An I.R. Study of Carbon Monoxide Fixation by Ni^+ Ions obtained by Photoreduction of a Nickel-exchanged Silica

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It is shown by i.r. spectroscopy, using mixtures of ^{12}CO and ^{13}CO, that isolated Ni^+ ions produced by u.v. irradiation in hydrogen at 77 K of an Ni-exchanged silica can form mono- or di-carbonyl adducts in the 10^{-5}—5 Torr range.

It has long been known that nickel ions in the unusual +1 oxidation state can be stabilized in zeolites.[1] Recently, Ni^+ ions have also been obtained on silica. These ions were prepared either by mild thermal reduction in hydrogen[2] or by photoreduction in hydrogen at 77 K[3] of a nickel-exchanged silica and characterized by their e.s.r. spectra. There was no indication that ferromagnetic or superparamagnetic nickel was formed during the reduction and Ni^{2+} ions were not detected. It is known, however, that these ions, if paramagnetic, may escape observation by e.s.r. spectroscopy at 77 K if short relaxation times are involved and also that it is difficult to detect nickel particles of a few ångstroms thick whatever the technique used.

In this work we have used i.r. spectroscopy as a more appropriate technique to detect the various oxidation states of nickel possibly present after treatment of a nickel-exchanged silica. Carbon monoxide was used as the probe molecule.

Since this study is related to a programme aimed at defining the active sites in olefin oligomerisation on nickel catalysts, it was felt to be important to perform the reduction at the lowest possible temperatures. As before,[3] the method recently described by Shelimov *et al.*[4] for supported molybdenum catalysts, involving u.v. irradiation in hydrogen at 77 K, has been adopted in the hope of preferentially stabilizing the Ni^+ oxidation state.

A nickel-exchanged aerosil with 2.7% of nickel by weight was prepared as previously described.[5] The sample was heated in oxygen (200 Torr) up to 700 °C, maintained at this temperature for 2 h, and finally vacuum treated (10^{-5} Torr) at 700 °C for 15 h. The photoreduction was carried out at 77 K in hydrogen (400 Torr) using a high-pressure mercury lamp. After 6 h of irradiation the sample which was light-brown after the activation pretreatment at 700 °C turned light-green.

After CO introduction at room temperature (5 Torr), the i.r. spectrum showed 3 bands at 2201, 2131, and 2083 cm^{-1}, Figure 1(a). The 2201 cm^{-1} band, which was also observed after CO adsorption on the anhydrous sample obtained after pretreatment at 700 °C, can be assigned to the stretching

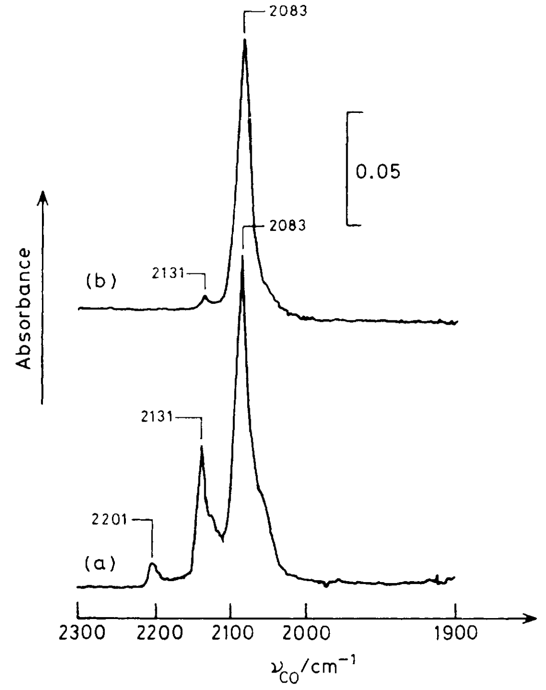

Figure 1. I.r. spectra obtained after exposure of a photoreduced 2.7% Ni exchanged silica to ^{12}CO at room temperature (a) under a pressure of 5 Torr (b) under a pressure of 10^{-5} Torr.

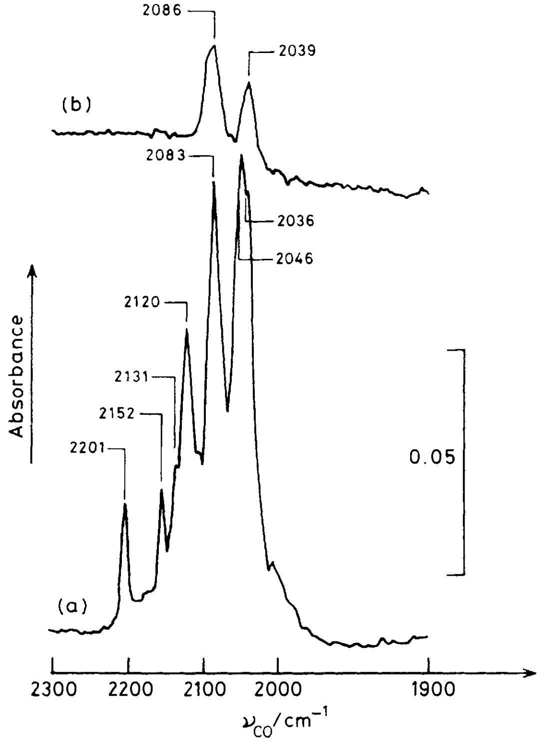

Figure 2. I.r. spectra obtained (a) after exposure of a photoreduced 2.7% Ni exchanged silica to a 1 : 1 mixture of $^{12}CO/^{13}C$ 90% enriched CO at room temperature under a pressure of 4.5 Torr and (b) after outgassing sample (a) at 150 °C for 20 h under 10^{-5} Torr.

vibration of CO bonded to Ni^{2+} ions. The two other bands may correspond to the dicarbonyl Ni^+ species obtained on an NiCaX zeolite[6] or on an Ni mordenite[7] although they are observed at lower frequencies. At low pressure (10^{-5} Torr), their intensity ratio was shown to vary considerably, Figure 1(b). In order to confirm the assignment of these bands (2131, 2083 cm^{-1}) to $Ni(CO)_2^+$, isotopic mixing experiments were carried out using a 50:50 mixture of ^{12}CO and 90% ^{13}C-enriched CO. Figure 2(a) shows the i.r. spectrum after the admission at room temperature of 4.5 Torr of the mixture. Table 1 summarizes the frequencies and assignments of the different carbonyl species.

Table 1

Wavenumber /cm^{-1}	Assignments
2201	Ni^{2+} (^{12}CO)
2152	Ni^{2+} (^{13}CO)
2131	Ni^+ (^{12}CO)(^{12}CO)
2083	
2120	Ni^+(^{12}CO)(^{13}CO)
2046	
(2084)	Ni^+(^{13}CO)(^{13}CO)
2036	
2086	Ni^+(^{12}CO)
2039	Ni^+(^{13}CO)

In addition to bands at 2201 and 2152 cm^{-1}, corresponding to ^{12}CO and ^{13}CO molecules bonded to Ni^{2+} ions, a group of five bands was observed instead of the two obtained in the presence of pure ^{12}CO. The number and position of these bands confirm the coupling of the oscillators and agree with the presence of a dicarbonyl Ni^+ species. The observation of five bands instead of six is well accounted for by the overlapping of the antisymmetric band of $Ni(^{12}CO)_2{}^+$ and the symmetric bands of $Ni(^{13}CO)_2^+$. Moreover, the relative intensity of the $Ni(^{12}CO)(^{13}CO)^+$ species (2120, 2046 cm^{-1}) is in agreement with the theoretical one since the probability of having this last species is *ca.* twice as large as for the other two.

When the sample was outgassed (10^{-5} Torr) at 150 °C for 20 h, there remained only two weak bands at 2086 and 2039 cm^{-1}, Figure 2(b). The frequency shift of 47 cm^{-1} between these bands is consistent with their assignment to monocarbonyl $Ni(^{12}CO)^+$ and $Ni(^{13}CO)^+$ entities (the calculated isotopic shift is 46 cm^{-1}). It can be noted that monocarbonyl Ni^+ species vibrate at almost the same frequency as the antisymmetric band of the dicarbonyl species. This result is quite different from that observed for NiCaX zeolite.[6] The high intensity of the 2083 cm^{-1} band at 10^{-5} Torr of CO pressure is thus accounted for by the coexistence of mono- and dicarbonyl Ni^+ species, Figure 1(b).

From a spectroscopic point of view, there is some ambiguity in the assignment of the 2086 cm^{-1} band to a monocarbonyl Ni^+ species since on supported Ni particles[8] and on matrix-isolated Ni clusters[9] the frequency of a linear bonded CO is observed at *ca.* 2080 cm^{-1}. However it must be stressed that this 2080 cm^{-1} band corresponds to saturation coverage while the 2086 cm^{-1} band when observed alone corresponds to a very low coverage [Figure 2(b): sample desorbed at 150 °C under 10^{-5} Torr for 20 h]. For matrix-isolated Ni clusters, in low coverage experiments, the frequency of isolated monoatomic Ni–CO is observed at 1996 cm^{-1}. Hence the presence of isolated Ni atoms or clusters produced by photoreduction at low temperature may be ruled out. Moreover, the green colour of the photoreduced sample and the absence of a ferromagnetic spectrum[3] indicate the existence of Ni^+ entities.

From this work, it has been shown that the photoreduction in hydrogen at low temperature of an Ni exchanged silica leads to the stabilization of Ni^+ ions without any observable nickel atoms, while the amount of non-reduced Ni^{2+} is low as shown by the weak intensity of the 2201 cm^{-1} band due to Ni^{2+}(CO). It must be emphasized that the exchange method used to introduce Ni^{2+} ions on silica, contrary to conventional impregnation methods, allows a better dispersion of these ions since after photoreduction only isolated Ni^{+} ions are formed, as detected from the frequency (ν_{CO}) of the carbonyl species.

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