

Production of $\text{Ru}(\text{CO})_5$ from Silica-Supported Ruthenium Catalysts Prepared by Cation Exchange

The author found the following phenomenon. After the CO flow had been passed through silica-supported Ru catalysts above room temperature, and then introduced into a dry-ice trap for 2 h, a yellow-orange substance could be observed with the naked eye on the wall of the trap. The existence of $\text{Ru}(\text{CO})_5$ was confirmed in the CO stream which was passed through the silica-supported ruthenium catalysts.

For the preparation of catalyst, the same method as in preceding papers (1, 2) was used. A $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ aqueous solution was prepared by the method reported by Allen *et al.* (3). $\text{RuCl}_3 \cdot \text{nH}_2\text{O}$ (0.1 g) was dissolved in water (10 ml); excess hydrazine hydrate (4 ml) was then slowly added, drop by drop, to this solution as it was being cooled in an ice bath. A vigorous reaction occurred evolving bubbles. In the initial stage, a blue or gray precipitate was observed. The precipitate gradually dissolved and the solution became dark red after 1-2 h. Because this solution decomposes slowly, the cation exchange must be performed immediately. The silica gels (BET surface area: $\text{SiO}_2\text{-N}$, 330 m^2/g ; $\text{SiO}_2\text{-30}$, 91 m^2/g) calcined at 500°C, were previously treated with an ammonia aqueous solution before the addition of the $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ solution. The cation exchange was performed overnight with occasional shaking. The dark red color of the liquid phase migrated to the solid silica. The exchanged catalysts were washed with water until no chlorine, ammonia, or hydrazine were detected, and then dried in a desiccator at room temperature. The catalyst should not be dried in air over room temperature.

Metal loading was determined by means

of the colorimetry of the Ru-thiourea for the $\text{Ru-SiO}_2\text{-30-2}$ (0.097 mg-atom Ru/g-cat) and by means of X-ray fluorescence for the $\text{Ru-SiO}_2\text{-N}$ (0.194 mg-atom Ru/g-cat).

All the catalysts were loaded in U-shaped tubes with vacuum-valves, reduced by a hydrogen flow (60-100 ml/min g-cat) at

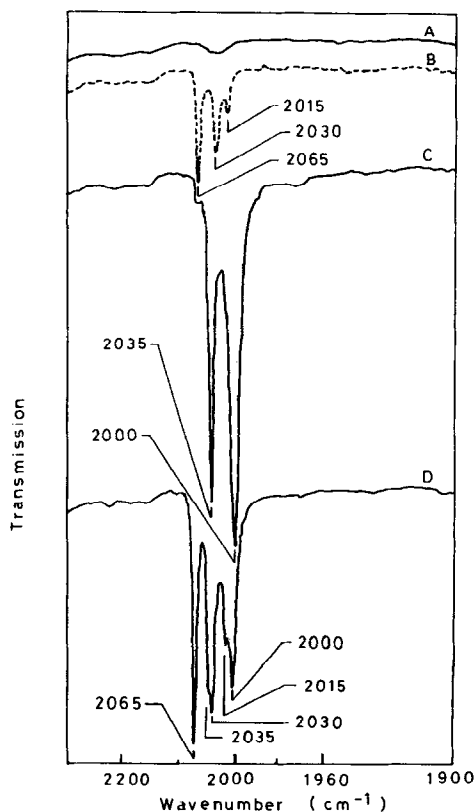


FIG. 1. Infrared spectra of gaseous product from $\text{Ru-SiO}_2\text{-N}$ at 90°C dissolved in n-heptane. (A) n-heptane; (B) $\text{Ru}_3(\text{CO})_{12}$ + n-heptane solution; (C) collected gaseous product in n-heptane under exclusion of light; (D) the same solution as (C) after 30 min exposure to sunlight.

300°C for 2 h, and evacuated below 0.001–0.0001 Torr (1 Torr = 133.3 Pa) at 300° for 2 h. All the flow gases were under atmospheric pressure.

The water contained in the CO was removed by a dry-ice trap. The CO flow (20 ml/min) was passed through the catalyst at 20–120°C, and then introduced into another dry-ice trap, in which 1.0 ml of n-heptane has previously been admitted. All light was excluded from the catalyst, the trap, and the connecting path. After 2 h of collection, the wall of the closed trap was washed with the 1.0 ml of n-heptane in a dark room. The catalyst remaining after the collection of the gaseous product was, while immersed in n-heptane, ground in a mortar, and filtered. The ir spectra were measured for the two kinds of n-heptane solutions with a Japan Spectroscopic Instrument, Model IRA-2. The Ru–SiO₂-N was used.

The EPR spectra were observed by the method described in a previous paper (2) at –140°C. The Ru–SiO₂-30-2 was used.

The irreversible CO-adsorption values CO/Ru_{total} (g-mol/g-atom) were 1.4 for Ru–

SiO₂-30-2 (1) and 2.0 for Ru–SiO₂-N, respectively.

Figures 1C and D illustrate the ir spectra of the gaseous product dissolved in n-heptane. CO (20 ml/min) was passed through Ru–SiO₂-N at 90°C for 2 h. The carbonyl-stretching bands at 2035 and 2000 cm^{–1} in Fig. 1C almost coincide with those of Ru(CO)₅ (4). The D spectrum has all the bands of B and C. This arises from the reaction

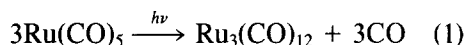


Figure 1 entirely agrees with the results reported by Calderazzo and L'Eplattenier who studied synthetic Ru(CO)₅ (4). The mass spectra of the same samples as D in Fig. 1 show a parent molecular ion [Ru₃(CO)₁₂]⁺ at *m/e* = 641 with the expected isotope pattern.

Figure 2 illustrates the temperature dependencies on the formation of gaseous Ru(CO)₅ and nonvolatile Ru-carbonyl from Ru–SiO₂-N. The intensities of absorbance were almost proportional to the amount of Ru(CO)₅ because a 0.1-mm KBr cell for the

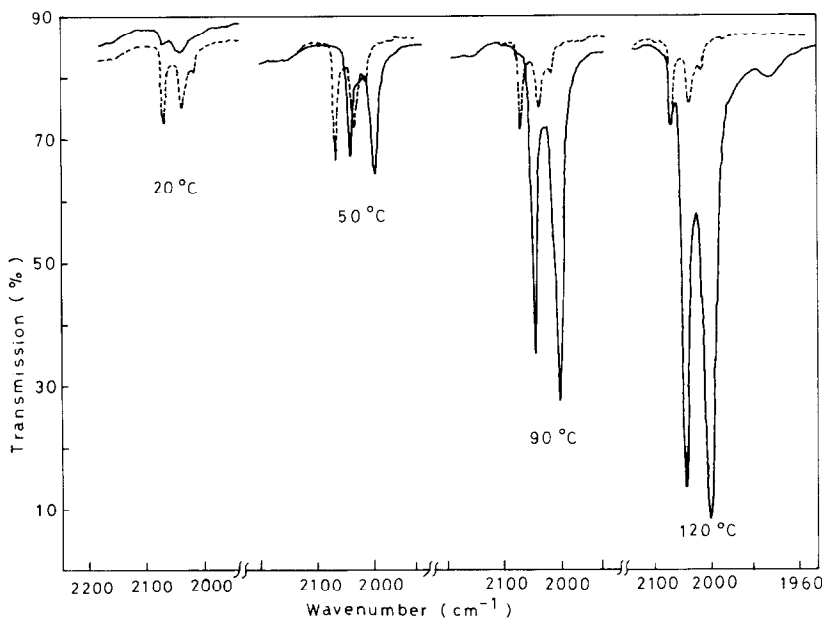


FIG. 2. Temperature dependencies on the formation of gaseous Ru(CO)₅ and nonvolatile Ru-carbonyl from Ru–SiO₂-N. Solid line: Ru(CO)₅ from the gas phase. Broken line: products extracted from Ru–SiO₂-N by n-heptane.

quantitative analysis and an almost constant amount of n-heptane were used. The solid and broken lines in Fig. 2 have the same bands as C and D, respectively, in Fig. 1. With the rise in the temperature, the $\text{Ru}(\text{CO})_5$ formation increases, but the amount of residual Ru-carbonyl decreases. A trace amount of $\text{Ru}(\text{CO})_5$ was observed at 20°C.

After the $\text{Ru-SiO}_2\text{-N}$ catalyst had been maintained in nonmobile CO (1 atm) at 90°C for 30 min, a N_2 flow of 20 ml/min was passed through the catalyst at 90°C and introduced into the trap at -78°C for 2 h. In the carbonyl-stretching region, no bands were detected for the n-heptane in the trap or for the n-heptane extracted from the catalyst. This shows that $\text{Ru}(\text{CO})_5$ and free Ru-carbonyls are not formed without the flow of CO.

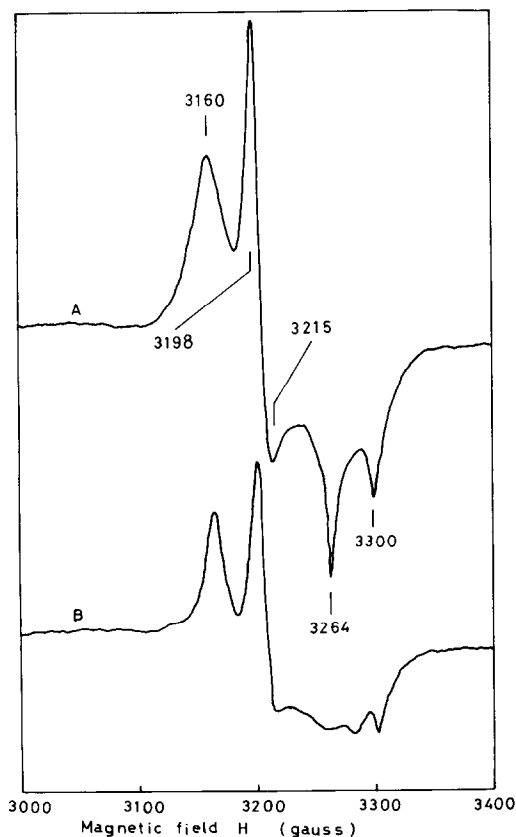


FIG. 3. EPR spectra of $\text{Ru-SiO}_2\text{-30-2}$ adsorbed CO at 30°C. (A) 104 Torr of CO coexist; (B) CO was evacuated at 30°C.

Goodwin and Naccache have reported that no EPR spectrum is produced on heating in CO (5). In the present study, however, EPR spectra were observed. Figure 3 illustrates the EPR spectra of CO-adsorbed $\text{Ru-SiO}_2\text{-30-2}$. In the present paper, the EPR signals are specified by using the top or bottom of the peaks. The results show that there are at least three kinds of states representing the strength of bonds between CO and Ru. The signals at 3160 and 3264 G arise from the irreversible and reversible adsorption of CO, respectively. Both the pair signal (3198, 3215 G) and the signal at 3300 G are assigned to the medium state. Neither $\text{Ru}_3(\text{CO})_{12}$ nor Ru-catalysts without the adsorbed CO produced EPR signals. $\text{Ru}(\text{CO})_5$ is probably also diamagnetic. Consequently, the existence of EPR signals shows that the CO-chemisorbed Ru are not free species like $\text{Ru}(\text{CO})_5$ or $\text{Ru}_3(\text{CO})_{12}$ but easily react with additional CO in the gas phase.

The characteristics of the catalysts described above arise from the method of catalyst preparation. The most important point in the preparation is that the cation exchange is performed using a $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ solution containing excess hydrazine rather than a $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ solution containing HCl.

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