

## Infrared Studies on the Formation of Isocyanate Surface Species over Unsupported Chromia

Supported chromia is an effective catalyst for the low-temperature reduction of NO with CO (1-4). In establishing a detailed mechanism of the reactions occurring on the catalyst surface, it is important to know more about the possible surface complexes formed. Whereas plenty of information is available in this respect on supported noble metal catalysts, relatively little is known about the surface species formed during the NO + CO reaction on oxide catalysts. We recently identified surface isocyanate complex on Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst during the NO + CO reaction (5). Surprisingly, the location of the isocyanate band in the ir spectra (2262-2242 cm<sup>-1</sup>) was almost the same as in the case of alumina-supported noble metals (6-8). From this it may be inferred that the vibration of the NCO hardly depends on the adsorbent, or that the NCO is located not on the active component, but rather on the alumina support. As NCO is a surface species possibly responsible for the undesired formation of NH<sub>3</sub> during automobile exhaust catalysis, establishment of its location and factors influencing its reactivity are of technological importance. *A deeper insight into the properties of surface NCO species may be expected from a study of its formation on the active component (noble metals, chromia) itself, without using a support.*

This cannot be done in the case of metals, however, due to their low transmittance. Nevertheless, from Cr<sub>2</sub>O<sub>3</sub> it is possible to make a transparent disk, which provides an opportunity for such an investigation to be carried out.

Cr<sub>2</sub>O<sub>3</sub> powder was produced by heating ammonium bichromate at 543 K for 2 hr in air. The final product can be characterized

as  $\alpha$ -chromia. Self-supporting wafers (10 × 30 mm) were pressed from the powdered and homogenized sample; their thickness was estimated as 10 mg/cm<sup>2</sup>. The pretreatments were as follows: (i) evacuation at 673 K for 90 min; (ii) oxidation with 100 Torr O<sub>2</sub> at 673 K for 30 min; (iii) evacuation at 673 K for 30 min; (iv) reduction with 100 Torr H<sub>2</sub> at 673 K for 30 min; (v) evacuation at 673 K for 30 min.

The gases used were of commercial purity. NO was further purified by fractional distillation before use. Isocyanic acid was produced by the reaction of potassium cyanate solution and sulphuric acid (9). The gas composition mainly used in the experiments was: 5% NO, 10% CO, and 85% N<sub>2</sub>.

Spectra were recorded with a double-beam spectrophotometer (Specord 71 IR, Carl Zeiss, Jena). The ir cell and the experimental details were described elsewhere (7, 8).

The chromia sample used catalyzes the NO + CO reaction above 523 K. At the beginning of the reaction N<sub>2</sub>O is formed, but the main products are N<sub>2</sub> and CO<sub>2</sub>. Figure 1 shows the ir spectrum obtained when the sample was treated with reacting gas mixture at 673 K. The spectra of adsorbed NO, CO, N<sub>2</sub>O, CO<sub>2</sub> are also shown. From comparison of the spectra it appears that the adsorption of an NO + CO gas mixture produces new strong bands at 2210 cm<sup>-1</sup>; this cannot be detected after the adsorption of any of the reactants or products of the NO + CO reaction.

Investigating the influence of the experimental conditions on the intensity of the 2210-cm<sup>-1</sup> band, we obtained the following results:

- (i) The lowest temperature of appearance

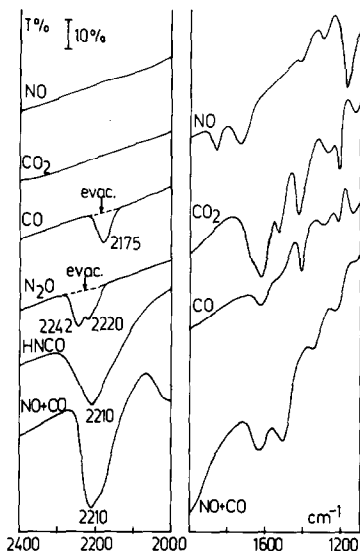


FIG. 1. Infrared spectra observed at 298 K after the adsorption of 10 Torr of different gases at 298 K and 100 Torr of an NO + CO gas mixture (mole ratio 1 : 2) at 673 K on reduced chromia.

of this band was 623 K. Upon increase of the adsorption temperature, the intensity of the band increased up to 723 K (Fig. 2).

(ii) The composition of the gas mixture also influenced the intensity of the 2210- $\text{cm}^{-1}$  band. It was not detected either in an NO excess or in a 1 : 1 mole ratio NO + CO mixture. In an excess of CO the intensity of the band increased with the CO content up to the composition NO : CO = 1 : 8.

(iii) The 2210- $\text{cm}^{-1}$  band was stable below 473 K during prolonged evacuation. Above 473 K its intensity decreased with the rise of the temperature (Fig. 2). At the same time  $\text{N}_2$ , CO, and  $\text{CO}_2$  were desorbed. On the infrared spectra a new band at 2150  $\text{cm}^{-1}$  was observed.

(iv) In the presence of  $\text{H}_2\text{O}$  the intensity of the 2210  $\text{cm}^{-1}$  band rapidly decreased. Mass-spectrometric analysis revealed that NCO reacted with water, yielding ammonia. Figure 2 also shows the effect of different gases on the intensity of the 2210- $\text{cm}^{-1}$  band. The half-time for disappearance of the 2210- $\text{cm}^{-1}$  band at 473 K was 80 min during evacuation and in CO, 60 min in NO,

13 min in  $\text{O}_2$ , 12 min  $\text{H}_2$ , and 6 min in water vapor.

In order to assign the 2210- $\text{cm}^{-1}$  band, labeled NO and CO were used. The observed shifts ( $\Delta\nu = -30 \text{ cm}^{-1}$  in  $^{15}\text{NO} + ^{12}\text{CO}$ ;  $\Delta\nu = -55 \text{ cm}^{-1}$  in  $^{14}\text{NO} + ^{13}\text{CO}$ ) make it evident that the species giving rise to the strong band at 2210  $\text{cm}^{-1}$  contains both carbon and nitrogen atoms. On the basis of these results as well as the properties of the band mentioned above, we assign the 2210- $\text{cm}^{-1}$  band to the vibration of an NCO species on a chromium ion. The 2150- $\text{cm}^{-1}$  band is tentatively assigned to Cr-CN species (10).

In the subsequent experiments isocyanic acid (HNCO) was adsorbed on chromia at 298 K. A strong band at 2210  $\text{cm}^{-1}$  was again produced (Fig. 1), which was stable under prolonged evacuation at 298 K. Mass-spectrometric analysis did not reveal any gaseous product during the interaction of HNCO with  $\text{Cr}_2\text{O}_3$  at 298 K. This result strongly supports the idea that the band observed at 2210  $\text{cm}^{-1}$  during the NO + CO reaction on chromia is due to the surface

Cr—NCO species. This result can be

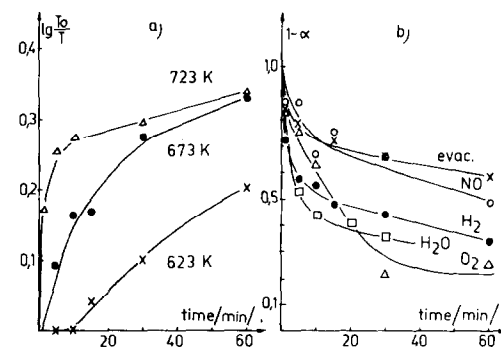


FIG. 2. (a) The intensity changes of the band at 2210  $\text{cm}^{-1}$  during the adsorption of an NO + CO gas mixture (100 Torr, mole ratio 1 : 2) on reduced chromia at different temperatures. (b) The decrease in intensity of the 2210- $\text{cm}^{-1}$  band on the effect of the prolonged evacuation and different gases (10 Torr) at 473 K. The isocyanate was produced at 673 K by the adsorption of the reacting gas mixture.  $\alpha = (a_0 - x)/a_0$ , where  $a_0$  = the initial intensity and  $x$  = the intensity at time  $t$ .

regarded as the first spectroscopic evidence for the existence of NCO species (formed in the NO + CO reaction) on the active component itself without using a support.

The fact that the vibration of NCO adsorbed chromia differs from that observed at 2262 and 2242  $\text{cm}^{-1}$  on  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  (5) may suggest that in the latter case the NCO was located not on the chromium ion but rather on the alumina. It does not seem likely that the chemical interaction between chromia and alumina would be so large as to account for the shift ( $\sim 40\text{--}50 \text{ cm}^{-1}$ ) in the vibration of the NCO band. The absence of the 2210- $\text{cm}^{-1}$  band on  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  in the entire temperature range indicates that the migration of NCO from chromia onto alumina is a very fast process. In this respect we may mention that, when  $\text{Cr}_2\text{O}_3/\text{SiO}_2$  was exposed to an NO + CO reaction mixture at 673 K, a strong NCO band was identified at 2210  $\text{cm}^{-1}$ , and only a very weak one at 2315  $\text{cm}^{-1}$  due to an Si-NCO species, indicating that in this case the migration of NCO from chromia to silica was hindered. With the rise of temperature the intensity of the band at 2210  $\text{cm}^{-1}$  decreased, whereas that at 2315  $\text{cm}^{-1}$  increased. This band proved to be stable even at 673 K. Adsorption of HNCO on silica produced also a strong band at 2313  $\text{cm}^{-1}$  (9).

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