Formation of an Acyl Species from Hept-1-ene and Carbon Monoxide on an Evaporated Nickel Surface

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Summary In a reaction which is apparently in contrast to insertion reactions of co-ordination complexes, carbon monoxide has been shown to react at room temperature with surface species obtained by hept-1-ene chemisorption on an evaporated nickel film to produce a surface species which i.r. evidence suggests is an acyl species, probably arising from C–O bond cleavage of the carbon monoxide and transfer of the oxygen atom on to a hydrocarbon species.

The reaction between chemisorbed hept-1-ene and chemisorbed carbon monoxide on an evaporated Ni film has been investigated by i.r. spectroscopy. We report the first experimental evidence that this reaction occurs at room temperature on a metal surface to produce an acyl species.

The catalytic Ni films were prepared by evaporation of the metal on NaCl windows in the presence of 10^{-1} Torr of CO, according to our procedure developed previously.[1] Chemisorbed CO on evaporated Ni films exhibits two strong bands at 2035 and 1890 cm^{-1},[1] attributed to C–O stretching vibrations of linear and bridging adsorbed CO, respectively (spectrum 1).

Addition of hept-1-ene at room temperature causes partial removal of CO from the Ni surface, as shown by the decrease in intensities of the i.r. bands; the remaining CO molecules were mainly in the bridging form. The frequencies of the two bands were lowered by 30 and 45 cm^{-1}, respectively, owing to release of electrons from the chemisorbed hept-1-ene species to the surface and then into the $2\pi^*$ antibonding orbitals of the chemisorbed CO, giving rise to a weaker C–O bond.[2] After 14 h, a new strong band appeared at 1570 cm^{-1}, which can be attributed only to a CO stretching vibration (spectrum 2).

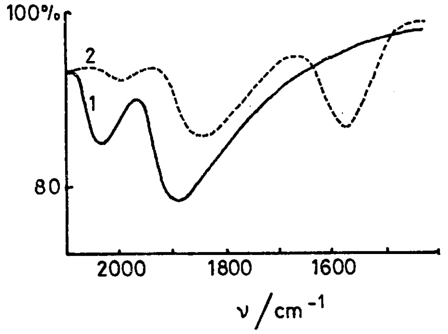

FIGURE. I.r. spectra of chemisorbed carbon monoxide on nickel. (1) initial spectrum; (2) after reaction with hept-1-ene for 14 h.

As shown by Blyholder *et al.*,[3] C_2H_4, CO, and H_2 interact at 100 °C on a Co surface to produce a carboxylate species, identified by two i.r. absorption bands at 1557 and 1435 cm^{-1} assigned, respectively, to the asymmetric and the symmetric stretching modes. In our case, the low frequency band in the 1400—1450 cm^{-1} region was missing. The 1570 cm^{-1} band that we observed cannot be attributed to a carboxylate species, but may be assigned to an acyl species for the following reasons. Firstly, acyl complexes of zero-valent transition metals are known to exhibit i.r. bands between 1560 and 1640 cm^{-1},[4] and secondly, in the case of the chemisorption of acetone on silica-supported cobalt samples, Blyholder *et al.*[5] have detected an i.r. band near 1590 cm^{-1} that they assigned to an acyl species.

The same experiments were performed using labelled ^{13}CO. The initial surface carbonyl complex of Ni exhibits i.r. absorption bands at 1990 and 1855 cm^{-1} in agreement with the expected isotopic shifts, but after introduction of hept-1-ene, the frequency of the new i.r. band assigned to the acyl species is unchanged at 1570 cm^{-1}; a frequency of 1535 cm^{-1} would be expected for a ^{13}C species. The acyl species formed is thus unlabelled; we propose that the acyl group is formed by transfer of the oxygen atom from a bridging chemisorbed carbon monoxide molecule to the carbon atom of neighbouring hydrocarbon surface species resulting from hept-1-ene chemisorption.

The formation of an acyl species proposed here is significantly different from the insertion reaction observed in co-ordination chemistry and could be of catalytic significance, particularly in the Fischer–Tropsch process, for which Ni is one of the catalysts.

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