Catalysis Letters Vol. 89, Nos. 1–2, July 2003 (© 2003)

Highly stable performance of methane dehydroaromatization on Mo/HZSM-5 catalyst with a small amount of H_2 addition into methane feed

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Received 21 February 2003; accepted 18 May 2003

With a small amount of H_2 ($3 \sim 6\%$) addition into methane feed, coke formation on 6 wt% Mo catalyst during the methane dehydroaromatization reaction was effectively suppressed and the catalyst stability was increased evidently under the reaction conditions of 1023 K, 0.3 MPa and 2520 mL g-MFI^{-1} h^{-1} of methane space velocity.

KEY WORDS: methane dehydroaromatization; Mo catalyst; H_2 addition; stability.

1. Introduction

In the last decade, a lot of research work focused on the methane dehydroaromatization reaction to form benzene and naphthalene not only for its effective utilization of natural gas as an alternative petrochemical feedstock but also for its hydrogen production for fuel cells [1–9]. At severe reaction conditions such as high reaction temperature and high space velocity, however, fast decrease in catalytic activity resulting from coke formation restricts its further industrial application. As we reported, a small amount of CO or CO_2 added into methane feed gas can remove the coke during the reaction and significantly enhance the stability [10,11]. Similarly, a suitable amount of O_2 or NO added into the feed gas also keeps the catalyst life a little longer [12,13]. However, these oxidative gases produce CO and CO_2 as by-products, which make it difficult to separate hydrogen from the reaction product. Recently, we reported that the highly stable performance of catalytic methane dehydroaromatization could be achieved by use of a periodic switching of methane with H_2 to remove coke under the same conditions as the reaction [14]. However, a large amount of hydrogen has to be used to keep stable activity. The studies of CO_2 and O_2 addition into methane feed also showed that H_2 was found to be responsible in part for the lowering rates of the deactivation in the methane pyrolysis reaction [12,15]. We report here that a small amount of hydrogen co-fed with methane effectively inhibits the formation of coke and stabilizes the catalytic activity at 1023 K. Further, this process serves as a method for an easy operation compared to the periodic switching and for an easy separation of hydrogen from a mixture of the reaction product.

2. Experimental

Honeycomb-type ZSM-5 (Meidensha Co., Japan) was heated at 723 K for 5 h to remove the adsorbed water in the ZSM-5 channel, cooled in vacuum and impregnated with aqueous solution containing a proper amount of ammonium molybdate for 30 min. After it was taken out and the weight change was measured, the catalyst was dried in vacuum and calcined at 773 K for 5 h. About 10 g (ϕ20 mm, height 130 mm) of 6 wt% Mo-loaded honeycomb ZSM-5 catalyst was charged into a high-pressure stainless steel reactor (20 mm i.d.). After carburization with a methane stream at 823 K for 30 min, the methane dehydroaromatization reaction with and without H_2 addition was performed under the conditions of 1023 K, 0.3 MPa and methane space velocity of 2520 mL g-MFI^{-1} h^{-1} in unit weight of MFI used. The products were analyzed by two on-line GCs equipped with FID and TCD detectors.

TG-TPO measurement was conducted on a TG/DTA/MASS system (Mac Science Co., TG-DTA 2020S). The O_2/He stream (flow rate: $O_2 = 15\,\text{mL min}^{-1}$ and $\text{He} = 100\,\text{mL min}^{-1}$) was fed on 30 mg of Mo/HZSM-5 catalyst in a fused alumina boat after being used in the reaction for 10 h. Then, the temperature was increased at a rate of 10 K min^{-1} and H_2O, CO and CO_2 were continuously monitored with a mass spectrometer (ThermoLab VG Gas) at $m/e = 18$, 28 and 44 respectively. Relative peak heights of H_2O and $CO + CO_2$ were calculated by considering the relative probability of ionization and the fragmentation for each compound.

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1011-372X/03/0700–0143/0 © 2003 Plenum Publishing Corporation

3. Results and discussion

Figure 1 shows the formation rate of benzene on 6 wt% Mo/HZSM-5 catalyst in the methane dehydroaromatization reaction with and without H_2 addition into methane feed gas. At 1023 K and 0.3 MPa, the catalytic activity without hydrogen addition into the feed decreased quickly after 10 h of the reaction to ca. 26% of the initial activity probably because of high coke formation. In contrast, by small amount of H_2 addition into the feed gas, the stability increased significantly. With 3.6, 6 and 9% (mol/mol) H_2 addition, catalytic activities kept 74, 88, and 93% of the highest activities, respectively, after 8 h of time on stream in the methane dehydroaromatization reaction. The highest catalytic activities decreased with increasing H_2 partial pressure because of thermodynamic limitation, as shown in figure 2. However, the formation rates of benzene with 3 and 6% H_2 addition into reactant feed were higher than that with no H_2 addition after 5 h of time on stream. Accordingly, the total amount of benzene production will be higher at long time on stream when H_2 was added into the reactant stream. As in benzene production, the formation rates of other products such as hydrogen (not shown), naphthalene and toluene were stabilized by the addition of H_2 into the feed, as seen in table 1. Table 1 also shows that the H_2 addition did not affect the product distribution in hydrocarbons.

The formation rate of H_2 coproduced with all hydrocarbons can be calculated from its stoichiometry; e.g., 9 and 16 moles of H_2 were coproduced with 1 mole of benzene and naphthalene, respectively. The ratio of H_2 formation rate of the experimentally obtained (H_2^{obs}) to the calculated (H_2^{calc}) as above was plotted against time on stream as shown in figure 3. The ratio should go down to unity at no coke formation. At the initial stage of the reaction, the ratio of H_2^{obs}/H_2^{calc} was higher than unity since additional H_2 was produced during the formation of the active phase, Mo_2C, for the reaction. The ratio of H_2^{obs}/H_2^{calc} was also higher than unity throughout the reaction when H_2 was not added into the feed, suggesting that methane was decomposed in forming the coke ($CH_4 = C + 2H_2$). On the other hand, the ratio decreased with an increase in H_2% in the feed and was kept stable with time on stream. It means that the coke formation was significantly suppressed by H_2 addition and reaction stability was increased. E. Iglesia and coworkers also studied the effect of H_2 addition into the reactant feed at 950 K and found the lower first-order deactivation rate constant at a higher H_2% in feed [15]. These results are consistent with this study at 1023 K.

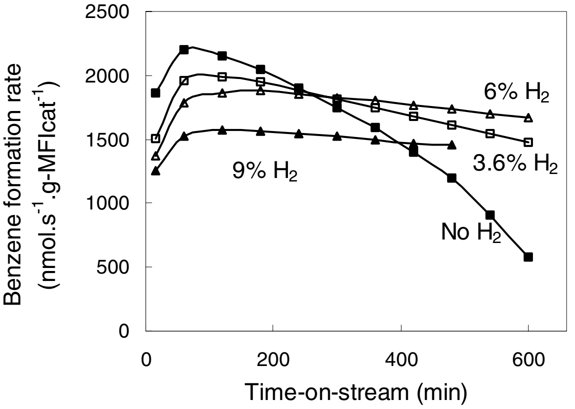

Figure 1. Formation rate of benzene in the methane dehydroaromatization reaction on 6 wt% Mo-loaded honeycomb ZSM-5 catalyst under flowing methane with 0, 3.6, 6, and 9% H_2 and under the conditions of 1023 K, 0.3 MPa and 2520 mL g^{-1}h^{-1} of CH_4 space velocity.

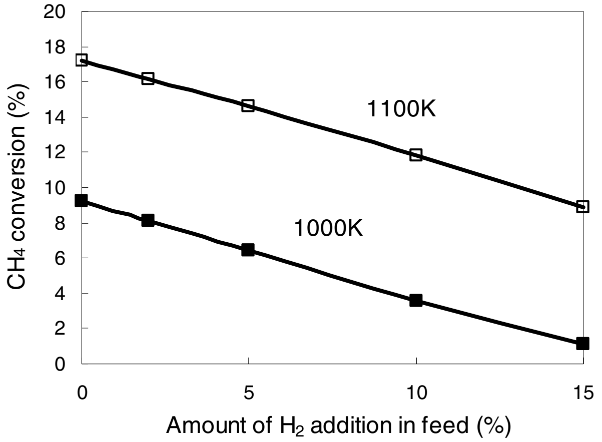

Figure 2. Effect of H_2 addition into methane feed on the equilibrium conversion of methane to benzene.

To further endorse the real reason resulting in the better stability of catalyst, TG-TPO measurements of the catalyst being used for 10 h of the reaction with or without H_2 addition into methane feed were conducted and the results are displayed in figures 4–6. It is obvious from the figures that the coke formation is suppressed by a small amount of H_2 addition into methane feed. After 10 h of the reaction under pure methane flow, ca. 2.4 mg of coke was formed on the catalyst. In contrast, only 1.7 and 1.1 mg of coke were produced on the catalyst during the methane dehydroaromatization reaction for 10 h under flowing methane with 3.6 and 6% H_2, respectively, as shown in figure 4. Figure 5 shows the corrected sum of peak height profiles of $CO + CO_2$ (CO_x) in TG-TPO experiments. The CO_x profile from Mo/ZSM-5 being used in pure methane stream consisted of two peaks at 790 and 870 K, which were attributed to the carbon associated with molybdenum and to carbonaceous deposits on the Brönsted acid sites of the zeolite, respectively [11,16]. In contrast, the other two CO_x profiles of catalysts used under methane with hydrogen only gave one peak at the low-temperature side. The result indicates that H_2 in feed

Table 1
Effect of H_2 addition into methane feed in the methane dehydroaromatization reaction on 6 wt% Mo-loaded honeycomb ZSM-5 catalysts

H_2 amount in feed (%)	CH_4 conversion (%)	Product distribution in hydrocarbons (%)			
		Benzene	Toluene	Naphthalene	$C_2 + C_2'$
0	12.7 (10.4)	75 (67)	4 (6)	9 (5)	10 (21)
3.6	11.0 (9.9)	77 (75)	5 (5)	9 (5)	8 (13)
6	9.5 (8.7)	76 (77)	4 (5)	10 (6)	9 (11)
9	7.6 (6.7)	75 (77)	4 (5)	9 (6)	10 (12)

[a] Reaction temperature: 1023 K, reaction pressure: 3 atm, methane specific velocity: 2520 mL g^{-1} h^{-1}.

[b] Data were taken at 120 min (480 min) of time on stream.

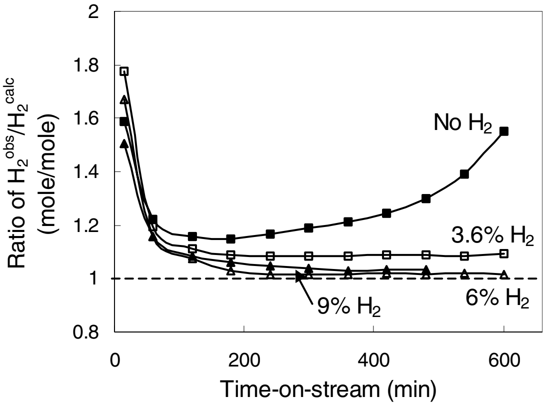

Figure 3. Ratio of H_2 formation rate of the experimentally obtained to the calculated from the formation rates of all hydrocarbon products in the methane dehydroaromatization under flowing methane with 0, 3.6, 6, and 9% H_2.

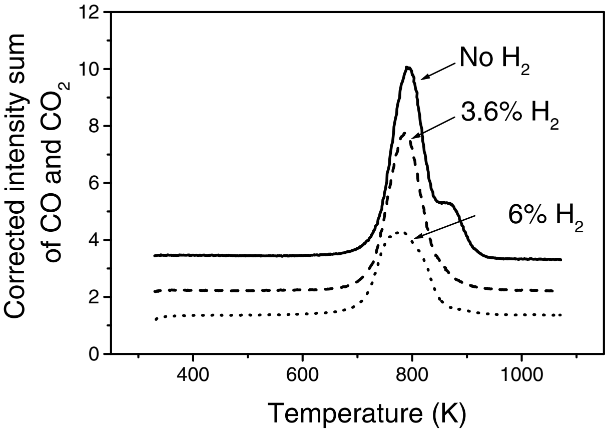

Figure 5. $CO + CO_2$ profiles in TPO experiments of catalysts used in the methane dehydroaromatization for 10 h under flowing methane with 0, 3.6, and 6% H_2.

suppresses the formation of coke formed on Brönsted acid sites. This is very important because it makes it possible to regenerate the used catalyst at lower temperature, where the sublimation of molybdenum oxide and the deterioration of the zeolite framework may be avoided. By comparing the CO_x profiles of figure 5 with the H_2O profiles of figure 6, the composition of coke could be estimated. With H_2 addition into the feed, the coke formed on the catalyst has a lower mole ratio of H/C.

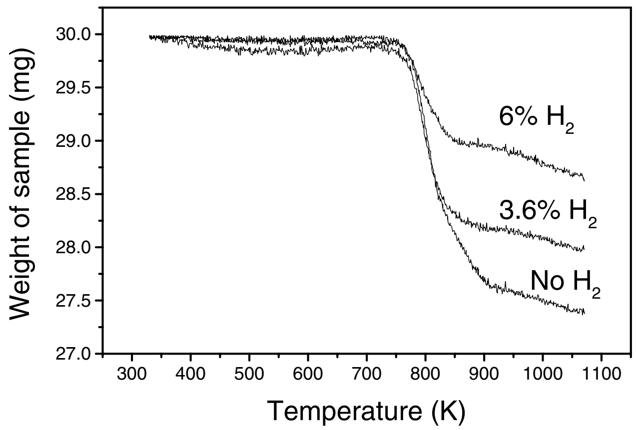

Figure 4. Weight changes in TPO experiments of catalysts used in the methane dehydroaromatization for 10 h under flowing methane with 0, 3.6, and 6% H_2.

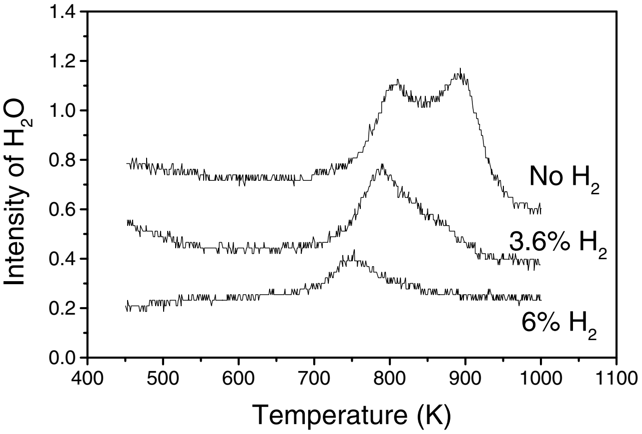

Figure 6. H_2O profiles in TPO experiments of catalysts used in the methane dehydroaromatization for 10 h under flowing methane with 0, 3.6, and 6% H_2.

4. Conclusions

In summary, a small amount of H_2 addition into methane feed is a very effective and simple method to suppress coke formation on the catalyst, especially the coke formed on Brönsted acid sites, during the methane dehydroaromatization reaction at 1023 K. As a result, the highly stable catalytic performance is achieved.

Acknowledgments

We appreciate the financial support from the New Energy and Industrial Technology Development Organization (NEDO) of Japan through the 2000-2002 FY Regional Consortium R&D Program for New Energy processes of NEDO (12S1001).

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