

ENHANCEMENT OF THE METHANOL FORMATION FROM CO AND H<sub>2</sub> OVER SUPPORTED  
RUTHENIUM CATALYSTS BY H<sub>2</sub>-H<sub>2</sub>O TREATMENT

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Supported ruthenium catalysts, which was treated by H<sub>2</sub>-H<sub>2</sub>O mixture at elevated temperatures, could produce methanol from CO and H<sub>2</sub> 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<sup>1</sup>, but has scarcely been reported to produce oxygen-containing products<sup>2,3</sup> 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<sub>3</sub>)<sub>6</sub><sup>3+</sup> ( Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> from Ventron ) in aqueous solution. A 1 wt.% Ru/Al<sub>2</sub>O<sub>3</sub> and a 4.5 wt% Ru/SiO<sub>2</sub> were prepared by immersing alumina (Aluminium oxide C, Aerosil) or silica (Aerosil) to an aqueous solution of RuCl<sub>3</sub> hydrate (Wako) followed by evaporation at 335K. The CO-H<sub>2</sub> reaction (P<sub>H<sub>2</sub></sub> = 40 KPa, P<sub>CO</sub> = 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<sub>2</sub>-H<sub>2</sub>O 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).

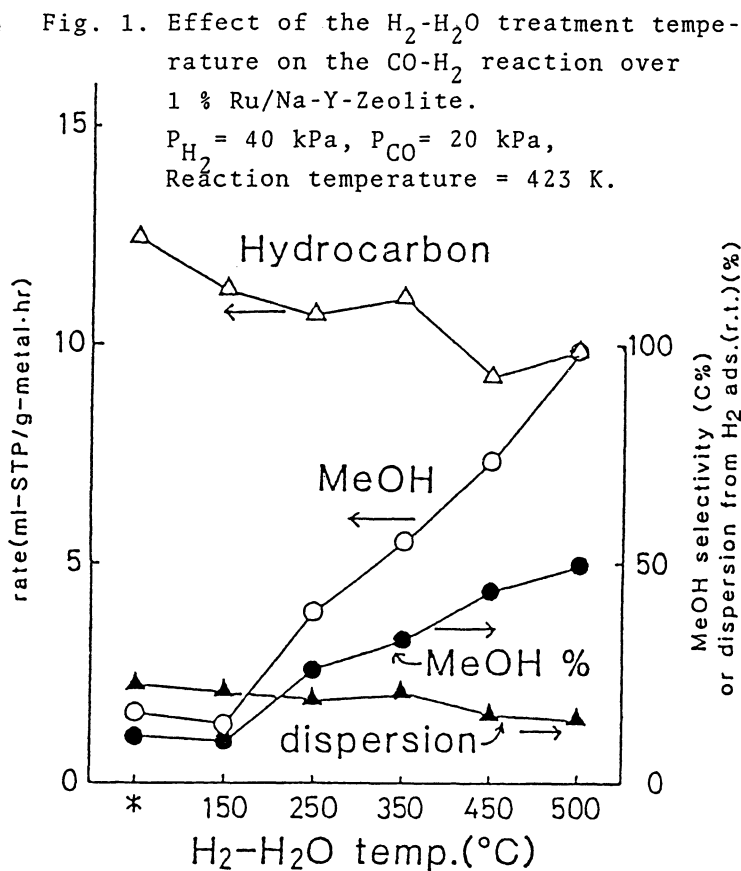
The catalytic activity of the zeolite-supported catalyst for the CO-H<sub>2</sub> reaction was examined as a function of the temperature of H<sub>2</sub>-H<sub>2</sub>O treatment. The

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).

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-



\* before  $H_2-H_2O$  treatment

Table 1. CO-H<sub>2</sub> reaction over various supported Ru catalysts

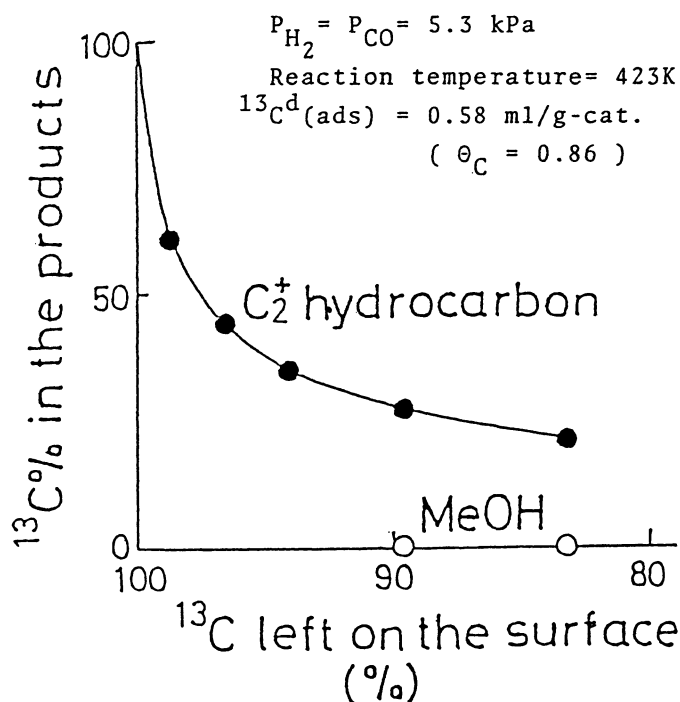
Treatments	Dispersion (%) (H <sub>2</sub> ads. at r.t.)			Rates			Selectivity <sup>c)</sup> for oxygenated compounds (%)
				MeOH (ml-STP/g-metal.hr)	DME <sup>a)</sup>	HC <sup>b)</sup>	
(Zeolite)							
H <sub>2</sub> -H <sub>2</sub> O	723K	45h	19	3.0	0.03	3.6	45
O <sub>2</sub> ox. H <sub>2</sub> red.	623K 573K	2h 6h	17	0.08	0.00	3.2	2
H <sub>2</sub> -H <sub>2</sub> O	723K	6h	9	1.2	0.00	1.6	43
(Alumina)							
H <sub>2</sub> -H <sub>2</sub> O	723K	17h	18	3.1	18.7	22.3	49
(Silica)							
H <sub>2</sub> -H <sub>2</sub> O	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 ( $2\text{CO} \longrightarrow \text{CO}_2 + \text{C(ads)}$ ) was carried out for one hour over the Ru/Na-Y-Zeolite catalyst at 573 K using <sup>13</sup>CO. Following the disproportionation reaction the catalyst was cooled to 423 K and molecularly adsorbed <sup>13</sup>CO was replaced by <sup>12</sup>CO.

Then a mixture of <sup>12</sup>CO and H<sub>2</sub> was introduced onto the catalyst and the <sup>13</sup>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<sub>2</sub> reaction without accumulated surface carbon. The <sup>13</sup>C content of the total C<sub>2</sub><sup>+</sup> hydrocarbon products was extrapolated to 100 % at the initial stage of the reaction, as reported already in the previous paper<sup>4</sup>, indicating the incorporation of the dissociative carbon into the hydrocarbon formation reaction. However, no <sup>13</sup>C was

Fig. 2. <sup>12</sup>CO-H<sub>2</sub> reaction after <sup>13</sup>C-deposition by <sup>13</sup>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<sub>2</sub> catalyst<sup>5</sup>. 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<sub>2</sub>-H<sub>2</sub>O treatment for the formation of ethanol and acetaldehyde from CO-H<sub>2</sub> reaction over Rh catalysts<sup>6</sup>, 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<sub>2</sub>-H<sub>2</sub>O 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<sub>2</sub>-H<sub>2</sub>O treatment may induce some electronic interaction between them to stabilize, for example, the ruthenium cation.

#### References

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