after reaction can be divided into a peak at lower and a peak

at higher temperature, which are attributed to carbon associated with molybdenum carbide derived from the complete methane decomposition and to carbonaceous deposits on the Brønsted acid sites of the zeolite mainly derived from adsorbed heavy aromatics, respectively [25]. When the profiles over Rh- and Pt-Mo/HZSM-5 were compared with that over Mo/HZSM-5, the peak area at lower temperature was not so different, but the peak at higher temperature was almost disappeared. Thus, it is reasonable to assume that the addition of noble metal suppresses the coke formation efficiently on the Brønsted acid sites of HZSM-5. This is the direct reason why the reaction stability was drastically improved by the addition of noble metal to the Mo/HZSM-5 catalyst.

3.3. Effects on noble metal addition on Mo/HMCM-22

Noble metal addition is effective to stabilize the reaction over Mo/HZSM-5 catalyst, and we also investigated the effect on Mo/HMCM-22 catalyst. Methane conversion and selectivity to hydrocarbon products over noble metal added Mo/HMCM-22 catalysts under 9% H_2 addition are listed in Table 3. This zeolite has smaller pore size than ZSM-5, and it is more difficult to produce larger aromatics due to the molecular shape selective effect. In this case, the naphthalene formation was not observed, and the selectivity to benzene was almost 80%. By the addition of noble metal, the selectivity to benzene was increased but the change was not as large as in the case of Mo/HZSM-5. Time course of benzene formation rates over noble metal promoted Mo/HMCM-22 are shown in Figure 4. Because the conversion was decreased and the increase of selectivity to benzene was small, the initial rate was decreased. The stability was improved, but the effect was not as drastic as in the case of HZSM-5.
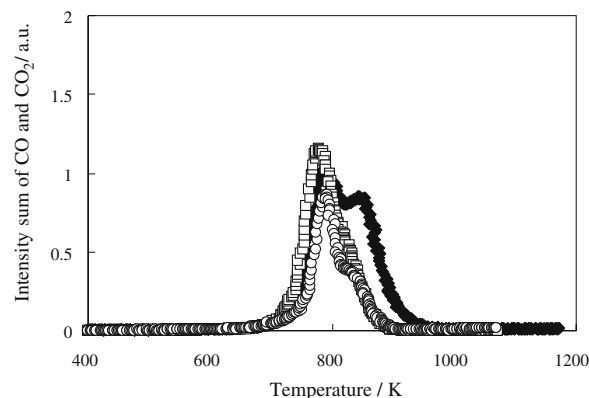

Figure 3. Sum of CO and CO_2 formation profiles during temperature programmed oxidation using noble metal added Mo/HZSM-5 catalysts (Rh or Pt/Mo = 0.2) after 50 h reaction runs with 6% H_2 addition. ◆: Mo/HZSM-5, □: Rh-Mo/HZSM-5, ○: Pt-Mo/HZSM-5.

Table 3
Methane conversion and selectivity to hydrocarbon products over noble metal added Mo/HMCM-22 catalysts under 9% H_2 addition

Catalysts	H_2 addition (%)	CH_4 conversion (%)	Hydrocarbon selectivity (%) (carbon base)				
			C_2	C_3	Benzene	Toluene	Naphthalene
Mo/HMCM-22	9	7.9	11.1	0	78.5	10.4	0
RhMo/HMCM-22	9	7.2	9.5	0	84.1	6.4	0
PtMo/HMCM-22	9	7.1	9.3	0	83.4	7.3	0

The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 ml g^{-1} h^{-1} of CH_4 space velocity. The data were taken at 3 h in time on stream.

3.4. Formation of α-MoC$_{1-x}$ by noble metal addition

XRD patterns of Mo/HZSM-5 catalysts and unsupported Mo carbides are shown in Figure 5. Normally, the thermodynamically stable phase β-Mo$_2$C, which has a hexagonally closed packed structure, is the main product of the direct carburization of Mo oxide (Figure 5-a, d): However, the metastable phase α-MoC$_{1-x}$, which has a face-centered cubic structure, was formed by the addition of noble metal. Bouchy *et al*. studied the different catalytic performance of β-Mo$_2$C and α-MoC$_{1-x}$ supported on HZSM-5 for methane dehydroaromatization [22, 23], and found that α-MoC$_{1-x}$ exhibited a more stable catalysis for this reaction. Thus, the formation of alpha carbide phase is also the reason why the reaction was stabilized by the addition of noble metal. These carbides did not change during the 50 h time on stream with H_2 addition.

Obviously, one of the roles of noble metal is to promote the formation of α-MoC$_{1-x}$ instead of β-Mo$_2$C. Lee *et al*. reported similar phenomenon: α-MoC$_{1-x}$ was prepared from 0.25 wt.% Pt added MoO$_3$ by the carburization with CH$_4$ + 4H$_2$ [26]. Usually, MoO$_3$ was reduced to MoO$_2$ in the methane and hydrogen mixed stream at 873–973 K, and MoO$_2$ transformed into β-Mo$_2$C, while the carburization temperature was kept at

973 K [27]. When Rh or Pt added MoO$_3$ was carburized under the same conditions, Rh or Pt was reduced to the metallic state before MoO$_3$ transformed into MoO$_2$. Then metallic Rh or Pt can be a catalyst to activate methane, and promotes MoO$_x$H$_y$C$_z$ (FCC structure) formation instead of MoO$_2$, which is known as a precursor of α-MoC$_{1-x}$ [22].
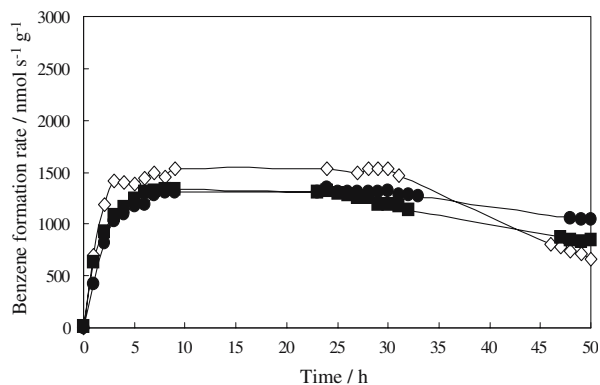

Figure 4. Time course of benzene formation rates over noble metal promoted Mo/HMCM-22 (Rh or Pt/Mo = 0.2). The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 ml^{-1} h^{-1} of CH$_4$ space velocity with 9% H$_2$ addition. ◇: Mo/HMCM-22, ■: Rh-Mo/HMCM-22, ●: Pt-Mo/HMCM-22.
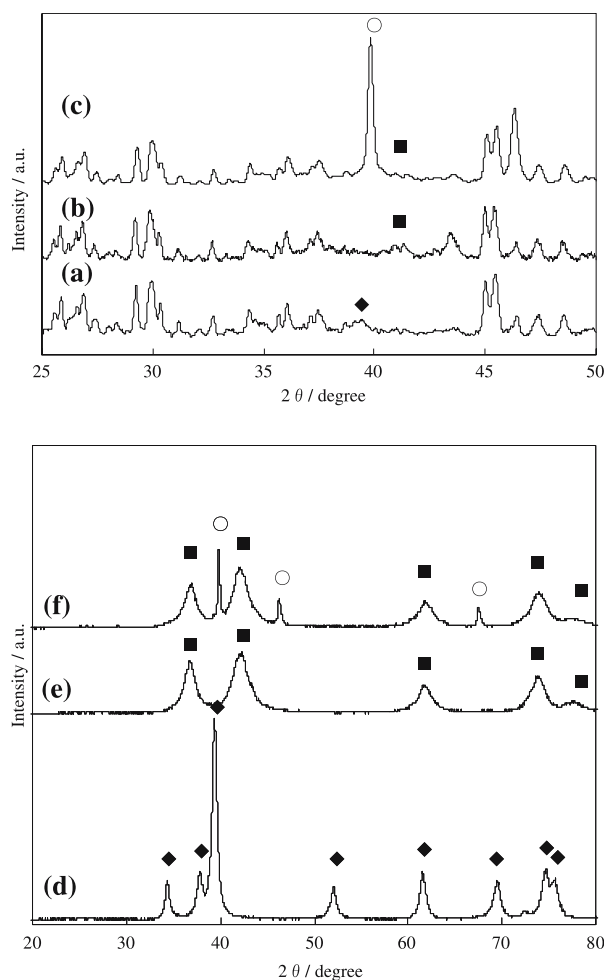
Figure 5. XRD patterns of Mo/HZSM-5 catalysts and unsupported Mo carbides. (a) Mo/HZSM-5 (b) Rh-Mo/HZSM-5 (c) Pt-Mo/HZSM-5 (d) Unsupported Mo carbide (e) Unsupported Rh-Mo carbide (f) Unsupported Pt-Mo carbide. These samples were carburized by CH$_4$ + 4H$_2$. ◆: β-Mo$_2$C, ■: α-MoC$_{1-x}$, ○: Pt.

We also discussed the relative location of noble metal with respect to Mo carbides. When we consider that noble metals promote the formation α-MoC_{1-x}, their location should be very close to molybdenum. Rh K-edge or Pt L_{III}-edge EXAFS experiments using the Rh- or Pt-Mo/HZSM-5 catalyst revealed that noble metal was present in the metallic state. Thus, noble metal did not form a bimetallic phase with molybdenum carbide.

3.5. Roles of noble metal

We discussed the roles of noble metal to the Mo/HZSM-5 catalyst using a schematic representation of the methane dehydroaromatization over noble metal promoted Mo/HZSM-5 which is shown in Figure 6. First, methane was activated to CH_x species selectively on the molybdenum carbide located in the pore of HZSM-5 zeolite (Figure 6, Reaction step 1). Then the activated hydrocarbons are condensed on the Brønsted acid site of ZSM-5 and benzene was produced (Figure 6, Reaction step 2). The heavier aromatics such as naphthalene were formed by successive reaction (Figure 6, Reaction step 3). However, there were undesirable reactions; coke formation by complete methane decomposition on molybdenum carbide (Figure 6, Undesirable reaction 1), and coke formation by heavy aromatics adsorption on the Brønsted acid site of HZSM-5 (Figure 6, Undesirable reaction 2). By the addition of noble metal, coke was effectively removed by hydrogenation and the reaction was drastically stabilized under H_2 added conditions (Figure 6, Role of noble metal 1). However, under non-H_2 added conditions noble metal promotes coke deposition and gives the catalyst no-positive effect. The selectivity to naphthalene was decreased and that to benzene was increased, possibly because the noble metal can catalyze the hydrogenolysis of heavy aromatics (Figure 6, Role of noble metal 2). However, when the naphthalene formation has already been suppressed, like in the case of Mo/HMCM-22, the effect of noble metal addition was no as drastic as in the case of HZSM-5. The formation of α-MoC_{1-x}, which has more stable catalytic performance, was also promoted instead of β-Mo_2C (Figure 6, Role of noble metal 3).

4. Conclusions

The effects of noble metal addition to the Mo/HZSM-5 catalyst are as follows.

(1) Coke is removed by hydrogenation and the reaction is drastically stabilized under H_2 added conditions by the addition of noble metal.
(2) The selectivity to benzene is increased and that to naphthalene is suppressed by the addition of noble metal, because the noble metal can catalyze the hydrogenolysis of heavy aromatics.
(3) The formation of α-MoC_{1-x}, which has more stable catalytic performance for methane dehydroaromatization, was also promoted instead of β-Mo_2C by the addition of noble metal.

Figure 6. Schematic representation of the methane dehydroaromatization over noble metal promoted Mo/HZSM-5.

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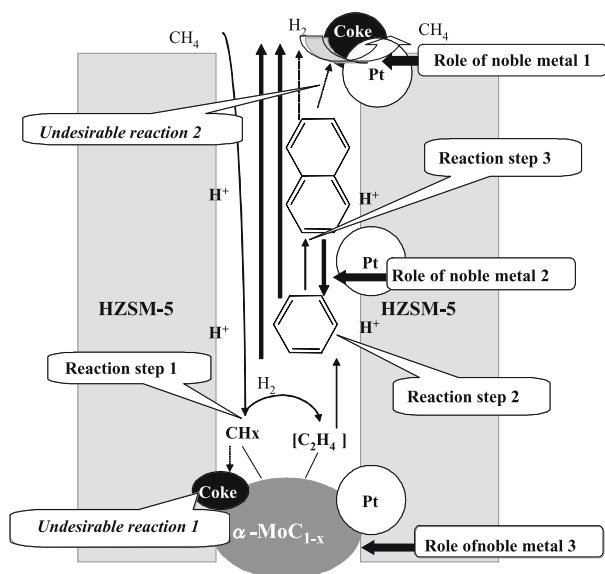[13] F. Solymosi, L. Bugyi and A. Oszko, Catal. Lett. 57 (1999) 103.

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