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ALCOHOL FORMATION IN CO HYDROGENATION OVER SUPPORTED RHENIUM

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Rhenium supported on CeO_2, TiO_2 or ZrO_2 showed high catalytic activity for CO hydrogenation and was found to produce sizable amount of alcohols along with hydrocarbons. The effects of catalyst support, reaction pressure and reaction temperature on the total conversion and the product distribution were examined.

Rhenium, which is a well known catalyst for hydrocarbon reforming, has also been known to catalyze CO hydrogenation to produce hydrocarbons[1,2,3] although detailed study on its catalytic activity for the reaction including the product distribution is yet to be published. The present paper reports the catalytic activity and selectivity of supported rhenium for the hydrogenation of carbon monoxide, paying special attention to the new fact, i.e., alcohol formation.

The catalyst of 7.7 wt % rhenium loading were prepared by impregnating various catalyst supports with aqueous solutions of perrhenium ammonate at room temperature followed by drying at 100°C in air for 18 hr. The resulting catalyst powder was pelleted, crushed and sieved to give particles between 1 to 2 mm in diameter and placed in a conventional flow-type high-pressure reaction vessel. The catalyst was reduced in situ with the reaction gas ($H_2/CO = 7/3$) at 300°C for 2 hr under the atmospheric pressure. Then the temperature and the pressure in the reactor were adjusted to desired values, and one hour later product sampling was started. The product gas was put through a condenser maintained at 0°C, and the condensate and the remaining gas were both analyzed by means of gas chromatography. The identification of the compounds produced was carried out by using JEOL-JMS-D-300 gas chromatographic mass spectrometer.

Table 1 lists the results of catalytic activity measurements of rhenium supported on various oxides. Column 3 shows that rhenium supported on CeO_2, TiO_2 or ZrO_2 gives relatively high conversion to hydrocarbons and alcohols, and column 6 shows that rhenium supported on SiO_2, CeO_2 or La_2O_3 has relatively high selectivity to alcohols. Separate experiments confirmed that these oxides without rhenium have negligible catalytic activities for the reaction under the present reaction conditions.

Table 1. CO Hydrogenation Activity and Selectivity of Rhenium Supported on Various Oxides (reaction conditions: temp.= 250°C, press.=20 kg/cm^2, s.v.= 1000/hr)

Support	Total Conversion (mol %)	Conversion to Hydrocarbons and Alcohols (mol %)	Selectivity**			
			Hydrocarbons	(CH_4)	Alcohols	(CH_3OH)
S.M.A.+A.C*	3.35	3.00	98.9	(31.3)	1.1	(1.0)
B_2O_3 + A.C.	2.97	2.79	97.3	(72.5)	0.3	(0.2)
GeO	3.78	3.68	95.3	(65.5)	4.7	(2.4)
SiO_2(ID)	1.77	1.65	85.2	(62.6)	14.8	-
γ-Al_2O_3	2.88	1.74	97.1	(52.3)	2.9	(1.4)
CeO_2	10.87	4.63	84.3	(54.7)	15.7	(13.5)
La_2O_3	0.49	0.25	74.6	(44.4)	25.4	(25.4)
TiO_2	12.03	7.24	97.1	(69.9)	2.9	(2.2)
ZrO_2	8.73	6.45	91.8	(75.6)	8.2	(6.8)
HY-Zeolite	1.62	1.37	100	(58.7)	0	(0)

*Silicomolybdic acid with activated carbon

**calculated as the molar ratio of each product (hydrocarbons, methane, alcohols or methanol) to the total amount of hydrocarbons and alcohols produced (CO_2 excluded)

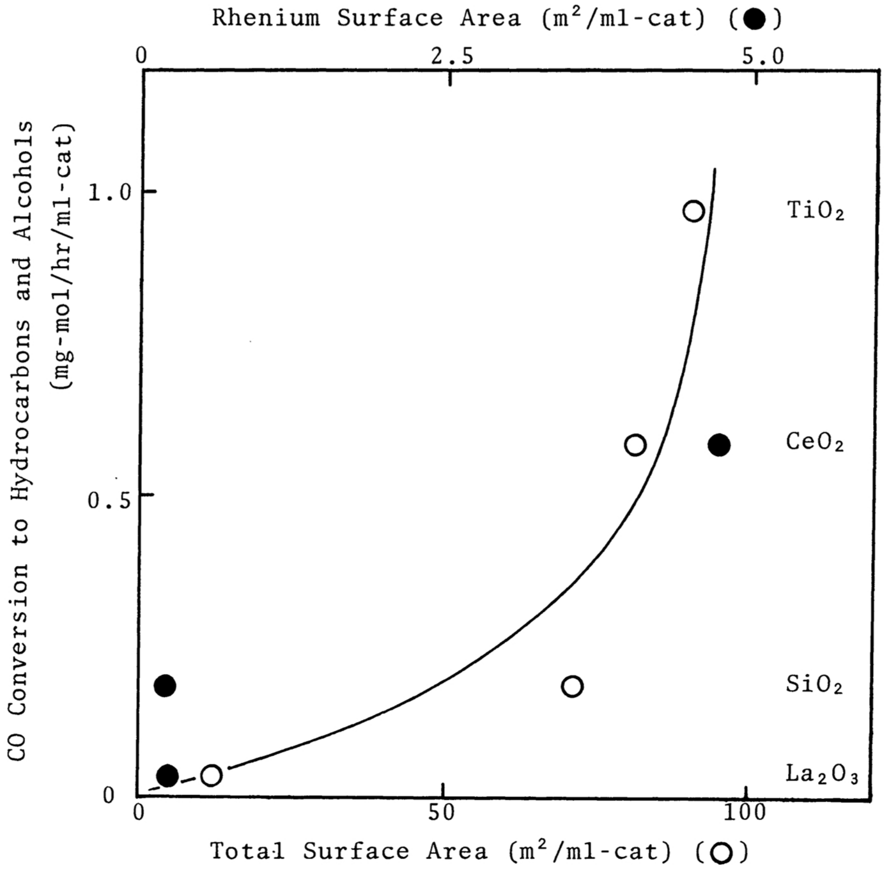

Figure 1. Catalytic Activity vs. BET and Metal Surface Area

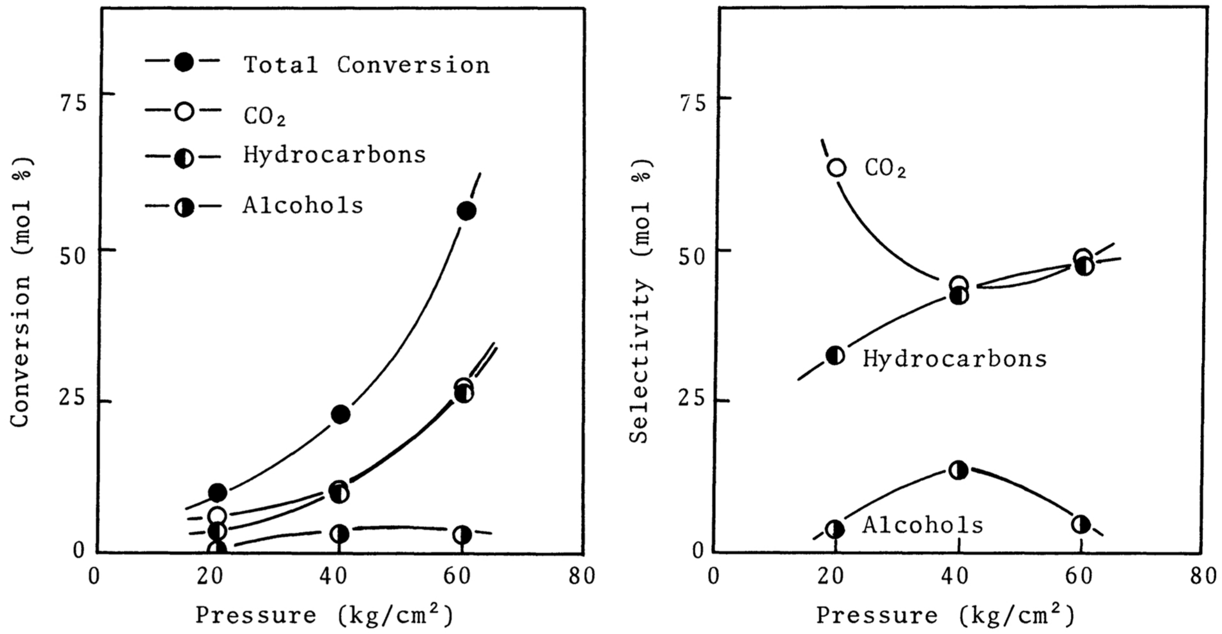

Figure 2. Pressure Dependence of CO Hydrogenation over Re-CeO_2 (temp.= 250°C, s.v.=1000/hr)

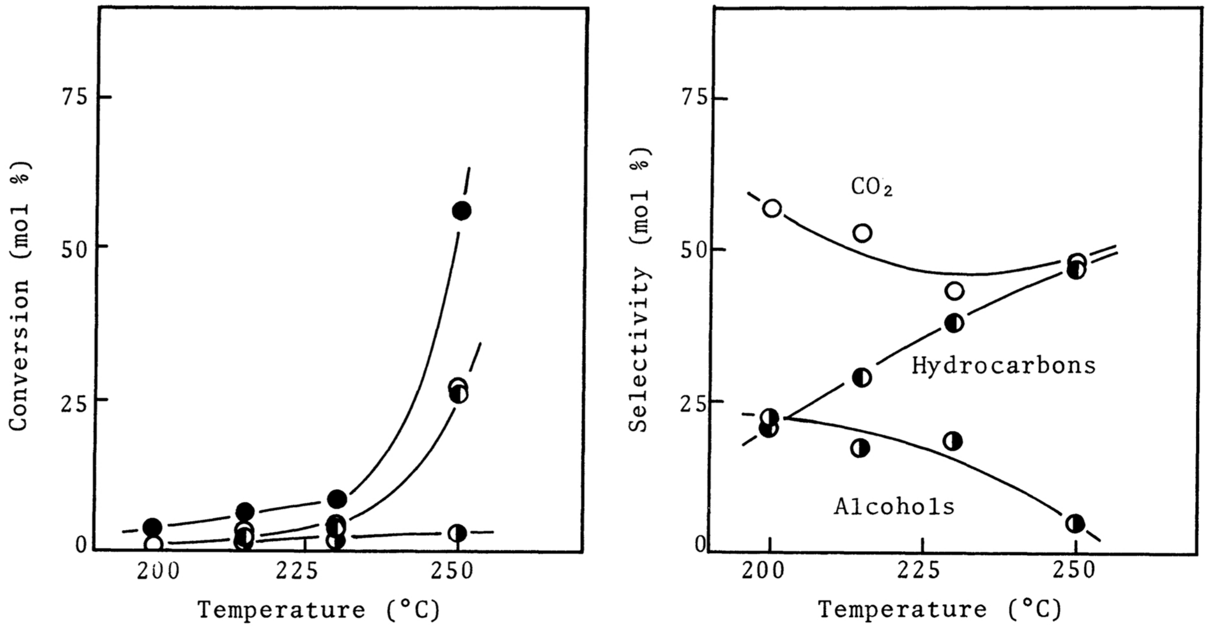

Figure 3. Temperature Dependence of CO Hydrogenation over Re-CeO_2 (press.= 60 kg/cm², s.v.= 1000/hr)

The BET and metal surface areas of some catalysts correlated well with their catalytic activities (conversion to hydrocarbons and alcohols) as shown in Figure 1. Here the total surface area is calculated on the basis of the bulk volume of catalyst, since the catalytic activity measurement was made with fixed volume of catalyst (2.0 ml catalyst bed). The area associated with each rhenium atom in the surface is assumed to be 7.6 Å^2.4) The positive correlation suggests that an improvement in the dispersion of rhenium may bring about higher catalytic activity, although the data is not yet conclusive.

Using Re-CeO_2 catalyst, which is unique in having relatively high catalytic activity and selectivity to alcohols, the effects of reaction conditions were examined. Rhenium-on-ceria catalyst showed constant catalytic activity for over 17 hr, and the following measurements were made within that period. Figures 2 and 3 compare the effects of reaction pressure and reaction temperature on the CO conversion and selectivity of the Re-CeO_2 catalyst. Total conversion increases from 11 to 66 mol % when reaction pressure is increased from 20 to 60 kg/cm^2 at 250°C. Selectivity to each product, however, follows complicated path: hydrocarbons increase as the pressure increases, alcohols have a maximum at around 40 kg/cm^2, and CO_2 has a minimum at around the same pressure. Temperature dependences of CO conversions show sharp increase above 230°C except the conversion to alcohols. The sharp increase in total conversion is mainly due to the increase in hydrocarbon production: although the amount of CO_2 produced increases with temperature, the selectivity to CO_2 tends to decrease as temperature increases as shown in Figure 3. It is noteworthy that the selectivity to alcohols is comparable to that to hydrocarbons at around 200°C, and Figure 3 suggests that below that temperature the reaction is favorable to the production of alcohols.

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