

Electronic Effects on CO Hydrogenation over Ru–Metal Oxide Catalysts

Yoshiharu Doi,* Hiroto Miyake, and Kazuo Soga

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

The electronic structure of supported Ru catalysts is markedly affected by the nature of the metal oxide support, and the specific activity of CO hydrogenation increases as the electron density of the Ru particles decreases.

The activity and product selectivity of CO hydrogenation over supported Ru catalysts are influenced by the nature of the support,^{1–3} the metal particle size,^{4,5} and the catalyst preparation.⁶ This has been attributed to changes in the electronic properties of the Ru particles due to metal–support interactions.^{1–6} However, no definite correlation between the catalytic properties and the electronic structure of the Ru particles has been shown. In this communication we report a distinct effect of Ru electron density on the specific activity of CO hydrogenation over Ru–metal oxide catalysts.

Supported Ru catalysts were prepared by impregnation of metal oxide with Na[Ru₃H(CO)₁₁] in methanol solution.³ The supported catalysts were activated by heating at 400 °C for 4 h

under vacuum. The content of Ru in the catalysts was 20 mg per g of catalyst. Seven different types of metal oxides were used as supports. SiO₂ (Davison 952, 350 m²/g), γ -Al₂O₃ (Nishio, 150 m²/g), MgO (Wako, 93 m²/g), and TiO₂ (Koso, 40 m²/g) were pre-treated by heating at 300–350 °C for 20 h under vacuum. Al₂O₃–SiO₂ and MgO–SiO₂ were respectively prepared by the reaction of AlEt₃ and MgEtBu with SiO₂,⁷ followed by treatment with O₂ (25 kPa) at 500 °C for 12 h. TiO₂–Al₂O₃ was also prepared by the reaction of Ti(OBu)₄ with Al₂O₃, followed by treatment with O₂ (25 kPa) at 500 °C. The mole ratios of M : Ru (M = Al, Mg, Ti) in the supported catalysts were in the range of 0.8 to 1.9.

The X-ray photoelectron spectra (X.p.s.) of the supported

Table 1. Binding energy and dispersion of Ru–metal oxide catalysts and their specific activities in CO hydrogenation.^a

Support	Binding energy Ru 3d _{5/2} /eV	Dispersion		Specific activity ^d	
		H/Ru ^b	H/Ru ^c	N(CO) × 10 ³ /s ⁻¹	N(CH ₄) × 10 ³ /s ⁻¹
TiO ₂	279.3	0.23	—	1.0	0.18
MgO	279.3	0.43	—	0.75	0.17
SiO ₂	279.9	0.33	0.36	3.1	2.2
MgO–SiO ₂	279.9	0.48	—	5.6	2.1
Al ₂ O ₃	280.1	0.31	—	5.0	1.6
TiO ₂ –Al ₂ O ₃	280.2	0.39	—	9.2	3.0
Al ₂ O ₃ –SiO ₂	280.2	0.55	0.51	15	4.7

^a Reaction conditions: CO + H₂ = 53 kPa, H₂:CO = 2:1, catalyst = 0.2–0.5 g, Ru = 2.0 wt%, 270 °C. ^b Fresh sample. ^c Sample after CO hydrogenation. ^d Based on H₂ uptake on fresh sample.

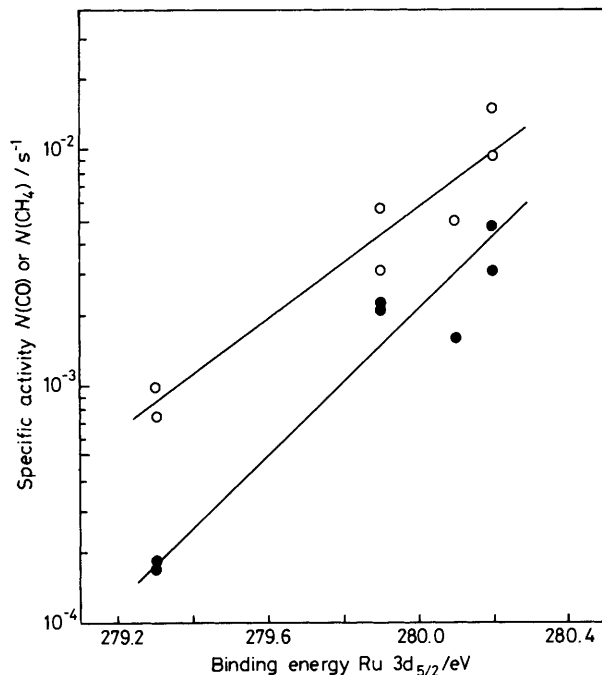


Figure 1. Correlation between binding energy Ru $3d_{5/2}$ and specific activity (N) of CO hydrogenation over supported Ru catalysts: $N(\text{CO})$ = molecules of CO converted (\circ) and $N(\text{CH}_4)$ = molecules of CH_4 produced (\bullet) per surface Ru per second.

catalysts were recorded on a Shimadzu electron spectrometer ESCA 750 with Mg-K_α excitation radiation. Sample preparation for X.p.s. measurements was performed in a glove box filled with nitrogen. The C (1s) line (E_b 284.5 eV) of the adsorbed diffusion pump oil was used as the standard peak. Measured binding energies were repeatable to ± 0.1 eV. The dispersions of Ru particles were determined from the equilibrium amount of H_2 adsorption by assuming that one hydrogen atom was adsorbed on each Ru atom on the surface. These results are given in Table 1. The electronic structure of Ru atoms is markedly affected by the metal oxides used as

supports. The Ru atoms on basic oxides such as MgO and TiO_2 are electron-rich, whereas those on acidic oxides such as $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{TiO}_2\text{-Al}_2\text{O}_3$ are electron-deficient. The strong acidity of $\text{Al}_2\text{O}_3\text{-SiO}_2$ was confirmed by the Al 2s peak (119.2 eV) at higher binding energy than that (118.0 eV) of Al_2O_3 . The dispersion of Ru particles on $\text{Al}_2\text{O}_3\text{-SiO}_2$ is higher than that on the parent SiO_2 . The Ru dispersion on $\text{Al}_2\text{O}_3\text{-SiO}_2$ support was almost independent of Ru concentration on the surface in the Ru loading range 0.5–5.0 wt%.

The CO hydrogenation was carried out at 270°C in a conventional circulating system³ ($\text{CO} + \text{H}_2 = 53$ kPa, $\text{H}_2 : \text{CO} = 2 : 1$); the products were analysed by gas chromatography. The specific activities, molecules of CO converted into hydrocarbons $N(\text{CO})$ or molecules of CH_4 produced $N(\text{CH}_4)$ per surface Ru atom per second, increase as the electron density of the Ru particles decreases (see Figure 1). The selectivity of methane formation increases slightly with decreasing electron density. These results may be interpreted by the mechanism of CO hydrogenation involving competitive adsorption steps of CO and H_2 over Ru particles.⁸ A decrease in Ru electron density must make CO adsorption weak and H_2 adsorption more competitive, increasing the surface concentration of adsorbed hydrides. This should increase the activity of CO hydrogenation, since adsorbed hydrides are involved in the rate-determining step.⁸

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