Amorphous AlPO₄ as Catalyst Support. 5. FTIR Study of CO Adsorbed on Transition Metal Ions Supported on Amorphous AlPO₄ and SiO₂*

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Amorphous AlPO₄ has been used as catalyst support for different 3d metals (Mn, Fe, Co, Ni and Cu) studied by CO IR spectroscopy. It was found that Mn(II), Fe(II) and Co(II) showed only one CO IR band each at 2199, 2180 and 2189 cm⁻¹, respectively. Ni(II) gave two bands at 2203 and 2193 cm⁻¹ at room or low temperatures. Cu(II) showed similar bands at 2220 and 2207 cm⁻¹. It was concluded that for all +2 cations the CO IR band is shifted some 10 cm⁻¹ higher on AlPO₄ compared with silica. This is an indication that these metal ions have lower electron density if supported on AlPO₄ as compared with silica gel. This effect is interpreted as due to binding of the +2 cations to the AlPO₄ via P–O surface groups, as previous noticed for Cr(II), and not to Al–O ones. An opposite shift was observed with Cu(II) at room temperature (CO on AlPO₄: 2121 cm⁻¹ and on silica: 2130 cm⁻¹). A second CO IR band on Cu(II) was noticed at low temperatures around 2160 cm⁻¹, which formed a doublet together with the band around 2124 cm⁻¹ (AlPO₄: 2123/2160 cm⁻¹, silica: 2125/2156 cm⁻¹).

The Phillips catalyst[2] consists of chromium(VI) on silica gel and is used industrially for the polymerization of ethylene. In our laboratory this catalyst (after reduction with CO)[3] has previously been studied,[4–9] and recently we have also investigated chromium on AlPO₄ by using carbon monoxide FTIR spectroscopy.[10] AlPO₄ has different kinds of hydroxyl groups[11] compared to silica gel. It was found that the surface consists of POH and several different kinds of AlOH groups. When chromium is added to the samples the chromium reacts (mainly) with POH groups and only rarely with AlOH.[10] It was also concluded that Al exists on the surface not only as four-coordinated, tetrahedral species (as one would expect), but also as five- and six-coordinated ones.[11]

Looking at the carbon monoxide IR region of the chromium/AlPO₄ catalyst there are some important differences compared with silica gel. The CO IR peaks from terminally bonded CO are generally shifted to higher wavenumbers by some 14 cm⁻¹. Since chromium is bonded to PO groups, and since phosphorus has a higher electronegativity than silicon, it has been concluded that the shift of the CO IR peaks is due to the higher Lewis acidity of chromium bonded to phosphorus via oxygen. In both catalysts terminally bonded CO [with an IR band at 2178 (silica) and 2192 cm⁻¹ (AlPO₄)] is converted to bridging ones (bands below 2160 cm⁻¹),[10] on cooling to low temperatures (−80 °C).

Another difference between Cr/AlPO₄ and Cr/SiO₂ catalysts is the more complicated pattern of the IR spectrum from bridging CO ligands at lower wavenumbers than CO gas (2143 cm⁻¹). This is explained by a more complicated surface structure of AlPO₄.

To better understand the structure of chromium surface species active for the polymerization of ethylene, it is necessary to study other 3d-metals on different supports (AlPO₄ and SiO₂) and compare the results with previous ones. The metals examined below are Mn, Fe, Co, Ni an Cu. Some of these (Mn, Fe, Co and Ni) have been studied before on SiO₂. Ni supported on Al₂O₃ is also investigated.

Experimental

Amorphous AlPO₄ was prepared from Al(NO₃)₃·6H₂O and (NH₄)₂HPO₄ (the Al:P ratio was 1:0.9 both in the starting mixture and the product).[11] An aqueous solution of these two substances was acidified with HNO₃ and then a gel formed by addition of a 25 % ammonia solution, so that the liquid became slightly alkaline.[10] The specific surface of the amorphous AlPO₄ was 140 m² g⁻¹ and the pore volume 0.3 cm³ g⁻¹. The SiO₂ used was "silica gel 60 (Merck 7733)". The preparation of the samples was either made in ethanol (AlPO₄) or in water (SiO₂) using the chlorides of the metal [Mn(II), Fe(II), Co(II), Ni(II) and Cu(I)]. Ethanol was used as the solvent with AlPO₄ since the use of water would destroy the specific surface. The samples contained 0.1 mmol metal per g AlPO₄ or per g SiO₂. XRD measure-
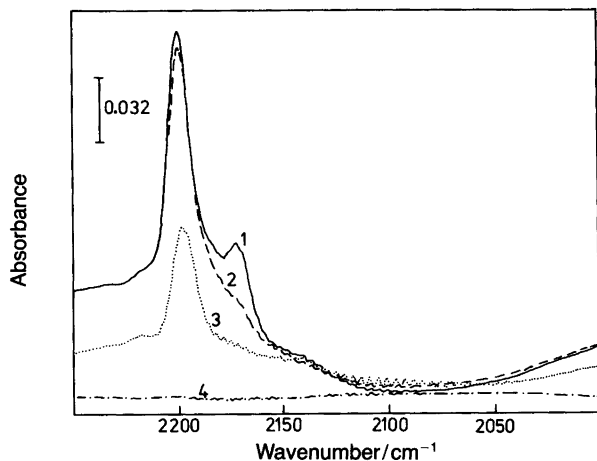
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Fig. 1. CO FTIR spectra of Mn on AIPO$_4$ heated to 800 °C in vacuum. Spectrum 1 was collected at −115 °C and 1 Torr CO, spectrum 2 at −80 °C and 1 Torr CO, spectrum 3 at room temperature and 80 Torr CO and spectrum 4 at room temperature and 10^{-3} Torr CO.

ments performed on AIPO$_4$ and on silica gel impregnated with chromium[11] showed that the samples are amorphous with no distinct lines in the diffractogram. No oxide particles could be detected.

It is known that halogens (Cl$^-$ and F$^-$) can cause shifts in the IR spectrum,[12] and since aluminium can form quite stable chlorides, XP spectra were recorded (with a KRATOS XSAM 800 instrument) on one of the impregnated samples, i.e. Fe/AIPO$_4$, both as dried at 120 °C and after heating to 800 °C in vacuum. It was found that no chloride could be detected after the impregnation in either of the two samples.

65 mg of the catalyst were pressed to a disc with a diameter of 2 cm and placed in an IR cell.[13] The catalysts were activated at 800 °C in vacuum (some at 500 °C) and, depending on which metal was used, either (a) directly cooled to room temperature or (b) oxidized (at 800 °C) with
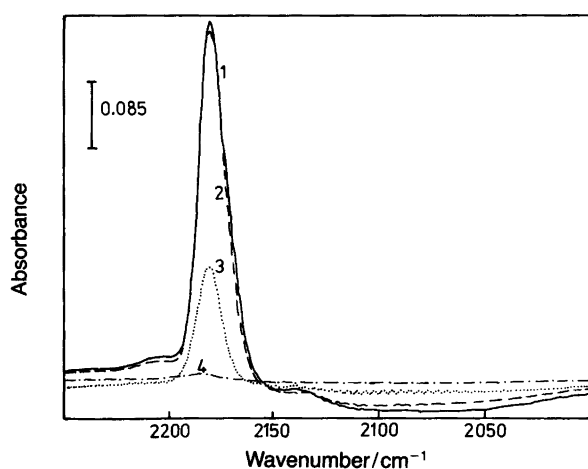

Fig. 2. CO FTIR spectra of Fe(II) on AIPO$_4$ heated to 800 °C in vacuum. Notation as in Fig. 1.
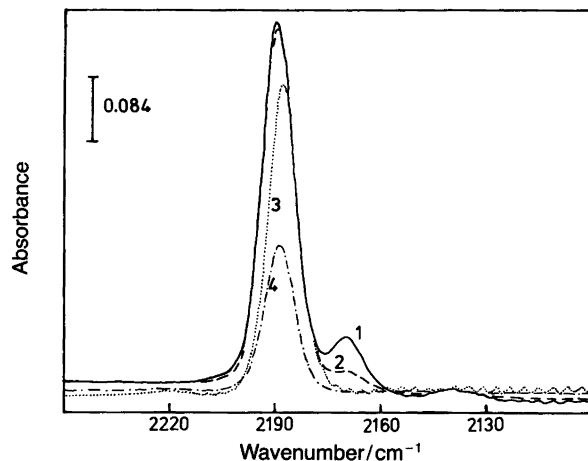

Fig. 3. CO FTIR spectra of Co on AIPO$_4$ heated to 800 °C in vacuum. Notation as in Fig. 1.

O$_2$, evacuated and then cooled to room temperature or (c) both oxidized with O$_2$ and reduced with CO (usually at 500 °C). The first IR spectrum was then taken at room temperature (c: after removal of the CO by evacuation at 500 °C). Thereafter the IR cell was filled with 80 Torr CO and more spectra were recorded at different temperatures. The FTIR spectra were collected on a Nicolet 20 SXC spectrometer. The resolution was 2 cm^{-1} and 1024 scans were averaged.

Results

The CO IR spectra of Mn on AIPO$_4$ (heated to 800 °C in vacuum, a) are shown in Fig. 1. Spectrum 3 (room temperature and 80 Torr CO) gives one main and one very weak peak. The former is at 2197 cm^{-1} and the latter one at 2202 cm^{-1}. On cooling to low temperature (spectrum 1: −115 °C and 1 Torr CO) the former increases and shifts to higher wavenumbers (2199 cm^{-1}) and the latter stays the same. A new peak at 2172 cm^{-1} appears which is assigned to CO adsorbed on P–OH.[10] This peak always arises under these conditions on AIPO$_4$. At room temperature and 10^{-3} Torr vacuum no peaks are detected (spectrum 4 in Fig. 1).

Using iron as the metal (on AIPO$_4$) and the samples heated to 800 °C in vacuum, again one major peak appears at room temperature and 80 Torr CO (Fig. 2, spectrum 3) at 2181 cm^{-1}. This peak shifts 1 cm^{-1} down and increases after cooling to low temperature (−115 °C, spectrum 1). Two other very small peaks are detected at 2203 and 2139 cm^{-1}. The latter of these two arises from CO clusters in the micropores of the support. When the sample is oxidized at 800 °C (b) no new peaks are found (spectra not shown). The main difference between these two pretreatments is found at low temperature (−115 °C), where the intensity of the large peak, now at 2183 cm^{-1}, is lowered markedly so that a peak at 2171 cm^{-1} can now be seen clearly. With both preparation methods only very weak peaks are detected at room temperature and 10^{-3} Torr CO pressure (Fig. 2, spectrum 4).
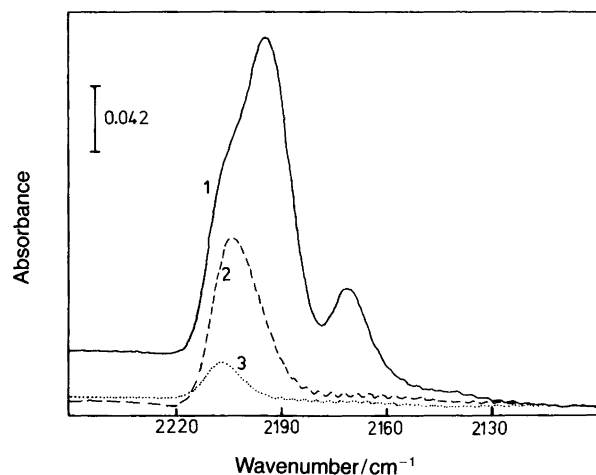
Fig. 4. CO FTIR spectra of Ni on AlPO₄ heated to 500 °C in vacuum. Spectrum 1 was collected at −80 °C and 1 Torr CO, spectrum 2 at room temperature and 80 Torr CO and spectrum 3 at room temperature and 10^{-3} Torr CO.

Cobalt on AlPO₄ (a) also gives only one peak at room temperature and 80 Torr CO, which is shown in Fig. 3, spectrum 3, situated at 2187 cm⁻¹. When the sample is cooled (−115 °C, spectrum 1) the peak increases a little in magnitude and shifts to 2189 cm⁻¹. The two other peaks, known from above, appear again at 2170 and 2139 cm⁻¹. At room temperature and 10^{-3} Torr vacuum, the peak at 2189 cm⁻¹ is still clearly seen but has decreased in intensity (spectrum 4).

Ni on AlPO₄ heated to 500 °C in vacuum (Fig. 4, spectrum 2) shows one peak at 2204 cm⁻¹ (room temperature and 80 Torr CO). This peak does not increase further on cooling to low temperatures (−80 °C and 1 Torr CO, spectrum 1), but becomes a shoulder with unknown intensity, most likely even lower than previously. Instead a new peak arises at 2194 cm⁻¹ whose intensity is larger than that of the former one. This may be due to a transformation of the species from the former peak to the latter one. The peak at 2170 cm⁻¹ is also again recognized. At room temperature and 10^{-3} Torr (Fig. 4, spectrum 3) only the peak at 2206 cm⁻¹ is left. Obviously the species giving rise to this peak is more stable at room temperature than the species with the CO IR peak at 2194 cm⁻¹, which is more stable at low temperatures.

The spectra of Ni on AlPO₄ heated to 800 °C in vacuum (a) are shown in Fig. 5. At room temperature and 80 Torr CO (Fig. 5, spectrum 3) there is one peak at 2203 cm⁻¹ which increases and shifts 2 cm⁻¹ higher at low temperatures (−80 and −115 °C, spectra 1 and 2, respectively). A second band is seen at 2193 cm⁻¹, and increases even more on cooling from −80 to −115 °C. At the same time the band at 2205 cm⁻¹ is slightly lowered in intensity. This again points towards a conversion of the species at higher wavenumbers into the one at lower wavenumbers. The two CO IR bands at 2169 and 2139 cm⁻¹ are again observed. At

room temperature and 10^{-3} Torr only a small residue of the CO IR band is left at 2205 cm⁻¹ (spectrum 4).

The inclusion of Ni on Al₂O₃ was made because of its industrial value as a hydrogenation catalyst. It is of interest to us to see how this support changes the IR spectra of CO adsorbed on Ni. In Fig. 6 the spectra of Ni on Al₂O₃ are shown, heated in vacuum to either 500 °C (spectra 2 and 4) or 800 °C (spectra 1 and 3). Starting with the sample heated to 500 °C in vacuum and recording the spectrum at room temperature and 80 Torr CO (spectrum 4) only one peak is observed at 2182 cm⁻¹. When the sample is cooled to −80 °C (spectrum 2) a major peak is seen at 2191 cm⁻¹ with a shoulder at 2180 cm⁻¹.

Preheating the sample to 800 °C and recording the spectrum at room temperature and 80 Torr CO, again only one peak is observed, but now at 2198 cm⁻¹. On cooling the sample, spectrum 1 in Fig. 6 gives one major CO IR peak at 2189 cm⁻¹ and a small shoulder at 2166 cm⁻¹. In Fig. 7 a spectrum from Ni on Al₂O₃, heated to 500 °C, is shown in the OH stretching range, where one medium sharp peak is observed at 3671 cm⁻¹ with a shoulder at 3724 cm⁻¹ and one very broad peak at 3597 cm⁻¹. A small peak at 3794 cm⁻¹ is also seen. Spectrum 1 in Fig. 7 was recorded at −80 °C and spectrum 2 at room temperature (vacuum). Spectrum 3 is the difference between these two spectra. Now a peak is observed at 3757 cm⁻¹, together with a broad negative and a broad positive band at 3706 and 3545 cm⁻¹, respectively.

Spectrum 4 in Fig. 7 corresponds to spectrum 3 in Fig. 7 with the difference that the sample has been heated to 800 °C in vacuum. Three negative peaks are observed at 3789, 3726 and 3685 cm⁻¹ and three positive ones at 3805, 3759 and 3604 cm⁻¹. A broad peak is also observed at 3553 cm⁻¹. The spectra corresponding to 1 and 2 in Fig. 7 are not shown. They do not show, however, the very broad band at about 3550 cm⁻¹ (which is expected). The peak at 3695
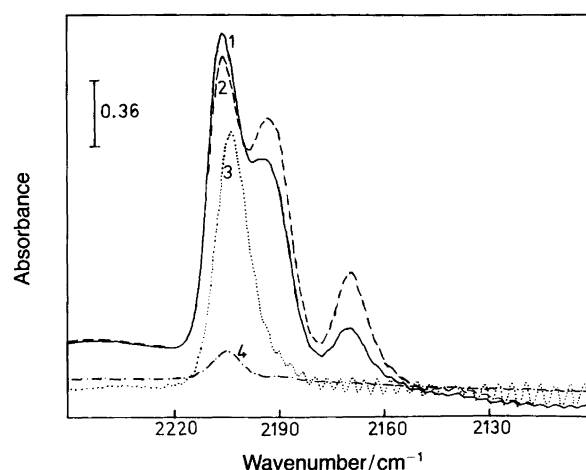

Fig. 5. CO FTIR spectra of Ni on AlPO₄ heated to 800 °C in vacuum. Spectrum 1 was collected at −80 °C and 1 Torr CO, spectrum 2 at −115 °C and 1 Torr CO, spectrum 3 at room temperature and 80 Torr CO and spectrum 4 at room temperature and 10^{-3} Torr CO.
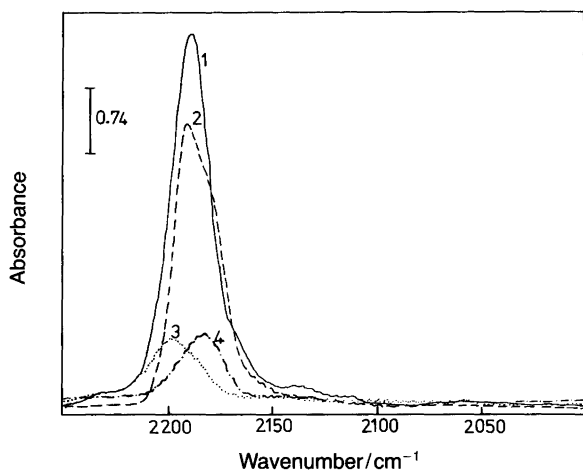
Fig. 6. CO FTIR spectra of Ni on Al$_2$O$_3$. The sample for spectra 2 and 4 was heated to 500 °C and the sample for spectra 1 and 3 was heated to 800 °C. Spectra 1 and 2 were collected at 1 Torr CO and −80 °C and spectra 3 and 4 were collected at 80 Torr CO and room temperature.

Fig. 8. CO FTIR spectra of Cu on AlPO$_4$ heated to 800 °C in vacuum. Spectrum 1 was collected at −115 °C and 1 Torr CO, spectrum 2 at −80 °C and 1 Torr CO, spectrum 3 at −50 °C, spectrum 4 at −15 °C, spectrum 5 at room temperature and 80 Torr CO, spectrum 6 at room temperature and 10^{-3} Torr CO and spectrum 7 at room temperature after evacuation at 200 °C for 120 s.

cm^{-1} has decreased, now having almost the same intensity as the peak at 3724 cm^{-1}.

Cu was investigated on both silica and AlPO$_4$. Fig. 8 shows Cu on AlPO$_4$ heated to 800 °C in vacuum (a). In spectrum 5 (room temperature and 80 Torr CO) there is a large band at 2121 cm^{-1} with a shoulder at 2131 cm^{-1}. There are also two smaller bands observed at 2179 and 2152 cm^{-1}. When the sample is cooled to −80 °C (spectrum 2) the former band at 2152 cm^{-1} increases greatly in intensity and splits into two shifted peaks at 2160 and 2163 cm^{-1}. The peak at 2121 cm^{-1} increases at the same time and is shifted
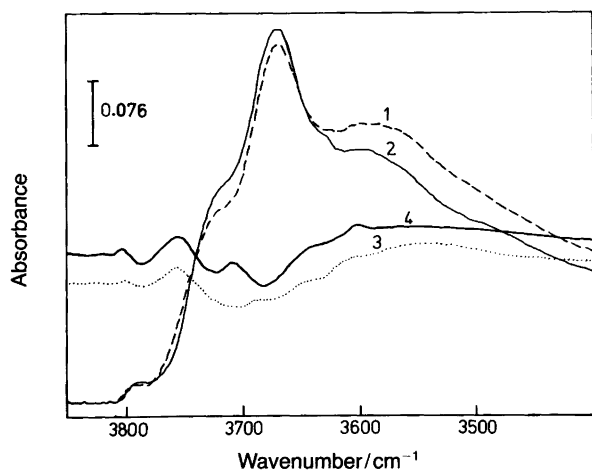
to 2123 cm^{-1}. No peak is detected in this spectrum at 2179 cm^{-1}, but instead two new peaks arise at 2204 and 2188 cm^{-1}. After evacuation to 10^{-3} Torr CO (spectrum 6 in Fig. 8) the peak at 2121 cm^{-1} also decreases and the shoulder at 2131 cm^{-1} becomes more prominent.

In Fig. 9 the spectra of Cu on AlPO$_4$ oxidized at 800 °C (b) are shown. At room temperature and 80 Torr CO (spectrum 3) one main peak arises at 2121 cm^{-1} with a shoulder at 2133 cm^{-1}. Two smaller peaks at 2206 and 2178

Fig. 7. FTIR spectra of the hydroxyl group region of Ni on Al$_2$O$_3$ heated to 500 °C in vacuum. Spectrum 1 was collected at −80 °C and 1 Torr CO, spectrum 2 at room temperature and vacuum and spectrum 3 is the difference spectrum (spectrum 1−spectrum 2). Spectrum 4 is the difference spectrum corresponding to spectrum 3, but here the catalyst was heated to 800 °C in vacuum.
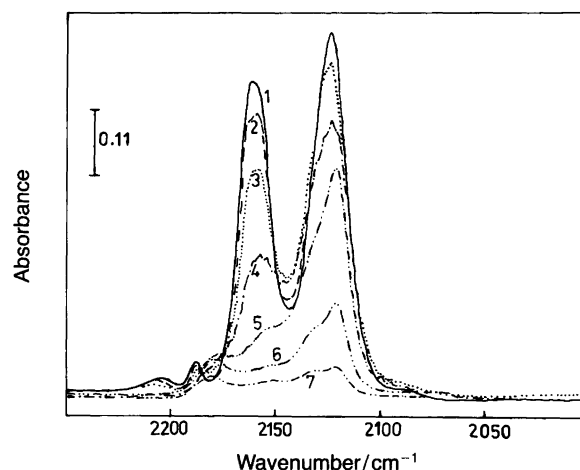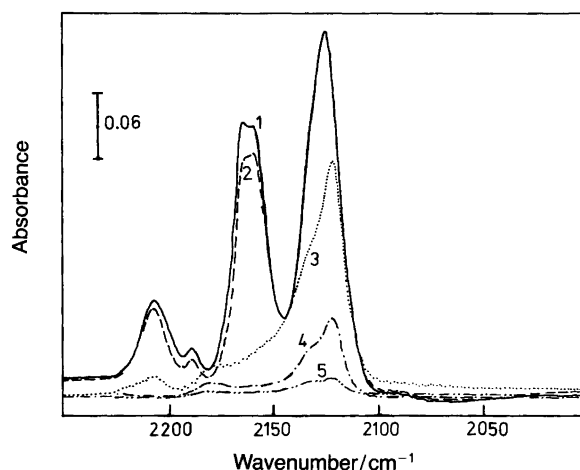

Fig. 9. CO FTIR spectra of Cu on AlPO$_4$ heated to 800 °C in oxygen. Spectrum 1 was collected at −115 °C and 1 Torr CO, spectrum 2 at −80 °C and 1 Torr CO, spectrum 3 at room temperature and 80 Torr CO, spectrum 4 at room temperature and 10^{-3} Torr CO and spectrum 5 after evacuation at 200 °C for 120 s.

cm⁻¹ are also noticed. When the sample is cooled to −80 °C (spectrum 2) the intensity of the peak at 2124 cm⁻¹ increases but a shoulder at higher wavenumbers can still be seen. A new peak with a doubled top is seen at 2163 and 2158 cm⁻¹ and a small peak at 2188 cm⁻¹ appears. The intensity of the peak at 2206 cm⁻¹ increases markedly. Further cooling does not yield any large additional changes. After a short heating to 200 °C and evacuation (spectrum 5 in Fig. 9) only three peaks of similar intensity are observed, at 2178, 2133 and 2121 cm⁻¹. A very weak band at 2220 cm⁻¹ is also noticed.

Cu on AlPO₄ reduced at 500 °C with CO (c) looks very much the same as without reduction (cf. Fig. 9). At room temperature and 80 Torr CO again one major peak at 2120 cm⁻¹, with a shoulder at 2131 cm⁻¹, was observed, together with two minor peaks at 2206 and 2178 cm⁻¹. When the sample was cooled to −80 °C the peak at 2123 cm⁻¹ increased and a new one with a double peak (at 2164 and 2158 cm⁻¹) was also noticed.

The investigation of Cu on silica was made because, although CO adsorbed on Cu/SiO₂ at room temperature has been studied by several groups[14–17] (Table 1), to our knowledge no low-temperature CO IR spectra have been described in the literature. The spectra of Cu on silica oxidized at 800 °C (b) are shown in Fig. 10. The spectrum at 80 Torr CO and room temperature (spectrum 2 in Fig. 10) has one large peak at 2131 cm⁻¹ and two small ones at 2158 and 2211 cm⁻¹. The latter peak has a shoulder at 2200 cm⁻¹. At −80 °C (spectrum 1) three bands are seen at 2128, 2156 and 2198 cm⁻¹, and they have all increased in intensity in comparison with room temperature. After evacuation to 10⁻³ Torr CO and at room temperature (spectrum 3) only one main band is left, at 2133 cm⁻¹, together with a shoulder at 2143 cm⁻¹. Three small residue bands can also be seen at 2212, 2181 and 2158 cm⁻¹.

When the sample was heated to 800 °C without oxidation (a) (spectra not shown) one main and two more peaks were detected at room temperature and 80 Torr CO (at 2130 cm⁻¹ and at 2161 and 2182 cm⁻¹). The spectra looked very much the same as those in Fig. 10, the only difference being the lack of peaks above 2185 cm⁻¹.

When the Cu/SiO₂ sample is reduced at 500 °C with CO (c) after oxidation at 800 °C (no spectra shown), the general appearance is almost identical to the sample heated to 800 °C in vacuum. At room temperature and 80 Torr CO the CO spectrum again showed one major peak and two minor ones. The former was at 2128 and the latter ones were at 2182 and 2160 cm⁻¹.

Discussion

The following interpretation of the CO IR bands is based on the CO stretching frequency from CO gas at 2143 cm⁻¹, which is taken as the base. CO is usually bonded to a metal or metal ion with a synergetic σ-bond–π-backbond. If a CO IR band is observed at higher wavenumbers than CO gas, the π-backbonding contributes less than the σ-bond, and if
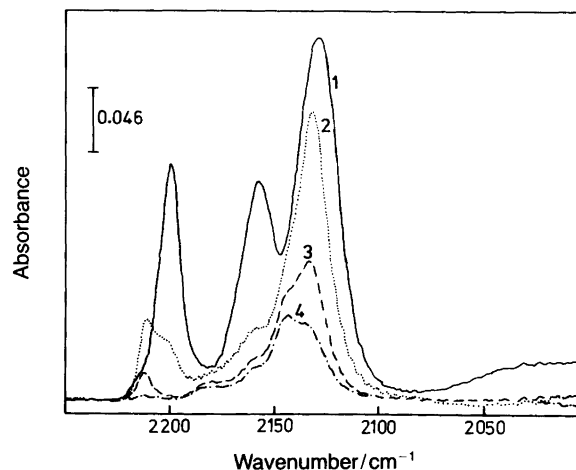

Fig. 10. CO FTIR spectra of Cu on SiO₂ heated to 800 °C in oxygen. Spectrum 1 was collected at −80 °C and 1 Torr CO, spectrum 2 at room temperature and 80 Torr CO, spectrum 3 at room temperature and 10⁻³ Torr CO and spectrum 4 after evacuation at 200 °C for 120 s.

the CO IR band is seen at lower wavenumbers the π-backbonding is more important than the σ-bond. An element with low electron density will therefore give a CO band at higher wavenumbers than would be the case for a more electron-rich element.

Discussing the assignment of the CO IR bands, a straightforward model of the structure of surface cations is used, as shown in Scheme 1. The metal ion is bonded to the surface via surface oxygen atoms (either from Si–O or Al–O/P–O groups). If the charge on the metal ion is +1, we assume that the ion can be bonded to one oxygen ion, and in some cases a second oxygen ion can donate electrons to the metal cation [strutures (a), (b) and (c) in the scheme]. If the metal ion instead has a charge of +2, it is likely to be bonded to two or three oxygen ions [structures (d), (e) and (f) in the scheme] in a similar way. Ligands can basically be bonded to the cation in two different configurations: trans and cis (Scheme 4). If the CO ligands are in the cis position, two IR-active CO vibrations are expected, while for a trans position one vibration is IR-active and the other is IR-inactive (it is instead Raman-active). In the case of the cis configuration, one can calculate the angle between the two
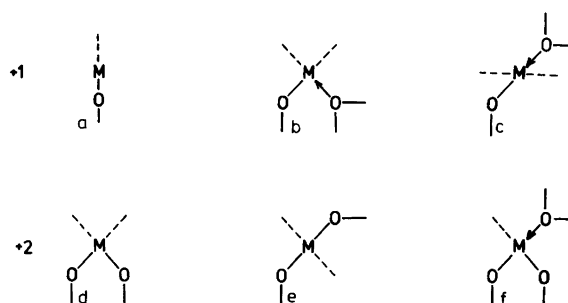
Scheme 1.

Table 1. Main CO IR bands from CO adsorbed on transition metal ions supported on amorphous AlPO$_4$ and silica gel.

Sample	Ions	AlPO$_4$	SiO$_2$
Mn	Mn^{2+}	2197/2199	2178/2192
			2190
Fe	Fe^{2+}	2181/2180	2171
Co	Co^{2+}	2187/2189	2176 (2188)
			2177/2191/2195
Ni	Ni^{2+}	2194	2180 (2195)
Cu	Cu$^+$	2121	2130
		2123/2160	2125/2156
	Cu^{2+}	2206	2198
		2220	2211

CO molecules from the intensities of the CO IR bands.[18,19] This gives a hint as to the coordination around the metal.

From investigations of CO adsorbed on chromium(II) on silica it is known[4,20] that an extra oxygen ligand at the cation [structures (d) or (e) in the scheme compared to structure (f)] shifts the CO vibration to higher wavenumbers by some 12 cm^{-1}. It should also be borne in mind that mixtures of the different surface structures in the scheme are possible.

Manganese on AlPO$_4$ shows only one peak. Since the metal charge is +2 the structures (d), (e) and (f) in the scheme with only one CO adsorbed are likely. It is, however, not possible to solve this structural problem. Even a *trans* configuration with two CO molecules at the Mn atom would fit our results. Compared to Mn on silica gel the CO IR band is shifted to higher wavenumbers by between 5 and 19 cm^{-1} (Table 1), depending on which CO IR band from Mn on SiO$_2$ is used for comparison.[13]

Fe on AlPO$_4$ heated to 800 °C gives only one large peak arising from one CO adsorbed on Fe(II). Here the same structural problem arises as before. The shift in comparison with silica gel is 10 cm^{-1} to higher wavenumbers (Table 1). When the sample was oxidized at 800 °C with O$_2$ to yield Fe(III) the only notable difference was that the intensity decreased. This can be explained by assuming that Fe(III) on AlPO$_4$ does not adsorb any CO.

Co on AlPO$_4$ also gives only one peak arising most likely from one CO adsorbed on cobalt. This CO band should be compared to the one for Co on silica gel, which is shifted to lower wavenumbers by 11 cm^{-1}, to 2176 cm^{-1} (Table 1).

Ni on AlPO$_4$, heated to 800 °C gave two CO IR peaks arising from two Ni–CO complexes, most likely with one and two CO ligands, respectively. By consideration of the results from a lower pretreatment temperature (Fig. 4), where the second peak dominated, we assign the two peaks to structures (e) and (f), respectively. On the basis of the CO IR spectra it was previously concluded that Ni(II) on silica gel forms *trans*-configurated surface species.[21] Comparing the CO IR-active band of the Ni–CO *trans* complex with two CO ligands on silica (2180 cm^{-1}) with that on AlPO$_4$ (2193 cm^{-1}), again a shift to higher wavenumbers was seen for AlPO$_4$.

Cu on silica gel heated to 800 °C gave two peaks, one of them only seen at low temperatures. They are assigned to CO adsorbed on Cu(I), which at room temperature is mainly coordinated to one CO (2131 cm^{-1}),[14–17] and two CO ligands at low temperatures. The adsorption of an additional CO ligand can also explain the shift by 6 cm^{-1} to lower wavenumbers of the first peak. This assignment would correspond to structure (a) or (b) in Scheme 1. Comparing the CO IR bands on Cu(I) at room temperature for the two supports it is noticed that AlPO$_4$ shows the CO IR band with the lower wavenumber (2121 as opposed to 2130 cm^{-1}). The two bands at lower temperatures are more difficult to compare because the CO IR band around 2160 cm^{-1} on AlPO$_4$ is split into two peaks. Considering in this case only the CO IR band pair with the largest splitting we compare 2123/2163 cm^{-1} with 2126/2156 cm^{-1} and observe that this splitting is somewhat larger for Cu(I) on AlPO$_4$ and that the mean value of the two bands (2143 cm^{-1}) is only slightly shifted from that on silica (2141 cm^{-1}).

As already mentioned above, the angles between two CO ligands can be calculated, and such angles are listed in Table 2. Structure (a) in the scheme with two CO ligands would give an angle close to 120° between the two CO molecules and structure (b) one close to 109 or 90° for a tetrahedral or square-planar configuration, respectively. It must also be considered that O^{2-} is rather large, a fact which might induce smaller angles than 120 and 90° between the two CO ligands. From Table 2 it is seen that the angle between the two CO molecules on AlPO$_4$ is smaller by some 10° compared with silica. This is an indication that Cu(I) surface compounds similar to structure (a) in Scheme 1 are changed in direction to structure (b) on using AlPO$_4$ instead of silica as the support.

When the Cu samples were oxidized at 800 °C one marked difference in the spectra is noticed: at room temperature a peak (2211 cm^{-1} on silica and 2220 cm^{-1} on AlPO$_4$) arising from Cu(II) is observed, which is assigned to one CO ligand, and a second peak (2200 cm^{-1} on silica

Table 2. The angle between the two CO ligands for Cu(I) surface ions calculated from the intensities of the two CO IR bands.[14]

Support and pre-heating procedures	Angle/°	
	−80 °C	−115 °C
Cu/SiO$_2$		
800 °C/vacuum	116	110
800 °C/O$_2$ (Fig. 11)	112	−^{a}
800 °C, 500 °C/CO	114	110
Cu/AlPO$_4$		
800 °C/vacuum (Fig. 9)	102	98
800 °C/O$_2$ (Fig. 10)	107	103
800 °C, 500 °C/CO	107	−^{a}

^{a}No spectrum was collected at −115 °C.

and 2207 cm^{-1} on AlPO$_4$) also from Cu(II) is seen, which is assigned to two CO ligands. Since there is only one peak, the two-coordinating species must adsorb the two CO ligands in the *trans* position. At low temperatures the two-coordinating species dominates completely, and at room temperature and 10^{-3} Torr CO the one-coordinating species is the only one observed.

On the basis of CO IR bands listed in Table 1 for +2 surface cations it is found that all bands are shifted to higher wavenumbers by some 10 cm^{-1} if AlPO$_4$ is used as the support instead of silica. This is an indication that these metal ions have lower electron density if supported on AlPO$_4$ as compared to silica gel. This can be explained again by the assumption that the cations are bonded to the surface via P-O$^-$, since phosphorus has a higher electronegativity than silicon. This effect was previously observed for Cr(II).[10] Our only example for +1 cations [Cu(I)] does not show such an effect.

Looking at the OH stretch region and the 500 °C Al$_2$O$_3$ sample (Fig. 7) the peak at 3794 cm^{-1} can be assigned, according to our previous hypothetical model,[11] to tetrahedrally coordinated aluminium ions. The same model predicts OH bands around 3768 and 3743 cm^{-1} for five- and six-coordinated aluminium ions. The shoulder at 3727 cm^{-1} in Fig. 7 is assigned to OH groups from six-coordinated aluminium ions, although this band is observed 16 cm^{-1} lower than predicted. A band for OH groups from five-coordinated aluminium ions is not observed in Fig. 7. The band at 3671 cm^{-1} is assigned to acidic AlOH with bridging oxygens, and the very broad band at 3597 cm^{-1} is assigned to AlOH with hydrogen bonding. In the difference spectrum of Fig. 7 the broad negative band around 3710 cm^{-1} and the broad positive band around 3550 cm^{-1} might be due to adsorption of CO on OH groups. The corresponding CO IR band is, however, not noticeable in spectrum 2 in Fig. 6. The negative peak at 3685 cm^{-1} (spectrum 4 in Fig. 7) and the broad positive band at 3550 cm^{-1} correspond, however, to the CO IR band at 2166 cm^{-1}, which is observed as a shoulder in Fig. 6. Similar phenomena have been observed previously with Si-OH-CO (2156 cm^{-1}) and P-OH-CO (2170 cm^{-1}).[11]

Conclusions

In this study it was found that the CO IR bands for +2 metal ions are generally shifted some 10 cm^{-1} towards higher wavenumbers on AlPO$_4$ as compared with silica gel. This is explained by the metal cation being bonded to the surface via P-O$^-$. For Mn, Fe and Co on AlPO$_4$, which showed only one CO IR band each, no particular structure

could be determined. Ni^{2+} on AlPO$_4$ and Cu(II) on both supports showed two CO IR bands. Cu(I) did not show the general shift to higher wavenumbers for AlPO$_4$ as compared to silica gel. Cu(I) gave one CO IR band at room temperature and two at low temperatures, which arise from one or two CO ligands at the same metal ion, respectively. The angle between the two CO ligands has been calculated and discussed with respect to the structure of the Cu(I) surface ion.

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