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Low Temperature CO Adsorption on Alum-Derived Active Alumina: An Infrared Investigation

Active aluminas are extensively used as adsorbents, catalysts, and catalyst supports. The relevant factors which determine the adsorptive and catalytic properties, such as crystal structure, surface area, and porous texture, and the chemical nature of the surface are largely determined by the precursor material used and the thermal treatment adopted.

Catalytic aluminas prepared by controlled thermolysis of aluminium hydroxides and oxohydroxides have been extensively studied (*1–6*) but materials prepared by thermal decomposition of aluminium oxosalts have so far received less attention. However, recent studies (*7–9*) have shown that thermolysis of aluminium sulfates can lead to high-surface-area aluminas with potential use as adsorbents and catalysts. We report here an IR study of CO adsorption on active alumina prepared by thermal decomposition of ammonium alum. The CO molecule is used to probe Lewis acidity which is related to catalytic activity (*10*) and is known to be structure dependent (*1*).

Ammonium alum (Koch-Light 99.97%) was subjected to thermolysis for 6 h at 1173 K. X-ray diffraction showed the resulting material to be γ-alumina with a defective spinel-type lattice in which all the cation vacancies are on octahedral sites. This corresponds to the structural notation $Al_8[Al_{13\frac{1}{3}}\square_{2\frac{2}{3}}]O_{32}$, octahedral sites being enclosed in square brackets. Chemical analysis showed a residual sulfur content of 0.5%, presumably due to tenaciously held SO_3. The BET surface area was 170 m^2g^{-1}, and nitrogen adsorption–desorption at 77 K revealed a mesoporous system consistent with the porosity being that of cylindrical pores with a most frequent pore radius of 10 nm and a unimodal radius distribution. Further details on the structural and textural characterization of this material were given elsewhere (*11*).

IR transmission spectra were recorded with a Perkin–Elmer 580 B spectrometer equipped with a data station. The alumina sample, in the form of a compressed self-supporting disk, was previously outgassed for 20 min at 1073 K under a dynamic vacuum (residual pressure $<10^{-4}$ Torr). This thermal treatment allows partial elimination of the sulfate impurities, as monitored by the intensity of the 1380-cm^{-1} band due to surface sulfates (*12, 13*). Further elimination was accomplished by reduction in H_2 at 1073 K and subsequent outgassing (three reduction cycles were performed). The sample thus prepared showed the characteristic spectrum of highly dehydroxylated γ-alumina with three very weak OH bands at 3800, 3740, and 3700 cm^{-1}, the first one being barely observable. From the point of view of the OH stretching-band fingerprint, the alum-derived γ-Al_2O_3 is very similar to γ-Al_2O_3 derived from other sources (vide infra).

Figure 1 shows the IR spectra, in the CO-stretching region, after dosing increasing amounts of CO to the γ-alumina sample kept at 77 K. The IR spectrum (dashed line) of CO adsorbed at 77 K on α-alumina, prepared as described by Morterra *et al.* (*14*), is also shown for comparison. Four partially overlapping bands (A, B, C, D), which grow in a different way upon increasing the CO pressure, are observed in the interval 2240–2130 cm^{-1}. Bands A, B, and

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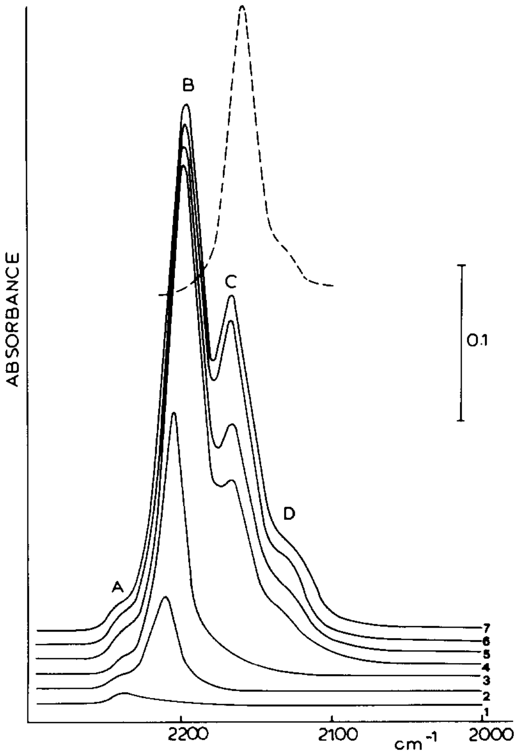


FIG. 1. Curves 1 to 7 correspond to increasing CO equilibrium pressures (at 77 K). Spectra 1 and 2: $P_{CO} < 10^{-2}$ Torr; spectrum 3: 2×10^{-2} Torr; spectrum 4: 2 Torr; spectrum 5: 6 Torr; spectrum 6: 20 Torr; spectrum 7: 60 Torr. Dashed curve: IR spectrum of CO adsorbed on α-Al_2O_3 at 77 K (P_{CO} = 40 Torr).

C have higher frequency than the free CO molecule and may consequently be assigned to CO bonded to Lewis acid centers of diffeent strength, as given below.

Band A (*2238 cm*$^{-1}$). This is the first one to appear at the lowest coverages and soon reaches its saturation intensity. This peak is present also at room temperature. The same band has been observed with similar intensity at room temperature on a γ-Al_2O_3 not derived by decomposition of aluminium sulfates (*15*), so in this respect γ-Al_2O_3 coming from different sources does not show substantial differences in surface properties. Under higher CO pressure band A appears as a weak shoulder on the main CO peak at 2210–2190 cm^{-1} (band B).

Band A has been assigned to CO σ-bonded to strong cationic Lewis acid sites (bonding energy ~50–60 kJ mol^{-1}) (*15, 16*). The population of these sites is very low (~0.06/100 Å^2) (*15*), i.e., less than 1% of the total number of surface cationic sites; consequently, they can be regarded as surface defects (*6, 15*) with strong Lewis acid character.

Band B (*2210–2190 cm*$^{-1}$). This is the second peak to appear upon increasing the CO equilibrium pressure at 77 K, and constitutes the most intense feature of the spectrum. The same peak is present also at room temperature but with much lower intensity. Inspection of the spectra of CO adsorbed at room temperature on γ-alumina obtained from a different source (*15*) shows that band B is similarly present at room temperature, with the same (very low) intensity. This again testifies to the fact that γ-aluminas obtained in different ways show very similar surface site distribution. The bonding energy of the species giving band B was estimated to be in the range 35–45 kJ mol^{-1} (*16*). On increasing the coverage the band B frequency changes gradually (a total negative shift $\Delta\bar{\nu} = -22$ cm^{-1} is observed) as a consequence of the building up of adsorbate–adsorbate interactions.

This phenomenon has been also observed for CO adsorbed on η-Al_2O_3 (*17*). Adsorbate–adsorbate interactions can be of the dynamic (dipole–dipole) type or of the static (chemical and electrostatic) type (*18–20*, and references therein). Dynamic interaction alone is known to cause an upward shift of the CO band. Static interactions usually behave in the opposite way. In the present case both types of interaction can be present, but the static ones are definitely predominant (because the observed shift is negative).

As lateral interactions die away after only a few lattice spacings, the large negative shift observed in this case suggests that B species are grouped into patches (or adsorbed on microfacets) where the distance between adsorbed molecules is not larger than a few interionic spacings in the solid.

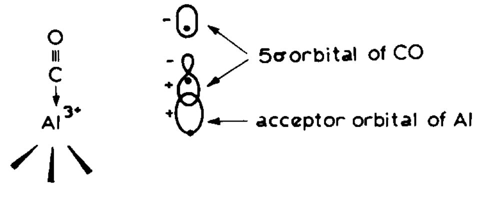
The high intensity of band B suggests that it corresponds to CO bonded to very common Lewis acid sites formed upon dehydroxylation of the γ-Al_2O_3 surface. We assign this band to CO σ-bonded to bulk tetrahedral Al^{3+} ions emerging on the surface. This is consistent with the absence of band B from the IR spectrum of CO adsorbed on α-Al_2O_3 (dashed line in Fig. 1) which has no tetrahedrally coordinated Al^{3+} ions. It should be noted that the ratio of the bulk tetrahedral to octahedral Al^{3+} ions in γ-Al_2O_3 is $8:13\frac{1}{3}$, yet band B is the most intense feature of the spectrum. This, however, is not necessarily a contradiction because enhanced covalency at the oxide surface could favor preferential exposure of tetrahedral ions.

The frequency of the peak of band B is 47 to 67 cm^{-1} higher than the corresponding stretching frequency of CO gas. This high value of the stretching frequency can be explained on the basis of the usual molecular orbital scheme involving the 5σ molecular orbital of the CO molecule (*21*) and an acceptor orbital of the Al_{tet} ion, with formation of a dative σ-bond as shown below in Scheme ***1***. The 5σ orbital of CO is slightly antibonding along the C–O bond; consequently, its depopulation upon σ-donation to the empty acceptor orbital of Al_{tet} strengthens the C–O bond, thus increasing the corresponding stretching frequency (*18, 20*).

The previous scheme can also explain the observed negative shift of the peak of band B when the CO coverage is raised. As briefly discussed before, CO adsorption on Al_{tet} Lewis acid sites results in charge donation to the alumina surface. This donated charge does not remain completely confined to the adsorbing center, but is partially delocalized through the solid (chemical effect) via an inductive mechanism with concomitant increase of the electron density (and decrease of the Lewis acid character) on the nearest, and also more distant, cationic sites. This is not a short range effect, but dies away in a few intercationic spacings (*18–20*). Incoming CO molecules find Al_{tet} sites with reduced σ-acceptor ability. Consequently, the strength of the Al_{tet}–CO σ-dative bond decreases with coverage, and so does the CO stretching frequency. It is worth mentioning that this interpretation scheme has been successfully applied to the assignment of the IR spectra of CO adsorbed on many oxides and halides (*18–20*) and is in agreement with the results obtained on η-Al_2O_3 (*17*).

Band C (2165 cm^{-1}). Band C begins to grow only when band B has nearly reached its maximum intensity. This fact suggests a lower interaction energy and, consequently, a smaller Lewis acid strength of the adsorbing center (on the basis of the frequency difference with respect to the free CO molecule the adsorption energy is estimated as ~20 kJ mol^{-1}) (*16*). The frequency of band C is very close to that of CO adsorbed on α-Al_2O_3. Consequently this band is readily assigned to CO weakly σ-bonded to (or more likely polarized by) octahedral Al^{3+} ions emerging on the surface.

The Al_{oct} sites are expected to be weaker Lewis acid sites than the tetrahedral ones. This is in agreement with a weaker interaction energy and the observed lower stretching frequency (only ~22 cm^{-1} shifted upward with respect to CO gas). The weakness of the σ-dative bond also justifies the absence of any appreciable frequency shift with coverage because (due to the weakness of the interaction) the CO oscillator does not appreciably respond to the change



SCHEME 1.

of coverage occurring at adjacent and more distant sites. This fact has been observed also in many other cases (*18–20*).

Band D (*2135–2140 cm*$^{-1}$). This band appears, as a broad shoulder, only at the highest CO equilibrium pressures. By analogy with the IR spectrum of CO in condensed phase (*22*), or physically adsorbed on oxides and halides (*18–20*), it is assigned to CO adsorbed via dispersion forces on the top of σ-bonded species (multilayer physical adsorption).

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