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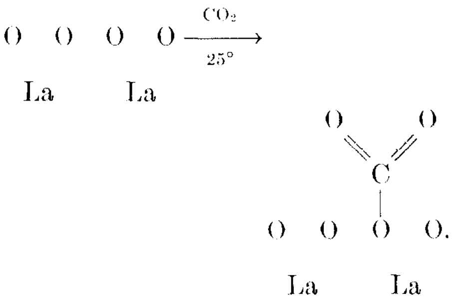
Infrared Study of Carbon Dioxide Adsorption on Lanthanum Sesquioxide and Trihydroxide

Although investigations of the catalytic properties of rare earth sesquioxides have multiplied in recent years (*1–5*), the primary modes of surface interactions on these materials remain largely undefined. Details of adsorption/desorption processes, for example, and of the natures of adsorbed species on Ln_2O_3 surfaces are sparse (*6*). As part of a continuing study of the fundamental catalytic and surface properties of basic lanthanide oxides, we have applied infrared and quantitative gravimetric techniques to to investigate the surface interactions of La_2O_3 and $La(OH)_3$ with carbon dioxide, and report pertinent results in the present communication.

$La(OH)_3$ and La_2O_3 were prepared using the "dehydration/rehydration" method described previously (*7*). Isothermal decomposition of the trihydroxide to the type A (hexagonal) sesquioxide occurs in two stages (passing through an oxyhydroxide, LaOOH, intermediate), and is complete within 10–12 hr at 300°C. No spectral evidence of either bulk or surface hydroxyls in the oxide remained above the latter temperature. BET-N_2 surface areas of La_2O_3 and $La(OH)_3$ following 16 hr evacuations at 800 and 100°C, respectively, were 7.5 and 18.5 m^2/g. Samples for infrared studies were fabricated from pressed discs of the hydroxide and had an optical density of 10 mg/cm^2 (dehydrated weight). Spectral resolution at <2000 cm^{-1} was better than 1.5 cm^{-1} in all cases. Descriptions of the infrared cell and electrobalance adsorption apparatus have been provided previously (*7*).

$CO_2 + La_2O_3$

Exposure of freshly calcined La_2O_3 to 50 Torr of dry CO_2 at 25°C caused the immediate appearance of infrared bands at 850 and 1060 cm^{-1} and a doublet with absorbance maxima at 1390 and 1500 cm^{-1} (Fig. 1) which attained 90% of their final intensities within 5 min. We ascribe these bands to the deformation, symmetric stretching, and antisymmetric stretching modes, respectively, of a unidentate carbonate species (*8*), formed by interaction of CO_2 molecules with basic oxide ions at the surface:



(1)

The relative breadth of the 1390–1500 cm^{-1} pair reflects the extent of heterogeneity of the surface O^{2-} ions. Quantitative adsorption measurements indicated that the level of surface coverage under these conditions was 7 to 8 CO_2 molecules/100 Å². For a typical (111) face of hexagonal La_2O_3, with $a = 3.94$ Å and $c = 6.13$ Å (*9*), this value corresponds to approximately 1 CO_2 molecule/surface O^{2-} ion. As expected, no evidence was observed for bicarbonate (HCO_3^-) species, due to the lack of surface hydroxyl groups on calcined La_2O_3, and the absence of bands in the region 1600–

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1800 cm^{-1} indicated that carboxylate (CO_2^-) formation also does not occur in this system.

The observed CO_2–La_2O_3 spectrum is in close agreement with that obtained by Filippova *et al.* (*10*) for CO_2 adsorption on type A Nd_2O_3, and, apart from the absence of O–H stretching bands due to crystalline water of hydration, is quite similar to the spectrum reported by Caro and co-workers (*11*) for bulk $La_2(CO_3)_3 \cdot 8H_2O$. The latter authors observed, in the region above 800 cm^{-1}, "non-OH" bands for this compound at 1460, 1360, 1075, and 850 cm^{-1} for ν_5, ν_1, ν_2, and ν_8, respectively, and attributed these to a unidentate coordinated CO_3 group. Rehydration with gaseous H_2O at 25°C of La_2O_3 contatining a carbonate surface layer occurred much more slowly (>72 hr for complete rehydration) than that of a "clean" La_2O_3 sample (2–3 hr). The relatively high concentration of surface CO_3^- structures evidently inhibits entry of H_2O molecules between the O^{2-} and $(LaO)_n^{n+}$ layers of the oxide, as normally occurs during the rehydration process (*12*). Intensities of the four CO_3^{2-} infrared bands did not decrease, however, even after quantitatively complete rehydration (discounting the unavailable surface layer of O^{2-} ions), indicating that the observed spectrum is that of a true surface carbonate species and is not due to bulk $La_2(CO_3)_3$ formation.

Evacuation for 6 hr at each of several temperatures up to 250°C (Fig. 1) caused a narrowing of the 1390–1500 cm^{-1} doub-

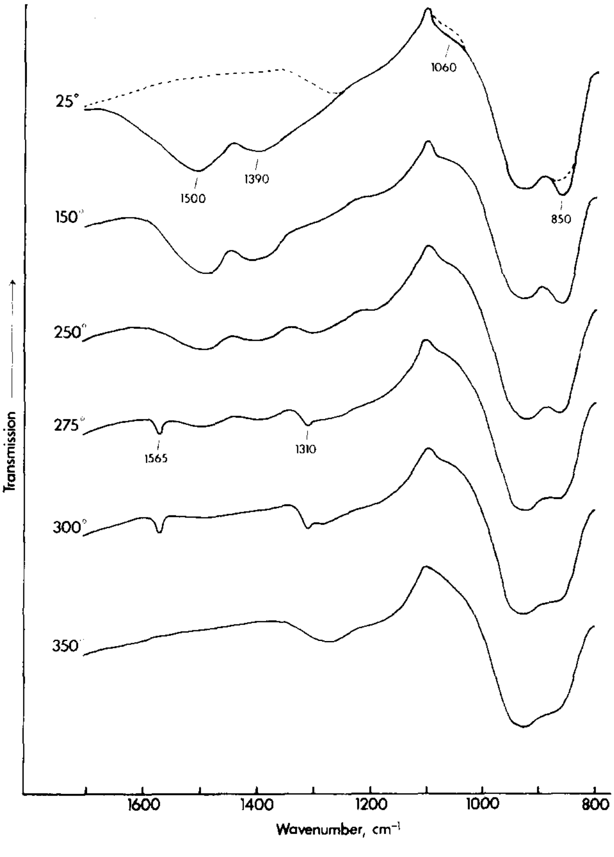


FIG. 1. Infrared spectra of CO_2 adsorbed on La_2O_3. La_2O_3 sample, calcined 16 hr *in vacuo* at 800°C [(– –) background spectrum], exposed to 60 Torr of dry CO_2 at 25°C for 1 hr, and then evacuated for 6 hr at each of the indicated temperatures (°C).

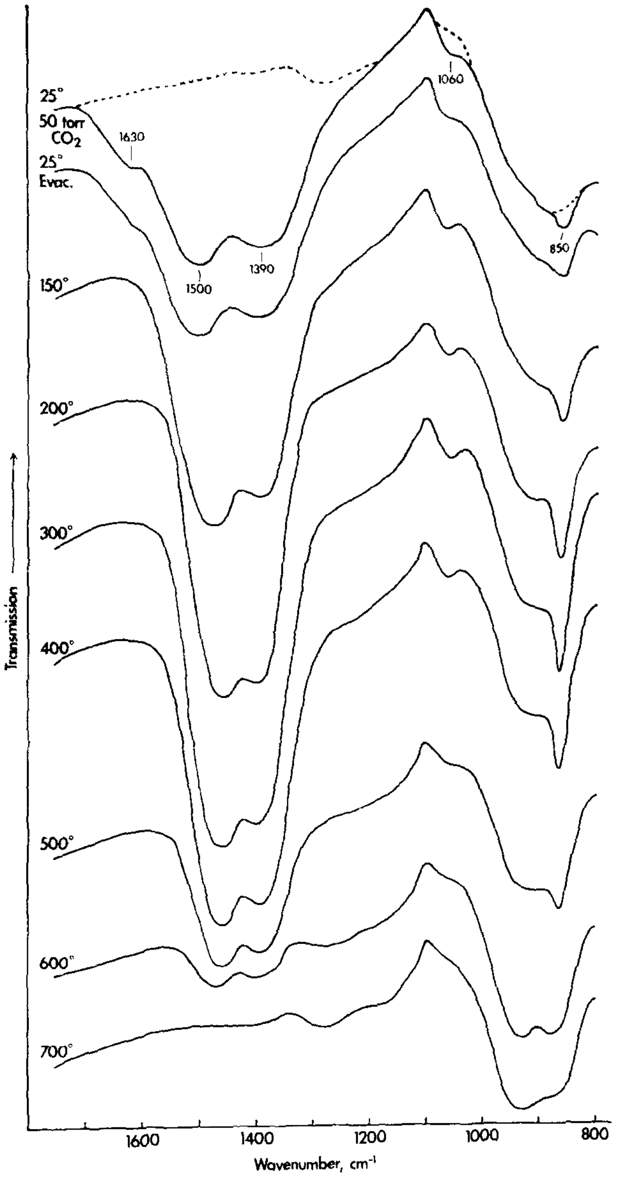
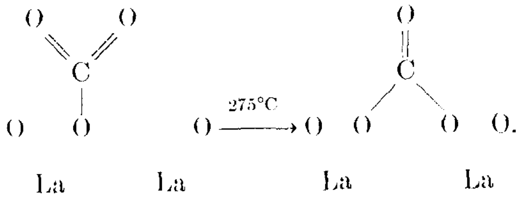


FIG. 2. Infrared spectra of CO_2 adsorbed on $La(OH)_3$. $La(OH)_3$ sample, calcined 16 hr *in vacuo* at 100°C [(- -) background spectrum], exposed to 50 Torr of dry CO_2 at 25°C for 1 hr, and then evacuated for 6 hr at each of the indicated temperatures (°C).

let and consequent shift of the apparent 1500 cm^{-1} band toward its true (lower) frequency, as well as a gradual decrease in intensity of all four CO_3^{2-} bands as CO_2 desorbed. Following evacuation at 275°C, weak bands appeared at 1310 and 1565 cm^{-1} which are due to bidentate carbonate entities (*8*) generated by rearrangement of unidentate structures as their surface population decreased:

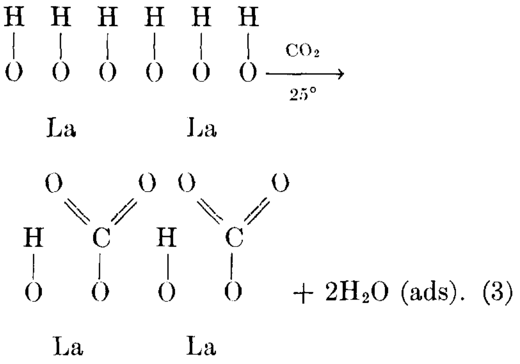


(2)

The surface coverage under these conditions was 1 to 2 CO_2 molecules/100 Å^2. Formation of such bidentate structures suggests the existence and accessibility of appropriate anion vacancies on the oxide surface. Spectral evidence for unidentate CO_3^{2-} species disappeared at 300°C and was followed by complete removal of the bidentate structures at ≥350°C.

$CO_2 + La(OH)_3$

Lanthanum trihydroxide contains at least two structurally dissimilar types of bulk hydroxide ions. The more weakly bound of these gives a relatively sharp infrared band at 3610 cm^{-1} and is preferentially removed during the first stage of $La(OH)_3$ dehydration (LaOOH formation) at 200°C (*7*). The other, hydrogen-bound, type is represented by a much broader infrared band with an absorbance maximum at 3590 cm^{-1} and is removed during LaOOH decomposition to the oxide at 300°C. Interaction of $La(OH)_3$ with CO_2 at 25°C causes proton displacement from and simultaneous condensation of surface OH^- ions of the second type, as shown by a marked decrease in intensity of the 3590 cm^{-1} band of $La(OH)_3$ following CO_2 adsorption (*7*):



(3)

Molecular water formed during this process remains physically adsorbed on the surface, as evidenced by a band that appears at 1630 cm^{-1} (Fig. 2), and is largely removed by brief evacuation at 25°C. The unidentate CO_3^{2-} species that result from reaction (3) are evidently identical to those obtained on La_2O_3 and give rise to the same four bands (850, 1060, 1390, and 1500 cm^{-1}) observed in Fig. 1. However, the extent of surface coverage (7 to 8 CO_2 molecules/100 Å^2) was virtually the same as that on the sesquioxide, the larger relative intensities of the bands in Fig. 2 compared to those in Fig. 1 being due to the higher surface area of the hydroxide.

Unlike the behavior of the CO_2–La_2O_3 system, however, evacuation at successively increasing temperatures, although accompanied by a narrowing of the 1390–1500 cm^{-1} doublet, caused a marked increase in the intensities of all four CO_3^{2-} bands at 150–200°C. Little further change occurred until ≥500°C, when all bands began to decrease, and evacuation at ≥700°C was required to remove all evidence of the carbonate species. The two stage of bulk hydroxide dehydration to the oxide, however, and consequent disappearance of OH^- bands at 3610 and 3590 cm^{-1}, still occurred at 200 and 300°C, respectively, and appeared to be virtually unaffected by the presence of the surface CO_3^{2-} layer. No evidence was observed in any of the spectra for the formation of bidentate carbonate species. At the high temperatures (600–700°C) required in this case to reduce the surface concentration of unidentate CO_3^{2-} to a sufficiently low level, the energetics of formation of the bidentate structures are evidently no longer favorable.

The apparently much greater stability of carbonate entities that result from CO_2 adsorption on $La(OH)_3$ compared to those formed on La_2O_3 implies a structural dissimilarity between the predominant surface species obtained in the two systems, and, moreover, one that persists during and after complete dehydration of the hydroxide. Rather than forming a simple unidentate CO_3^{2-} species, as occurs on La_2O_3, interaction of CO_2 with $La(OH)_3$ may, for example, generate a surface layer of lanthanum hydroxycarbonate, similar to the bulk compound obtained by decomposition of $La_2(CO_3)_3 \cdot 8H_2O$ (*13*):

$$La(OH)_3 + CO_2 \xrightarrow{25°C} (LaOH)CO_3 + H_2O. \quad (4)$$

CO_3^{2-} entities in the lamellar hydroxycarbonate sutructure are bridge-bonded between adjacent (LaOH) layers. Subsequent thermal treatment at 150–200°C effects a decomposition of $(LaOH)CO_3$ that accompanies the first stage of $La(OH)_3$ dehydration and forms the corresponding oxycarbonate species (*13*):

$$2(LaOH)CO_3 \xrightarrow{150\text{–}200°C} (LaO)_2CO_3 + CO_2 + H_2O. \quad (5)$$

The CO_3^{2-} groups in $(LaO)_2CO_3$, although apparently retaining their essential unidentate character, are bridged between $(LaO)_n^{n+}$ layers and would be expected to be more stable and difficult to remove than the corresponding species on an unmodified La_2O_3 surface:

$$(LaO)_2CO_3 \xrightarrow{600\text{–}700°C} La_2O_3 + CO_2. \quad (6)$$

The increasing spectral intensities observed in Fig. 2 at 150 and 200°C may be due to changes in extinction coefficients of the CO_3^{2-} vibrational modes that accompany reaction (5).

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REFERENCES

1. Tosun, G., and Rase, H. F., *Ind. Eng. Chem. Proc. Res. Develop.* **11**, 249 (1972).

2. Minachev, K. M., "Catalysis," p. 219. North-Holland, Amsterdam, 1973.

3. Hattori, H., Inoko, J., and Murakami, Y., *J. Catal.* **42**, 60 (1976).

4. Read, J. F., and Perkins, E. W., *J. Catal.* **42**, 443 (1976).

5. Khodakov, Y. S., Nesterov, V. K., and Minachev, K. M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, **9**, 2012 (1975).

6. Read, J. F., *Canad. J. Chem.* **50**, 490 (1972).

7. Rosynek, M. P. and Magnuson, D. T., *J. Catal.* **46**, 402 (1977).

8. Hair, M. L., "Infrared Spectroscopy in Surface Chemistry." Dekker, New York, 1967.

9. Westrum, E. F., *in* "Progress in the Science and Technology of the Rare Earths," Vol. 1, Pergamon, New York, 1964.

10. Filippova, A. A., Davydov, A. A., and Shchekochikin, Y. M., *Kinet. Katal.* **14**, 1333 (1973).

11. Caro, P. E., Sawyer, J. O., and Eyring, L., *Spectrochim. Acta* **28A**, 1167 (1972).

12. Bacquet, G., Bouysset, C., and Escribe, C., *J. Solid. State Chem.* **18**, 247 (1976).

13. Dexpert, H., Schiffmacher, G., and Caro, P. E., *J. Solid State Chem.* **15**, 301 (1975).

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