

Pronounced Effect of Particle Size on Selectivity Observed for Carbon Monoxide Hydrogenation over Ruthenium–Alumina Catalysts

Zheng-Zhong Lin,^a Toshio Okuhara,^{*b} Makoto Misono,^b Kazuyuki Tohji,^c and Yasuo Udagawa^c

^a Faculty of Chemistry, Xiamen University, Fujian, China

^b Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

^c Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444, Japan

The size of Ru crystallites affected markedly the selectivity for CO hydrogenation in contrast to previous reports; small particles (10 Å) produced significant proportions of higher hydrocarbons and large single crystallites (110 Å) gave mainly methane.

The catalytic activity and selectivity of supported or single crystal metal catalysts are often sensitive to the metal particle size.^{1,2} However, in Fischer–Tropsch synthesis over Ru/Al₂O₃, it has been reported that the carbon number distribution is independent of the ‘dispersion’ of Ru.^{3–5} We now find that, in contrast, the selectivity is markedly different for small and large particles.

Ru/Al₂O₃ catalysts were prepared from Ru₃(CO)₁₂ as described previously.³ The catalysts were reduced with 101 kPa of H₂ at 723 K for 2 h (this treatment will be abbreviated as R). Some were further oxidized at 773 K with 13 kPa of O₂ and were again reduced at 723 K (abbreviated as R–O–R). Transmission electron microscopy (T.E.M.) and extended X-ray absorption fine structure (E.X.A.F.S.)

measurements were carried out as described elsewhere.^{6,7} E.X.A.F.S. spectra were measured at room temperature after the samples had been reduced *in situ* at 673 K. Hydrogenation of CO was performed in a flow reactor at 533 K at 101 kPa (H₂/CO = 2) as described previously.⁶ Hydrogenolysis of butane was carried out in a closed circulation system at 5.5 kPa of butane and 10.9 kPa of H₂ at 373 K.

The selectivities and turnover frequencies (T.O.F.) for hydrogenation of CO and hydrogenolysis of butane over 2.5% Ru/Al₂O₃ after R and R–O–R are given in Figure 1. Considerable differences in selectivity are apparent; the weight percentage of methane obtained in the CO hydrogenation was about 40% after R, but was >80% after R–O–R. The carbon number distribution was confirmed to be independent

Table 1. Characterization of Ru on 2.5% Ru/Al₂O₃.^a

Pretreatment ^b	Diameter/Å			E.X.A.F.S. data ^c	
	Adsorption ^d	E.M. ^e	X.R.D. ^f	$r/\text{Å}^g$	N^h
R	10	n.d. ⁱ	n.d. ⁱ	2.59 ± 0.02	6.1 ± 1
R-O-R	83	110	140	2.65 ± 0.02	12.6 ± 1.5

^a Prepared from Ru₃(CO)₁₂. ^b R, reduction with H₂ at 723 K; R-O-R, oxidation with O₂ at 773 K and reduction with H₂ at 723 K after R. ^c From curve fitting method. ^d From H₂ adsorption at 298 K. ^e From electron microscopy. ^f From line width of X-ray powder diffraction peak. ^g Interatomic distance of Ru (nearest atom neighbours). The value for bulk Ru is 2.66 Å. ^h Average co-ordination number of Ru. The value for bulk Ru is 12. ⁱ Not detected.

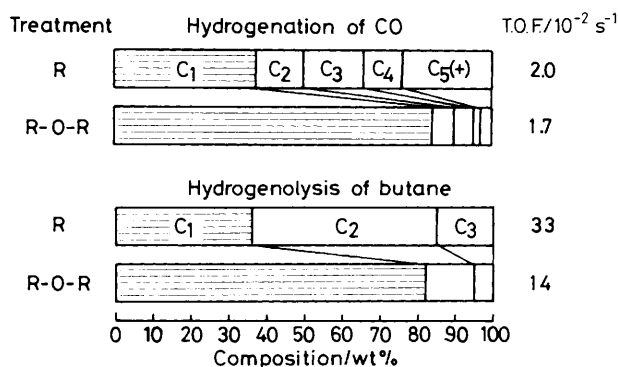


Figure 1. Selectivities and turnover frequencies for hydrogenation of CO and hydrogenolysis of butane over 2.5% Ru/Al₂O₃ prepared from Ru₃(CO)₁₂. Reaction conditions: hydrogenation of CO: 533 K, 1 atm, H₂/CO = 2; hydrogenolysis of butane: 373 K, 16.5 kPa, H₂/butane = 2. Pretreatment conditions: R: reduction with H₂ at 723 K, R-O-R: oxidation with O₂ at 773 K and reduction with H₂ at 723 K after R.

of the extent of conversion in the conversion range 5–35%. In the hydrogenolysis of butane, the selectivity was also quite different for the two pretreatments. Distributions of products for 4% Ru/Al₂O₃ after R and R-O-R were essentially the same as for 2.5% Ru/Al₂O₃ after R and R-O-R, respectively.

Ru particles on Ru/Al₂O₃ were characterized by H₂ adsorption, T.E.M., E.X.A.F.S., and X-ray powder diffraction (X.R.D.); the results are summarized in Table 1. It has previously been shown for 4% Ru/Al₂O₃ that the particle size did not change significantly after use of the catalyst for CO hydrogenation.³ After R, the particle size of Ru on 2.5% Ru/Al₂O₃ (and 4% Ru/Al₂O₃) was estimated to be about 10 Å from H₂ adsorption. These particles were too small to be detected by T.E.M. and X.R.D. E.X.A.F.S. spectra for 4% Ru/Al₂O₃ are shown in Figure 2. Only one peak due to Ru-Ru bonds was found after the two different treatments. The co-ordination number of Ru on Ru/Al₂O₃ (Table 1) was about 6 after R, which is consistent with particles of 10 Å diameter.⁸ After R-O-R, the Ru size was 83–110 Å (from H₂ adsorption and T.E.M.). X.R.D. peaks of Ru were intense and the particle size estimated from X.R.D. was comparable with that from T.E.M., showing that those Ru particles are single crystallites. The high co-ordination number of 12 observed after R-O-R (E.X.A.F.S., Table 1) also supports the particles being large crystallites. X.R.D. showed that the oxidation of Ru/Al₂O₃ with O₂ at 773 K led to RuO₂ crystallites with a diameter of 200 Å. These facts demonstrate that small Ru particles (after R) were transformed into large crystallites (after R-O-R) via the formation of RuO₂ crystallites as illustrated in Scheme 1.

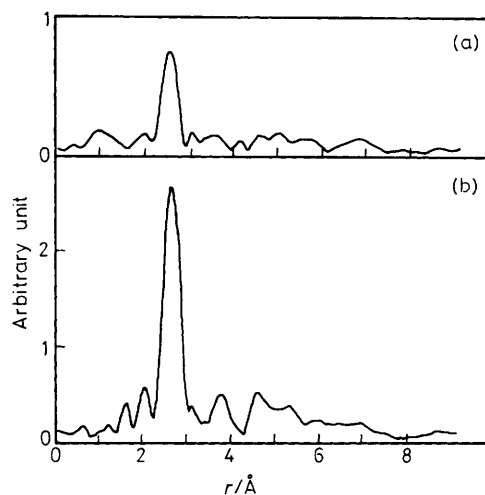
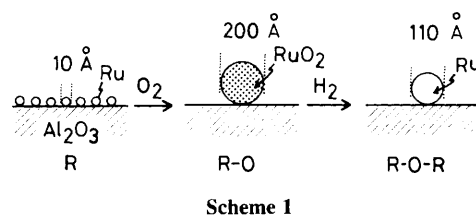


Figure 2. Fourier transforms of the E.X.A.F.S. spectra of (a) 4% Ru/Al₂O₃ after R and (b) 4% Ru/Al₂O₃ after R-O-R. 4% Ru/Al₂O₃ was prepared from Ru₃(CO)₁₂. R: reduction with H₂ at 723 K; R-O-R: oxidation with O₂ at 773 K and reduction with H₂ at 723 K after R. The E.X.A.F.S. data are for the extended fine structure beyond the K absorption edge of Ru.



The change of the selectivity given in Figure 1, therefore, may be caused by this change in the Ru particles; small particles produced higher hydrocarbons and large crystallites gave mainly methane in CO hydrogenation. In accordance with this, unsupported Ru crystallites (3000 Å) produced mainly methane in CO hydrogenation.^{4,9} Previous studies claimed that the carbon number distribution in the product of CO hydrogenation was independent of the particle size measured by H₂ adsorption. These studies all used Ru/Al₂O₃ samples which were prepared from RuCl₃ and treated only with H₂. We also obtained similar results for 0.5–10 wt% Ru/Al₂O₃ prepared from RuCl₃ (Ru particles 20–80 Å). According to our previous data, the Ru particles of these catalysts were aggregates of fine particles.¹⁰ Therefore, the difference in the morphology of Ru particles probably explains why previous investigators observed little dependence of selectivity on the Ru dispersion. The R-O-R treatment of these catalysts transformed the Ru particles into

single crystallites and the selectivity became similar to the case of Ru/Al₂O₃ [from Ru₃(CO)₁₂] after R–O–R.

With regard to the changes in the selectivity, it may be necessary to consider metal–support interactions. Iwasawa *et al.*¹¹ reported on the basis of an E.X.A.F.S. study that Ru particles on Ru/Al₂O₃ interacted strongly with the surface of Al₂O₃ to form Ru–O–Al bonds, whereas Ru–O bonds were not detected for Ru/SiO₂. They accounted for the difference in the selectivity for CO hydrogenation between the two supports by the difference in metal–support interaction. However, as shown in Figure 2, no Ru–O bond was observed even for Ru/Al₂O₃ when it was reduced *in situ*. Therefore, the interaction between Ru and Al₂O₃ may not be primarily important in the present work. Further, the Ru–Ru peak of Ru/Al₂O₃ observed by E.X.A.F.S. after R changed completely to the Ru–O peak on the exposure of the catalyst to air at room temperature.

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