Effects of Rhodium Addition to Mo/HZSM-5 Catalyst for Methane Dehydroaromatization

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Rhodium added 6 wt % Mo/HZSM-5 catalyst (Rh/Mo = 0.2) exhibited highly stable and active performances in the methane dehydroaromatization reaction at 1023 K under 0.3 MPa with 2700 mL g^{-1} h^{-1} of the methane feed with 6% hydrogen addition due to the effective suppression of the coke deposition on the Brønsted acid sites of HZSM-5.

Recently, methane dehydroaromatization is considered as the one of the most important reaction from the viewpoints of utilization of methane related gases such as natural gas, biogas, and methane hydrate, producing aromatic compounds as petrochemical feedstock and hydrogen for fuel cell society. We have previously reported that Mo_2C/HZSM-5 and Re/HZSM-5 catalysts exhibit high activity and selectivity towards benzene and naphthalene, as shown in Figure 1.[1–4] Molybdenum carbide or rhenium metal activates methane, and condensation of activated methane occurs on the Brønsted acid site of ZSM-5 producing aromatics due to the shape selectivity effect.

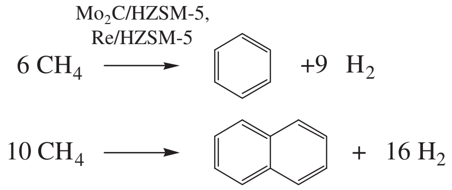

Figure 1. Methane dehydroaromatization over Mo_2C/HZSM-5 and Re/HZSM-5 catalysts towards benzene and naphthalene.

Nevertheless, these catalysts were readily deactivated during the pure methane dehydroaromatization process owing to the serious coke deposition reducing the pore size of HZSM-5 zeolite support. To overcome this problem, we have investigated effects of a few percent of CO_2 or H_2 addition to the methane feed and revealed that it promoted remarkably the catalyst stability owing to the efficient removal of coke under the working conditions.[3,4] Here, we report that the optimum addition of noble metals, such as Rh and Ru, to the Mo/HZSM-5 gives the effective improvement of the catalyst stability due to efficient removal of coke under the reaction with H_2.

The 6 wt % Mo/HZSM-5 catalyst was prepared by conventional impregnation technique. NH_4-ZSM-5 zeolite ($SiO_2/Al_2O_3 = 40$, Tosoh. Co., Japan) was added into an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Kanto Chem. Co.). When Rh or Ru was added to the catalyst, $RhCl_3\cdot 3H_2O$ (Kanto Chem. Co.) or $RuCl_3\cdot nH_2O$ (Kanto Chem. Co.) was used as a precursor. An aqueous solution of this compound was mixed with the solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and by co-impregnation technique they were loaded on the NH_4-ZSM-5 at the same time. After removal of the water solvent using an evaporator, the samples were calcined under air stream at 823 K for 8 h. By the thermal decomposition NH_4ZSM-5 was changed to HZSM-5 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ transformed into molybdenum oxide. Then the samples were carburized before the reaction. 0.3 g of the sample was fixed in the U-tube quartz reactor and was heated up to 973 K under 50 mL min^{-1} of $CH_4 + 4H_2$ stream with 5 K min^{-1} of heating rate, and then it was kept at 973 K for 2 h. After the carburization, the gas stream was switched to 15 mL min^{-1} of $9CH_4 + Ar$ reactant gas with or without 6% hydrogen in methane base, the total pressure was increased to 0.3 MPa, and the temperature was increased up to 1023 K within 10 min, and then the methane dehydroaromatization was performed. All the products were analyzed by on-line FID-GC (for hydrocarbons) and TCD-GC (for CH_4, H_2, and Ar). The molybdenum carbide phases on the HZSM-5 were analyzed for phase identification by X-ray diffraction (XRD), using a Rigaku MiniFlex with a Cu Kα monochromatized radiation source. Temperature programmed oxidation (TPO) was performed using a TG/DTA/MASS system (Mac. Science. Co., TG-DTA2020S) to characterize the deposited carbon on the used catalyst. The experimental conditions were as follows: 30 mg of the used catalyst, O_2/He stream consisted of $O_2 = 4$ mL min^{-1} and He = 100 mL min^{-1}, and 10 K min^{-1} of heating rate.

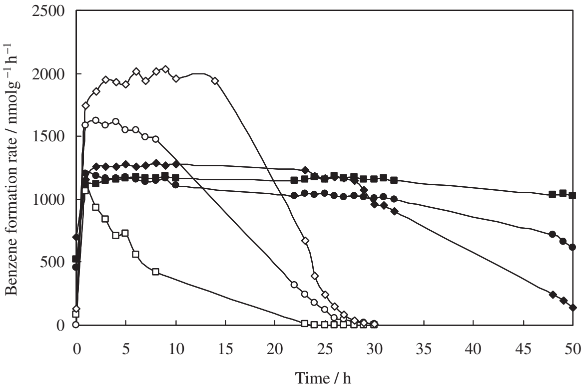

Figure 2. Time course of benzene formation rates over Mo/HZSM-5, Ru-Mo/HZSM-5, and Rh-Mo/HZSM-5 catalysts carburized by $CH_4 + 4H_2$. The reaction was performed under conditions of 1023 K, 0.3 MPa and 2700 mL g^{-1} h^{-1} of CH_4 space velocity with or without 6% H_2 addition. Solid symbols show the data with 6% H_2 addition, and open symbols show the data without H_2 addition. ◆, ◇: Mo/HZSM-5, ●, ○: Ru-Mo/HZSM-5, ■, □: Rh-Mo/HZSM-5.

Time course of benzene formation rates over Mo/HZSM-5, Ru–Mo/HZSM-5, and Rh–Mo/HZSM-5 catalysts carburized by $CH_4 + 4H_2$ are shown in Figure 2. When the reaction was performed without H_2 addition, the initial benzene formation rate over Mo/HZSM-5 was approximately 2000 nmol s^{-1} g^{-1} (CH_4 conversion: 8.5%), but after 14 h the catalyst started to be deactivated. The addition of Rh or Ru was not effective under the reaction condition without H_2 addition. The benzene formation rates were decreased and the stability during the reaction was not improved. The possible reason is that methane was decomposed to carbon and hydrogen over Rh or Ru particles, and then the benzene formation rate was decreased and the catalyst was deactivated faster. Then the effects of the noble metal addition into the catalyst were investigated under the reaction condition with 6% H_2 addition. When 6% H_2 was added into the methane feed, the methane conversion and the benzene formation rates were decreased because of equilibrium reason,[3] for example, the initial benzene formation rate over Mo/HZSM-5 was approximately 1300 nmol s^{-1} g^{-1} (CH_4 conversion: 7.5%). In this condition, Mo/HZSM-5 has much higher stability comparing with the case of non-hydrogen reaction condition; after 22 h the catalyst started to be deactivated. When Rh or Ru was added to Mo/HZSM-5 catalyst, the stability during the reaction run was drastically improved, especially, the benzene formation rates over the Rh-Mo/HZSM-5 (approximately 1200 nmol s^{-1} g^{-1}) was not decreased drastically within 50 h reaction run (CH_4 conversion: 7.0%). This drastic improvement for the catalyst life is clearly observed in time course of the naphthalene formation rates. Naphthalene is considered as a precursor of graphite, which reduces the pore size of HZSM-5, and its formation rate is decreased faster than that of benzene because of molecular shape selectivity effects.[5] The naphthalene formation rate over Mo/HZSM-5 was decreased drastically (approximately 700 to 0 nmol s^{-1} g^{-1} in 30 h); however, that over Rh–Mo/HZSM-5 was kept to be observed during the reaction run (approximately 300 to 60 nmol s^{-1} g^{-1} in 50 h). After all, the addition of the noble metal was very effective to keep the stability of the catalytic activity, only when the reaction was performed under the hydrogen-added condition. Rh and Ru are known as good catalysts for activation of hydrogen and hydrogenation of carbon species, and these abilities can give the catalyst stability, removing the deposited coke with added hydrogen.

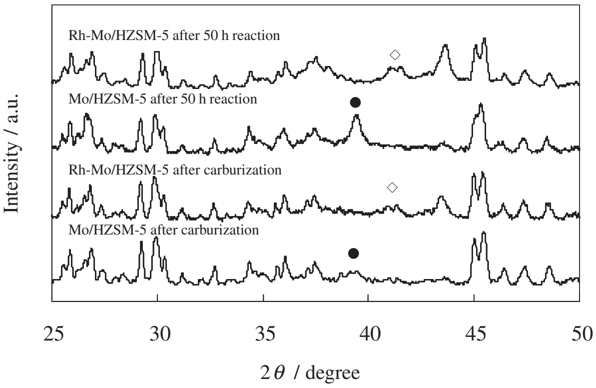

Figure 3. XRD patterns of Mo/HZSM-5 and Rh–Mo/HZSM-5 catalysts. ●: β-Mo_2C, ◇: α-MoC_{1-x}.

XRD patterns of Mo/HZSM-5 and Rh–Mo/HZSM-5 catalysts are shown in Figure 3. Normally, β-Mo_2C is the main product by the direct carburization from MoO_3; however, by the addition of Rh α-MoC_{1-x} was formed. Lee et al. have reported the similar phenomenon; α-MoC_{1-x} was prepared from 0.25 wt % Pt added MoO_3 by the carburization with $CH_4 + 4H_2$.[6] α-MoC_{1-x} is more stable catalyst for the methane dehydroaromatization,[5] thus, one of the role of Rh is a promoter to form α-MoC_{1-x} instead of β-Mo_2C. These carbides did not change during the reaction.

To investigate the ability of Rh to remove the deposited carbon during the reaction, temperature programmed oxidation experiments (TPO) using the used catalyst (50- or 30-h reaction run with or without 6% hydrogen addition, respectively) were performed. Sum of Co and CO_2 formation profiles during TPO experiments using Mo/HZSM-5 and Rh–Mo/HZSM-5 catalysts after reaction runs are shown in Figure 4. When the Rh–Mo/HZSM-5 was used under the reaction condition without H_2 addition, much more amount of CO*x* was detected comparing with the Mo/HZSM-5 catalyst, thus, the methane feed was decomposed to carbon and hydrogen completely over Rh particle. However, under the H_2 added reaction condition the total amount of the carbon species on the Rh–Mo/HZSM-5 was less than that on the Mo/HZSM-5. The CO*x* profiles from Mo/HZSM-5 catalysts used in the reactant gas consisted of two peaks at lower and higher temperature, which were attributed to the carbon associated with molybdenum and to carbonaceous deposits on the Brønsted acid sites of the zeolite respectively.[3,7] When the profile over Rh–Mo/HZSM-5 was compared with that over Mo/HZSM-5, the peak area at lower temperature was not so different, but the peak at higher temperature was smaller than that in the case of Mo/HZSM-5. Thus, we concluded that Rh suppresses the coke formation efficiently on the Brønsted acid sites of HZSM-5.

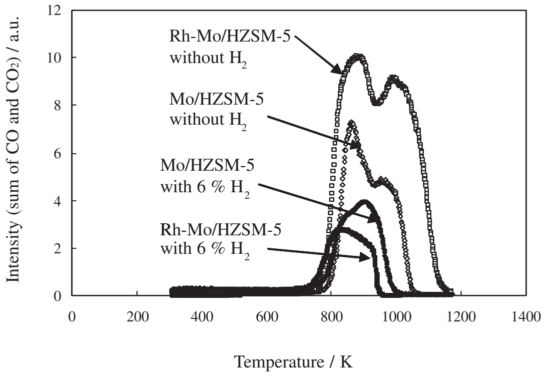

Figure 4. Sum of CO and CO_2 formation profiles during temperature programmed oxidation experiments using Mo/HZSM-5 and Rh–Mo/HZSM-5 catalysts after reaction runs. The reaction was performed for 50 or 30 h, with or without 6% H_2 addition. Solid symbols show the data with 6% H_2 addition, and open symbols show the data without H_2 addition. ◆, ◇: Mo/HZSM-5, ■, □: Rh–Mo/HZSM-5.

In summary, the addition of Rh to the Mo/HZSM-5 catalyst gives the catalyst stability drastically under H_2 added reaction, suggesting it is a good catalyst for re-hydrogenation of deposited carbon only when hydrogen was fully supplied to the methane feed.

References and Notes

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