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Marked role of carbon monoxide in the formation of benzene during CH_4–CO reaction over Rh/SiO_2 catalysts

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Temperature-programmed desorption (He-TPD) and temperature-programmed reaction with hydrogen (H_2-TPR), carbon monoxide (CO-TPR) or methane (CH_4-TPR) were carried out to elucidate the benzene formation mechanism as well as the role of CO during CH_4–CO reaction over SiO_2-supported Rh catalysts. The steady-state surface for the CH_4–CO reaction was different from that of the CH_4 decomposition reaction. The existence of benzene-like adsorbed species as "building blocks" was demonstrated on the CH_4–CO reaction surface, while no such higher hydrocarbon adsorbed species was detected in the case of the CH_4 decomposition surface. On the contrary, in CO-TPR experiments various unsaturated hydrocarbons were released from the steady-state CH_4 decomposition surface, which was not the case from the CH_4–CO reaction surface. It is concluded that adsorbed CO may play an important role to enhance the C–C bond formation of carbonaceous species, which correlates deeply with the novel phenomenon of selective benzene formation in the CH_4–CO reaction.

KEY WORDS: benzene formation; silica-supported Rh catalyst; CH_4–CO reaction; temperature-programmed reaction.

1. Introduction

A growing interest has been noted concerning the transformation of methane into higher hydrocarbons and oxygenates as an alternative to petroleum. Three different research directions have been proposed for this purpose as follows: indirect reforming of methane into synthesis gas by steam, carbon dioxide or partial oxidation; oxidative coupling of methane to C_2 hydrocarbons and partial oxidation to CH_3OH and HCHO; non-oxidative oligomerization of methane to higher hydrocarbons and aromatics.

In the third category, Wang *et al.* first demonstrated that methane conversion of 7–10% could be achieved and benzene was formed with 90% selectivity over $MoO_3/ZSM-5$ catalysts [1,2]. Solymosi *et al.* also reported 80% selectivity for benzene formation and 8–10% conversion of methane over $Mo_2C/HZSM-5$ catalysts [3]. Since then, a large number of investigations have been published in the dehydroaromatization reaction of methane over W/HZSM-5 [4], W-Zn/HZSM-5 [5], Mo-Pt/HZSM-5 [6] and Mo-Ru/HZSM-5 [7], etc. However, the conversion of methane is rather low due to the thermodynamic limitation of higher hydrocarbon formation.

To overcome this limitation, Amariglio *et al.* [8] and van Santen *et al.* [9] demonstrated the possibility of higher hydrocarbon formation from methane by means of a two-step reaction. In the first step some kinds of surface carbonaceous species were accumulated by the flow of methane on Group VIII catalysts in the temperature range 450–800 K, and subsequently in the second step accumulated carbonaceous species were subjected to H_2 flow resulting in the production of C_1–C_8 hydrocarbons at 300–400 K.

We have reported already that benzene was selectively synthesized among hydrocarbons (more than 80% selectivity) in CH_4–CO reaction at 600–700 K over Group VIII metal catalysts [7,8]. When only methane was introduced onto the catalyst, ethane was formed mainly due to the coupling reaction of methane, and in the case of CO only carbon dioxide was released due to the disproportionation reaction of CO. Accordingly, both CH_4 and CO were required for the formation of benzene. In the present study the mechanism of benzene formation and the role of CO during CH_4–CO reaction were investigated in depth by means of TPD and TPR techniques.

2. Experimental

The 5 wt% silica-supported Rh catalyst was prepared by impregnating SiO_2 (Aerosil silica 300) into an aqueous solution of $RhCl_3{\cdot}3H_2O$ (Nakarai Tech.). The 0.3 g of Rh/SiO_2 was put into a U-shaped reaction vessel (30 ml), which was connected to a closed gas circulation system (total volume 350 ml, gas circulation rate 40 ml/min), and reduced by 200 torr of H_2 at 673 K for 6 h. The particle size and dispersion of the Rh metal thus prepared were 29.6 Å and 37.1%, determined by H_2 adsorption (OMNISORP-100CX) at room temperature. The CH_4–CO reaction or CH_4

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decomposition reaction was carried out for 2 h in a closed gas circulation system (partial pressure of each reactant 10 torr) with a liquid N_2 cold trap to gather the products and shift the equilibrium of the reaction. After that, the reactor was cooled down to room temperature and evacuated for 5 min before TPD or TPR experiments. For TPD experiments, 10 torr of He was introduced onto the steady-state reaction surface in the closed gas circulation system with a liquid N_2 cold trap, and the catalyst temperature was increased slowly (1.7 K/min) from room temperature to 623 K. The same procedures were taken for temperature-programmed reactions with hydrogen (H_2-TPR, 10 torr), carbon monoxide (CO-TPR, 10 torr) or methane (CH_4-TPR, 10 torr). At a certain temperature gaseous CO, H_2, and CH_4 were analyzed by gas chromatography with a thermal conductivity detector equipped with a Molecular Sieve 13X column. Other hydrocarbon products collected in the liquid N_2 cold trap were analyzed by a frame ionization detector with a Porapak N column, and another TCD gas chromatography (Porapak Q column) was applied for the measurement of CO_2. To verify the absence of concentration gradients as well as diffusion limitations in the catalyst bed, the amount of the catalyst and the circulation rate were varied between 0.1–0.5 g and 10–50 ml/min respectively, but no changes of the product distribution were observed in the TPD and TPR experiments.

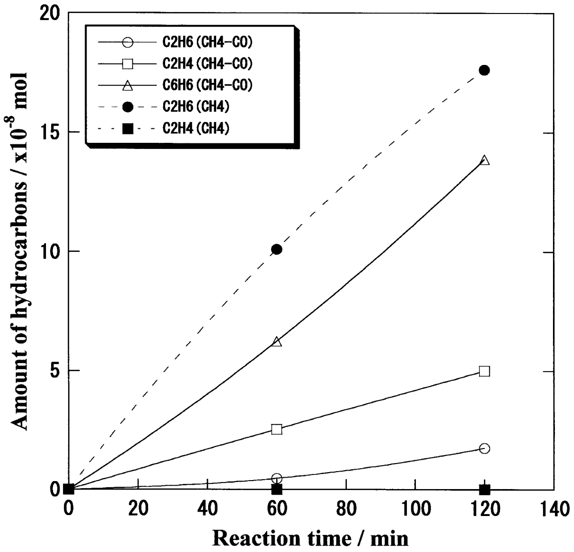

Figure 1. Time courses of ethane, ethylene, and benzene formation in CH_4–CO and CH_4 decomposition reactions over Rh/SiO_2 at 632 K. Solid line: CH_4–CO reaction. Broken line: CH_4 decomposition.

3. Results and discussion

Figure 1 represents the time courses of CH_4–CO and CH_4 decomposition reactions over freshly reduced 5 wt% Rh/SiO_2 catalyst. In the former case, a substantial amount of CO_2 was formed (not plotted in the figure) accompanied by ethane, ethylene, and benzene. On the other hand, only ethane and a trace amount of ethylene were formed and no benzene was detected in the latter case. Accordingly, the steady-state surface of the CH_4–CO reaction seems to be different from that of the CH_4 decomposition reaction. To clarify this point, He-TPD, H_2-TPR, and CO-TPR experiments were carried out over these steady-state surfaces.

As shown in figure 2, during TPD experiments over the steady-state CH_4–CO reaction surface, desorbed

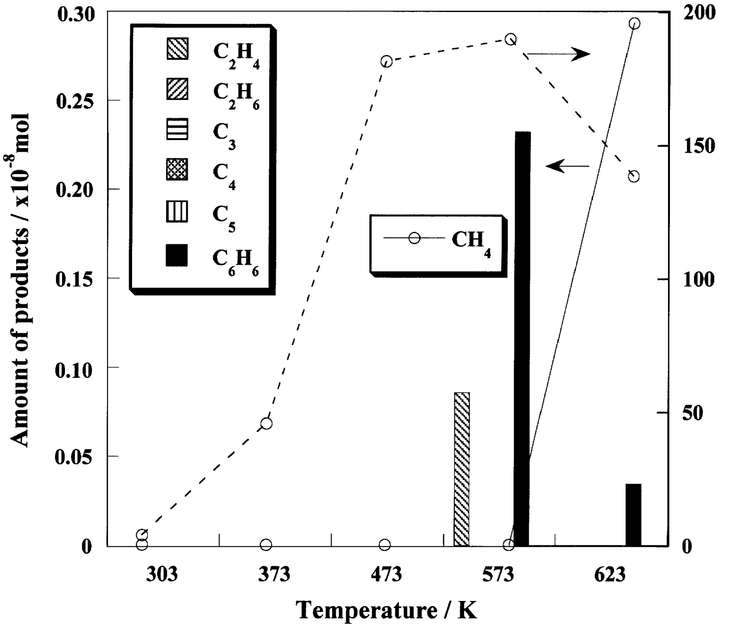

Figure 2. Product distribution in TPD over steady-state surfaces of CH_4–CO and CH_4 decomposition reaction over Rh/SiO_2. CH_4–CO reaction: solid line for CH_4 and bars for C_2–C_6 hydrocarbons. CH_4 decomposition reaction: broken line for CH_4.

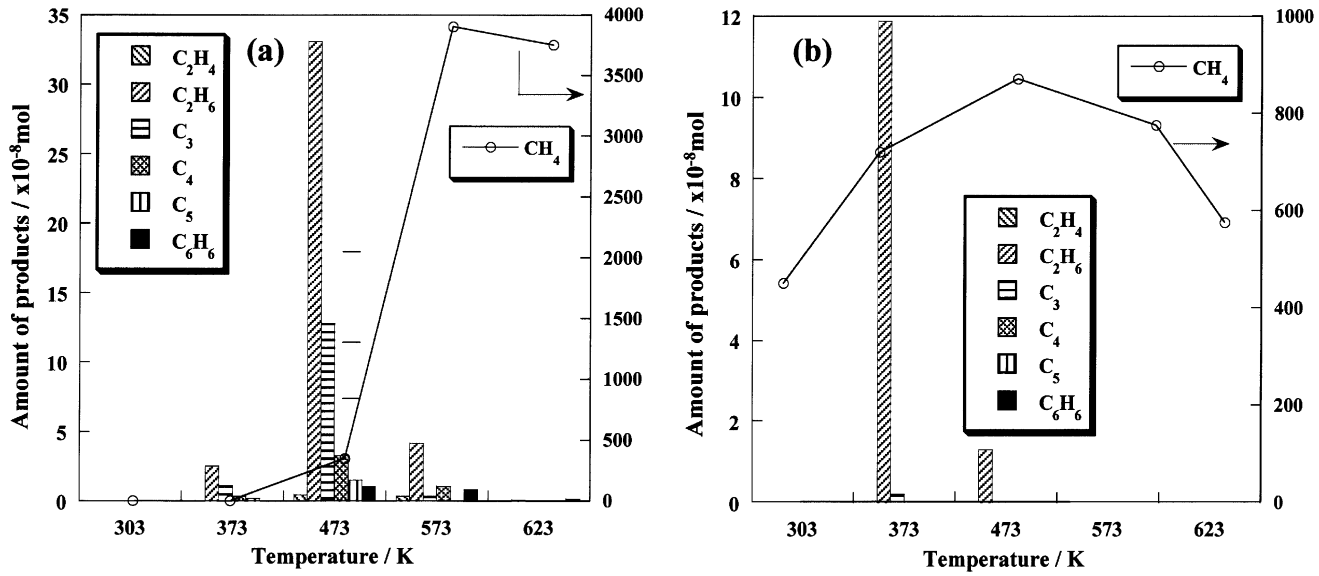

Figure 3. Product distribution in CH_4-TPR over steady-state surfaces of (a) CH_4–CO reaction and (b) CH_4 decomposition reaction over Rh/SiO_2.

products were ethylene and benzene at 573 K and methane and benzene at 623 K, implying the accumulation of benzene-like adsorbed species as building blocks over Rh surfaces. On the other hand, during TPD experiments over the CH_4 decomposition reaction surface, only methane was desorbed (dotted line in the figure). Amariglio *et al.* [9] reported that methane was only desorbed during TPD after CH_4 decomposition reaction over silica-supported Pt or Ru catalyst, which coincides well with our result over Rh/SiO_2 and indicates that the CH_4–CO reaction surface is entirely different from the CH_4 decomposition surface. On the other hand, in the CH_4-TPR experiment over the steady-state CH_4–CO reaction surface, a one order of magnitude larger amount of benzene than that of TPD was formed, accompanied by the formation of ethane and ethylene, which indicates the supply of hydrogen or carbon atoms from CH_4 to the adsorbed building blocks at 623 K. According to isotopic tracer experiments by Choudhary *et al.*, showing that carbon of methane is not readily incorporated into benzene [10], it is reasonable to suppose that hydrogen atoms are supplied to benzene-like adsorbed species. Furthermore, since the amount of benzene released during CH_4-TPR is one order of magnitude larger than that during the TPD experiment, it is concluded that the rate-determining step of benzene formation is the supply of hydrogen atoms to benzene-like adsorbed species.

Figures 3(a) and (b) represent the profiles of H_2-TPR over the steady state CH_4–CO and CH_4 decomposition reaction surfaces, respectively. From both surfaces, a large amount of methane was formed, accompanied by small amounts of various saturated hydrocarbons. In the case of the steady-state CH_4–CO reaction surface, considerable amounts of C_4–C_6 hydrocarbons were detected, indicating the hydrogenolysis of benzene-like adsorbed species during the H_2-TPR experiment. Although Amariglio *et al.* [11] and van Santen *et al.* [12] reported that hydrocarbon products up to C_8 unit were released in H_2-TPR from the CH_4 decomposition reaction surface at 473 K on Pt, Co, Ru or Rh metals, only the hydrocarbons up to C_3 units were released in the present study, as seen in figure 3(b). This is probably because of the deactivation of carbonaceous adsorbed species during the CH_4 decomposition process at higher temperatures (623 K). In the H_2-TPR experiment the total amount of surface carbon species hydrogenated up to 623 K was much more over a CH_4–CO reaction surface than a CH_4 decomposition surface, but the opposite result was obtained in the TPD experiment. Accordingly it is seen that significantly H-deficient carbonaceous species were accumulated during the CH_4–CO reaction compared to the CH_4 decomposition surface.

The results of CO-TPR over a steady-state CH_4–CO reaction surface are shown in figure 4(a). It is interesting to note that small amounts of methane and benzene were released at 373 and 623 K respectively, although no methane was released up to 573 K in the case of the TPD experiment as shown in figure 2. This may be achieved by taking hydrogen atoms away from neighboring carbonaceous species, which suggests a marked role of adsorbed CO in CH_4–CO reactions. This effect was quite pronounced in the case of CO-TPR over the steady-state surface of the CH_4 decomposition reaction. As shown in figure 4(b), various unsaturated hydrocarbons were released by introducing CO onto the steady-state CH_4 decomposition surface, whereas only methane was released in the TPD experiments as shown in figure 2. These results strongly suggest that, in the absence of CO, disproportionation of adsorbed CH_x species can take place on the vacant metal sites,

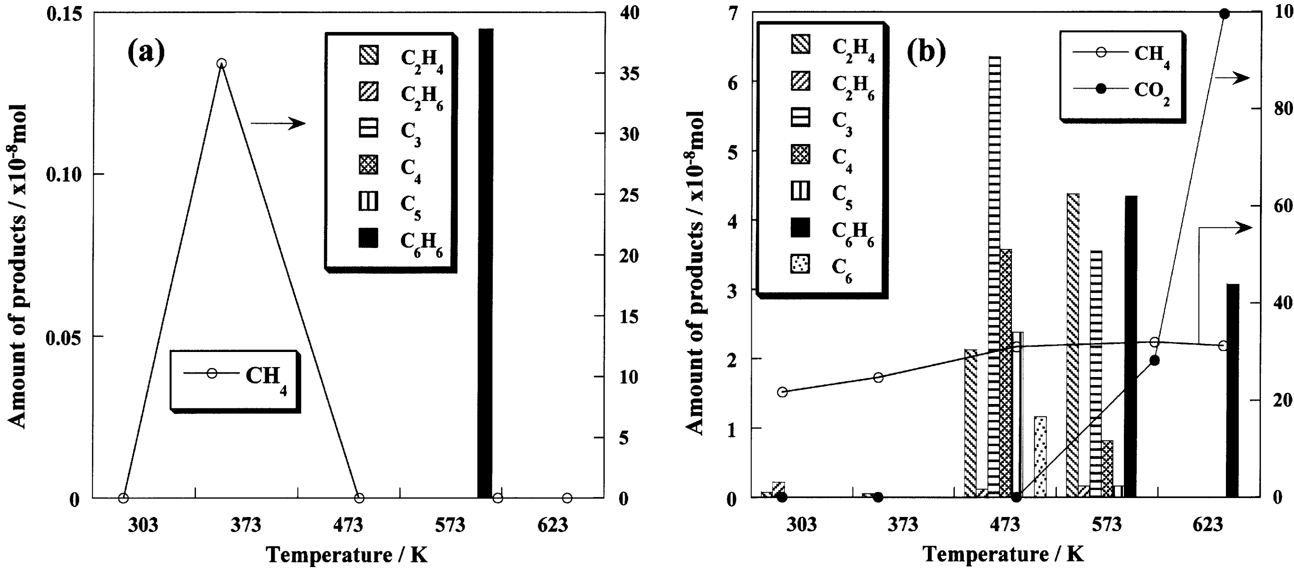

Figure 4. Product distribution in CO-TPR over steady-state surfaces of (a) CH_4–CO reaction and (b) CH_4 decomposition reaction over Rh/SiO_2.

resulting in the formation of CH_4 and more H-deficient adsorbed carbonaceous species. On the contrary, in the presence of gaseous CO, adsorbed CO may prevent this process, promote the C–C bond formation between adjacently adsorbed C_1 or C_2 fragments and let them desorb associatively. This tendency was dependent on the partial pressure of CO and diminished under the lower partial pressure of CO than saturated adsorption (1–3 torr), suggesting that blocking the vacant sites available for C–H or C–C bond cleavage is the main role of adsorbed CO.

Madix and Burke reported that when only C_2H_4 is adsorbed on the hydrogen-preadsorbed Fe(100) surface without co-adsorbed CO, formation of ethyl groups took place accompanied by ethylene formation at 170 K and no ethane was released [13]. However, the co-adsorption of CO and ethylene led to the formation of ethane at 170 K. From these results they considered that the role of adsorbed CO was to stabilize ethyl groups without dehydrogenation and to put aside hydrogen atoms from the Fe(100) surface. Amariglio *et al.* [14] have studied a possible insertion of CO into the adsorbed species prepared by CH_4 decomposition in the sequential TPR experiments of the CH_4/CO or $CH_4/CO/H_2$ over Pt/SiO_2 catalyst [14]. Although no oxygenates were obtain in their experiments, desorption of numerous alkanes and alkenes was unexpectedly induced by CO. They concluded that CO not only occupied the vacant sites but could also push aside hydrocarbonaceous adsorbed species and substitute for them, causing C–C bond lengthening due to alkyl-coupling through associative desorption. These effects are quite similar to our present TPR study and may also be operating in the case of benzene formation in CH_4–CO reaction, by behaving as a kind of framework. Ceyer *et al.* [15] have published that the conversion of methane to benzene occurs over a hexagonal spot of Ni(111) as the template for benzene formation. Accordingly, it is considered that a template for benzene formation may also be required in the CH_4–CO reaction, such as hexagonal spots of Rh(111), and adsorbed CO around there may also assist the oligomerization of CH_x species.

4. Conclusions

1. A CH_4–CO reaction surface is different from a CH_4 decomposition surface: on the former surfaces, benzene-like adsorbed species are formed as "building blocks", but only C_1 and C_2 adsorbed species are present on the latter surfaces.
2. The total amount of accumulated carbon species is much more over a CH_4–CO reaction surface than a CH_4 decomposition reaction surface, which is much more hydrogen-deficient during a CH_4–CO reaction than CH_4 decomposition.
3. The role of CO is to displace carbonaceous species from the metal surface and cause associative desorption involving nearby C_xH_y and H adsorbed species and/or neighboring C_xH_y adsorbed species.
4. Benzene formation during a CH_4–CO reaction may be attributable to the oligomerization of surface H-deficient C_1 and/or C_2 units in the framework of adsorbed CO.

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