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Catalytic Properties of Thorium Oxide in the Oxidation of Carbon Monoxide

I. Calorimetric Confirmations of Adsorption and Catalysis Processes

MICHÈLE BREYSSE, BERNARD CLAUDEL,
MARCEL PRETTRE, AND JEAN VERON

*Institut de Recherches sur la Catalyse, 39, Boulevard du 11 Novembre 1918,
69-VILLEURBANNE, France*

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Adsorptive and catalytic properties of thoria have been reexamined in the light of some new microcalorimetric experiments. It has been shown that oxygen can be weakly adsorbed under a neutral form, that chemisorption heat of carbon monoxide on *n*-type thoria linearly decreases with the logarithm of the adsorbed volume, and that carbon dioxide is chemisorbed under two forms, one of which is an intermediary in carbon monoxide oxidation, the other one being an inhibitor of this catalysis.

INTRODUCTION

Catalytic properties of thoria have long been explored in the oxidation, dehydrogenation, and degradation reactions, mainly of organic chemistry (*1*). The present work will be concerned with its catalytic role in the oxidation of carbon monoxide, which was chosen as a test reaction owing to its relative simplicity and to the ease with which its kinetics can be followed.

We have already reported elsewhere (*2–4*) the mechanism we found for this catalysis, on the basis of kinetic experiments connected with measurements of electrical conductivity. Our purpose is now to present some additional evidence, mainly founded upon calorimetric results, for the different steps involved in this catalysis.

EXPERIMENTAL METHODS

Preparation of the Samples

Thoria has been prepared either from thorium nitrate (*2, 3*), according to the overall reaction:

$$Th(NO_3)_4 \cdot 5\,H_2O \rightarrow ThO_2 + 4\,NO_2 + O_2 + 5\,H_2O$$

or from thorium oxalate (*4*), according to the overall reaction:

$$Th(C_2O_4)_2 \cdot 6\,H_2O \rightarrow ThO_2 + 2\,CO + 2\,CO_2 + 6\,H_2O.$$

We shall designate in the sequel by ThO_2"*N*" and ThO_2"*O*" the thoria samples descended from nitrate or oxalate, respectively. Their surface areas, as measured by the BET method, are, respectively, equal to 70 ± 5 m²/g and 30 ± 2 m²/g. In either case, the samples, when prepared in an apparatus other than this one in which they are used as catalysts, are first heated at 500°C in air, in order to burn the hydrocarbons they quite readily adsorb. Then, in all cases, they are heated again at 500°C for 20 hr either under vacuum or under an argon flow. After this treatment, they will be designated by "*A*" (e.g., ThO_2"*NA*" or ThO_2"*OA*").

When they are subsequently heated at 500°C for 5 hr under 200 Torr of hydrogen, and degassed at the same temperature for 16 hr under 10^{-5} Torr (or under an argon flow), they will be called solids "*B*" (e.g., ThO_2"*NB*" or ThO_2"*OB*").

When the sample is named only by ThO_2"*A*" or ThO_2"*B*", it means that the results are the same whichever the starting salt may be.

Calorimetric Determinations

Differential adsorption heats have been measured in a microcalorimeter (*5*) to which a volumetric set-up (*6*) has been adapted. Some of the measurements (for example CO adsorption) have been performed in a Calvet microcalorimeter. The introduction of small amounts of gas (included between 0.02 and 0.1 cm^3/STP) is repeated until the final pressure is about 2 Torr. The evaluated error on adsorption heat is close to 5%. The volumetric apparatus allows the determination of adsorption isotherms which will be reported in the following sections. In the case of CO adsorption, some results are expressed by the fraction of surface covered, θ, assuming that the area covered by a CO molecule is 16 Å^2.

EXPERIMENTAL RESULTS

Adsorption of the Gases

Oxygen. Previous study (*4*) has shown that thoria "*A*" contains strongly chemisorbed oxygen which can, wholly or partly, be removed by a reducing treatment: when submitted to treatment "*B*", ThO_2"*NA*" loses an average of 0.440 mg/g (7.26×10^{-3} g-atom O per mole ThO_2) and ThO_2"*OA*" an average of 0.775 mg/g (12.8×10^{-3} g-atom O per mole ThO_2) (Fig. 1). Such losses are far too large to be ascribed to a bulk nonstoichiometry (which cannot exceed 4×10^{-5} g-atom O per mole (*7*)), and hence were attributed to strongly chemisorbed oxygen.

Thoria "*B*" can readsorb an amount of oxygen close to the amount strongly chemisorbed on thoria "*A*", but it has been concluded from gravimetric and conductimetric experiments that this adsorption of oxygen on thoria "*B*" occurs through a weak bond; although there is indeed a weight increase due to the adsorption, there is no concomitant change in electrical conductivity. Calorimetry confirms that there is no heat evolved after the first minute (what happens during the first minute is related to the equilibration of the surface which has undergone treatment "*B*").

Carbon monoxide. Thoria "*A*" has strongly chemisorbed oxygen on its surface; this oxygen is likely to react with carbon monoxide when the latter is admitted onto the solid and the occurrence of this reduction could have been checked (*4*).

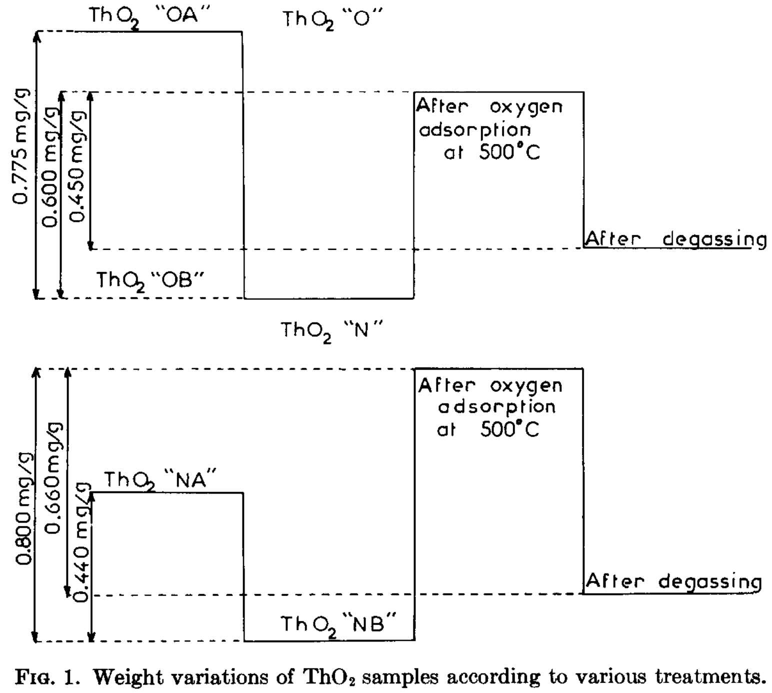


FIG. 1. Weight variations of ThO_2 samples according to various treatments.

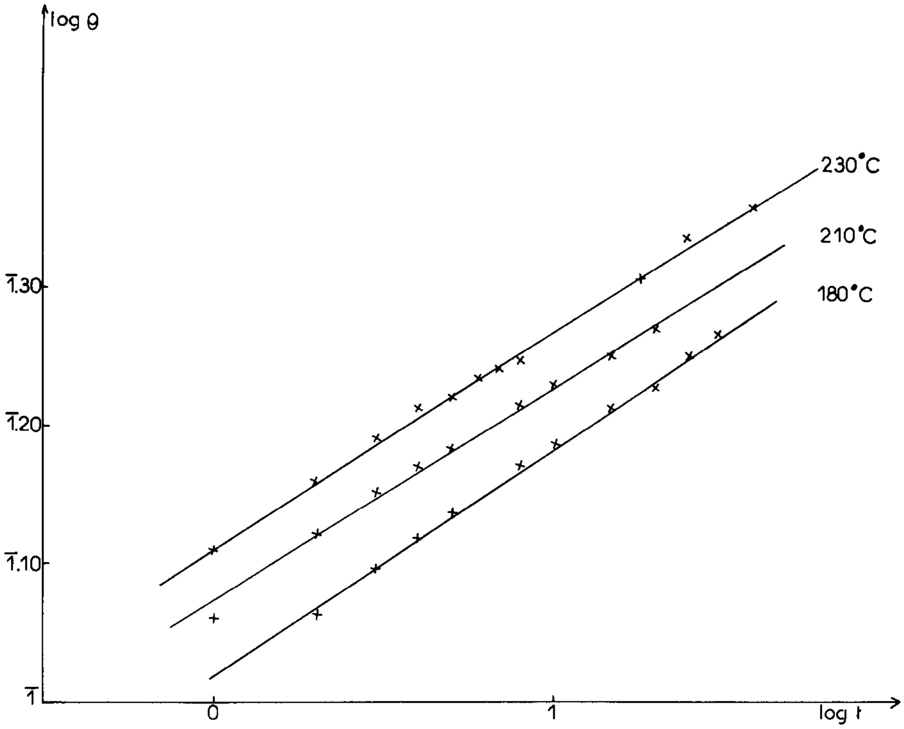


FIG. 2. Linear transforms of adsorption kinetics of CO on thoria "*B*," in the representation log θ vs log t (time t is expressed in min).

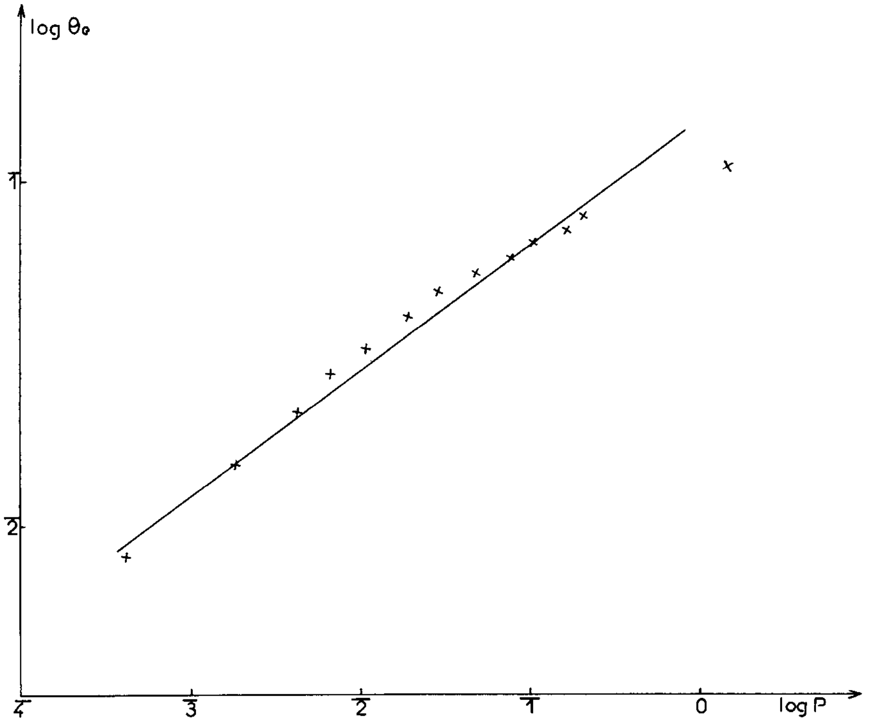


FIG. 3. Isotherm of CO adsorption on ThO_2"*B*," at 200°C, according to the Freundlich law.

Therefore, chemisorption of CO can be studied in its pure state on thoria "*B*", because there is in this case no interference with previously adsorbed oxygen. And then it is found that the adsorption is completely reversible; all the chemisorbed amount can be desorbed as CO by evacuation at the same temperature. A second adsorption yields the same value for the heat evolved and the same isotherm.

Satisfying straight lines are obtained when the adsorption kinetics are drawn in the representation $\log \theta$ vs $\log t$ (Fig. 2), thus showing that:

$$\log \theta = (1/m) \log t \tag{1}$$

with a value of m close to 6 at each working temperature.

Likewise, when the isotherm is represented by plotting $\log \theta_e$ as a function of $\log P$, a good straight line is gotten (Fig. 3), pointing out the apparent validity of Freundlich's law:

$$\theta_e = P^{1/n}, \tag{2}$$

with $n = 3$ in our case.

Microcalorimetry shows that the chemisorption heat is a linear function not of the adsorbed volume, but of its logarithm (Fig. 4).

Carbon dioxide. The differential heat of adsorption of carbon dioxide has been measured at 200°C. It decreases from the initial value of 42 kcal/mole (Fig. 5). Adsorption isotherm drawn according to Temkin's law exhibits two nearly linear branches (Fig. 6). The break can be interpreted by two adsorption modes; the first, which is the stronger one, includes the first ten amounts of CO_2 on Fig. 5. The second corresponds to an initial heat of 27 kcal/mole, and the volume of CO_2 adsorbed according to this latter mode can be reversibly removed and added (second adsorption of Figs. 5 and 6).

Origin, "*N*" or "*O*", and previous treatments, "*A*" or "*B*" of thoria do not influence the features of CO_2 chemisorption. But in each case, CO and CO_2 compete with each other on the same adsorption sites; as a matter of fact, previous adsorption of a definite volume of CO_2 reduces accordingly the volume of CO subsequently chemisorbed.

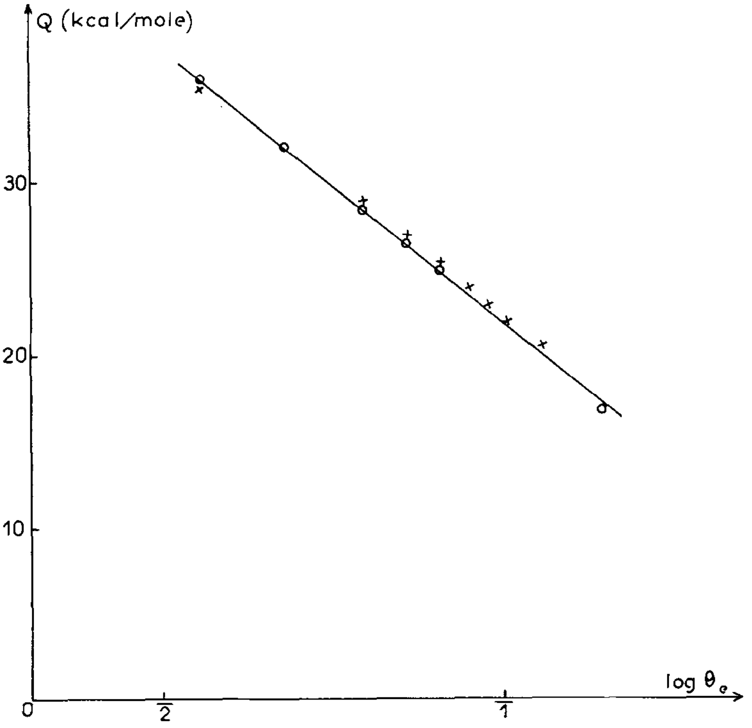


FIG. 4. Variation of the chemisorption heat of CO on ThO_2"*B*" as a function of $\log \theta$, at 200°C.

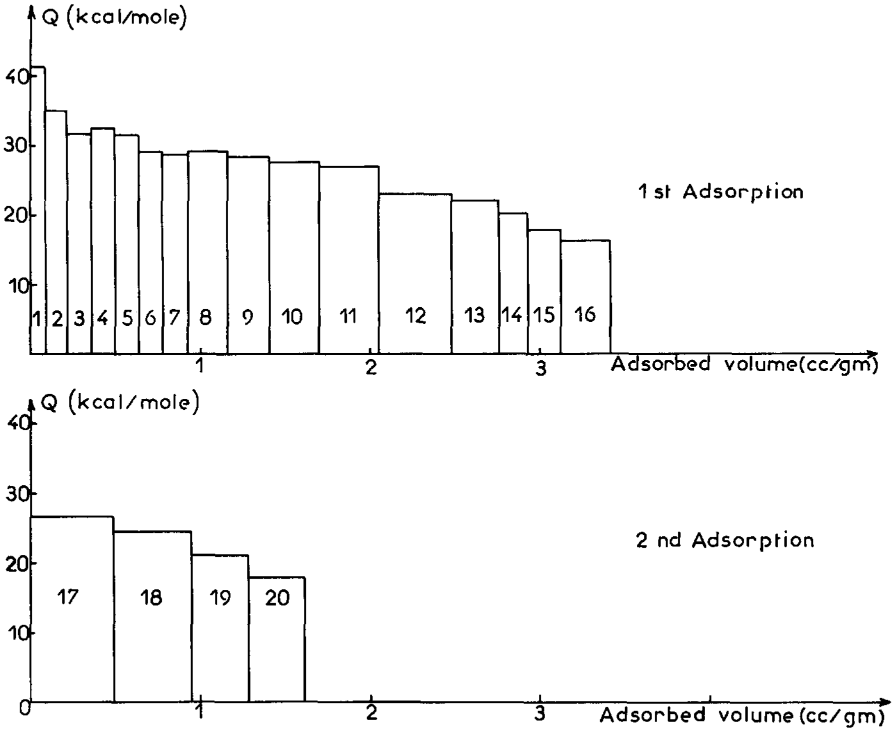


FIG. 5. Heat evolved during the adsorption of CO_2 on ThO_2"*NA*" at 200°C.

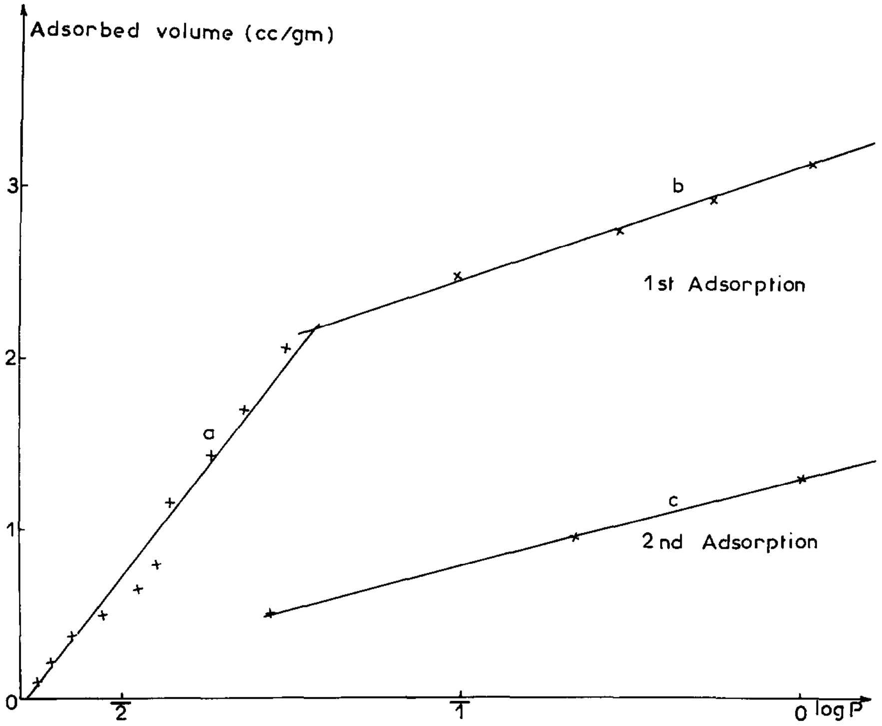


FIG. 6. Linear transform of adsorption isotherm of CO_2 on ThO_2"*NA*".

Inhibiting Role of Carbon Dioxide during the Catalysis of Carbon Monoxide Oxidation

Previous kinetic studies of thoria "*NA*" (*2, 3*) and of thoria "*OB*" (*4*) have shown that carbon dioxide was an inhibitor of the oxidation of carbon monoxide. Microcalorimetry confirms that this inhibiting action occurs even when a liquid-nitrogen trap is used, but not located in the immediate neighborhood of the catalyst. As a matter of fact, if CO_2 did not remain adsorbed at all, the heat evolved by the reaction would be the same as that of the homogeneous reaction, i.e., 68 kcal/mole of CO. If, on the contrary, CO_2 remained completely chemisorbed, the maximum reaction heat would be 110 kcal/mole, the maximum heat evolved by the chemisorption of one mole of CO_2 being equal to 42 kcal/mole (Fig. 5). And indeed, the reaction heat decreases from 88 kcal/mole down to a value very close to 68 kcal/mole for the fourth addition (Fig. 7), after which it remains practically constant. Thus a fraction (estimated near to 0.9 cm^3/g of catalyst in the present case) of CO_2 formed during the first three additions remains chemisorbed, all the CO_2 formed after the fourth one being desorbed.

When CO_2 is previously adsorbed, and the reaction heat measured, it is found to be equal to 68 kcal/mole from the very start (Fig. 7).

This experimental study proves that the fraction of surface covered by CO_2 during catalysis at the steady state essentially depends on the CO_2 pressure *in the immediate neighborhood* of the catalyst, and therefore on the location of the trap and on the design of the apparatus.

DISCUSSION

Adsorption of the Gases

Oxygen. The heat evolved during oxygen adsorption on thoria "*B*" remains nil although gravimetry shows that there is a weight increase. This constitutes another proof of the weak-bond character of this adsorption, the possibility of which has

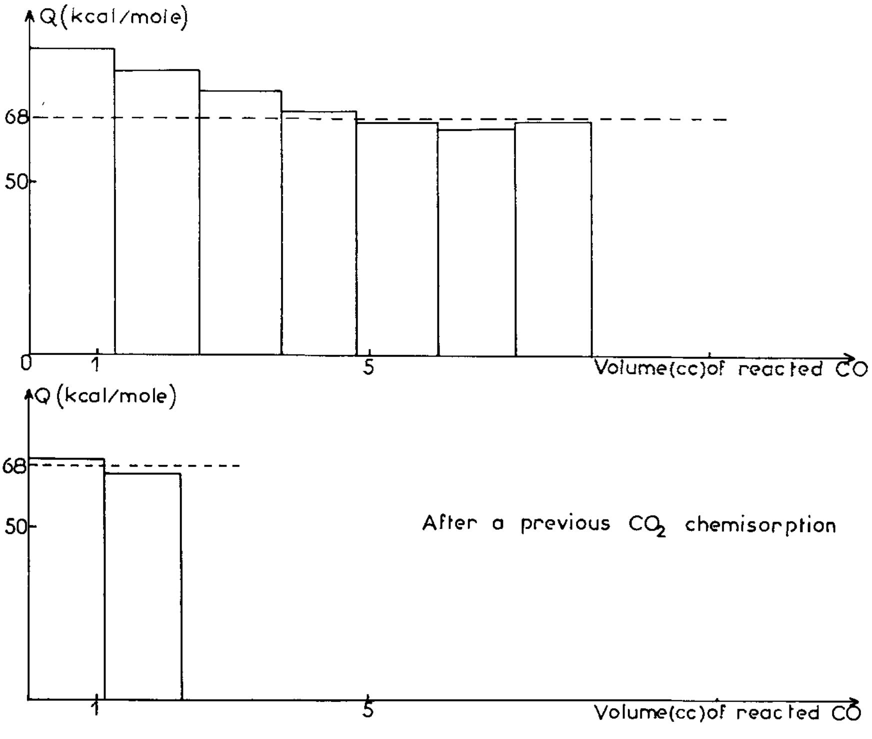


FIG. 7. Heat evolved during the reaction catalyzed by ThO_2"*N*" (stoichiometric mixture introduced by small amounts at 250°C).

been predicted a long time ago (*8*), and since, found for other adsorbents, e.g., ZnO (*9*).

It is noteworthy that, again in accordance with theoretical predictions (*10–12*), the passage from the weak adsorption to the strong one can be observed (*4*) if the adsorbent is allowed to remain in the presence of oxygen for about 20 hr.

The physical nature of the neutral and charged species involved is still a pendent question.

Carbon monoxide. The striking feature of carbon monoxide adsorption on thoria "*B*" is the logarithmic dependence of adsorption heat as a function of the adsorbed volume, connected with the validity of Freundlich's law.

This can be related to earlier work (*13*) devoted to the change of work function, $\Delta\varphi$, of semiconductors with the fraction, θ, of surface covered. It has indeed been observed that when an accumulation space charge region is created during adsorption, which is just the case of CO (donor) adsorbed on thoria "*B*", a *n*-type semiconductor (*4*), $\Delta\varphi$ varies linearly with log θ. This variation has been theoretically derived from a charge transfer model of adsorption (*14*). If we admit that the surface energy level of adsorbed CO species does not change during adsorption, then the heat of adsorption Q varies as $\Delta\varphi$ does (*15*), and so the experimentally observed variation of Q is justified.

It is worth recalling that i.r. spectroscopy shows that the CO chemisorption sites are oxygen atoms, and that superficial carboxylates are then formed (*16*, *17*).

Carbon dioxide. Microcalorimetry proves that CO_2 can be adsorbed in two different ways, and this is consistent with earlier works: Pitt (*18*) had already concluded from a thorough study of CO_2 adsorption on thoria within a temperature range 100–500°C that two types of adsorption occur. The first appears only at temperatures below 200°C and corresponds to an entropy decrease of —44 cal deg^{-1} mole^{-1}. Pitt considers this form of adsorbed carbon dioxide to have no degree of freedom of translation and of bidimensional rotation. At higher temperatures, a second type of adsorption is observed, which corresponds to an entropy decrease of —7 cal deg^{-1} mole^{-1} only. Pitt assumes that this relatively mobile species is formed by a bond between CO_2 and a superficial oxygen atom.

The recording of i.r. spectra of chemisorbed CO_2 confirms the existence of two types of adsorption (*16*, *17*). Formation of the absorption bands is observed already at room temperature, and these bands correspond to two species, bidentate and monodentate carbonates, (Fig. 8) the stability of which is completely different; the bidentate carbonate is partially removed by a mere evacuation at room temperature, and the corresponding bands completely disappear at 180°C. The monodentate carbonate is much more stable, being eliminated by heating *in vacuo* only at 500°C.

If we compare these previous data with our present calorimetric results, we can conclude that the stronger adsorption mode which corresponds to the first ten additions of CO_2 (Fig. 5) is to be referred to the monodentate carbonate, and the weaker one to the bidentate.

The small change of electrical conductivity (*2*, *4*) during CO_2 chemisorption corresponds to the acceptor character of this species. It must be pointed out, however, that these conductivity measurements have been made in the simultaneous presence of the two forms of adsorbed CO_2. If the strongly chemisorbed monodentate is likely

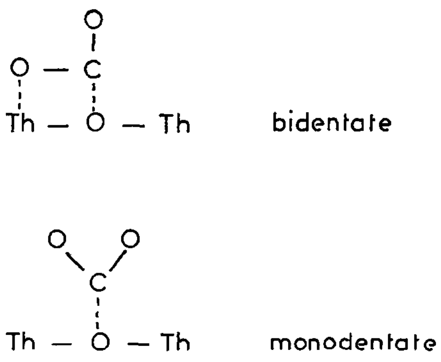


FIG. 8. Bidentate and monodentate forms of CO_2 adsorbed on thoria. (- - - designates a chemisorption bond.)

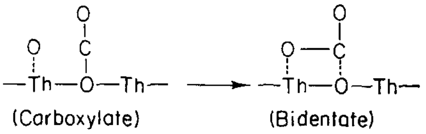
to be negatively ionized, the polarization of the bidentate form, if any, is unknown.

Inhibiting Role of Carbon Dioxide

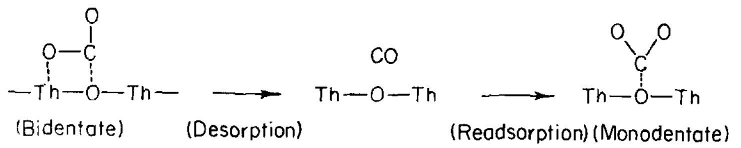
Present study confirms earlier data according to which carbon dioxide inhibits carbon monoxide oxidation on thoria, because both species compete with each other on the same adsorption sites. Infrared spectrophotometry detects the action of oxygen on previously chemisorbed CO above 225°C. In the absence of a liquid-nitrogen trap, the characteristic bands of the bidentate carbonate and of the monodentate are observed. Simultaneously, the absorptions due to the carboxylate species begin to vanish.

In the presence of a liquid-nitrogen trap located in the reactor loop very close to the catalytic bed, the diminishing, then the vanishing of the carboxylate band is observed without the carbonate bands becoming visible.

These spectral modifications give a clue to what happens during catalysis. Carbon monoxide chemisorbed in the form of a carboxylate species reacts upon chemisorbed oxygen to yield a bidentate, weakly fixed carbonate:



As a matter of fact, the direct passage from the carboxylate to the monodentate species is unlikely, because it involves the simultaneous rupture and formation of chemical bonds, and we assume that the observed monodentate carbonate is formed after a desorption of CO_2 followed by its further readsorption:



This process seems very likely on a porous catalyst, in the absence of, or far from, a condensation trap.

CONCLUSION

Joined with already used techniques, microcalorimetry throws some light on the behavior of adsorbed species on the thoria surface, behavior which must be taken into account in any further discussion of the catalytic mechanism in which they are involved:

1. Oxygen can be adsorbed in a weak and neutral form, which can be transformed into strongly adsorbed, charged species.
2. When carbon monoxide is adsorbed on *n*-type thoria, a Freundlich-type isotherm is obeyed, the chemisorption heat decreasing as the logarithm of the adsorbed volume.
3. Carbon dioxide exists at the surface under two different forms. Bidentate carbonate is formed first during catalysis, but is not the inhibiting agent, since, being weakly chemisorbed at temperatures where catalysis occurs, it is immediately desorbed. But gaseous CO_2 thus formed can be readsorbed under the form of a monodentate carbonate, which is the true inhibitor.

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