The Chemisorption of Carbon Monoxide on Various Transition Aluminas

Giuseppe Della Gatta,[1] Bice Fubini,[1] Giovanna Ghiotti,[2]
and Claudio Morterra[2]

University of Turin, Turin, Italy

Carbon monoxide chemisorption was investigated at 36°C on four transition aluminas (η, γ, θ, Alon C) by means of microcalorimetry and infrared spectroscopy. On all the aluminas coverages are fairly low, and the interaction only involves a coordination to surface cations. There is evidence for two families of admolecules, characterized by different stretching frequencies ($\Delta\bar{\nu} \sim 30$ cm^{-1}) and adsorption heats (14 and 2 kcal/mole, respectively).

The same species are found on all the aluminas although in different amounts. In particular the remarkable differences observed between η-alumina and γ-alumina seem to parallel their different catalytic activity.

INTRODUCTION

In an earlier paper (1) devoted to obtaining a better understanding of the surface properties of transition aluminas we investigated the combined use of the two rather different techniques of adsorption microcalorimetry and vibrational spectroscopy in respect of water adsorption. We concluded that the adsorption of a molecule different from water should also be used, as water adsorbed through different mechanisms, reacted with the surface and led to strong lateral interactions. Carbon monoxide was therefore chosen, since it is known to chemisorb on aluminas in such small amounts (2, 3) that lateral interactions involving the whole surface are unlikely. Secondly, it does not physically adsorb nor interact with surface hydroxyls, at least at the temperatures employed here. Thirdly,

[1] Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Torino, Via Pietro Giuria 9, 10125 Torino, Italy.

[2] Istituto di Chimica Fisica, Facoltà di Scienze, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy.

it is the only simple molecule that interacts with the surface maintaining its chemical individuality. This last apparently contradicts what has been previously reported by other authors (2, 4, 5) who observed that the chemisorption of CO produced surface carbonates, but there are the exceptions of O'Neil and Yates (6) and Borello et al. (7) who only observed bands in the 2150–2250 cm^{-1} range. In the present paper, four different transition aluminas were used, including a nonporous material, whose behavior closely resembles that of Peri's alumina [compare, for example, CO spectra of Ref. (2) and of Fig. 1D below], but no trace of carbonate formation was ever observed, neither at room nor at higher temperatures.

As far as the characterization of surface properties is concerned, the use of CO adsorption is likely to be helpful in throwing light on the Lewis acidity, which is known to vary from alumina to alumina (8) and which is considered to be related to the catalytic activity (9).
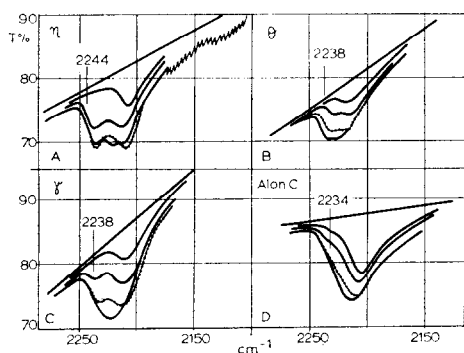
FIG. 1. Infrared spectrum due to the adsorption of 40 Torr of CO on four aluminas. Dehydration temperatures are, in order of increasing intensity, 400, 500, 600, 740°C. The spectrum relating to 600°C pretreatment has been marked differently for the sake of clarity. For dehydration below 400°C only the spectrum of the gas was observed. In one case only (A) this was not subtracted, in order to show its contribution to the total intensity. (A–D) The frequency of the most resistant component is reported.

EXPERIMENTAL METHODS

The apparatus and the method of study both for the calorimetric and the ir technique have already been described (7, 10).

η-Alumina was obtained from the same batch prepared for preceding investigations (1) and similarly for θ-alumina (11). γ-Alumina was kindly supplied by Professor A. Cimino, and was prepared following the method proposed by McIver et al. (8). Alon C[3] was given by Professor M. J. D. Low.

Surface characteristics, which will be described in detail elsewhere, are summarized in Table 1.

[3] Alon C is a microspherical, nonporous, high area alumina manufactured by Cabot Corp., Boston, and is considered to be either a γ-alumina or a mixture of γ- and δ-alumina phases. Very few data are reported relative to it, as this material was only introduced for comparison with other authors' aluminas on which CO oxidation was observed. In fact no agreement has so far been achieved on the structural characteristics of this alumina and, in view of the importance of the crystalline structure in catalytic activity stressed by McIver et al. (9), any reasoning on its behavior would seem to be of little contribution.

CO adsorption was also checked on two well-crystallized α-alumina specimens (16 and 25 m² g⁻¹, respectively), but no uptake was observed either spectroscopically or gravimetrically.

Calorimetric and volumetric measurements were performed as follows: a first adsorption run (run 1) was conducted up to a chosen pressure on the sample outgassed at the proper temperature, followed by desorption, and then a readsorption (run 2) and a subsequent desorption were conducted in order both to evaluate an irreversible fraction, if present, and to confirm measured data. Adsorption runs were stopped when uptake of the gas became so small as to make any further adsorption increase unreliable.

Adsorbed amounts were also checked by microgravimetric technique. On θ-alumina only the first adsorption–desorption run was carried out, as no difference from η-alumina was found.

Sample dehydration temperatures for calorimetry were chosen on the basis of ir data and were 400 and 740°C for η-Al₂O₃, 740°C for θ-Al₂O₃, and 580 and 740°C for γ-Al₂O₃. 400°C corresponds to the beginning of adsorptive activity, 740°C is the activation temperature at which the maximum number of adsorbed species is evidenced, and the range 580–740°C corresponds, for γ-alumina, to the appearance in the spectrum of a discrete component.

Calorimetric measurements were carried out at 36°C, so as to be as close as possible to the thermal conditions of white samples in the ir beam.

TABLE 1

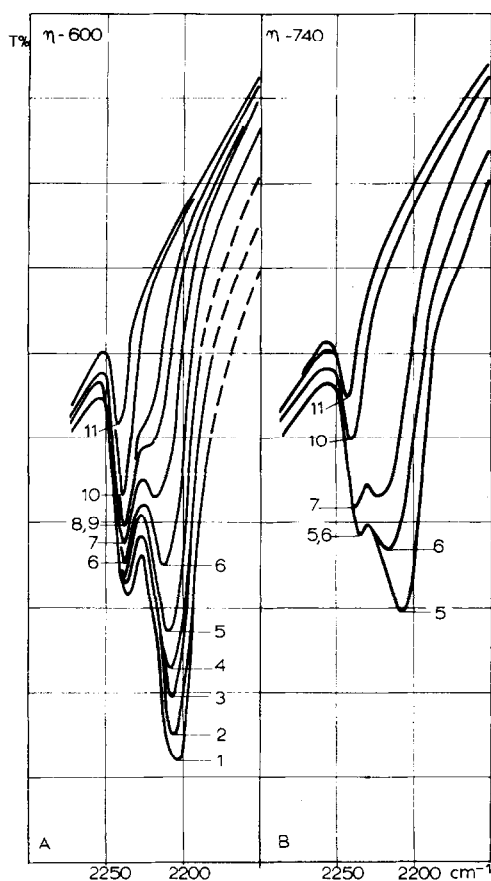| Alumina	Surface area (m² g⁻¹)	Porosity
η	220	Mesopores
θ	70	Macropores
γ	140	Meso–macropores
Alon C ($\gamma + \delta$)	100	Absent

FIG. 2. Infrared spectrum of CO adsorbed on η-Al$_2$O$_3$ dehydrated at 600°C (A) and 740°C (B) at different pressures. Pressures (Torr): (1) 200; (2) 175; (3) 150; (4) 125; (5) 100; (6) 50; (7) 25; (8) 8; (9) 3; (10) 1 × 10^{-2}; (11) degassed 10 min. The spectra have been recorded with an approx 2.5 times ordinate scale expansion.

Carbon monoxide was high purity grade and was passed through a liquid nitrogen cold trap before use.

RESULTS

A. Infrared Spectra

Figure 1 shows the spectrum in the 2100–2300 cm^{-1} range due to adsorption of CO (40 Torr) on four aluminas (1 Torr = 133.3 N m^{-2}). As these spectra were obtained with samples of different thickness, they can only show the qualitative evolution of bands with dehydration.

The chemisorption of CO on all the four materials was confirmed (7) to be conditioned by preliminary dehydration. In particular, no adsorption was detected on samples dehydrated below 400°C.

It can be seen that:

a. For activation at 400°C only one CO band is formed on each sample, whose position varies between 2203 and 2215 cm^{-1}.

b. From 500°C up, a second species appears at higher wavenumbers (2235–2245 cm^{-1}) which is quite scarce and poorly resolved on Alon C.

c. Above 600°C either the apparent maximum of the lower absorbing species shifts upwards or a new distinct component grows, whose frequency is intermediate between the two already mentioned. Meanwhile, the intensity of the highest and of the lowest species is either constant or decreases somewhat on η- and γ-alumina. This behavior is also observed on θ-alumina if CO is contacted with the material activated at 800°C (spectrum not reported in Fig. 1).

Figures 2 and 3 show on an expanded scale the different behavior of η- and γ-Al$_2$O$_3$ and the effect of increasing the activation temperature from 600 to 740°C. In particular it can be noted that:

a. There is a much stronger dependence of η- than of γ-alumina on CO pressure, as in the former case the adsorbed amount goes on increasing up to 200 Torr, while in the latter the very small increase is mainly an artefact and is due, at the higher pressures, to the contribution of the gaseous phase. In Fig. 2 most of the increase of the high frequency component is due to strong band overlapping, the actually growing species being the low frequency one. In Fig. 2B no spectra are reported relative to pressures above 100 Torr, as the evolution of the low ν component with pressure is much the same in the two samples.

b. A higher adsorbing activity of the η-phase is much clearer here than it was in Fig. 1, as comparable samples were used

and more severe expansion conditions were necessary on γ- than on η-alumina to obtain similar band sizes.

c. The existence of a fraction not removed by a 10 min degassing at room temperature is evidenced on both materials. The spectral position is indicated in Fig. 1, and the amount is higher on η- than on γ-phase alumina. This result was also confirmed on a quantitative basis.

d. Minor spectral features suggested by Fig. 1 are here emphasized by the scale expansion. In particular on η-Al$_2$O$_3$ a small decrease of the 2244 cm^{-1} and of the 2205 cm^{-1} components is caused by raising the

FIG. 4. Infrared spectrum of the OH stretching region of η-Al$_2$O$_3$ dehydrated at 600°C. (1) Background; (2) 3 Torr of CO added; (3) 200 Torr added.

activation temperature from 600 to 740°C, together with a moderate increase of a component of intermediate frequency. Microgravimetric experiments show that, in such conditions, the specific activity is either unchanged or slightly decreases, suggesting the beginning of a site-conversion process already postulated (9) to explain a similar evolution of catalytic activity with dehydration. On the γ-phase the first effect is inferior, or nonevident, while the appearance of a new component at about 2225 cm^{-1} is much more clearly evidenced.

Figures 1–3 show the only spectral modifications produced upon CO adsorption, except for a small effect observed in the surface hydroxyl region which is reported in Fig. 4 for η-Al$_2$O$_3$ dehydrated at 600°C. The 3786 cm^{-1} OH band is reversibly perturbed, with a shift to 3780 cm^{-1}, to an extent that varies with CO coverage. The perturbation already occurs with the small pressures which merely produce the high frequency CO component (see Fig. 2). No perturbation is observed on 400°C-dehydrated samples, which only yield the lower ν CO component, even though in that case the 3786 cm^{-1} band has about its maximum intensity (1, 12). The OH perturbation is thus likely to be
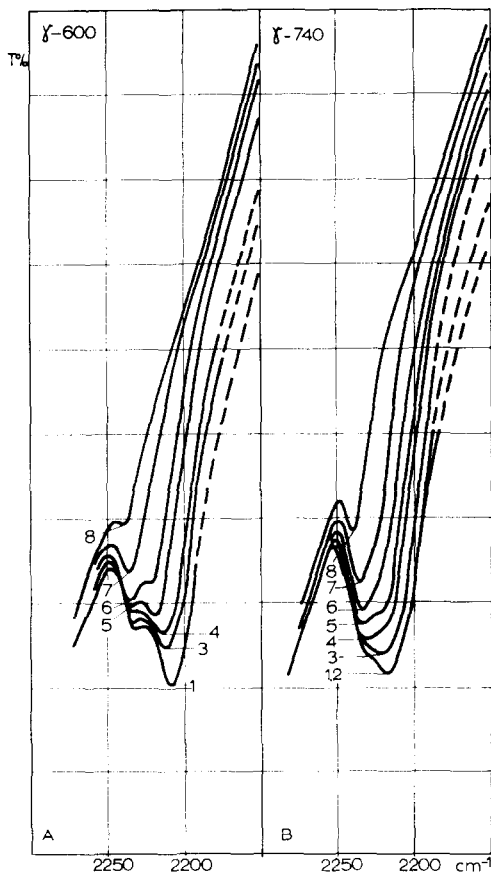

FIG. 3. Infrared spectrum of CO adsorbed on γ-Al$_2$O$_3$ activated at 600°C (A) and 740°C (B) at different pressures. Pressures (Torr): (1) 200; (2) 150; (3) 100; (4) 70; (5) 50; (6) 20; (7) 3; (8) 1 × 10^{-2}. The spectra have been recorded with an approx 7 times ordinate scale expansion.
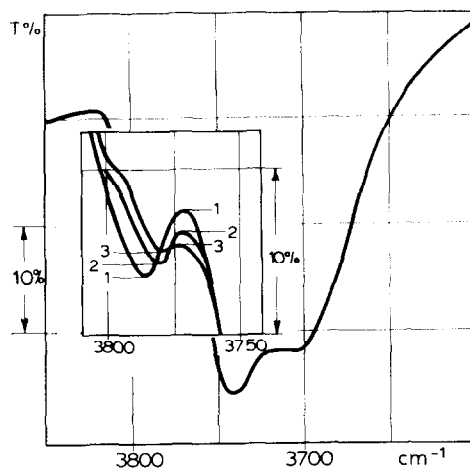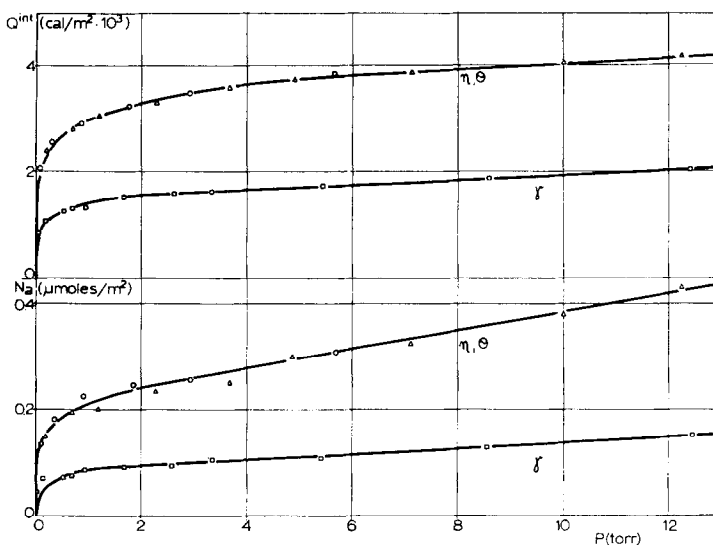
FIG. 5. Calorimetric and volumetric isotherms of CO on η ($\triangle$), θ ($\bigcirc$), and γ ($\square$) alumina dehydrated at 740°C.

due to the CO species which absorbs at the higher frequency.

B. Calorimetric and Volumetric Measurements

Figure 5 shows the first run of calorimetric and volumetric isotherms on η-, θ-, and γ-alumina activated at 740°C; the adsorption is reported up to 13 Torr, as at this pressure no further appreciable uptake was observed on γ-Al$_2$O$_3$, while for η-Al$_2$O$_3$ a regular increase was still observed for pressures as high as 40 Torr.[4] It can be noted that:

a. The specific activity of η- and θ-Al$_2$O$_3$ coincide, both as regards adsorbed amounts and evolved heats. This seems to suggest that, despite the change of crystalline structure, surface area and porous texture, a fairly similar distribution of cationic sites is maintained at least as far as the most acidic ones are concerned.

b. The chemisorption on γ-Al$_2$O$_3$ is very different, both in specific activity and in

[4] In the whole pressure range explored and for each material heat of adsorption peaks were of the "instantaneous" type (lasting $\sim$15 min) thus indicating a nonactivated process.

overall trend of the adsorption isotherm, which was found to fit a Langmuir plot whose monolayer value coincides well with the maximum uptake observed.

The much lower activity of γ-alumina is believed to indicate that, although η- and γ-phase alumina possess the same crystalline structure, remarkable differences probably exist in the concentration of the most acidic cationic sites.

In Fig. 6 the adsorption integral heats plot is reported. Only the experimental points of run 1 of each alumina are shown, not to overcrowd the plot, as all adsorption and desorption data fit the same curve. The major feature is that the adsorption on three different materials yields only one curve of integral heats, except for the final points of γ-Al$_2$O$_3$. The curve is mainly made up of two nearly linear parts separated by a very restricted transition range, suggesting two different forms of adsorption, each characterized by a constant differential heat. On γ-Al$_2$O$_3$ only the higher energy one is present.

Differential heats, which we normally evaluate by a computer differentiation method, were instead obtained from the slope of the two linear parts. The low

FIG. 6. Integral heat of adsorption of CO on η- ($\triangle$), θ- ($\bigcirc$), and γ- ($\square$) alumina, dehydrated at 740°C. p_η and p_γ are the CO equilibrium pressures corresponding to the indicated coverages on these aluminas.

coverage adsorption turns out to possess a rather high bonding energy ($q^{\mathrm{diff}} = 14$ kcal/mole), while the high coverage one is characterized by a very low energy ($q^{\mathrm{diff}} \sim 2$ kcal/mole). The first straight line points to the origin, so that the existence of adsorption phenomena of different energy at lower coverages seems likely to be ruled out.

The fraction adsorbed with low energy is fairly abundant on η-alumina, and seems to be so on θ-alumina as well, while on γ-alumina it is almost entirely missing. In fact only the last few points seem to suggest the beginning of a low energy range of a very small extent, if compared with η-alumina at the same pressure (e.g., see the arrows in Fig. 6 showing $p_\gamma = 12$ Torr and $p_\eta = 10$ Torr). This overall behavior agrees with infrared results.

The strong chemisorption process ends on η-alumina at coverages between 0.15 and 0.2 molecules/100 Å² (beginning and end of the transition range, respectively) while on γ-alumina it ends at about 0.06 molecules/100 Å². The concentration of the weakly held species is, on η-alumina, between 0.30 and 0.35 molecules/100 Å² at 40 Torr, and increases at 150 Torr by about 20%.

The above reported concentrations confirm what has been previously observed (2),

i.e., that only very few cationic sites are able to chemisorb CO.

Other activation temperatures have also been examined, namely 400°C for η and 580°C for γ, to check the influence on CO adsorption of higher surface hydration conditions. η-Alumina degassed at 400°C, which only exhibits a weak band at 2205 cm⁻¹ (Fig. 1A), adsorbed unreliably small quantities that correspond to the evolution of approximately one third of the heat due to the weakly held amount on the 740°C sample. The quick reversibility observed was also comparable with that of the low energy species, so that a correspondence between this and the lower frequency infrared band is suggested.

Figure 7, lower section, shows calorimetric isotherms (all adsorption and desorption runs) on γ-Al₂O₃ activated at 580 and 740°C. It is observed that:

a. Points referring to the samples dehydrated at the two temperatures fit the same curves within the experimental error, as they do in the case of volumetric isotherms (not reported). This would seem to suggest that the new band formed at 2225 cm⁻¹ on raising the activation temperature, does not mean much in quantitative terms, at least in the pressure range explored for
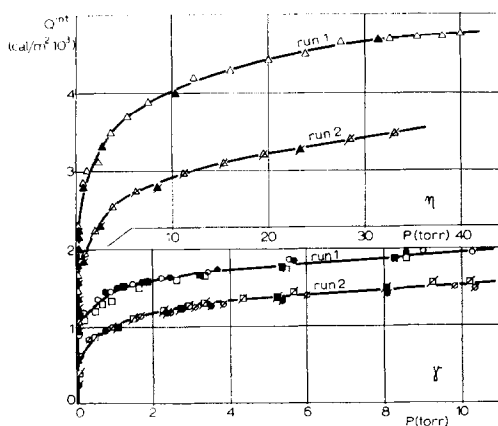
Fig. 7. Calorimetric adsorption–desorption isotherms of CO on γ-Al$_2$O$_3$ dehydrated at 580°C ($\bigcirc$) and 740°C ($\square$) (lower abscissa scale), and on η-Al$_2$O$_3$ dehydrated at 740°C ($\triangle$) (upper abscissa scale). Full points refer to desorption.

the isotherms. In fact the 2225 cm^{-1} band (see Figs. 2 and 3) is evident only at high pressures for which the quantitative data were not obtained.

b. The non-coincidence of Run 1 and 2 indicates that a fraction, though quite small (0.018 molecules/100 Å^2), is not removed at the experimental conditions. The last step of the desorption run was a direct pumping off of the calorimetric cell, which gave rise to a very slow thermal emission that lasted over 5 hr, and clearly corresponded to a strongly activated species evidenced by the small band remaining in the spectrum at 2238 cm^{-1}.

Calorimetric isotherms (all adsorption and desorption runs) on η-Al$_2$O$_3$ activated at 740°C are reported in the upper section of Fig. 7. The existence of a fraction not removed on degassing is clearly evidenced and turns out to be some three times more abundant than on the γ-Al$_2$O$_3$ (0.054 molecules/100 Å^2).

DISCUSSION

The assignment of CO stretching bands in the 2150–2250 cm^{-1} region to carbon monoxide molecules linked to coordina-

tively unsaturated surface cations through σ-dative bonds has already been discussed (7) and is also proved by the complete inhibition caused by preadsorption of strong bases such as pyridine (12).

As CO is a soft base and as aluminum does not possess d-electrons available for back-donation, the formation of carbonyl-like structures on the surface of transition aluminas is believed to reveal small but observable amounts of strongly acidic sites.

Following a preadsorption of pyridine, the activity towards CO starts being restored after the removal of the adsorbed base at temperatures as high as 300°C (12) so that a strict correspondence between CO sites and the strongest Lewis acidity is further evidenced.

The presence of three σ-coordinated species indicates a certain variety of these sites both within each alumina phase and among different phases.

In this respect, the OH perturbation (Fig. 4) ascribed to the highest absorbing CO species indicates that the involved Al ion either possesses the hydroxyl in its coordination sphere, or lies just next to it.

The presence of at least two forms of adsorption is confirmed by calorimetric results. All the proposed data give sufficient evidence for the assignment of the sharp high frequency band to the high energy species, and of the broader and likely complex absorption band at lower frequencies to the weak adsorption.

In fact, on η-alumina the transition from strong to weak adsorption occurs for CO pressures between 3 and 5 Torr: curves 8 and 9 of Fig. 2A show that, in this range, the appearance of low frequency bands is the only appreciable spectral change.

On the other hand on γ-alumina calorimetric data only refer to pressures up to 13 Torr, in which conditions only the high frequency band is appreciably present (curves 6 and 7 of Fig. 3B). As for the appearance at higher pressures of a certain amount of lower frequency bands, a weak

adsorption is in fact suggested to begin by the last points in Fig. 6.[5]

As on both aluminas the non-desorbable amount corresponds to a fraction of the band at highest frequency, the correspondence between the high frequency band and the strongly held species is further shown.

In this respect it should be considered how to reconcile the existence of the non-removable fraction with the constancy of strong adsorption differential heats. This constancy makes the existence of a true irreversible phase hard to admit, but entropic and kinetic factors should also be taken into account. While the former are not easily accounted for, there is enough experimental evidence from thermokinetics that the desorption process becomes so slow as to imply times whose length is experimentally unreasonable. Besides, the porous nature of η- and γ-alumina could be thought to play some role when the surface concentration left is of the order of 1 CO molecule/ porous cavity. However, a small "hard-to-remove" fraction is also observed on the nonporous Alon C, so that it seems likely that several factors are acting together.

It was shown that the strongly adsorbing sites are, on η-Al$_2$O$_3$, three times as many as on γ-Al$_2$O$_3$, while for the weakly adsorbing ones the ratio is definitely higher. In fact the second process only barely begins on the γ-phase, and the increased intensity of spectra in Fig. 3B from curve 5 to curve 1 is found to correspond to a very small uptake, as also shown by the shape of the adsorption isotherm in Fig. 5.

It is therefore suggested that the different activity exhibited by the two phases in some catalytic reactions (9) is probably to be sought in the population of the sites

responsible for the low frequency absorptions. The population of "strong" sites absorbing at 2238–44 cm^{-1} is not sufficiently different in the two phases to justify what is often observed in the catalytic work.

Moreover, the dehydration temperatures normally employed in catalytic studies (3, 13, 14) correspond to conditions in which the high frequency CO bands are not yet very abundant. However, the sites responsible for the high frequency CO species would seem to have some catalytic connections as well in that, for some reactions, the need of a nearby hydroxyl has sometimes been invoked (13, 15).

CONCLUSION

The interaction of carbon monoxide with pure well-characterized transition aluminas does not lead to any oxidation or disproportionation, as only a σ-coordination to surface cations is observed.

Very few such sites are involved; they reveal the existence of an exceptionally strong Lewis acidity of limited extent, following on the absence, in aluminum ions, of d-electrons and on the insulating nature of aluminas. Two families of CO adsorbing centers are brought into evidence, characterized by quite different bond strengths. Although no CO adsorption heats were previously determined for aluminas, a few other oxides have been studied (16, 17) that might be used for comparison. Disregarding transition metal oxides, whose adsorption heats are obviously high, it is found that the high energy CO species on alumina (14 kcal/mole) is comparable with the heats observed on ZnO, although in that case a CO oxidation is probably produced and the electronic properties are very different. The low energy species (2 kcal/ mole) is, on the contrary, comparable with a physical adsorption, though a dative coordination is still involved in the adsorption. In fact a plain physisorption is inconsistent with CO stretching frequencies so much higher than that of the gas (18,

[5] Note that the high sensitivity of spectral data brings into evidence even small amounts of all species, provided individual frequencies are different and extinction coefficients are of the same order of magnitude, while the formation of small quantities of low energy species together with higher amounts of strong species, as suggested by curve 7 of Fig. 3B, is bound to be unobserved in plots such as that of Fig. 6.

19), with inhibition by preadsorption of specific adsorbates, and with the gaseous nature of carbon monoxide at room temperature.

The same adsorbed species are found on all aluminas, only minor differences being observed in the CO stretching frequencies but greater ones in the adsorbed amounts. This clearly follows from the common coordinative nature of aluminum ions in all transition aluminas, among which only distribution differences are likely to be found. The structure itself seems not to play a primary role, as strict similarities are found between η- and θ-alumina, while γ-alumina behaves quite differently. It is therefore suggested that the CO adsorbing sites ought to be sought for in the cationic configuration whose population is known to be favored on η- and θ-alumina, i.e., in the tetrahedral coordination (*20, 21*). This assignment is confirmed by the lack of activity towards CO in α-alumina. Furthermore the big difference in catalytic activity between η- and γ-alumina would come from the different coordinative distribution in the two phases. In particular, of the two CO adsorbed species the low energy one exhibits a population ratio between η- and γ-Al_2O_3 comparable with the activity ratio reported by several authors and is thus suggested as corresponding to the family of catalytically active sites.

ACKNOWLEDGMENTS

REFERENCES

1. Borello, E., Della Gatta, G., Fubini, B., Morterra, C., and Venturello, G., *J. Catal.* **35**, 1 (1974).

2. Peri, J. B., *J. Phys. Chem.* **72**, 2917 (1968).

3. Saunders, P. C., and Hightower, J. W., *J. Phys. Chem.* **74**, 4232 (1970).

4. Parkyns, N. D., *J. Chem. Soc. A* 1910 (1967).

5. Little, L. H., and Amberg, C. H., *Canad. J. Chem.* **39**, 535 (1961).

6. O'Neil, C. E., and Yates, D. J. C., *J. Phys. Chem.* **65**, 901 (1961).

7. Borello, E., Cimino, A., Ghiotti, G., Lo Jacono, M., Schiavello, M., and Zecchina, A., *Discuss. Faraday Soc.* **52**, 149 (1971).

8. MacIver, D. S., Tobin, H. H., and Barth, R. T., *J. Catal.* **2**, 485 (1963).

9. MacIver, D. S., Wilmot, W. H., and Bridges, J. M., *J. Catal.* **3**, 502 (1964); and references therein.

10. Della Gatta, G., Fubini, B., and Venturello, G., *J. Chim. Phys.* **70**, 64 (1973).

11. Della Gatta, G., Fubini, B., and Venturello, G., *in* "Thermochimie," Vol. 201, p. 565. CNRS, Paris, 1972.

12. Borello, E., Garrone, E., Ghiotti, G., and Morterra, C., presented: Autumn Meet. Chem. Soc., Norwich, 1973.

13. Larson, Y. G., and Hall, W. K., *J. Phys. Chem.* **69**, 3080 (1965).

14. Rosynek, M. P., Smith, W. S., and Hightower, J. W., *J. Catal.* **23**, 204 (1971).

15. Van Cauwelaert, F. H., and Hall, W. K., *Trans. Faraday Soc.* **66**, 454 (1970).

16. Fripiat, J., Chaudisson, J., and Jelly, A., *in* "Chimie-Physique des Phénomènes de Surface," p. 113. Masson and Cie, Paris, 1971.

17. Thomas, J. M., and Thomas, W. J., *in* "Introduction to the Principles of Heterogeneous Catalysis," p. 367. Academic Press, New York, 1967.

18. Smith, A. W., and Quets, J. M., *J. Catal.* **4**, 163 (1965).

19. Zecchina, A., Ghiotti, G., Cerutti, L., and Morterra, C., *J. Chim. Phys.* **68**, 1479 (1971).

20. Pines, H., and Haag, W. O., *J. Amer. Chem. Soc.* **82**, 2471 (1960).

21. Lippens, B. C., and Steggerda, J. J., *in* "Physical and Chemical Aspects of Adsorbents and Catalysts" (B. G. Linsen, J. M. H. Fortuin, C. Okkerse and J. J. Steggerda, Eds.), p. 190. Academic Press, London, 1970.