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ON THE DIFFERENCE IN REACTION PATHWAYS OF STEAM REFORMING OF METHANOL OVER COPPER-SILICA AND PLATINUM-SILICA CATALYSTS

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Steam reforming of methanol $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ proceeded through different pathways over copper-silica and platinum-silica catalysts. This was ascribed to the difference in the reactivities of formaldehyde intermediates formed in the reaction over these catalysts.

Steam reforming of methanol proceeded with high selectivity over copper-containing catalysts.[1] On the other hand, the selectivity obtained over transition metal catalysts were much lower than that obtained over copper-containing catalysts.[2] In connection with these results, it was worth noting that the dehydrogenation of methanol proceeded in a different manner over these catalysts. Methyl formate and hydrogen were selectively produced over copper-containing catalysts whereas carbon monoxide and hydrogen were exclusively produced over transition metal catalysts.[3] These differences were ascribed to the difference in the reactivity of formaldehyde formed as intermediate in the course of the dehydrogenation over these catalysts.[4,5]

In the present work, copper-silica and platinum-silica catalysts were both adopted for steam reforming of methanol. It is shown that the reactivity of formaldehyde is markedly affected by the kind of the catalyst and the steam reforming proceeds through the different pathways over these catalysts.

Experiments were carried out in a flow system at atmospheric pressure, and the outlet concentrations of the reactant and the products were determined by gas chromatography. Copper-silica catalyst (10 wt% Cu) was prepared by ion exchange of silica hydroxyls with tetrammine copper (II) cations, dried at 110 °C overnight and calcined at 500 °C for 3 h. Platinum-silica catalyst (1 wt%) was prepared from tetrammine platinum (IV) cations in the same manner as copper-silica catalyst.

Steam reforming of methanol occurred with high activity and high selectivity over copper-silica catalyst. Selectivity of the steam reforming was in the range of 95 to 100% at 150 - 250 °C. Carbon monoxide and methyl formate were detected with a trace amount of formaldehyde as by-products. When carbon monoxide was fed over the catalyst in the course of the steam reforming, no reaction occurred with this species. In like manner, methyl formate or formaldehyde was fed with methanol and water, and it was found that these species participated in the steam reforming. Methyl formate was hydrolyzed and the formic acid formed was decomposed to carbon dioxide and hydrogen. Both reactions occurred rapidly at higher temperatures, whereas at lower temperatures the hydrolysis occurred sluggishly. On the other hand, formaldehyde was found to react with water rapidly over whole temperature range studied. This species was converted into methanol, carbon dioxide and hydrogoen. On the basis of these findings and the previous results[5)] as to the formation of methyl formate by dehydrogenation of methanol, it was, therefore, concluded that the reaction proceeded through the pathways as

$$CH_3OH \rightarrow HCHO \xrightarrow{H_2O} HCOOH + CH_3OH \rightarrow CO_2 + H_2 \qquad (A)$$

and

$$CH_3OH \rightarrow HCHO \xrightarrow{CH_3OH} HCOOCH_3 \xrightarrow{H_2O} CH_3OH + HCOOH \rightarrow CO_2 + H_2 \qquad (B)$$

Pathway (A) was preferentially operative in the steam reforming in particular at lower temperatures, whereas pathway (B) was also involved in the reaction at higher temperatures. The same experiments were carried out over platinum-silica catalyst. Carbon monoxide was produced to an appreciable extent together with carbon dioxide and hydrogen. The selectivity of the steam reforming was estimated to be 10 to 20% at 150 - 220 °C. Formaldehyde decomposed to carbon monoxide and hydrogen rapidly either in the presence or in the absence of methanol. When experiments were carried out with formaldehyde and water at various space times, carbon dioxide was produced together with carbon monoxide and hydrogen. The latter two species produced in 1 to 1 ratio at shorter space times and the formation of carbon dioxide was practically negligible. As the space time increased, the formation of carbon monoxide decreased and that of carbon dioxide increased. Figure 1 illustrates the results obtained when carbon monoxide was fed with the mixture of methanol and water. In contrast to the results obtained on copper-silica catalyst, the outlet partial pressure of carbon dioxide increases to an appreciable extent in the presence of carbon monoxide although that of hydrogen decreases. When carbon monoxide was cut off from the mixture, the outlet compositions reverted to their orginal values. Water gas shift reaction was evidently involved in the reaction over platinum-silica catalyst. In these respects, it was concluded that steam reforming of methanol proceeded through the pathways

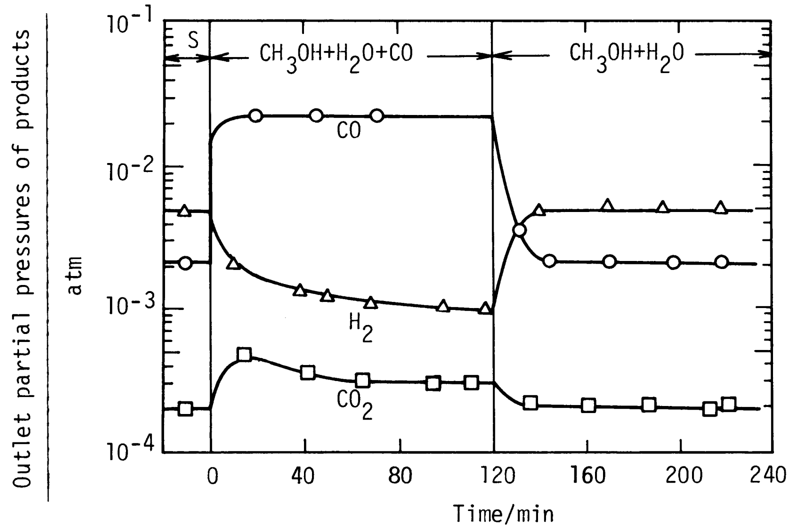

Fig. 1. Effect of carbon monoxide upon steam reforming of methanol over 1 wt% Pt/SiO_2. S in the figure denotes a steady state attained in the mixture of methanol and water ; Reaction temperature : 220 °C.

$$CH_3OH \longrightarrow HCHO \longrightarrow CO + H_2 \xrightarrow{H_2O} CO_2 + H_2O$$

over platinum-silica catalyst. No reaction occurred between formaldehyde and water or methanol over platinum-silica catalyst. This species was simply decomposed to carbon monoxide and hydrogen, and the carbon monoxide was converted to carbon dioxide and hydrogen by reaction with water. From these findings, it was demonstrated that steam reforming of methanol proceeded through the different pathways over copper-silica and platinum-silica catalysts. As suggested by Miyazaki and Yasumori4) in the dehydrogenation of methanol, formaldehyde was possibly held on these catalysts in different manner, so that the pathway of the steam reforming was strongly affected by the catalysts used.

References

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