Dehydrogenation of methane over Mo/ZSM-5. Effects of additives in the methane stream

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The dehydrogenation of methane was carried out over a Mo/ZSM-5 catalyst. It was revealed that the purity of the methane was very critical for the evaluation of the catalyst activity. In order to study the phenomenon, the effects of the addition of O_2, CO_2, CO or H_2 to the feed were investigated. A small amount of O_2 increased the amounts of aromatic compounds and CO produced. The addition of H_2 scarcely affected the conversion of methane, but it prevented the deactivation of the catalyst, i.e., benzene production remained constant during a 6 h test.

KEY WORDS: methane; dehydrogenation; Mo/ZSM-5; additives.

1. Introduction

Recently, the catalytic conversion of methane into valuable chemicals has attracted much attention, because methane is expected to be a major raw material for higher hydrocarbons. The dehydrogenation of methane in the absence of oxygen is one of the methods to produce aromatic compounds and higher hydrocarbons. The Mo/ZSM-5 catalyst invented by Wang *et al.* in 1993 [1] is one of the promising catalysts for this process and has already been investigated by many research groups [2]. The research is roughly divided into two categories. One is research related to catalyst preparation and possible reaction variables, and the other is that related to the characterization of the catalysts and reaction mechanisms. As for the catalyst preparation and reaction variables, Mo/ZSM-5 prepared from $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ by an impregnation method is generally accepted as one of the best catalysts for the dehydrogenation and aromatization of methane [3–8]. Other metals (Zn, W, Fe, V, Cr, Co, Re) on ZSM-S [9–14] and the promoter effect of the additive metals (Ru) to Mo/ZSM-5 [15] were also investigated. Ichikawa and co-workers demonstrated that the addition of CO and CO_2 to the methane feed promoted stability for the production of benzene and naphthalene with time on stream [16]. They also reported that high activity and stability were achieved under pressurized methane conditions (0.3 MPa) with the addition of CO_2 (5%) [17]. Recently the effects of CO_2, CO and H_2 co-reactants were reported by Iglesia and co-workers [18]. In the studies on the characterization of the catalyst, the conditions of the Mo species were analyzed by XPS [19,20], XAS [21], EPR [22], thermal analyses [23,24], IR and raman spectroscopy [25,26] and NMR [27,28]. Based on these studies, it is accepted that Mo_2C is responsible for the methane activation. In spite of the presence of many studies, little has been reported about the reaction feed gases except the studies already mentioned [16–18].

In this study, the effect of methane purity on the activity of the catalyst was first investigated. As it was revealed that the purity of methane was very critical for the evaluation of the catalyst activity, the effects of the addition of various gases to the methane feed on the catalytic activity were investigated.

2. Experimental

2.1. Materials

All the chemicals were used as received. Two grades of methane of different purities (Takachiho Trading Co. Ltd., Japan) were used, that is, 99.99% (impurities: $O_2 < 0.002\%$, $N_2 < 0.005\%$, $CO_2 < 0.001\%$, $C_2H_6 < 0.002\%$) and 99.0% (impurities: $O_2 < 0.03\%$, $N_2 < 0.25\%$, $CO_2 < 0.40\%$, $C_2H_6 < 0.01\%$). The nitrogen used was of research grade (99.999%) (impurities: $CO < 0.5$ ppm, $CO_2 < 0.5$ ppm, $O_2 < 0.5$ ppm, $H_2O < 1$ ppm, $Ar < 1$ ppm).

2.2. Catalyst preparation

Mo/ZSM-5 (3 wt%) was prepared by the impregnation method. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.166 g) was dissolved in 15 ml of distilled water. Zeolite (Toso Co. Ltd., HSZ-840NHA, Si/Al = 78.8) was immersed in the solution and stirred at 353 K for 2 h. The resulting

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solid was dried at 383 K for 20 h and calcined at 773 K for 6 h under a flowing mixture of N_2 (30 ml/min) and O_2 (30 ml/min).

2.3. Catalytic test

The dehydrogenation of methane was carried out in a continuous gas flow fixed-bed reactor (quartz, 14 mm i.d.) under atmospheric pressure with 1 g of Mo/ZSM-5 (particle size between 24 and 35 mesh) at 973 K. The inlet feed was a mixture of methane (27 ml/min) and N_2 (3 ml/min). N_2 was used as the internal standard. The additive gas (O_2 or CO_2) was introduced through a silica capillary tube (0.05 mm i.d.). This concentration was controlled by the pressure at the inlet of the capillary tube and was determined by gas chromatography. Each concentration of CO and H_2 was controlled by a mass flow controller. The aromatic compounds were trapped by passage through a cold ethanol trap (273 K) for 30 min, and the ethanol solution was analyzed using a capillary gas chromatograph (Shimadzu GC-14A) equipped with an OV-1 column (0.25 mm × 50 m). Quantitative analyses of ethane, CO, methane and N_2 were carried out using a gas chromatograph (Hitachi 263-30) equipped with Polapac Q (2 m) (for the analysis of CO_2 and ethane) and active carbon (2 m) (for the analysis of CO, CH_4 and N_2). The conversion of methane was obtained from the difference between the amounts of the inlet methane and outlet methane. Preliminary experiments showed that a large amount of CO was mostly produced during the first hour after the start of the reaction. This would be due to the possible reduction process of MoO_3 to Mo_2C [27]. Therefore, the catalytic activity was typically evaluated by the amounts of the products during a 5 h test (time on stream: from 1 to 6 h).

3. Results and discussion

3.1. Effect of the purity of methane

Figure 1 shows the effects of the purity of methane on the production of aromatic compounds, ethane and CO during a 4 h test (time on stream: from 1 to 5 h). The 99.0% pure methane produced a large amount of CO, while the 99.99% pure methane produced no CO. These results indicated that the methane impurities affected the amounts of the products. Therefore, the effects of the various additional gases in the inlet methane on the activity of Mo/ZSM-5 were next investigated.

3.2. Effect of the addition of O_2 to the feed

When we investigated the effects of the various additional gases to the feed, the starting time of adding the gas to the feed was initially examined using O_2. When O_2 (0.49%) was added to the feed from the start of the reaction, only CO and CO_2 were obtained during the 6 h test. This was possibly due to the inhibition of the formation of Mo_2C, which was demonstrated as the active species for the dehydrogenation of methane to give aromatics. As a result, the mixture of methane and N_2 (internal standard) was passed through the catalyst for the first 0.5 h in order to activate the catalyst, and then additional gas was added. Figure 2 shows the effect of the addition of O_2 on the activity. The addition of a small amount of O_2 (0.49%) increased the amount of benzene produced. A 0.49% O_2 addition gave the maximum amount of benzene. The addition of O_2 up to 1.11% slightly decreased the production of benzene, while the addition of O_2 (10%) was reported to inhibit the production of benzene [29]. The amount of CO produced increased with an increase in O_2, while no CO_2 was observed. The addition of more than 0.49% of O_2 decreased the conversion of methane, while an increasing amount of CO was produced. Figure 3 shows the effect of the addition of O_2 on the total amounts of the consumed CH_4 for 5 h, the total amounts of the products represented by the equivalent moles of CH_4, and the difference in the two values. From 0 to 0.49% O_2 concentrations, the subtraction of the total amount of the products from that of the consumed CH_4 gives positive values, which decreased with an increase in the O_2 concentration. This indicates that the difference corresponds to the carbon deposition on the catalyst surface during the reaction. On the other hand, the difference gives negative values from 0.66 to 1.1% O_2 concentrations. This indicates that carbon deposited

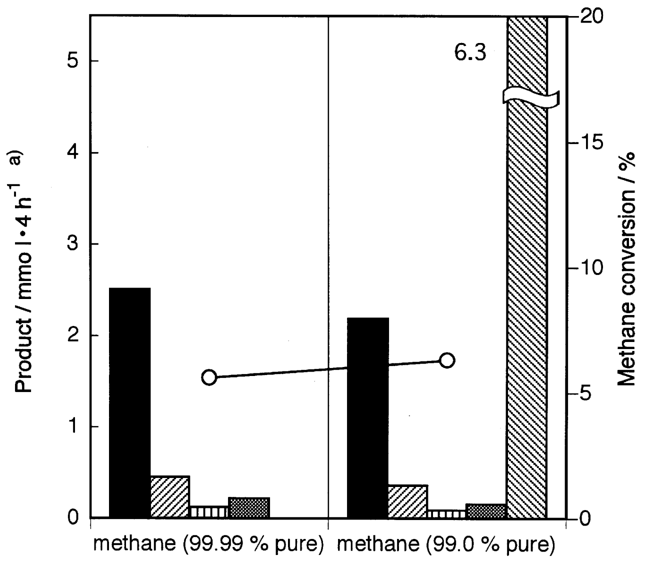

Figure 1. Effect of the purity of methane used: ■, benzene; ▨, naphthalene; ▥, toluene; ▩, ethane; ▧, CO; ○, conversion of methane. CO_2 was not detected in the outlet feed. (a) Products during the 4 h test (time on stream: from 1 to 5 h).

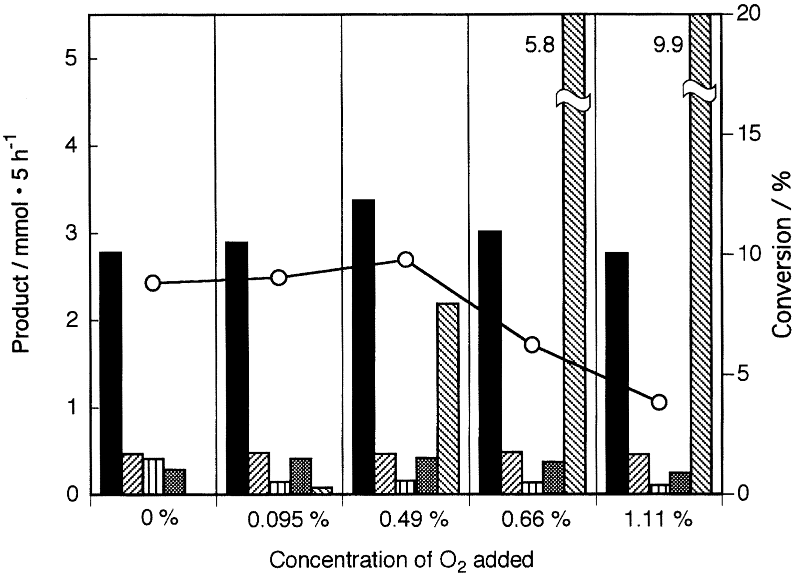

Figure 2. Effect of the addition of O_2 to the feed: ■, benzene; ▨, naphthalene; ▥, toluene; ▩, ethane; ▧, CO; ○, conversion of methane. The methane used was 99.99% pure. CO_2 was not detected in the outlet feed.

during the activation process prior to the reaction could react with added O_2 and produce CO.

3.3. *Effect of the addition of CO_2 to the feed*

Figure 4 shows the effect of the addition of CO_2 on the activity. The conversion of methane increased from 5 to 10% by the addition of CO_2 up to 0.66% and then decreased at greater CO_2 concentrations. The amounts of benzene were almost constant with the addition of CO_2 up to 1.4%. The increase in the methane conversion in spite of the constant production of benzene could be caused by the deposition of carbon on the catalyst surface. The addition of 5% CO_2 significantly decreased the production of benzene, while CO increased with an increasing amount of CO_2. Liu *et al.* also reported the effect of CO_2 addition to the feed [16]. They demonstrated that the addition of 1.6% CO_2 improved the stability of the catalyst and that double the number of moles of CO were produced with respect to the added CO_2. Our results indicated that 0.66% CO_2 also improved the stability of benzene production (figure 5). Therefore, the addition of a small amount of CO_2 (0.66%) would be more favorable for the production of a lower amount of CO. The production of CO would be explained by the reforming process ($CO_2 + CH_4 = 2CO + 2H_2$) or the reverse Boudard reaction ($CO_2 + C = 2CO$) [29]. It can be presumed that the reverse Boudard reaction could be dominant because the amount of CO produced increased when the amount of CO_2 was increased, while the conversion of methane decreased.

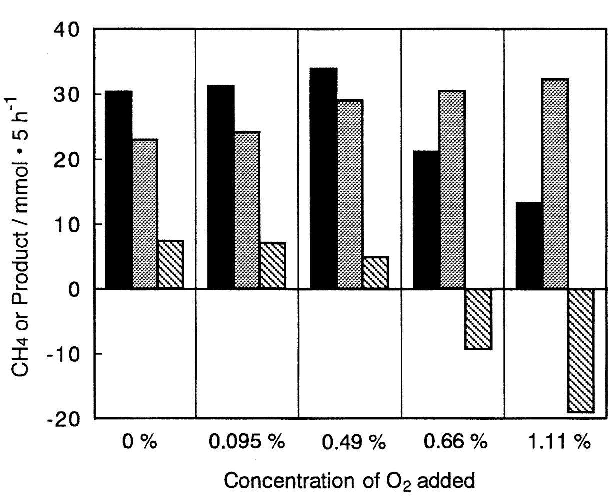

Figure 3. Effect of the addition of O_2 to the feed: ■, A: the amount of consumed CH_4; ▩, B: the total amount of the product (represented by the equivalent moles of CH_4); ▧, A − B.

3.4. *Effect of the addition of CO to the feed*

Figure 6 shows the effect of CO addition on the activity. We studied the effects of CO concentration from 5 to 30%. The conversion was almost constant up to a 30% addition of CO. The amounts of benzene and naphthalene produced significantly increased on addition of 5% CO. Aromatic compound production increased with the addition of 10% CO, while it decreased at concentrations from 20 to 30%. Liu *et al.* reported that the addition of CO improved the stability of the catalyst [16]. Less catalyst deactivation at concentrations from 5 to 30% CO was also confirmed by this study.

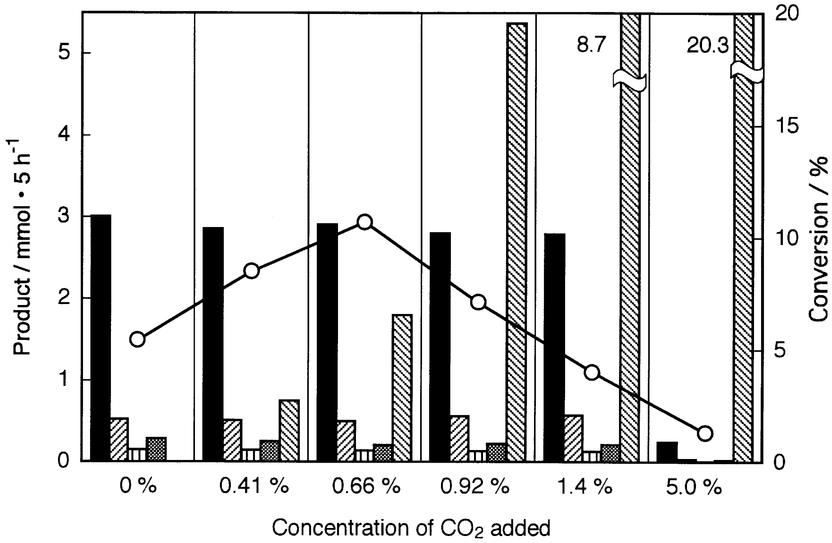

Figure 4. Effect of the addition of CO_2 to the feed: ■, benzene; ▨, naphthalene; ▥, toluene; ▩, ethane; ▧, CO; ○, conversion of methane. The methane used was 99.99% pure. CO_2 was not detected in the outlet feed up to a 1.4% CO_2 concentration.

3.5. *Effect of the addition of H_2 to the feed*

Figure 7 shows the effect of H_2 addition (10%) on the amount of the products. During the 5 h test, the addition of H_2 did not affect the methane conversion and the amounts of the aromatic compounds produced. However, the addition of H_2 reduced the deactivation of the catalyst. With the addition of 10% H_2 to the feed, the amount of benzene formed remained almost constant during the 5 h test. As for the production of naphthalene, the amount gradually decreased, but the slope of the decrease curve with time on stream was smaller than that in the absence of H_2. Considering the equilibrium of the aromatization of methane, the addition of H_2 is unfavorable to the production of the aromatic compounds. However, the addition of H_2 could possibly contribute to preventing catalyst deactivation by reducing the surface carbon deposit. Hence, the addition of H_2 could contribute to increasing the total amount of aromatic compounds.

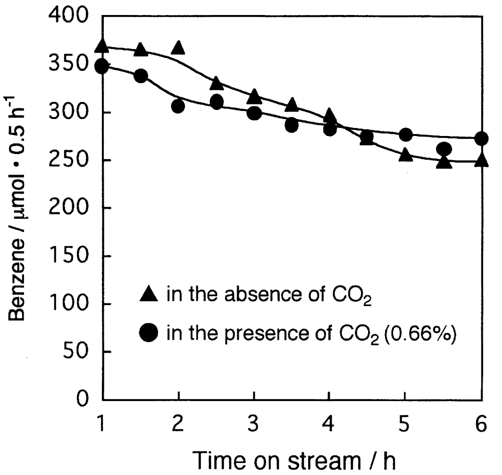

Figure 5. Effect of the addition of CO_2 on benzene production. The methane used was 99.99% pure.

3.6. *Discussion of the effects of the various additives*

The methane conversion was increased with the addition of a small amount of O_2 or CO_2 and then decreased with more O_2 or CO_2. The amount of CO produced was simply increased by the addition of continued O_2 or CO_2. The similarity between the results for O_2 and those for CO_2 could be attributed to the oxidizing property of O_2 and CO_2. Figures 2 and 3 show that up to 0.49% O_2, the amount of deposited carbon was reduced by the addition of O_2 and that the production of benzene increased. With more than a 0.66% O_2 addition, carbon deposited in advance would be consumed and a large amount of CO was produced. It would be desirable that the amount of carbon deposited during the activation process prior to the reaction does not increase and does not decrease during the reaction. This condition would be achieved by an O_2 addition between 0.49 and 0.66%. This is the reason why the maximum amount of benzene was produced at an O_2 addition of 0.49%. In the case of the addition of CO_2, results similar to figure 3 were observed. Therefore, CO could be produced by the combustion of deposited carbon with O_2 or the reverse Boudard reaction with CO_2 [29]. The addition of a large amount of the oxidizing gases would result in the reoxidation of Mo_2C. Wang *et al.* demonstrated from XPS data that Mo_2C was reoxidized by exposure of the activated Mo/ZSM-5 catalyst to 10% CO_2 at 973 K [4]. The concentration of

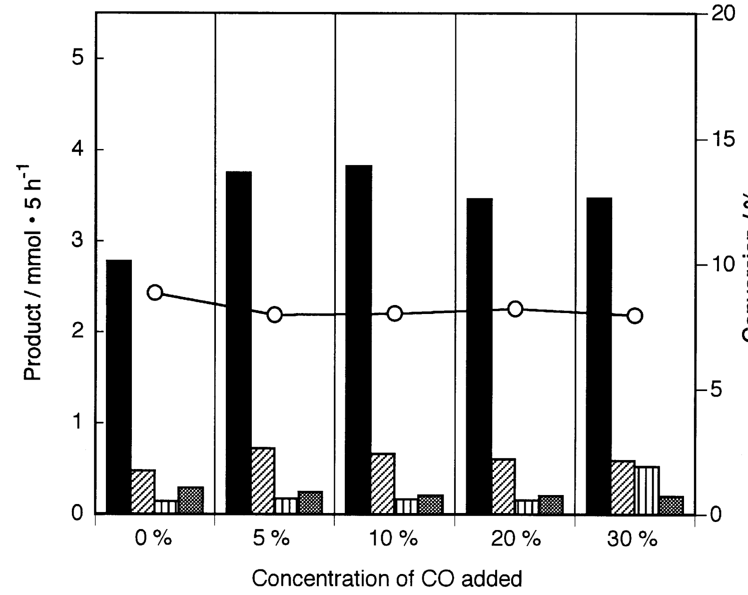

Figure 6. Effect of the addition of CO to the feed: ■, benzene; ▨, naphthalene; ▥, toluene; ▩, ethane; ○, conversion of methane. The methane used was 99.99% pure. CO_2 was not detected in the outlet feed.

O_2 and CO_2 in this study was so small that the deposited carbon could be consumed in preference to Mo_2C. This could be supported by the fact that the amount of Mo (3% loading) was less than the amount of CO produced. The addition of CO or H_2 did not affect the methane conversion, but contributed to the stability of the catalytic activity. As Mo_2C would be the active species in the catalyst, the amount of surface carbon may be critical for the catalytic activity. CO and H_2 would regulate the amount of carbon on the surface. The analyses of the amount of consumed CH_4 and the total amount of products in the case of H_2 addition indicate that the deposited carbon did not increase after the 5 h test. As CO strongly adsorbs on the Mo surface [30], it would inhibit excess carbon deposition on the surface due to regulation of the smaller methane coverage. H_2 could increase the value of n in CH_n(a) dissociative surface species of methane by the dissociative adsorption of H_2. The CH_n(a) species having large n would prevent its easy conversion into inactive carbon deposits.

The impurities in methane affected the activity of the Mo/ZSM-5 catalyst. Especially, the oxidative impurities increased the production of CO. This study revealed that the oxidative impurities in methane were critical to the aromatization of methane over the Mo/ZSM-5 catalyst.

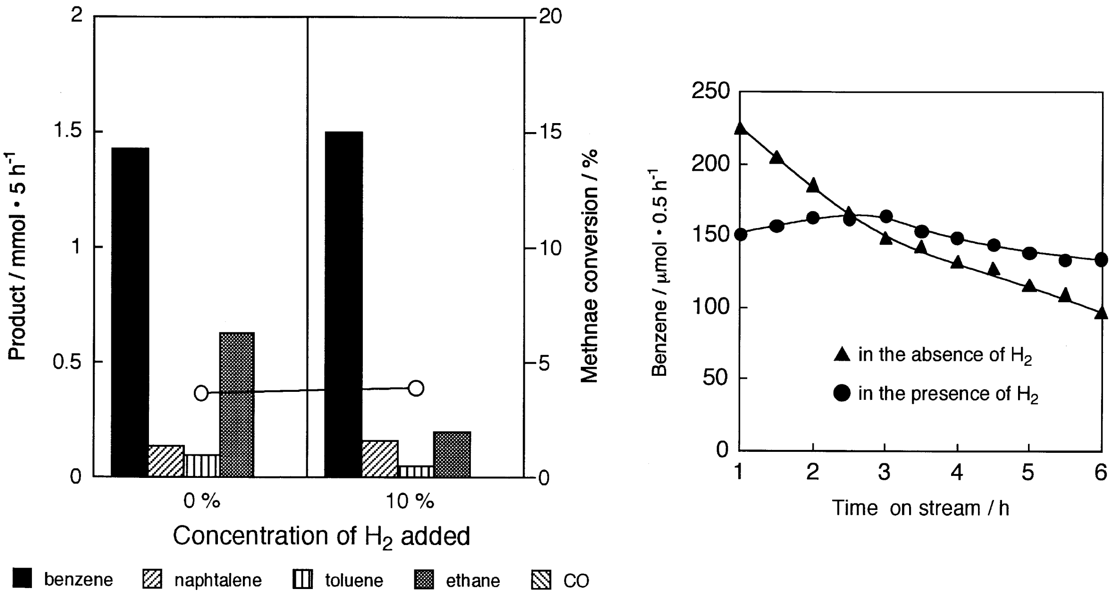

Figure 7. Effect of the addition of H_2 to the feed: ○, conversion of methane. The methane used was 99.99% pure. CO_2 was not detected in the outlet feed.

4. Conclusion

The dehydrogenation of methane was carried out over a Mo/ZSM-5 catalyst. The tests using two grades of methane revealed that the purity of methane was very critical for the evaluation of the catalyst activity. The effects of the addition of O_2, CO_2, CO or H_2 to the feed were then investigated. By mixing an appropriate amount of the additive gas in the reaction feed, it was possible to increase the amounts of aromatic compounds produced and inhibit the deactivation of the catalyst.

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