

Catalytic Properties of Non-Stoichiometric Uranium-Thorium Mixed Oxides in Carbon Monoxide Oxidation

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Non-stoichiometric uranium-thorium mixed oxides, of general formula $U_xTh_{1-x}O_{2+y}$, have an important catalytic activity in carbon monoxide oxidation between 250 and 350°C. Kinetic study of the reaction is consistent with a mechanism based on oxidation-reduction of the catalysts surface. A detailed reaction pattern is proposed and discussed, where oxygen interstitial atoms play the essential role.

INTRODUCTION

Statistical substitution of Th^{4+} cations by U^{4+} in the cubic face-centered lattice of thoria is feasible at all contents when substituted uranium remains quadrivalent (1). But solid solutions constituted in this way may oxidize (2) by oxygen inclusion in the central interstitial sites of the fluorite-type cell (3) (1/2, 1/2, 1/2 positions). Simultaneously, some uranium cations take V or VI oxidation states. Thus are obtained non-stoichiometric solid solutions of general formula $U_xTh_{1-x}O_{2+y}$, in the cation sublattice of which U^{4+} ions of variable valence are diluted in a matrix of Th^{4+} ions of fixed valence; the solid solutions exhibit some of the widest ranges of stoichiometry in a single phase known in oxide chemistry, and show a remarkable structural stability (4).

Existence of oxygen interstitial ions, noted O_{Δ}^{-} , confers physico-chemical (5) and adsorbant (6, 7) (towards CO, O_2 and CO_2 gases) properties to mixed oxides different from that of pure thoria (8). We indicated previously (6, 7) that these ions participate directly in the catalysed reaction mechanism, which develops by successive surface oxidations and reductions. The rate-determining elementary step of this process is probably reduction by carbon monoxide.

The present work is concerned with the

kinetic study of carbon monoxide oxidation; its objective is to confirm the previously proposed mechanism. After having disclosed the experimental methods we have been using, we shall report our results which will be discussed at the end of the paper.

EXPERIMENTAL

Materials

Purity of the original materials (uranyl and thorium nitrates) and reactants used for mixed oxalates preparation has been controlled by emission spectroscopy (5). Purity of gaseous reactants, supplied by Air Liquide Company, has been checked by mass spectrometry (5).

^{18}O -enriched oxygen which has been used for isotopic labelling studies was provided by Miles Laboratories (Research Products Department, Elkhart, Indiana) in 100-cm³ cylindrical borosilicate glass bulbs, under atmospheric pressure.

Samples Preparation

Mixed oxides $U_xTh_{1-x}O_{2+y}$ are obtained by thermal decomposition in air at 500°C for 24 hr of the corresponding dihydrated mixed oxalates $U_xTh_{1-x}(C_2O_4)_2 \cdot 2H_2O$. These salts are themselves prepared by coprecipitation of uranium IV and thorium

nitrate mixtures in oxalic acid under rigorously controlled conditions (9). Chemical composition of the phases gotten from calcination is determined by chemical analysis following procedures described by Bressat (10). X-ray diffraction experiments show that the oxides are single-phase and study with an electron probe micro-analyser proves that the cation molal fraction on the surface is close to the nominal one (5).

Kinetic Study of the Catalytic Reaction

The apparatus is classical for investigation of a reaction kinetics by the quasi-static method, in which variations of the total pressure are measured in a constant volume (11). This set has already been described by Veron (12). The reactor consists of a pyrex tube placed in a vertical furnace; the catalyst is uniformly spread in thin layers on a many-plates boat in order to minimize heat or matter diffusion phenomena.

The reaction is carried out between 250 and 350°C with initial reactants pressures lower than 350 Torr. The carbon dioxide pressure is maintained below 10^{-8} Torr by use of a liquid nitrogen trap, except when influence of the reaction product on kinetics is investigated. We have used in every experiment a same amount of catalyst (1.5 g) which corresponds to a total area varying from 30 to 35 m² according to the catalyst. Catalytic activities are related to the same active surface area, that is, 35 m².

Preliminary Treatment of the Samples

We have shown (5) that the amount of interstitial oxygen ions existing in the fluorite-type crystalline structure of mixed oxides tightly depends on the sample previous treatment. We apply to our solids, before every kinetical experiment, the following thermal procedure:

1. Heating in air at 400°C for 4 hr.

2. Desorption under 10^{-6} Torr vacuum at 450°C for 24 hr, which leads to partial elimination of interstitial oxygen. Table 1 gives results of *in situ* chemical analyses of various oxides.

These solids shall be used for kinetic study of the catalytic reaction.

TABLE 1
RESULTS OF CHEMICAL ANALYSES OF PREPARED MIXED OXIDES

Nomenclature	x	y Before pretreatment	y After pretreatment
Solid A	0.0112	0.0071	0.0060
Solid B	0.028	0.019	0.016
Solid C	0.052	0.036	0.032
Solid D	0.065	0.047	0.042
Solid E	0.094	0.071	0.062
Solid F	0.192	0.151	0.133

RESULTS

Table 2 indicates employed notations along this paper.

The same notations, bearing 0 index (p_0, θ_0) will be relative to initial time.

We operate first in the presence of the liquid nitrogen trap and we suppose that the reaction rate is given by the following relationship:

$$v = -\frac{dp}{dt} = kp^\alpha p'^\beta \quad (1)$$

the integrated form of which is, for excess oxygen mixtures:

$$p_0^{1-\alpha} - p^{1-\alpha} = (1-\alpha)k't \quad (2)$$

with $k' = k(p'_0)^\beta$

and for CO excess mixtures:

$$p'_0^{1-\beta} - p'^{1-\beta} = \frac{1-\beta}{2} k''t \quad (3)$$

with $k'' = k(p_0)^\alpha$

1. Order with Respect to Carbon Monoxide

The initial order α_0 . It has been determined for the reaction catalyzed by solids

TABLE 2
EMPLOYED NOTATIONS

	Gas		
	Carbon monoxide	Oxygen	Carbon dioxide
Partial pressures	p	p'	p''
Fractions of surface covered	θ	—	—
Partial orders	α	β	—

A and C containing various initial concentrations in interstitial oxygen. Initial oxygen pressure p'_0 ($p'_0 = 138$ Torr) being kept constant, carbon monoxide initial pressures p_0 are allowed to vary. For these two samples, α_0 is close to 0.75 at 300°C.

The order α during the reaction. This has been determined in the following way: Oxygen pressure p' is kept fixed at the value corresponding to the vapor pressure at liquid nitrogen temperature ($p' = 160$ Torr). α is represented by the slope of the straight lines: $\log(-dp/dt) = f(\log p)$. Figure 1 shows that this order does not vary with chemical composition of the oxides at 300°C and approaches 0.75.

The integration method (expression 2) leads to the same result; moreover, it permits one to observe that α is not temperature dependent in the considered temperature range for a particular oxide (oxide C, Fig. 2).

In situ chemical analyses of mixed oxides during the catalysis step reveal that, in case of such excess oxygen gaseous mixtures,

solids keep a stable oxidation state until the end of the reaction (solid C: curve ① Fig. 3).

2. Order with Respect to Oxygen

The initial order β_0 . This has been determined in the same way as for carbon monoxide, by maintaining p_0 constant and equal to 210 Torr and by varying p'_0 beyond 15 Torr. In presence of solids A and C at 300°C, β_0 is very low and cannot be distinguished from zero.

The order β during the reaction. It must be measured using gaseous mixtures containing a great excess of carbon monoxide, so that pressure p could be accepted constant along the reaction. But, following the time dependence of interstitial oxygen content in catalyst C (submitted at 300°C under 245 Torr initial pressure to a mixture of composition $6\text{CO} + \text{O}_2$), we observe (Fig. 3, curve ②) a very fast initial re-oxidation as quickly as the gaseous mixture is introduced. After a flat of about 10 min, a reduction reaction occurs up to a maxi-

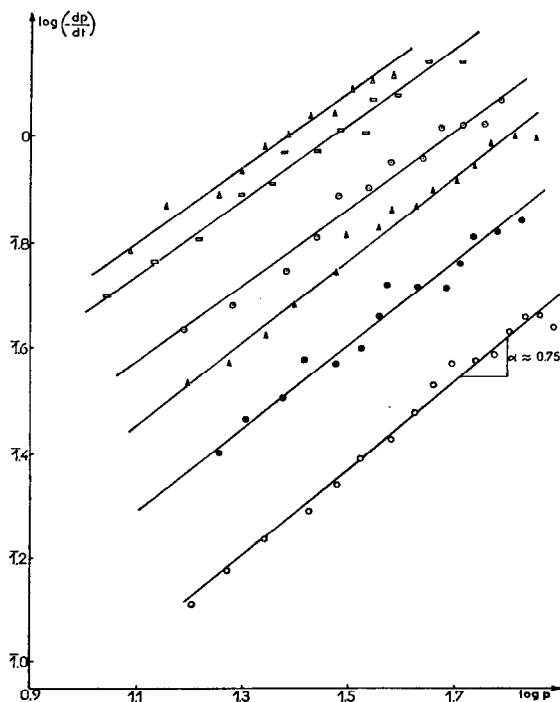


Fig. 1. α partial order determination for various oxides at 300°C — $p_0 \approx 80$ Torr. (○) solid A; (●) solid B; (▲) solid C; (◻) solid E; (△) solid F.

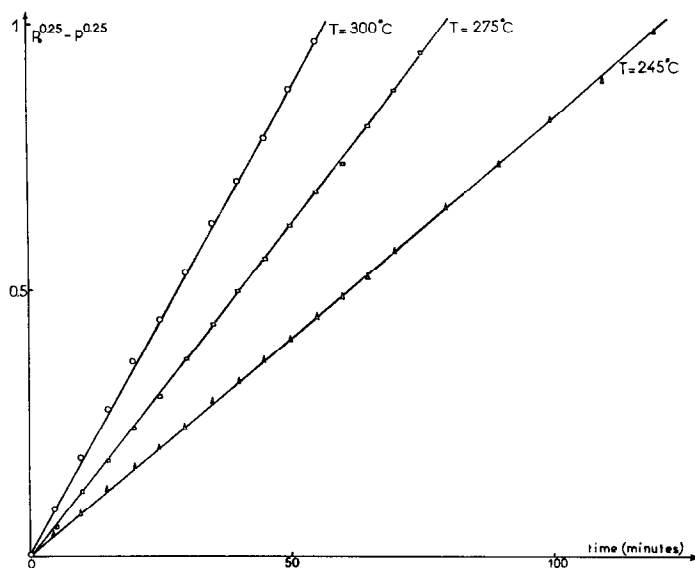


FIG. 2. Linear-transformed kinetic curves according to the integration method at various temperatures on oxide C.

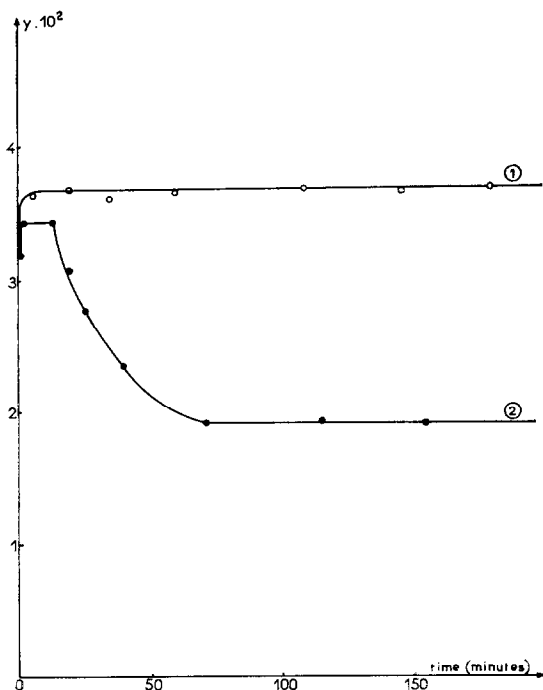


FIG. 3. Chemical composition change (non-stoichiometry y) of catalyst C versus time: Curve ①: oxide C submitted to an excess oxygen mixture ($CO + 2O_2$) under 210 Torr initial pressure at $300^\circ C$; curve ②: oxide C submitted to an excess CO mixture ($6CO + O_2$) under 245 Torr initial pressure at $300^\circ C$.

imum reduction state reached after about 70 min. The existence of this reduction phenomenon is directly confirmed by color change of the solid (yellow or brown to white) during catalysis as soon as oxygen pressure p' becomes lower than about 15 Torr: this color change is a sign of loss of the surface in interstitial oxygen ions.

For a particular catalyst (oxide C), the reaction rate: $v = -dp/dt$ is a function of pressure p' as indicated on Fig. 4. Straight lines are obtained by plotting $1/v$ (in $\text{Torr}^{-1} \times \text{min}$) versus $p'^{-1/2}$, but these straight lines present, for every temperature, an abrupt increase in the slope which corresponds to a pressure $p' = p'_s \approx 15$ Torr (temperature dependent).

These observations on the catalytic behavior of oxide C are valid for the whole range of mixed oxides A to F, but critical pressure p'_s corresponding to the slope change of straight lines on Fig. 4 depends on the solid and on the CO pressure and temperature.

3. Overall Order

Starting from the stoichiometric mixture under an initial pressure of 210 Torr at $300^\circ C$, we found that the overall order $\alpha + \beta$ is constant from one oxide to another

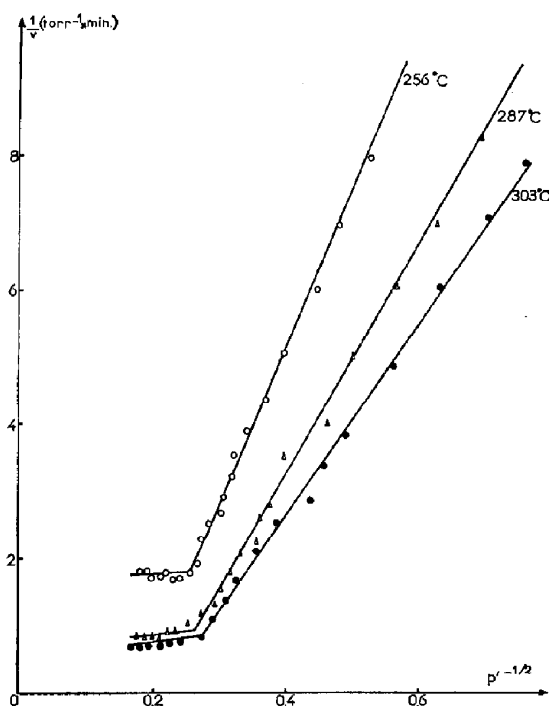


FIG. 4. Plot of $1/v$ versus $p'^{-1/2}$ at various temperatures (catalyst C). Mixture composition: $6\text{CO} + \text{O}_2$. Initial pressure: 245 Torr.

(Fig. 5) at every temperature in the chosen range and is equal to 0.75 (Fig. 6), that is the same value as the partial order α measured by employing an excess oxygen gaseous mixture.

This equality suggests that β is almost zero when mixtures containing a high enough oxygen pressure are used.

In the interpretation of our results, it will be convenient to distinguish:

1. Catalyses with gaseous mixtures at the contact of which oxides keep a constant oxidation state all along the reaction (after an initial setting in equilibrium).

2. Catalyses with excess CO mixtures at the contact of which oxides undergo a continuous chemical composition change.

4. Catalysis Activation Energies

The apparent activation energy of carbon monoxide oxidation can be calculated from the Arrhenius expression for specific rate:

$$k = k_0 e^{-E/RT} \quad (4)$$

Specific rate k has been determined on solids A to F at various temperatures and

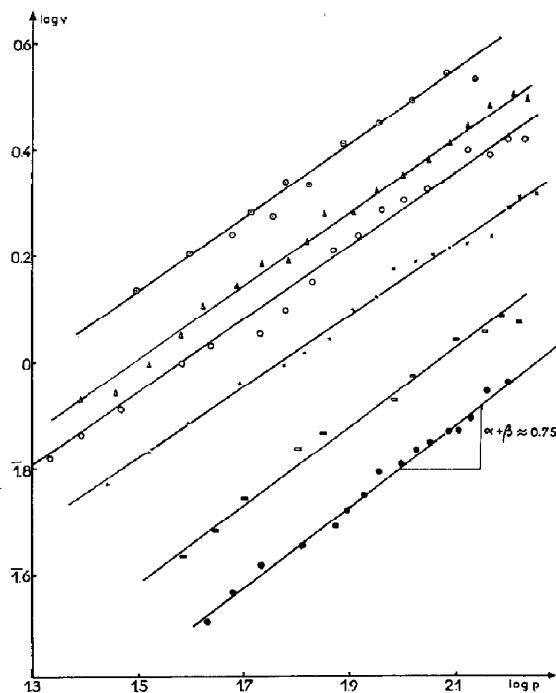


FIG. 5. $\alpha + \beta$ overall order determination for various oxides at 300°C . (●) solid A; (□) solid B; (×) solid C; (○) solid D; (△) solid E; (⊙) solid F.

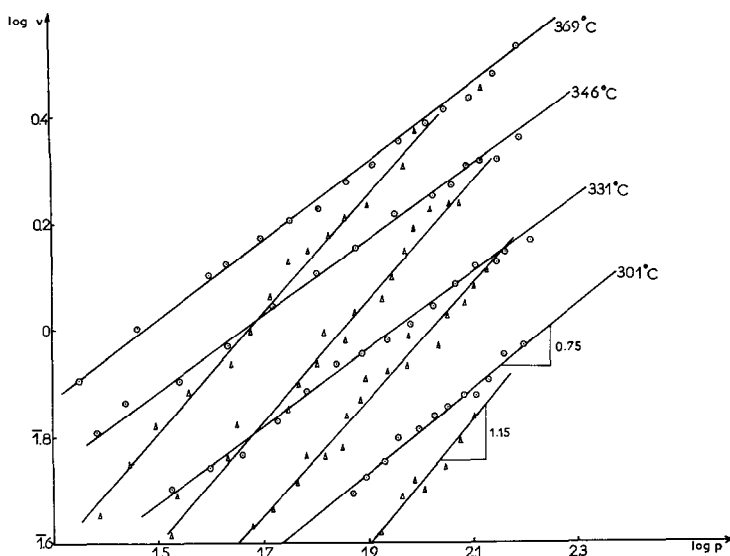


FIG. 6. Temperature dependence of overall order on catalyst A submitted to a stoichiometric mixture under 210 Torr initial pressure. (\odot) In the presence of the liquid nitrogen trap; (\triangle) without liquid nitrogen trap.

with a mixture of initial composition $CO + 2 O_2$. The values of found apparent activation energy E' are reported in Table 3.

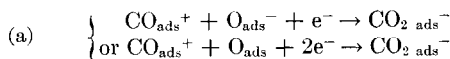
Energy E' decreases with increasing initial content of interstitial oxygen in the oxides. For a particular catalyst, the initial value of E' does not vary with the composition of the reaction mixture containing oxygen pressures greater than 15 Torr, the solid being previously reduced or not.

TABLE 3
CATALYSIS APPARENT ACTIVATION ENERGIES E'

Studied solid	E' (kcal \times mole $^{-1}$)
A	10.0 ± 0.3
B	8.5 ± 0.3
C	8.0 ± 0.3
D	7.5 ± 0.3
E	6.1 ± 0.2
F	4.5 ± 0.2

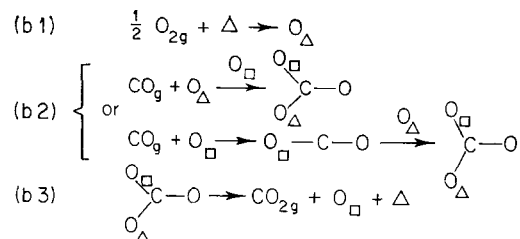
INTERPRETATION AND DISCUSSION OF THE RESULTS

Claudel and coworkers (13), (8) have interpreted the catalytic role of pure thoria in carbon monoxide oxidation admitting that the low step is:



according as oxygen is chemisorbed as anion or as neutral atom. In both cases, this step makes use of the electrons from the solid and is therefore under the dependence of the electronic properties of the latter.

Our preceding studies (6, 7, 14) on uranium-thorium mixed oxides afforded indication that interstitial oxygen may be a chemisorption site for CO. In particular, infra-red spectroscopy showed the existence of the transient species:



(O_{\square} being a normal oxygen atom of the anion sub-lattice).

Our present hypothesis is that the formation of this superficial entity plays an ever increasing role when the concentration in uranium increases. The mechanism becomes then:



Δ being a vacant superficial site.

That means that the catalysis evolves through successive oxidations and reductions of the surface, which are bound, through the O_{Δ} , to the valency states of *localized* uranium atoms, and not principally to charge transfer between adsorbate and adsorbent as a whole.

The following arguments seem to support this hypothesis:

1. Curve ① of figure 3 can be explained if it is assumed that the oxidation rate according to reaction (b 1);

$$v_1 = k_1 p^4(\Delta) \quad (5)$$

being very high, the catalyst immediately gets a maximum oxidation state imposed by the mutual pressures of the two gases and by the temperature. When this oxidation state has been reached (in a few 10 sec), the slower velocity of step (b 2):

$$v_2 = k_2 \theta(O_{\Delta}) \quad (6)$$

governs kinetics; this one is not influenced any more by oxygen pressure since (O_{Δ}) can be considered as being constant. That implies zero order with respect to oxygen during the reaction.

Under such conditions, the relationship expressing the catalytic reaction rate is simple:

$$v = - \frac{dp}{dt} = k'_2 \theta, \quad (7)$$

with $k'_2 = k_2(O_{\Delta})$

This relationship corresponds under our experimental conditions to a partial order equal to 0.75.

2. Let us consider Figs. 3 and 4. Until the end of the initial step on curve 2 (Fig. 3)—corresponding to oxygen pressure $p' = p'_s$ close to 15 Torr—velocity v does not depend on p' (Fig. 4). But, as soon as p' becomes lower than p'_s , the catalyst is reduced during the reaction because the oxidation of the solid by oxygen of the gaseous mixture becomes slower than its reduction by carbon monoxide. Thus,

oxidation rate v_1 being given by relation (5), the linear dependence of $1/v$ versus $p'^{-1/2}$, when p' is lower than p'_s is obvious. This dependence implies a dissociative action of oxygen between 250 and 350°C. The apparent activation energy, determined from the slopes of the straight lines (for $p' < p'_s$) of Fig. 4 is equal to 8 kcal/mole, in accordance with Table 3.

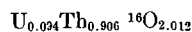
3. The apparent activation energy of the catalysis passes through a maximum when x increases (Fig. 7). This maximum can be explained if it is supposed that uranium ions at higher oxidation states at first slow down the reaction (a) by trapping the electrons, but, at a higher concentration, accelerate the reaction (b 2) by supplying the O_{Δ} atoms.

4. Participation of O_{Δ} atoms to the catalytic action, as indicated by pattern (b) has been checked by isotopic labelling experiments. The method consists in changing partially superficial $^{16}O_{\Delta}$ atoms of a solid solution to $^{18}O_{\Delta}$; carrying out the catalytic reaction on such a labelled oxide, we should see formation of $C^{16}O^{18}O$ molecules due to CO chemisorption on those $^{18}O_{\Delta}$ atoms if our hints were valid. The employed catalyst is solid E. So as to minimize possible exchange reactions in gaseous or chemisorbed phase, we have chosen the temperature of 250°C to perform the experiments, and solid-gas interactions do not exceed 5 min.

Solid E has been submitted to the following operations:

1. Reduction under 400 Torr hydrogen pressure at 450°C for 24 hours.

2. Desorption under 10^{-6} Torr vacuum at 450°C for 24 hr: this desorption allows to remove adsorbed hydrogen and water formed along the first stage. This reduction procedure gives a superficially reduced solid named solid E_1 which has the overall formula:



(y value being measured thermogravimetrically by means of a Sartorius balance).

3. Oxidation by an isotopic mixture containing 79.2 atoms percent of ^{18}O isotope, under atmospheric pressure; after this

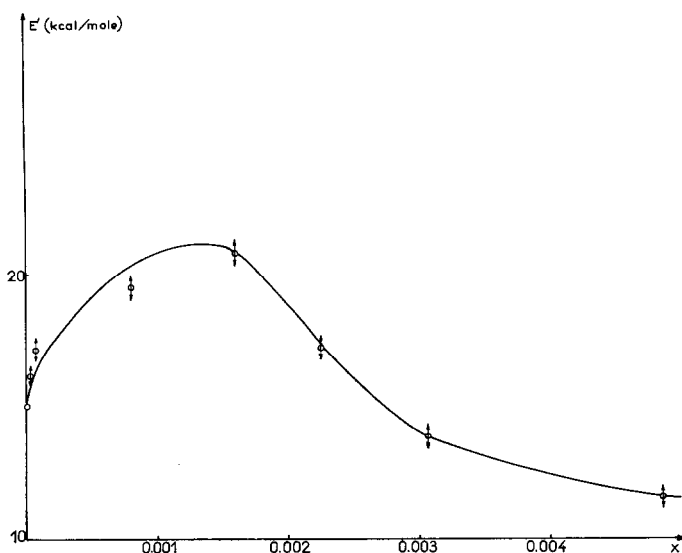
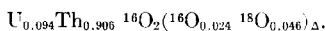


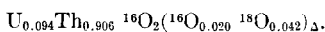
FIG. 7. Maximum of the apparent activation energy at $x \approx 0.0014$ for uranium low-concentrated catalysts.

treatment, the sample has the following formula:

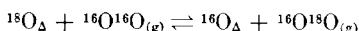


This oxide, solid E_2 , is heated under a 10^{-6} Torr vacuum to $450^{\circ}C$ for 12 hr in order to remove oxygen eventually chemisorbed on the surface.

Final solid E_3 presents, after this labeling procedure, the formula:

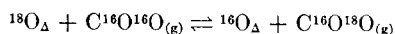


We have first checked that reaction:



does not occur at a significant rate at $250^{\circ}C$ if natural gaseous oxygen is kept in contact of the solid containing $^{18}O_{\Delta}$ under a 50-Torr pressure for 5 min. In the gaseous phase, the enrichment ratio ^{18}O /total O does not exceed 0.26% under these conditions.

The exchange reaction between gaseous CO_2 and interstitial oxygen, carried out under the same conditions:



does not occur either under a 100 Torr CO_2 pressure. The enrichment ratio $^{46}CO_2$ /

total CO_2 in gaseous phase is 1% after 5 min.

The catalytic reaction on sample E_3 has been studied at $250^{\circ}C$ with an excess natural oxygen mixture $CO + 2O_2$, under 210 Torr. Reactants are kept in contact of the oxide for 5 min only, after which the catalyst is suddenly cooled down to room temperature. The gaseous phase is then analyzed by mass spectrometry; chemisorbed gases on solid are collected in a mercury drop-pump (15) and analyzed in the same way. The O_{Δ} content of the solid is obtained from chemical analysis, and the $^{18}O_{\Delta}$ /total O_{Δ} ratio is calculated from reduction of the mixed oxide by CO and measurement of the $^{46}CO_2$ /total CO_2 ratio.

Table 4 represents the balance of gotten experimental results, the atom-grams numbers being related to one gram of oxide E_3 . It has been assumed that every molecule of carbon dioxide was obtained from one superficial O_{Δ} atom.

The total number of ^{18}O atoms recovered after catalysis (line 6) is close to the number of atoms initially present in solid E_3 (line 1). The enrichment in ^{18}O of CO_2 formed along the reaction is important and proves the participation of O_{Δ} to the formation mechanism of the reaction product.

TABLE 4
 CATALYSIS BALANCE ON SOLID E₃

		Numbers of atom-grams of ¹⁸ O	Enrichment of formed CO ₂ in ¹⁸ O: $\frac{^{18}\text{O}}{\text{total O}}$
1	In solid E ₃ before catalysis (¹⁸ O _A)	15.8×10^{-5}	—
2	After catalysis, in gaseous phase under the form of CO ₂	2.6×10^{-5}	22.5%
3	After catalysis, in chemisorbed phase under the form of CO ₂	2.1×10^{-5}	23.1%
4	After catalysis, in the solid under the form of O _A	7.3×10^{-5}	—
5	Miscellaneous (¹⁸ O in gaseous phase, ³⁰ CO...)	1.3×10^{-5}	—
6	Sum 2 + 3 + 4 + 5	13.3×10^{-5}	—

Furthermore, the collection of chemisorbed gases has shown that no chemisorbed carbon monoxide exists under CO form on the solid during catalysis: the whole chemisorbed CO is desorbed as CO₂.

CONCLUSION

Our kinetic studies of CO oxidation catalysed by U_xTh_{1-x}O_{2+y} solid solutions are consistent with the hypothesis that the reaction mechanism (b) becomes predominant already at relatively low uranium contents. At higher uranium concentrations the reaction develops through the intermediacy of interstitial superficial oxygen atoms, so that the solid may be considered as an "oxygen sponge."

The case of these mixed oxides seems to be a good example on one hand of a type of catalysis by oxygen exchange between the solid and the gaseous phase, and, on the other hand, of the influence of relatively small amounts (0.14%) of foreign element.

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