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SELECTIVE FORMATION OF METHANOL OVER WATER-TREATED RANEY RUTHENIUM

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Methanol was obtained as a main product from CO and H_2 over water-treated Raney-Ru, although hydrocarbons were exclusively obtained over Ru powder. The C-base selectivity to methanol was 73% at 353 K under a total pressure of 600 Torr (1 Torr = 133.3 Pa). The selectivity was increased with an increase of the Al content. XPS studies showed that the surface Al was oxidized by water treatment above 473 K, which was necessary for methanol formation.

Ru metal surface is known to dissociate CO bond easily, which enables supported Ru catalysts to be effective for methanation or Fischer-Tropsch synthesis. Although, there are several Ru systems which give oxygen containing compounds,$^{1-4)}$ the reasons have not been discussed well. Since the Raney type catalyst has concentrated surface metal atoms comparing with the supported catalysts, it is suitable for surface measurements such as XPS, which would clarify the state of active site.

The mostly used alloy has a composition of $Ru_{21}Al_{79}$, which is mainly composed with both Ru_4Al_{13} and $RuAl_6$ phases. The crashed alloy was leached with KOH solution, and washed several times with decantation until the solution showing pH7, followed by 5 times washing with decantation further. In order to control the amount of residual Al, KOH concentration, leaching time (5 min to 3 h) and temperature (273 to 373 K) were varied. The leached sample powder was transferred to the catalyst chamber together with the water. It was evacuated for 10 h at room temperature, and treated with circulating H_2O(ca. 20 Torr)-He(200 Torr) gas mixture at various temperatures for 10 h. The water vapor was trapped with liquid nitrogen temperature for 2 h, and evacuated for 2 h at the treatment temperature. The reaction was carried out by using a conventional circulation system mostly at

353 K and under the pressure of 600 Torr of H_2/CO(=3/1) gas mixture. Methanol and hydrocarbons with the carbon number of 1 to 7 were recovered as products and analyzed by a gaschromatography. The activity of the catalyst was almost identical during 10 h of the run except for the first 1 h. After each reaction run and hydrogen adsorption measurement, a part of the catalyst sample was transferred to a side arm of the reactor and sealed off. The sealed sample was moved to XPS apparatus (Shimadzu ESCA 750) for the measurements.

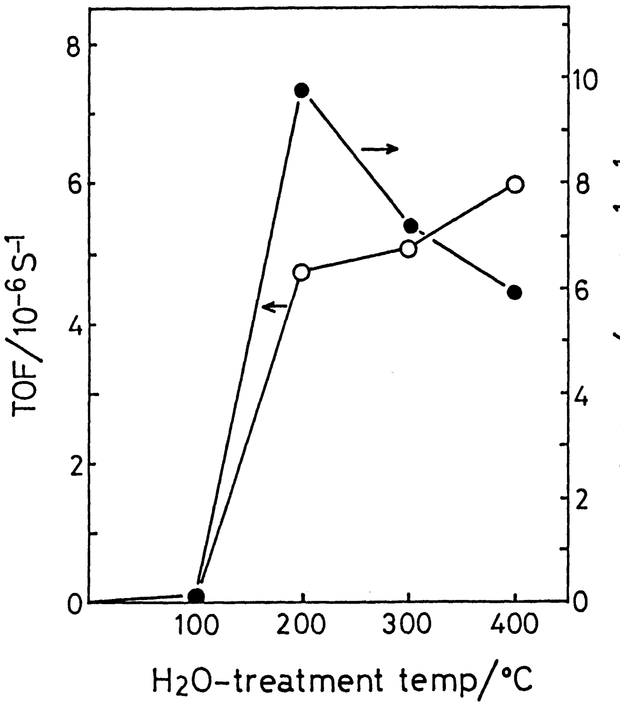

Fig. 1. Activity and turnover frequency of MeOH formation over Raney-Ru as a function of H_2O-treatment temperature. Reaction condition; CO+3H_2 = 600 Torr, 353 K.

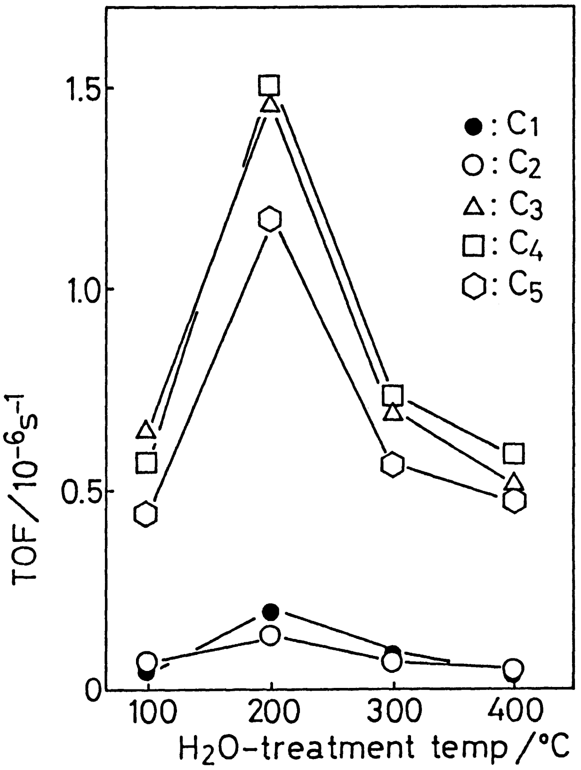

Fig. 2. Turnover frequency (TOF) of hydrocarbon formation over Raney-Ru as a function of H_2O-treatment temperature. Reaction condition; CO+3H_2 = 600 Torr, 353 K.

CO hydrogenation reactions were carried out over the Raney-Ru which was leached at 373 K for 3 h by 5 mol dm^{-3}-KOH solution and treated with water vapor at various temperatures. Al content measured by XPS was 24±2 mol%. The turnover frequencies of methanol and hydrocarbon production at 353 K are plotted as a function of H_2O treatment temperature in Figs. 1 and 2. Hydrocarbons were produced exclusively over the sample treated at 373 K, without yielding any methanol. When the sample was treated above 473 K, methanol was produced as a main product. No other oxygenated hydrocarbon was observed. The catalyst had the maximum activity for hydrocarbon formation when it was treated at 473 K as is shown in Fig. 2. The XPS spectra of the samples treated with water at various temperatures were shown in Fig. 3. Ru was observed to be mostly in metallic because the binding energy of $Ru3d_{5/2}$ was 280.0 eV.$^{5)}$ The state of Al was changed from metallic (117.3 eV for Al2s) to Al^{3+} (119.1 eV for Al2s) by the water-treatment above 473 K. An active site for methanol formation was considered to be generated during the mild oxidation of the surface by water-treatment above 473 K. It seems that the activity for hydrocarbon formation has also some relation to the extent of oxidation of the surface.

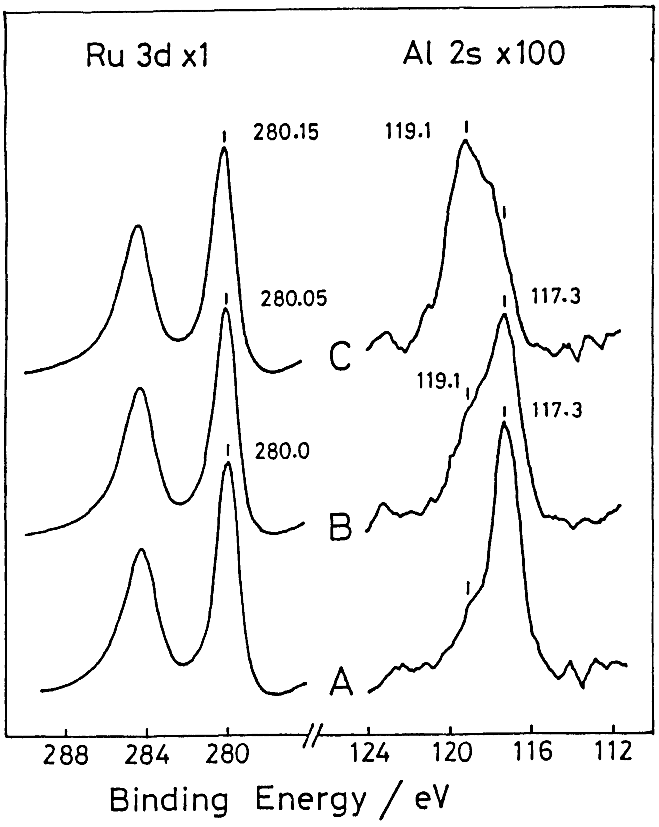

Fig. 3. Al2s and Ru3d XPS spectra of various Raney-Ru samples after H_2O-treatment at 373 K (A), 473 K (B), and 673 K (C).

Raney-Ru with various Al contents were prepared by changing the leaching condition. A sample of Ru powder without Al was also used. Al content was analyzed by both XPS and adsorption techniques. CO hydrogenation reactions were carried out at 353 K over the water-treated (473 K) samples. A C-base selectivity for methanol increases with an increase of residual Al content as is shown in Fig. 4. The maximum selectivity was 73% for methanol.

The following two factors were found in order to get methanol over Raney-Ru from these findings. 1) The surface should be composed both Ru and Al (especially in rich Al concentration). 2) The surface should be oxidized moderately. Thus the active site for methanol formation over Raney-Ru is considered to be such as -

Ru-Al^{3+}- (model A) or -Ru^{x+}-Al^{3+}- (model B). Although the XPS results showed that Ru was reduced after the reaction (model A), a part of surface Ru atom of which concentration is below the limit of XPS sensitivity might be oxidized (model B). Cationic species has been reported to exist on Pt/$Al_2O_3$$^{6)}$ and be responsible for methanol formation over Pd/SiO_2.$^{7)}$ Since the escape depth of Ru3d electron corresponds about 5 layers of Ru surface, the XPS information about surface active site may be diluted. The state of active site cannot be determined only by an XPS measurement. However, an important factor to obtain methanol over Ru catalyst was clarified.

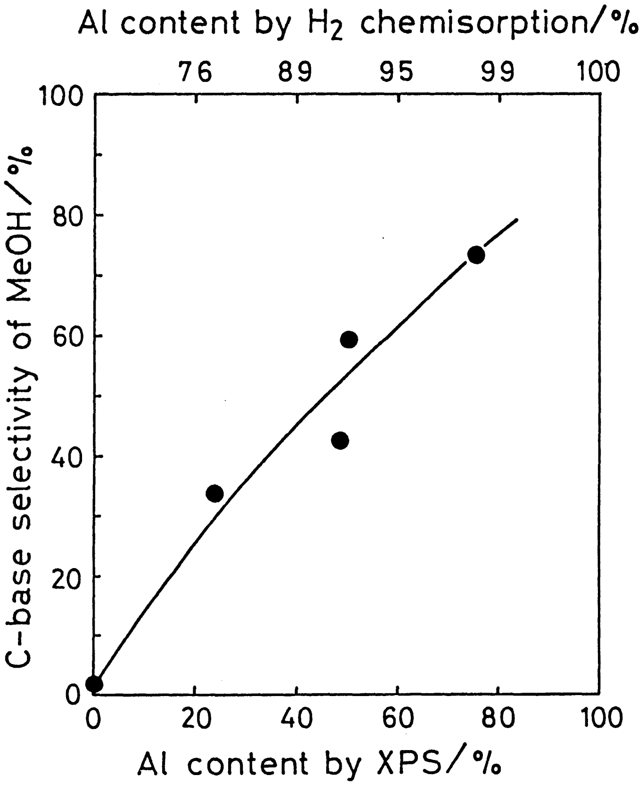

Fig. 4. Activity of MeOH formation over water-treated Raney-Ru as a function of Al content. Reaction condition; CO+3H_2 = 600 Torr, 353 K.

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