A Surface Complex produced on Supported Rhenium Catalysts during High-pressure Hydrogenation of Carbon Monoxide

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A high-pressure *in situ* i.r. study revealed the presence of two sets of linear- and bridge-bonded CO on Re–TiO_2, one set of which is stable against evacuation up to 523 K and shows a constant intensity ratio between its linear and bridged species.

Rhenium-containing catalysts are known to be active in the hydrogenation of CO,[1—3] although there are only a few[4] reports of i.r. spectra of CO adsorbed on these catalysts. Reported here is the presence of several adsorbed CO species and the formation of a surface complex on Re–TiO_2 and Re–ZrO_2 under high-pressure CO hydrogenation conditions.

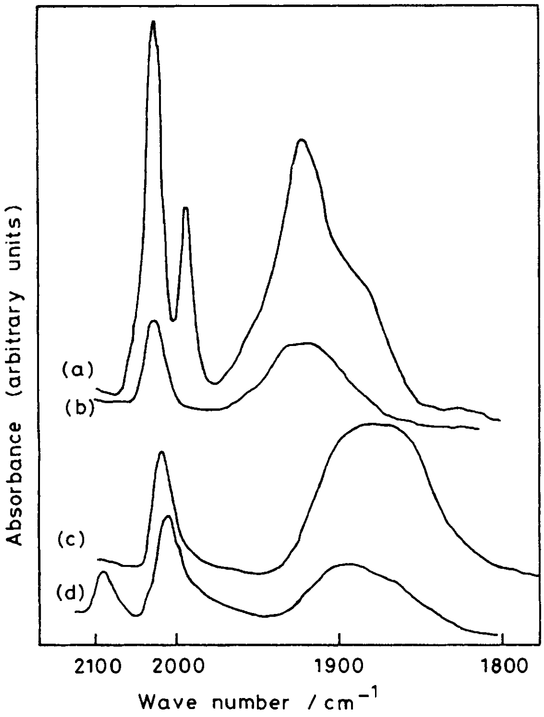

Figure 1. I.r. spectra of CO adsorbed on supported rhenium. For details see text.

Spectrum (a) in Figure 1 is an *in situ* i.r. spectrum of Re–TiO_2 (1.0 wt % Re) exposed to 1.0 MPa of CO at 385 K for 15 min and then evacuated at room temperature. The high-pressure i.r. cell was constructed by the method of Hicks *et al.*[5] Four absorption peaks are apparent in the spectrum, two in the linear (2030 and 1995 cm^{-1}) and two in the bridged (1920 and 1885 cm^{-1}) CO stretching region. Evacuation of this sample at 400 K decreases the intensity of these peaks and also eliminates the low wave-number absorption due to the linear species. Evacuation at 523 K for 0.5 h gives spectrum (b), in which the low wave-number absorption due to the bridged species is also eliminated while the intensities of the

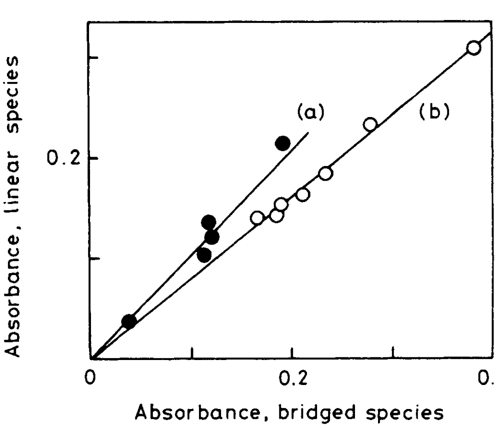

Figure 2. Correlations between the two peak absorbances of the stable species, (a) used Re–TiO_2, (b) used Re–ZrO_2.

other peaks are reduced. The remaining peaks are stable against longer evacuation at this temperature or exposure to air at room temperature. Thus these four absorption peaks are differentiated into two sets, each including absorptions due to the linear and bridged CO species: one stable set (2030 and 1920 cm^{-1}) and one set that is not (1995 and 1885 cm^{-1}). The stable species give the higher wave-number set. No information on the specific Re lattice planes on which the CO might be adsorbed is available in the literature.

Screening (by the conventional KBr method) of catalysts which had been used for high-pressure CO hydrogenation[2] showed that these stable species were formed on Re when it is dispersed on TiO_2 or ZrO_2, with slightly different i.r. peak positions. Spectrum (c) is of spent Re–ZrO_2 (KBr method). An interesting feature of these stable species is that the absorbances due to the linear and bridged species, observed in the screening of catalysts used under various conditions, give linear correlations which go through the origin, as shown in Figure 2, depending on the kind of support used. These correlations are indicative of the presence of a particular stoicheiometry for these stable linear and bridged species, possibly formation of a carbonyl or subcarbonyl complex. This speculation is consistent with the fact that similar i.r. peaks can be produced by impregnating ZrO_2 with rhenium pentacarbonyl, as shown by spectrum (d) in Figure 1. We also note that there are three rhenium carbonyl complexes reported, $[Re(CO)_3(OH)]_4$,[6] $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$,[7] and $[H_6Re_4(CO)_{12}]^{2-}$,[8] which exhibit carbonyl peaks in positions similar to the present stable entity.

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