

An Infrared Spectroscopic Study of the Formation of Isocyanate Species on Ru/Al₂O₃

Supported noble metals are effective catalysts in the reduction of NO with CO and H₂ (1). However, only Ru catalysts exhibit high selectivity for the formation of nitrogen, the other noble metals producing various amounts of ammonia in addition to N₂ (1, 2).

The unique behavior of Ru is reflected in its virtual inability to form surface isocyanate in the catalyzed reaction of CO and NO (3). Isocyanate ir bands are formed with high intensities on all noble metals except Ru, where the band is very weak or entirely absent. As it has been assumed that the formation of a surface isocyanate intermediate and its hydrolysis is a possible pathway to NH₃ (3), the absence of isocyanate on Ru seems to corroborate this view. The formation of NH₃ in the reactions of surface isocyanate with water on supported Pt and Pd catalysts has been confirmed using a combined infrared and mass-spectrometric technique (4, 5).

Recent observations, however, have shown that the catalytic behavior of Ru depends on its surface state (6). On oxidized Ru only a minimal amount of NH₃ is formed above 450°C, whereas the reduced state produces a large amount of NH₃. Investigating the catalytic reduction of NO with CO in the presence of exhaust gases, Voorhoeve and Trimble (7) found two peaks, at 270 and 350°C, in the NH₃ yield. From the behaviors of the peaks it was concluded that the first is due to CO-assisted, and the second to H₂-assisted, NH₃ formation.

On the basis of these results, it seemed

important to investigate more closely the surface interaction of NO and CO and the possible formation of isocyanate complexes over Ru under different conditions.

The catalyst was produced by the impregnation of Degussa P 110 C1 Al₂O₃ with Koch-Light RuCl₃·3H₂O. After impregnation, the sample was dried at 120°C for 16 hr. The Ru content of the catalyst was 5% (by weight). The powdered material was pressed into a 10 × 30-mm self-supporting disc with an optical density of 20 mg/cm². Before use, the disc was preheated at 400°C for 1.5 hr. Any further pretreatments were made in the ir vacuum cell.

NO (Matheson Gas Products) was used after "freeze and pump" pretreatment. N₂ (99.95%) and CO (99%) were introduced into the cell through a trap at -190°C.

A Specord 71 ir spectrometer was used to record the ir spectra. The resolution was better than ±5 cm⁻¹.

REDUCED SURFACES

The preparation of reduced surfaces was as follows: (i) exposure of the sample to 100 Torr of O₂ at 400°C for 30 min; (ii) evacuation of the sample at 400°C for 15 min; (iii) exposure of the sample to 100 Torr of H₂ at 400°C for 30 min; and (iv) evacuation of the sample at 400°C for 15 min.

This pretreatment was almost the same as used by Unland (3).

When 100 Torr of a reaction mixture of 5% NO, 10% CO, and 85% N₂ was introduced onto the reduced surfaces, bands indicative of the formation of surface iso-

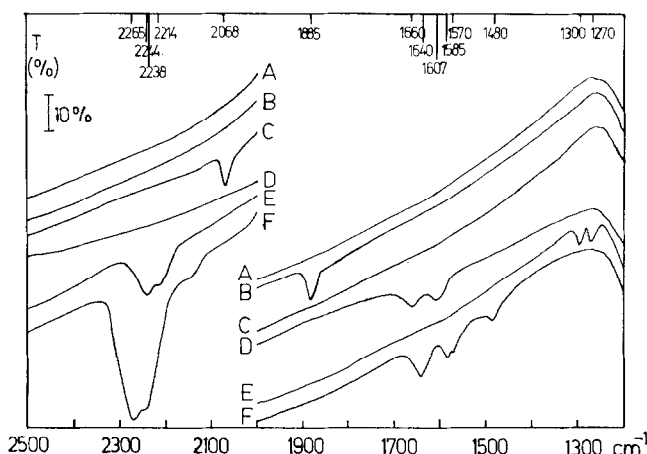


FIG. 1. Infrared spectra observed at room temperature after dosing the reduced 5% Ru/Al₂O₃ sample with different gases and with 100 Torr of a reacting mixture (5% NO, 10% CO, and 85% N₂) at 250°C. (A) cleaned sample; (B) 5 Torr of NO; (C) 10 Torr of CO; (D) 10 Torr of CO₂; (E) 5 Torr of N₂O; (F) 5% NO + 10% CO + 85% N₂. The adsorption time was 60 min.

cyanate complexes appeared at 2265 and 2244 cm⁻¹ (Fig. 1). No such bands appeared in the spectra when pure gases (NO, CO, and CO₂) alone were used. After the adsorption of N₂O, two bands at 2238 and 2214 cm⁻¹ appeared. These bands, however, were very weak and disappeared after evacuation at room temperature. According to the investigations of Unland (3) on noble metals, a strong band, assigned to covalently bonded isocyanate [-NCO]

appeared at 2259–2267 cm⁻¹, while a band of medium intensity, tentatively assigned to anionic isocyanate [NCO]⁻, was located at 2148–2239 cm⁻¹. Accepting the assignments of Unland, the band at 2265 cm⁻¹ can be ascribed to -NCO, and the band at 2244 cm⁻¹ to [NCO]⁻. In addition, we observed a band at 2150 cm⁻¹ which is very likely due to adsorbed CO (8).

The intensities of the bands at both 2265 and 2244 cm⁻¹ were very sensitive to the

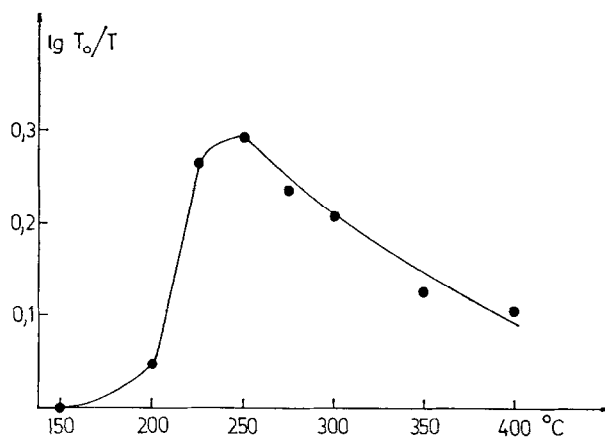


FIG. 2. Dependence of the intensities of the band at 2265 cm⁻¹ (observed at room temperature) on the temperature of dosing reduced 5% Ru/Al₂O₃ sample with 100 Torr of a 5% NO, 10% CO, and 85% N₂ mixture. The adsorption time was 30 min.

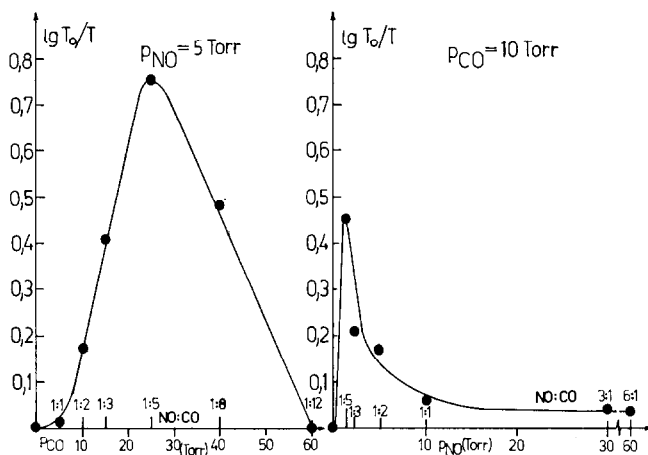


FIG. 3. Dependence of the intensity of the band at 2265 cm^{-1} on the partial pressure of CO and NO in the reacting gas mixture. The reduced 5% Ru/Al₂O₃ sample was dosed with 100 Torr of reacting gas mixture (NO + CO + N₂) at 250°C. The adsorption time was 30 min.

temperature. The band at 2244 cm^{-1} was somewhat more stable and became dominant at higher temperatures. The band at 2265 cm^{-1} appeared with well-measurable intensity even at 200°C. The intensity of the band increased with the adsorption time and finally reached a steady value. With the rise of the temperature the intensity of this band increased up to 250°C but subsequently decreased (Fig. 2). At 400°C a slight decrease was observed in the intensity after a certain reaction time. No isocyanate bands appeared in the spectra above 400°C.

Mass-spectrometric analysis of the gas phase indicated that a reaction between NO and CO occurs on this Ru sample even at 200°C. The reaction products are N₂, CO₂, and a small amount of N₂O.

The composition of the reacting gas mixture greatly influences the formation of isocyanate (Fig. 3). At the optimum temperature of isocyanate formation, 250°C, maximum intensity was obtained at a NO:CO ratio of 1:5. Further increase of the CO excess (the partial pressure of NO was kept constant at 5 Torr) inhibited formation of the isocyanate complex. The intensity of the band due to isocyanate was also less in a NO excess (in this case the partial

pressure of CO was kept constant, at 10 Torr), but bands due to isocyanate were detected even at a NO:CO ratio of 6:1. If we assume that a prerequisite of the formation of isocyanate is the dissociation of adsorbed NO, which requires vacant adjacent sites, it is obvious that occupation of these adjacent sites by either CO or NO suppresses the dissociation of NO and hence the formation of surface isocyanate. We mention here that a small band assigned to a surface isocyanate was reported on reduced Ru-silica when adsorbed CO was slowly displaced by NO (9).

OXIDIZED SURFACES

The pretreatment of the catalyst was performed in the same way as before, except that the last step, reduction with H₂, was omitted. When a gas mixture with a NO:CO ratio of 1:2 was used, the band due to covalently bonded isocyanate appeared only above 300°C. At 400°C the highest value was obtained at the very beginning of the interaction of the solid sample with the reacting gases.

Accordingly, a significant difference in isocyanate formation exists between reduced and oxidized Ru/Al₂O₃ even in this case when the reduction and oxidation of

Ru was milder than in the former cases (6, 7). Nevertheless, this is not unique behavior for Ru, as the same was observed in the cases of Pt and Pd catalysts at higher temperatures (5, 10).

The stability of the isocyanate band at 2265 cm^{-1} produced at 250°C was investigated under constant evacuation at $175\text{--}400^\circ\text{C}$. It appeared that the surface isocyanate is very unstable on Ru at higher temperatures. The half-time for disappearance of the peak at 300°C was about 1 min, compared to 60 min on Pt and 160 min on Pd.

According to the results presented, isocyanate complexes are easily formed on 5% Ru/ Al_2O_3 surfaces at lower temperatures; at 250°C the intensity of the isocyanate band on Ru is not much less than that on Pt surfaces. The basic differences between the two metals are that isocyanate is formed with maximum intensity on Ru at 250°C and on Pt at 325°C , and that it is much more unstable on Ru than on Pt, which makes its detection at high temperatures difficult.

As isocyanate was formed with maximum intensity at almost the same temperature for which the CO-assisted NH_3 formation displayed a maximum in the catalytic reduction of NO with CO (7),

it seems very likely that at lower temperatures NH_3 is formed through isocyanate intermediates, whereas at higher temperatures these species do not play any role.

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