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Effective coke removal in methane to benzene (MTB) reaction on Mo/HZSM-5 catalyst by H_2 and H_2O co-addition to methane

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The catalytic dehydro-aromatization reaction over Mo/HZSM-5 catalyst was drastically stabilized by the co-addition of 5.4% H_2 and 1.8% H_2O to methane feed at 750 °C, 0.3 MPa and methane space velocity of 3000 mL g^{-1} h^{-1}, suppressing the coke formation effectively, compared with single hydrogen or steam addition.

KEY WORDS: methane dehydro-aromatization; Mo catalyst; H_2 addition; H_2O addition.

1. Introduction

Since the initial discovery in 1993 [1], the methane dehydro-aromatization on Mo catalyst has already been known as an effective utilization of natural gas to produce hydrogen and petrochemical products; however, the fast catalyst deactivation due to the serious coke formation at high reaction temperature is a big obstacle for its industrial application [2–9]. Thus, in the last several years many researchers focused on the suppression of the coke formation on Mo catalyst [10–16]. Except the CO_2/CO addition [3], a small amount of hydrogen or steam addition to methane feed was also proved to be able to improve the catalyst stability effectively [11,14]. The added hydrogen can react with the coke, especially the deposited carbonaceous which is burnt-off in oxygen at high temperature [8,11]. However, a high amount of hydrogen addition suppresses the reaction activity markedly, due to the equilibrium shift. On the other hand, we have also reported that a proper amount of steam addition can also reduce the coke formation amount and enhance the stability of catalyst markedly; and it can also increase the hydrogen formation amount at the same time (methane decomposition reaction $CH_4 = [C] + 2H_2$, water gas shift reaction $[C] + H_2O = CO + H_2$, and steam reforming reaction $CH_4 + H_2O = CO + 3H_2$ as a whole). However, excess steam addition oxidizes the active species Mo_2C and cause a little dealumination of zeolite support, resulting in the destruction of catalyst active structure and the decrease of catalyst stability [14]. Thus, neither the excess hydrogen addition nor excess steam addition can be used here to achieve further stability of Mo catalyst. In this work, in order to avoid the disadvantages of excess hydrogen or steam addition and to obtain further higher catalyst stability and higher hydrogen formation rate, the co-addition of proper amount of hydrogen and steam was used to suppress the coke formation on Mo catalyst during reaction. In addition, the deposited coke on the used catalysts in different reactions was characterized by temperature-programmed oxidization technique method.

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2. Experimental

Honeycomb type ZSM-5 (containing 20% binder, Meidensha Co., Japan) was heated at 723 K for 5 h to remove the adsorbed water in ZSM-5 channel, cooled in vacuum and impregnated with aqueous solution containing proper amount of ammonium molybdate. After being taken out and measured the weight change, the catalyst was dried in vacuum and calcined at 773 K for 5 h. About 14 g (ϕ 20 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 methane stream at 823 K for 30 min, the methane dehydro-aromatization reaction with and without H_2 addition and steam addition were performed under the conditions of 1023 K, 0.3 MPa and methane space velocity of 3000 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.

The deposited carbon on the used catalysts was characterized by TG-TPO experiment conducted on a TG/MASS System (Mac Science Co., TG-DTA 2020S). The experiment conditions are as follows: 30 mg of the used catalyst, O_2/He stream consisted of $O_2 = 15$ mL/min and He = 100 mL/min, and 10 K min^{-1} of a heating rate. CO and CO_2 were continuously monitored with a mass spectrometer (ThermoLab VG Gas) at $m/e = 28$ and 44, respectively. Relative peak height of $CO + CO_2$ was calculated by considering the relative

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probability of ionization and the fragmentation for each compound.

3. Results and discussion

Prior to study on the effect of co-addition of hydrogen and steam to methane feed, the effect of different amount of steam addition was investigated at 1023 K under 0.3 MPa. As shown in figure 1, proper amount (1.8% to CH_4 feed) of steam addition improved the reaction stability markedly, while the excess steam addition (2.3% to CH_4 feed) caused a fast deactivation of the catalyst, which might be resulted from the Mo_2C oxidization and steam dealumination of zeolite support [14].

With steam addition to the methane feed and under the reaction conditions of 1023 K and 0.3 MPa, the principal methane reactions are as follows:

$$CH_4 = [C] + 2H_2 \quad \Delta G = -22\,\mathrm{KJ/mol}\,(1023\,\mathrm{K}) \quad (1)$$

$$H_2O + [C] = CO + H_2 \quad \Delta G = -11\,\mathrm{KJ/mol}\,(1023\,\mathrm{K}) \quad (2)$$

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta G = -33\,\mathrm{KJ/mol}\,(1023\,\mathrm{K}) \quad (3)$$

$$CH_4 = 1/6C_6H_6 + 3/2H_2 \quad \Delta G = +22\,\mathrm{KJ/mol}\,(1023\,\mathrm{K}). \quad (4)$$

Compared the Gibbs energy of the steam reforming reaction (3) and methane dehydro-aromatization reaction (4), the steam reforming reaction (3) can be occurred much easier at the gas inlet part of the catalyst layer. Considering one unit of steam can produce three units of hydrogen from the methane steam reforming reaction, the effect of steam addition might be similar to the effect of three times amount of hydrogen addition. It has already been proved by the similar benzene formation performances under the conditions of 1.8% steam addition and 5.4% hydrogen addition (figure 2). Another noticeable thing is that the amount of hydrogen formation in the case of steam addition was much higher than that formed in the hydrogen added reaction (as shown in figure 3).

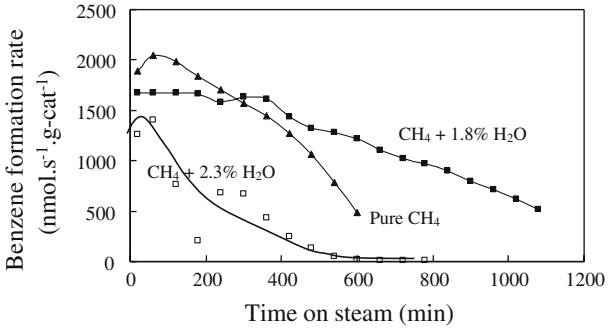

Figure 1. Benzene formation performance with different amount of steam addition to methane feed.

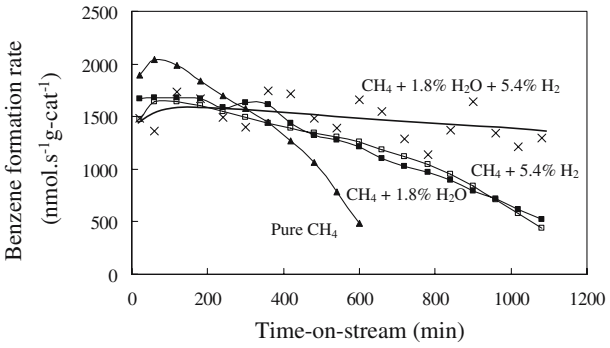

Figure 2. Benzene formation performance in reaction without or with different amount of hydrogen or/and steam addition to methane feed.

In order to achieve further stabilization of the methane dehydro-aromatization on Mo catalyst, the co-addition of 5.4% hydrogen and 1.8% steam to methane feed was performed under the conditions of 1023 K, 0.3 MPa and methane space velocity of 3000 mL g-MFI^{-1} h^{-1}. Just as we expected, the much more stable benzene formation performance (figure 2) and much higher hydrogen formation rate (figure 3) were obtained. After 18 h reaction run, the benzene formation activity was decreased to ca. 30% or 27% of the initial activity with single hydrogen or steam addition, respectively. On the other hand, with the co-addition of steam and hydrogen into the methane feed, the benzene formation activity kept ca. 86% of the highest activity after 18 h reaction run, and the hydrogen formation performance was much more stable than those in reactions with single 1.8% steam addition and with single 5.4% hydrogen addition.

In order to compare the coke formation performance on Mo catalysts used in reactions under different conditions, all the used catalysts were taken out after 18 h reaction run and then characterized by TG-TPO experiment. As shown in figure 4, basically, there are

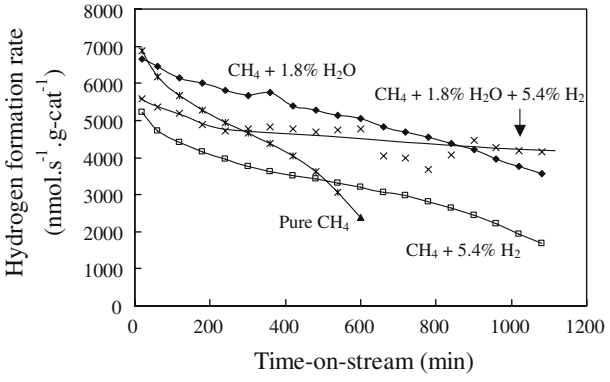

Figure 3. Hydrogen formation performance in reaction without or with different amount of hydrogen or/and steam addition to methane feed.

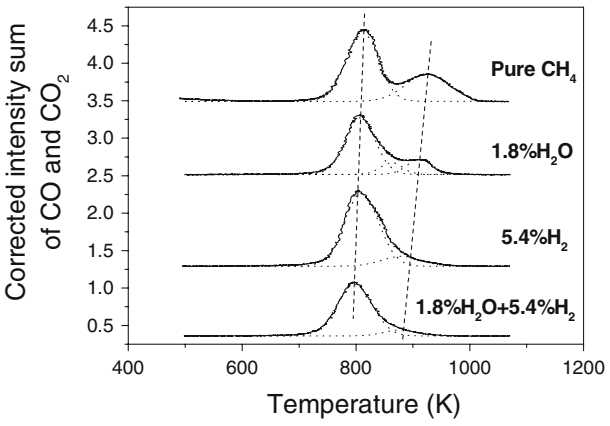

Figure 4. TPO-CO_x profiles of the catalysts used in reaction without or with different amount of hydrogen or/and steam addition to methane feed.

two major carbon deposited on the Mo catalyst. The high temperature coke is usually attributed to the aromatic type of coke deposited on the Brønsted acid site, which is usually responsible for the deactivation of Mo catalyst. The low temperature coke is the carbon deposited on/close to Mo_2C species, which is derived from the deep-condensation of methane [9,11,13,16]. Table 1 shows the data of calculated coke formation amount on the catalysts in reaction under different conditions. After 18 h of the reaction under pure methane flow, about 3.8 mg coke was formed on the catalyst, which was highest and led to the fastest catalyst deactivation among the conditions used in this study. On the contrary, only 1.8 mg coke was produced on the catalyst used in the reaction with the co-addition of hydrogen and steam, especially, the aromatic type of coke was effectively removed by the added hydrogen and steam together, resulting in the most stable catalytic performance of catalyst.

From table 1, it can be also find that the formation amount of low temperature coke was similar under the methane flow with single hydrogen addition (2.2 mg) and single steam addition (2.1 mg); while the formation amount of high temperature aromatic type of coke was much different, 0.8 mg under steam added methane flow and 0.2 mg under hydrogen added methane flow, respectively. The aromatic type of coke formation was suppressed more effectively by the hydrogen addition. This result indicates that the coke removing abilities of steam and hydrogen are somewhat different. However, the interesting thing is that the catalysts under steam added methane flow and hydrogen added methane flow had a similar deactivation rate, although much more amount of coke was formed on the catalyst under steam added methane flow (figure 4 and table 1). It implies that the catalyst deactivation is not simply corresponded to the amount of the coke formed on Mo catalyst. Actually, whatever the steam addition was excess or not, a slight steam dealumination of zeolite was observed on the catalyst used in reaction with steam addition [14]. Thus the pore mouth size of the zeolite channel might be enlarged slightly, which permits much more amount of coke to be formed on the catalyst before its deactivation. It is possible that the high amount of coke formed on the catalyst under the steam added methane flow did not result in a high deactivation rate of the catalyst.

Additionally, a reaction with the co-addition of excess steam (2.4%) and hydrogen (6%) was carried out at 1023 K. As shown in figure 5, the co-added 6% hydrogen markedly stabilized the benzene formation performance in the reaction with excess steam addition (2.4% to CH_4 feed). It indicates that the destruction of the active species on Mo catalyst by the added steam into the methane feed was clearly suppressed by the co-added hydrogen, which might be another function of the co-added hydrogen, except its high coke removing ability. This result is consistent to the work reported by Anna R.S. Darujati *et al.*, hydrogen addition was found to strongly inhibit Mo_2C oxidation by steam at high temperature and increase the oxidation onset temperature clearly [17].

Table 1
The coke formation amount on the Mo catalysts used in different reactions

Reactions	Coke formation amount on catalysts (mg/30 mg-catalyst)		
	Low temperature	High temperature	Total[a]
Pure CH_4 (18 h)	2.5	1.3	3.8
CH_4 + 1.8% H_2O (18 h)	2.2	0.8	3.0
CH_4 + 5.4% H_2 (18 h)	2.1	0.2	2.3
CH_4 + 5.4% H_2 + 1.8% H_2O (18 h)	1.7	0.1	1.8

[a]Data obtained from TGA experiments.

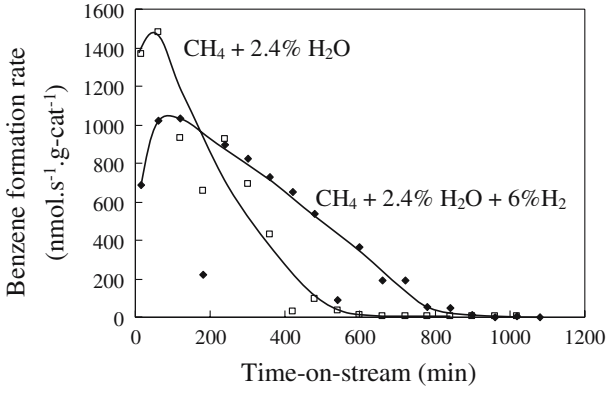

Figure 5. The effect of the co-added hydrogen on benzene formation performance in the reaction with excess steam addition.

4. Summary

With the co-addition of hydrogen and steam to methane feed, the coke formation was further effectively suppressed than in the reaction with single hydrogen or steam addition, and much more stable methane dehydro-aromatization performance was obtained. Much higher hydrogen formation rate was also obtained than that in single hydrogen added reaction. Further more, the destruction of catalyst by steam dealumination during the reaction was also suppressed by the hydrogen addition.

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