Synthesis of Benzene from Methane and Carbon Monoxide over Silica-Supported Rh, Ru and Pd Catalysts

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(Received May 12, 1997; CL-970371)

Benzene was formed selectively among hydrocarbons produced in CH_4-CO reaction over silica supported Rh, Ru and Pd catalysts at 573-723 K under atmospheric pressures, although CO_2 was the main product, which was formed by the disproportionation of CO. Addition of H_2 to CH_4-CO reaction accelerated the rate of benzene formation several times, and the selectivity increased considerably.

Direct conversion of methane into other useful products has been an issue of great attention. By far the most promising reaction routes have been oxidative coupling of CH_4 to form C_2H_6, and reaction with CO_2 to form CO and H_2. Recently another interesting attempt has been made to activate methane under non-oxidative conditions and convert it into higher hydrocarbons and aromatic compounds.[1,2] Over supported Pt and Ru catalysts, dehydrogenation of methane occurred readily to form H_2 and surface carbon.[3] Subsequent hydrogenation of the surface carbon gave several higher hydrocarbons and even benzene. More attractive results have been reported in similar reactions over MoO_3/ZSM-5, MoO_3/SiO_2 and Mo_2C/ZSM-5 catalysts, where benzene can be formed with high selectivity (60-100%) at 973 K.[4,5]

In the present study we investigated CH_4 and CO reaction over silica supported Rh, Ru and Pd catalysts at 573-723 K under atmospheric pressures. We found that benzene is formed selectively among hydrocarbons, although CO_2 is the main product of this reaction.

The metal (5 wt%) supported catalysts used in this work were prepared by impregnation of a silica sample (Aerosil 300) into $RhCl_3$, $RuCl_3$ or $(NH_4)_2PdCl_4$ solution. After drying, 0.5 g of the catalysts was reduced by hydrogen in a closed gas circulation system with liquid nitrogen cold trap, while the temperature was slowly raised to 723 K and maintained constant at 723 K for 12 h. The metal dispersions were determined by hydrogen adsorption at room temperature and the following values were obtained: Rh=49 %, Ru=28 % and Pd=12 %, respectively. Before each run, the catalyst was reduced with 26.7 kPa of hydrogen at 723 k for 6 h. The reaction was carried out in a closed gas circulation system under atmospheric pressures. A liquid nitrogen cold trap was employed in the circulation system to gather the primary products. The composition of the gas phase during the reaction was followed by TCD gas chromatography (molecular sieve column), and the gathered products in the cold trap were analyzed by FID (porapak Q) except for CO_2 which was analyzed by TCD (porapak Q). The formation of benzene was confirmed by mass spectroscopy as well as infrared spectroscopy.

Figure 1 demonstrates the time course of the CH_4-CO reaction (1.33 kPa each) over a freshly reduced Rh/SiO_2 catalyst at 623 K. At the initial stage of the reaction, a considerable amount of CO_2 was formed accompanied with the decrease of gaseous CO and the accumulation of surface carbon. The rates of C_2H_6, C_2H_4 and C_6H_6 formation were more than one order of magnitude smaller than that of CO_2 formation. After 30 min the rates of CO_2, C_2H_6 and C_2H_4 formation decreased considerably, but the rate of C_6H_6 formation increased slightly and stayed almost constant for more than ten hours. The dotted line in the figure represents the rate of CO_2 formation when only CO was introduced onto the freshly reduced catalysts. Its coincidence with that for CH_4-CO reaction may indicate that CO_2 is formed mainly by the disproportionation of CO. On the other hand, when only CH_4 was introduced onto the freshly reduced catalysts, C_2H_6 was formed faster than the case of CH_4-CO reaction, but benzene was not detected at all during prolonged reaction period. These results strongly suggest that both CO and methane were required for benzene formation.

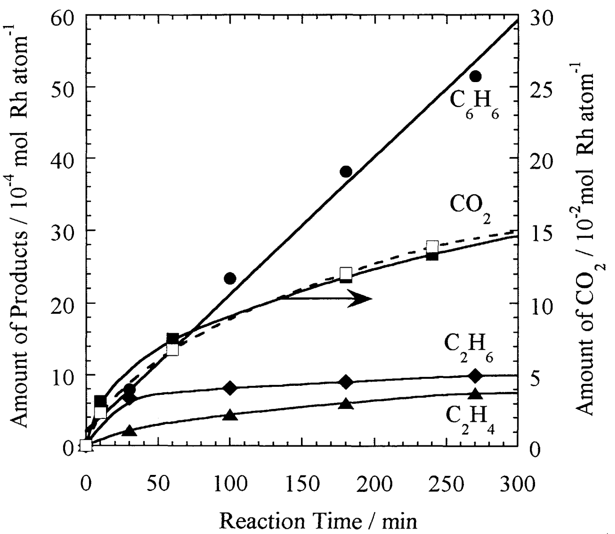

Figure 1. CH_4 - CO reaction over 5wt% Rh/SiO_2 at 623K.

Similar reaction profiles were obtained in the cases of Ru/SiO_2 and Pd/SiO_2 catalysts. The reaction rates as well as the selectivity in the later stage of CH_4-CO reaction (steady state; where the coverage of surface carbon increased very slowly) over various catalysts are summarized in Table 1. The most active catalyst for benzene formation was Rh/SiO_2, and the selectivity increased to about 10 % in the later stage of the reaction, where the amount of accumulated surface carbon was approximately 60 % of surface Rh atoms (steady state). A similar rate of benzene formation was observed over Ru/SiO_2, yet the disproportionation of CO to form CO_2 was much faster than the case of Rh/SiO_2. Accordingly, the selectivity for benzene formation remained within a few percent at the steady state, where the amount of accumulated surface carbon was about 130 % of surface Ru atoms. The situation was different in the

Table 1. TOF and selectivity in the steady state of CH_4-CO reaction over various catalysts at 623 K

Catalysts	TOF / $10^{-7}s^{-1}$				Selectivity / %			
	C_2H_4	C_2H_6	C_6H_6	CO_2	C_2H_4	C_2H_6	C_6H_6	CO_2
Rh/SiO_2								
(a)	0.28	0.24	3.33	28.2	0.9	0.8	10.4	88.0
(b)	4.06	5.17	11.8	118	2.9	3.7	8.5	84.9
Ru/SiO_2								
(c)	0.09	0.05	2.00	155	0.6	0.3	1.3	97.8
(d)	1.23	4.07	14.5	570	0.2	0.7	2.5	96.6
Pd/SiO_2								
(a)	0.6	47.8	1.75	689	0.1	6.5	0.2	93.2

(a) CH_4=CO=1.3kPa, (b) H_2(0.13kPa) was added to (a),
(c) CH_4=1.3kPa,CO=4.0kPa, (d) H_2(0.13 kPa) was added to (c).

case of Pd/SiO_2, where the rate of C_2H_6 formation was faster than benzene formation even in the steady state, perhaps because of the absence of the inhibition by accumulated surface carbon.

Pressure dependence of the initial rate of benzene formation upon the partial pressure of CH_4 and CO was investigated at 623 K for Rh/SiO_2. The empirical reaction orders for CH_4 and CO were 1.0 and -1.0 respectively, which indicates that strongly adsorbed CO may inhibit the adsorption of methane. As summarized in Table 1, it is interesting to note that the addition of a small amount of H_2 (0.13-0.27 kPa) during CH_4-CO reaction accelerated the formation of benzene several times, which suggests that the supply of hydrogen through the dissociation of methane would be the key step of this reaction. To investigate the role of methane in benzene formation more clearly, $^{12}CH_4$-^{13}CO (1:1, total pressure=2.67 kPa) reaction was carried out at 623 K over freshly reduced Rh/SiO_2 catalyst, and the isotopic distribution in benzene was followed by mass spectroscopy. After 26 h, isotopic distribution in formed benzene was as follows: $^{13}C_6H_6$=20%, $^{13}C_5{}^{12}CH_6$=55% and $^{13}C_4{}^{12}C_2H_6$=25%. This result indicates that carbon atoms in benzene mainly come from CO, but some from methane as well. After the brief evacuation at 623 K, hydrogen was introduced onto the carbon accumulated surface. The isotopic distribution of the formed methane by the hydrogenation of the surface carbon was $^{13}CH_4$=55% and $^{12}CH_4$=45%. These results indicate that not only the carbon of CO but also that of methane participate in this reaction.

To clarify the mechanistic difference between CO-H_2 and CH_4-CO reactions, the former reaction was carried out over freshly reduced Rh/SiO_2 catalyst by changing the reaction temperature and the ratio of CO and H_2. After 1 hour, the obtained product distributions were analyzed using Schulz-Flory equation as plotted in Figure 2. In the case of 1:1 ratio CO-H_2 reaction (1.33 kPa each) at 603 K, C_1-C_5 hydrocarbons were formed, which obeyed Schulz-Flory equation. At the same time,

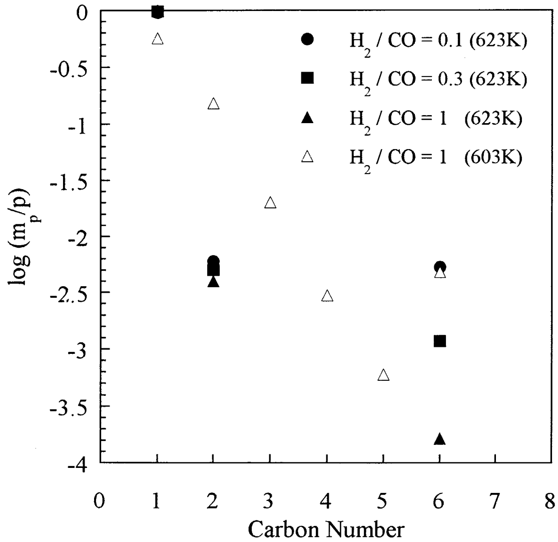

Figure 2. Schulz Flory Plots of CO-H_2 reaction over 5wt% Rh/SiO_2.

considerable amount of benzene was formed, maybe through the reaction between CO and formed methane, and did not obey the equation. The situation was completely different when the reaction temperature was raised to 623 K. In the case of 1:1 ratio reaction (H_2 = CO = 1.33 kPa), the main products were methane and C_2 hydrocarbons with a certain amount of benzene, but C_3-C_5 hydrocarbons were scarcely observed. By decreasing the partial pressure of H_2 to 0.40 and 0.13 kPa, the reaction rate was decreased considerably, but the selectivity for benzene was increased sharply as seen from the plots. These results strongly suggest that the C_1 building blocks for benzene formation may be different from those for other hydrocarbon formation. The former could be CH(a), and the latter CH_2(a) species, whose concentrations strongly depend on the amounts of surface carbon and hydrogen as well as reaction temperatures.

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