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ENHANCEMENT OF THE METHANOL FORMATION FROM CO AND H_2 OVER SUPPORTED RUTHENIUM CATALYSTS BY H_2-H_2O TREATMENT

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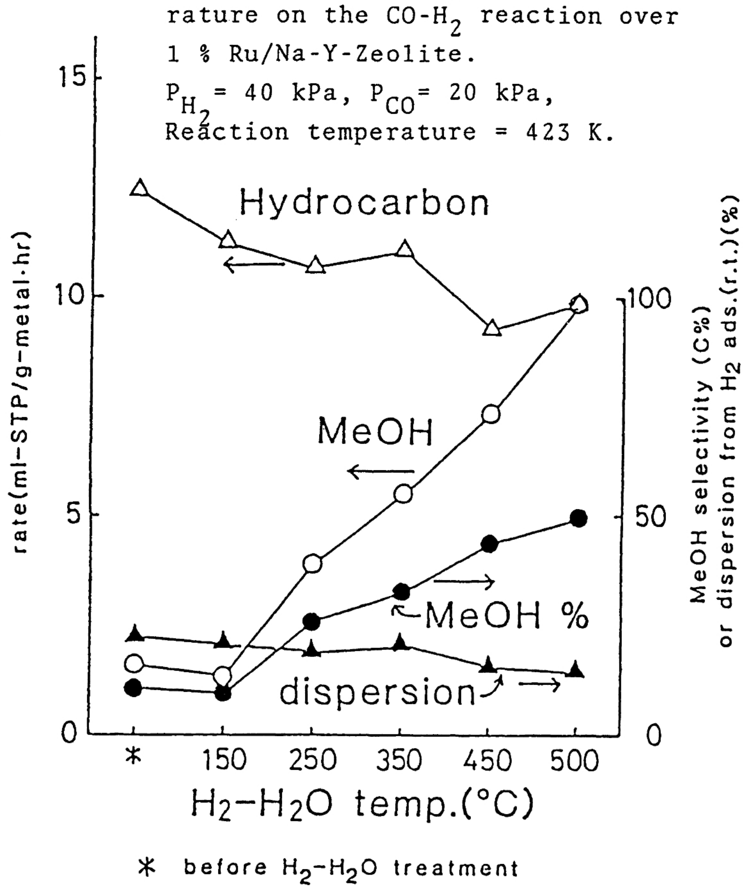
Supported ruthenium catalysts, which was treated by H_2-H_2O mixture at elevated temperatures, could produce methanol from CO and H_2 with 50% selectivity, and the nature of the active sites for methanol formation on these catalysts was discussed.

Ruthenium metal is well known as one of the most active catalysts for hydrocarbon formation from synthesis gas[1], but has scarcely been reported to produce oxygen-containing products[2,3] so far. We report here for the first time, that methanol formation can be drastically enhanced by a pretreatment of some supported ruthenium catalysts with hydrogen-water mixture gas at elevated temperatures.

A 1 wt.% Ru/Na-Y-Zeolite was prepared by cation exchange of Zeolite (Linde) with $Ru(NH_3)_6{}^{3+}$ ($Ru(NH_3)_6Cl_3$ from Ventron) in aqueous solution. A 1 wt.% Ru/Al_2O_3 and a 4.5 wt% Ru/SiO_2 were prepared by immersing alumina (Aluminium oxide C, Aerosil) or silica (Aerosil) to an aqueous solution of $RuCl_3$ hydrate (Wako) followed by evaporation at 335K. The CO-H_2 reaction (P_{H_2} = 40 KPa, P_{CO}= 20 KPa) was carried out in a closed gas circulation system equipped with a liquid nitrogen cold trap. Product analysis was carried out by gas chromatography. For isotope labelled experiments, the products were separated into each component by gas chromatography prior to mass spectral analysis. The H_2-H_2O treatment was performed in the same closed gas circulation system with a mixture of hydrogen (60 KPa) and water vapor (saturated vapor pressure at room temperature).

The catalytic activity of the zeolite-supported catalyst for the CO-H_2 reaction was examined as a function of the temperature of H_2-H_2O treatment. The activity for methanol formation increased gradually by raising the H_2-H_2O treatment temperature as shown in fig. 1. On the other hand, the activity for hydrocarbon formation decreased to a small extent, corresponding approximately to the decrease in ruthenium dispersion, which was estimated from the amount of adsorbed hydrogen at room temperature and the amount of ruthenium loaded on the support. These results suggest that the formation of hydrocarbon and methanol proceed on different active sites of the catalyst. The activity change with extended reaction period was also examined and the amount of formed methanol exceeded, without considerable decrease, more than twice of the number of total ruthenium metals in the catalysts (more than ten times of that of surface metal atoms), which clearly indicates that this reaction is catalytic. Methanol formation was not influenced by prolonged hydrogen treatment at 593 - 723 K, but was completely suppressed by O_2 treatment at 623 K, which was regenerated by subsequent H_2-H_2O treatment at 723K (table 1).

Fig. 1. Effect of the H_2-H_2O treatment temperature on the CO-H_2 reaction over 1 % Ru/Na-Y-Zeolite.
P_{H_2} = 40 kPa, P_{CO} = 20 kPa,
Reaction temperature = 423 K.



* before H_2-H_2O treatment

Catalytic activities of the CO-H_2 reaction over alumina- and silica-supported catalysts were also examined. Just after the reduction by hydrogen treatment at 773 K, these catalysts did not produce any oxygen-containing products. As shown in table 1, the H_2-H_2O treatment of the alumina-supported ruthenium catalyst produced a considerable amount of dimethylether (up to 50% selectivity on the carbon number basis), which may be produced by the successive dehydration of methanol on alumina. On the contrary, only a small amount of oxygenated compounds were detected in the reaction over the silica-supported catalyst even after the H_2-H_2O treatment.

To elucidate the differences between the mechanism of methanol and hydro-

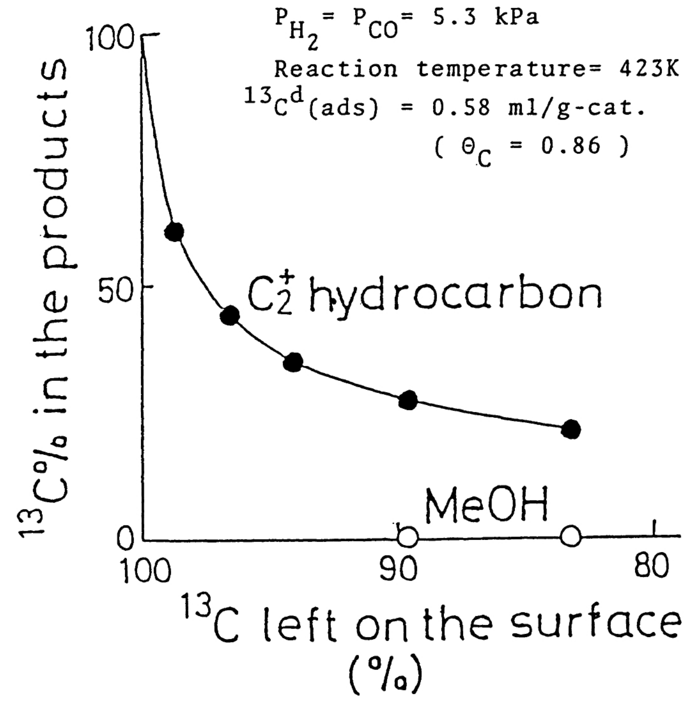
Table 1. CO-H_2 reaction over various supported Ru catalysts

Treatments			Dispersion (%) (H_2 ads. at r.t.)	Rates MeOH (ml-STP/g-metal.hr)	DME[a)]	HC[b)]	Selectivity[c)] for oxygenated compounds(%)
(Zeolite)							
H_2-H_2O	723K	45h	19	3.0	0.03	3.6	45
O_2 ox. H_2 red.	623K 573K	2h 6h	17	0.08	0.00	3.2	2
H_2-H_2O	723K	6h	9	1.2	0.00	1.6	43
(Alumina)							
H_2-H_2O	723K	17h	18	3.1	18.7	22.3	49
(Silica)							
H_2-H_2O	723K	3h	26	0.26	0.00	36.9	1

a) DME = dimethylether, b) HC = hydrocarbon, c) DME+MeOH / all products

carbon formation, the Boudouard reaction ($2\ CO \longrightarrow CO_2 + C(ads)$) was carried out for one hour over the Ru/Na-Y-Zeolite catalyst at 573 K using ^{13}CO. Following the disproportionation reaction the catalyst was cooled to 423 K and molecularly adsorbed ^{13}CO was replaced by ^{12}CO. Then a mixture of ^{12}CO and H_2 was introduced onto the catalyst and the ^{13}C content in the reaction products at 423 K was analyzed with time using the mass spectrometer. The results are shown in fig. 2. Hydrocarbons and methanol were formed with the similar rates to those of the CO-H_2 reaction without accumulated surface carbon. The ^{13}C content of the total C_2^+ hydrocarbon products was extrapolated to 100 % at the initial stage of the reaction, as reported already in the previous paper[4], indicating the incorporation of the dissociative carbon into the hydrocarbon formation reaction. However, no ^{13}C was

Fig. 2. ^{12}CO-H_2 reaction after ^{13}C -deposition by ^{13}CO disproportionation(at 573 K) over 1 % Ru/Na-Y-Zeolite.



detected in the produced methanol, which suggests that alcohol formation proceeds via hydrogenation of non-dissociative carbon monoxide, as has been reported already by Katzer et. al. in the case of Rh/TiO_2 catalyst[5]. These results also support the conclusion that hydrocarbons and methanol are formed via different reaction pathways on different reaction sites of the catalysts.

Iwasawa et. al. reported similar effect of H_2-H_2O treatment for the formation of ethanol and acetaldehyde from CO-H_2 reaction over Rh catalysts[6], but the structure of their active sites was not clarified yet. In this study, we investigated the XPS of Ru/Na-Y-Zeolite catalyst, which did not show any significant chemical shift of any elements before and after the H_2-H_2O treatment. At present, the nature of the active sites for methanol formation is not clear, but they may be located on the support at the boundary with the ruthenium metal and the H_2-H_2O treatment may induce some electronic interaction between them to stabilize, for example, the ruthenium cation.

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