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THE EFFECT OF STRONG INTERACTION BETWEEN Ru AND Al_2O_3 ON THE ACTIVITY FOR CARBON MONOXIDE HYDROGENATION OVER Ru/Al_2O_3

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Hydrogenation of CO over Ru/Al_2O_3 was examined. It was found for the first time, that when the catalyst was strongly reduced, the CO conversion activity for the CO-H_2 reaction increased and surface Ru on strongly reduced catalyst was determined to be electronegatively charged, by X-ray photoelectron spectroscopy (XPS).

Ruthenium is known to be one of the most active catalyst for the CO-H_2 reaction among group VIII metals. The specific activity of supported Ru catalysts for methanation and CO conversion decreased with increasing Ru dispersion.[1,2,3] With titania supported Ru catalyst which chows the strong metal-support interaction (SMSI), higher hydrocarbons are produced in the hydrogenation of CO.[4] In this paper, we will report that on Ru/Al_2O_3, when the catalyst is strongly reduced by H_2, the specific activity of the CO conversion in the CO-H_2 reaction increased. In order to elucidate the cause of the increase in the activity of the catalyst, we have observed the catalyst surface by X-ray photoelectron spectroscopy (XPS) and found that Ru was ionically charged by the interaction with Al_2O_3 support in a strongly reduced state.

Catalysts were prepared by impregnating an aqueous solution of $RuCl_3$ into χ-Al_2O_3 to make ca. 1 wt% Ru loaded ones. The catalysts were reduced with N_2H_4 (1 wt% aqueous solution) followed by the reduction in flowing H_2 ar 300°C (hereafter 300-Ru/Al_2O_3) and 600°C (hereafter 600-Ru/Al_2O_3) before use. The surface area and pore volume of both catalysts thus prepared were determined to be 165 m^2/g and 0.45 cc/g, respectively. Dispersion of Ru was determined by CO adsorption, assuming the ratio between surface Ru and the amount of adsorbed CO to be unity. For the reference of the electronic state of Ru, we prepared Ru-Al alloy by melting Ru and Al powder together, the weight ratio of which was unity. X-ray powder diffration of this alloy showed the Ru_4Al_{13} structure. The CO-H_2 reactions were carried out using an isothermal type micro reactor, of which the temperature of the catalyst bed was controlled within ± 0.5 °C during the CO-H_2 reaction at 300 °C. The gaseous products were analyzed by gas chromatography. X-ray photoelectron spectroscopic measurement was carried out using a V. G. ESCALAB 5.

The examples of the CO conversion on 300-Ru/Al_2O_3 and 600-Ru/Al_2O_3 during the

$CO-H_2$ reaction are shown in Fig. 1. Details of the reaction conditions are listed below it. As is shown in Fig. 1, the activity of CO conversion on 600-Ru/Al_2O_3 is higher than that on 300-Ru/Al_2O_3. In both cases, the activity decreases from the initial value and becomes constant after about 500 min. The amount of gaseous products detected by the gas chromatography showed that 99.5% of the CO consumed was converted to hydrocarbon species, after the CO conversion reached the constant value. When a catalyst used for 1000 min was reduced at 300 °C in flowing H_2, the amount of CO conversion was restored to the initial value. This fact suggests that as the $CO-H_2$ reaction takes place, carbon species begin to accumulate on the surface and then the activity decreases. However, the carbon deposition and the $CO-H_2$ reaction to form hydrocarbons occur simulteneously and the amount of surface carbon balances at a certain level to give a constant activity.

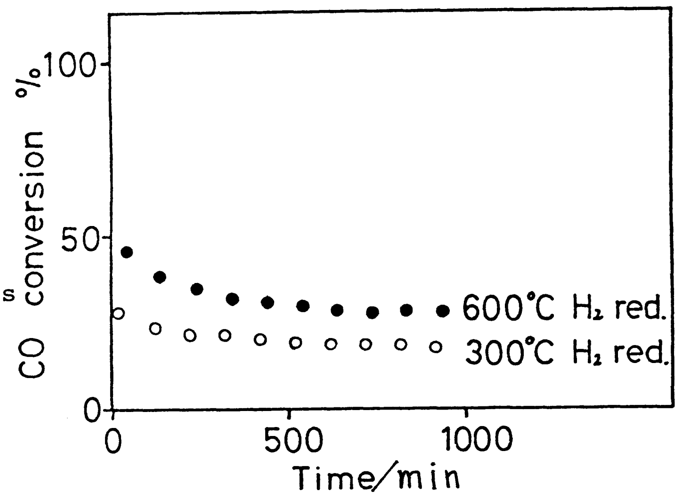

Fig. 1. CO conversion in $CO-H_2$ reaction over Ru/Al_2O_3 at 300 °C.
○; 300-Ru/Al_2O_3 and
●; 600-Ru/Al_2O_3.
Total pressure; 10 $kgw/cm^2\cdot G$,
CO; 30 mlSRP/min, H_2; 150 mlSTP/min
and N_2; 240 mlSTP/min.

As the activity of the CO hydrogenation reaction over the supported Ru catalysts strongly depends on the Ru dispersion,[1,2,3] the turn over frequency (TOF) of CO conversion versus Ru dispersion of Ru/Al_2O_3 were plotted (Fig. 2). TOF was calculated from the value of CO conversion taken at 1000 min. The activity of both catalysts, 300-Ru/Al_2O_3 and 600-Ru/Al_2O_3, declined as the Ru metal dispersion increased. However, the 600-Ru/Al_2O_3 showed higher activity than that of 300-Ru/Al_2O_3. This difference is more extensive in the higher dispersion regions.

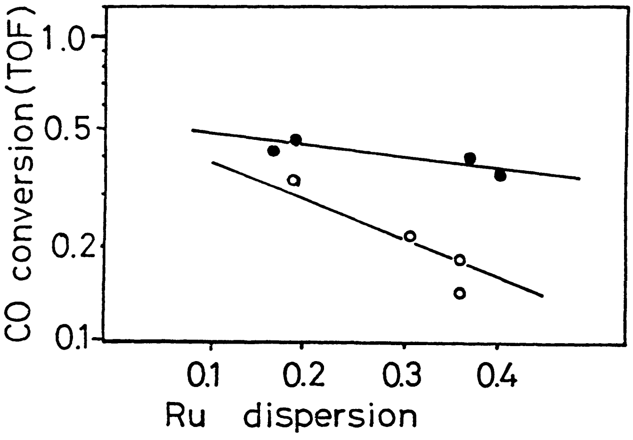

Fig. 2. Changes in the CO conversion (TOF) against the dispersion of Ru on Ru/Al_2O_3. ○ ; 300-Ru/Al_2O_3 and
●; 600-Ru/Al_2O_3.

In order to elucidate the effect of the reduction temperature on the state of the supported catalyst, we have studied the pore structure, surface area and surface contaminations. Those factors were similar for both catalysts. The electronic state of Ru on the catalysts was studied by XPS and the results are shown in Fig. 3. The peak of Ru 3d 5/2 before H_2 reduction (Fig. 3c) showed two peaks at 277.8 eV and 281.3 eV. When the catalyst was reduced at 300°C with H_2 (Fig. 3d), the peak at 281.3 eV shifted to 280 eV. Further reduction at 600 °C with H_2 (Fig. 3e) showed that the peak at 277.8 eV increased and a small peak also appeared at about 280 eV. In order to identify these peaks, the XPS of Ru metal and Ru-Al alloy were taken (Fig. 3a and 3b). The peak of Ru 3d 5/2 at 280 eV was identical with that observed for Ru metal. This peak was due to Ru^0 state. The peak at 281.3 eV was due to oxidized Ru state.[5)] However, the peak at 277.8 eV (Ru^*) had binding energy 2 eV smaller than that of Ru^0 state. In the case of Ru-Al alloy, Ru 3d 5/2 was observed at 277.8 eV, which was identical with Ru^* on supported catalyst. In Ru-Al alloy, Al 2p peaks were detected at 71.0, 72.3 and 73.8 eV. The peak at 73.8 eV decreased after Ar^+ sputtering for 3 min, where other peaks at 71.0 and 72.3 eV increased. This indicated that these peaks were due to the Ru-Al alloy and that at 73.8 eV was due to the surface oxidized Al species. The peak at 71.0 eV was due to Al^0, which existed excessively in the alloy. The Al 2p at 72.3 was observed in higher binding energy than that of Al^0. For Ru-Al alloy, Ru 3d 5/2 was observed at lower binding energy than that of Ru^0 state, and Al 2p at higher than that of Al^0 state. This indicates a certain amount of charge transfer from Al to Ru in this alloy. However, the large shift in the binding energy of Ru 3d 5/2 should be considered as the sum of charge transfer shift and the relaxation shift.[6)] Similar state of Ru could be formed on the surface of the 600-Ru/Al_2O_3 catalyst, though the Al 2p at 72.3 eV was not observed in this case, because of the large peak due to the Al_2O_3 support. On the other hand, the Ru 3d 5/2 peak of 300-Ru/Al_2O_3

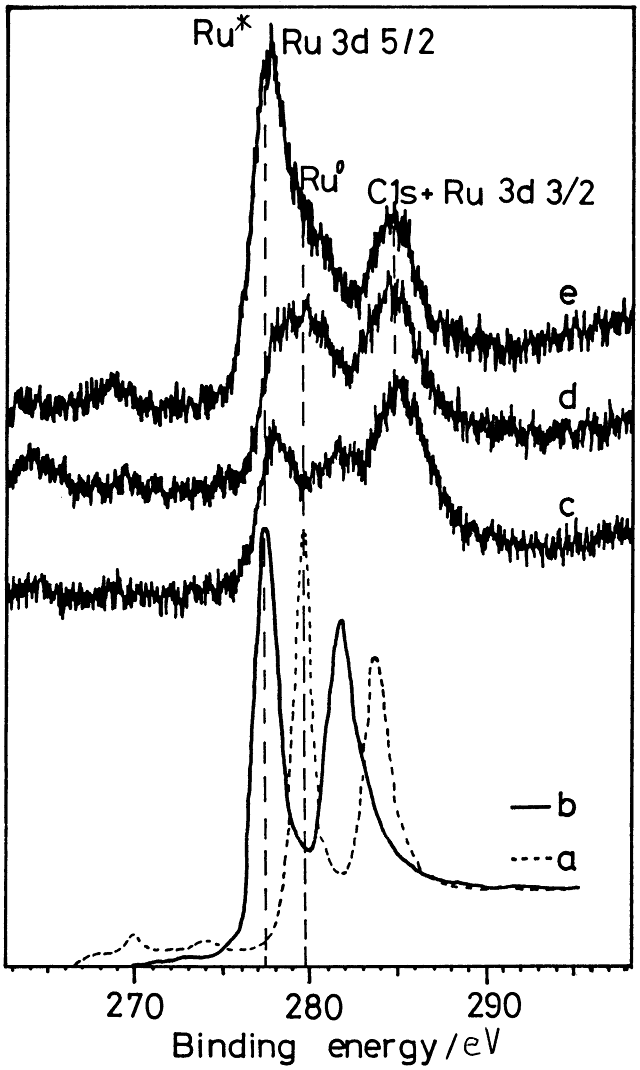

Fig. 3. X-Ray photoelectron spectra of Ru 3d region. Binding energy of Ru/Al_2O_3 was determined by Al 2p=73.8 eV, which was corrected from the Au evaporated Al_2O_3 sample assuming Au 4f 7/2=83.7 eV. a) Ru metal, b) Ru-Al alloy, c) Ru/Al_2O_3 after reduction with N_2H_4, d) c) was treated under H_2 flow at 300 °C for 3 h, e) H_2 reduction of c) at 600 °C for 3 h.

(Fig. 3d) showed the strongest peak at 280.0 eV, so the surface Ru in this catalyst was mostly in the Ru^0 state (including some amount of Ru^*).

Here we have shown for the first time that when a Ru/Al_2O_3 catalyst was reduced with H_2 at 600 °C, the electronic state of the surface Ru changed to $Ru^{\delta-}$. As a result, the activity of CO conversion in $CO\text{-}H_2$ reaction increased compared with the 300 °C H_2 reduced catalyst, of which the surface Ru was in Ru^0 state. The reason for the enhancement of the reaction is discussed in connection with the state of Ru. The product distribution for hydrocarbons higher than C_2 showed almost identical inclination in the Shlz-Flory plot for both $600\text{-}Ru/Al_2O_3$ and $300\text{-}Ru/Al_2O_3$. This suggests that the process of chain growth in the $CO\text{-}H_2$ reaction was not affected by the change in the electronic state of Ru. On the other hand, when Ru is in the Ru^* state, which is considered to be electronegatively charged, the adsorbed state of CO might change and the C-O bond could be weaken by the increase of the backdonation from Ru. This might result in increasing the carboneous species which could be the initiating species of the $CO\text{-}H_2$ reaction.

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