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Oscillating Oxidation of Propene on Copper Oxides

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Bistability may be displayed by the system Cu–O used as a catalyst of propene oxidation under isothermal conditions and at low extents of reaction. This results from possible conversion of one Cu oxide into another under reacting conditions and from partial overlapping of the conditions of kinetic stability of both oxides. The phase changes of the solid are identified by X-ray analysis and are made visible by the strikingly different colors of the oxides. Under well-defined conditions, where the mass of the sample (Cu obtained from bulk CuO by reduction under a H_2 flow at 400°C for 2 h), grain size, residence time, and composition of the reactant mixture belong to an appropriate range, thermochemical oscillations are observed. CO_2 formation, much more exothermic and oxygen-consuming than that of acrolein, is favored on CuO and causes overheating of the solid. Reducing conditions are then created, leading to Cu_2O formation. On the latter oxide, acrolein is favored, so that less O_2 is consumed and the temperature decreases, which allows the reoxidation of the solid. Particularities of the oscillating behavior can be interpreted in relation to the structural imperfections which are likely to result from repeated oxidations and reductions of the catalyst.

I. INTRODUCTION

Most studies of oscillating heterogeneous catalytic reactions are devoted to CO or H_2 oxidation and the catalysts involved are most often metals among which Pt is a frequent example.

The present work reports on the oxidation of propene catalyzed by Cu oxides. An interesting feature of hydrocarbon oxidations is that they may follow different paths. In the experiments which will be described here, carbon dioxide and acrolein were the main products. In this reaction as in any other oxidation reaction an essential question concerns the true chemical nature of the solid catalyst, at least in its surface region, under reacting conditions. As Mars and Van Krevelen (*1*) assumed in their well-known and accepted model, the catalyst surface is in effect involved in redox processes. In a flow reactor, the constant feed of reactants keeps the system in a stationary state which is away, and frequently far, from equilibrium. As a result, the chemical state of the surface, and therefore of the underlying solid as well, is under kinetic and not thermodynamic control and cannot be easily anticipated. In the present case, when the initial state of the solid was CuO, reduction to Cu_2O (or even Cu) had to be considered with an increasing C_3H_6/O_2 ratio. Conversely, even if metallic in its initial state, the catalyst could turn, at least on its surface, into one or another oxide under reacting conditions with an appropriate C_3H_6/O_2 ratio.

Redox mechanisms of catalytic oxidations remain essentially formal if phase transitions involving the solid catalyst are not considered as one of their possible natural consequences. Wagner (*2*) showed that such phase transitions had to be expected when keeping the temperature constant and progressively modifying the composition of the reactant mixture. As a consequence, bi- (or multi-) stability and associated hysteresis effects should be obtained since the differing kinetic properties of the various surfaces will give rise to differing compositions of the reactant mixture which, in turn, will give rise to critical

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surface conditions that lead to solid-state transitions.

Riekert *et al.* (*3*) first showed the relevance of this analysis in the case of copper oxides dispersed on a support and used as catalysts in the oxidation of propene. The present paper first confirms this point in the case of the same reaction, catalyzed by initially pure CuO. X-ray-diffraction analysis allowed us to verify that hysteresis is effectively due to the reduction of cupric oxide or to the oxidation of cuprous oxide. Another consequence of such a bistability is the occurrence of oscillations under a suitable set of operating conditions.

II. EXPERIMENTAL

II.1. Catalyst

In its initial state the catalyst was made of CuO (Merck Ref. 2764; pro analysi; 0.8–2 mm), ground and sieved. Its specific surface area was determined at 77 K from both the Kr adsorption isotherm obtained by using classical physisorption equipment and the CH_4 adsorption isotherm established *in situ* by a dynamic method. The two values so obtained were in good agreement (1.4 and 1.26 $m^2\ g^{-1}$, respectively). The distribution of pore diameters, as determined by mercury penetration (Carlo Erba porosimeter), was narrow with an average of 3×10^3 Å. The specific surface area which can be deduced from a histogram of pore distribution by using the cylindrical pore model is 2.02 $m^2\ g^{-1}$. When necessary, the oxide was reduced to Cu by flowing H_2 at 400°C for 2 h. The resulting metal powder displayed an increased surface area (1.9 $m^2\ g^{-1}$), as measured by the dynamic method which was considered the best suited here. The average pore diameter was also increased (4×10^3 Å), leading to a calculated surface area equal to 3.05 $m^2\ g^{-1}$. Reduction by C_3H_6 caused modifications of the surface area and of the average pore diameter which were not significantly different.

As shall be seen from the following, the initial CuO turned to a mixture of both oxides or to Cu_2O or even to Cu under the influence of the reactant mixture. Conversely, the initial Cu might oxidize superficially to Cu_2O or CuO or a mixture of both oxides. The phase changes of the solid were made visible by striking changes of color and were characterized as often as possible by X-ray diffraction (CGR diffractometer; Ni-filtered Cu*Kα* radiation) (Fig. 1). The diffractograms obtained were compared to the reference diffractograms corresponding to pure CuO, Cu_2O, or Cu (Fig. 2).

II.2. Reactor

The reaction was carried out in a continuous-flow system. The reactor was a U-shaped Pyrex tube (i.d. 4 mm) placed inside a cylindrical silica tube. An electric resis-

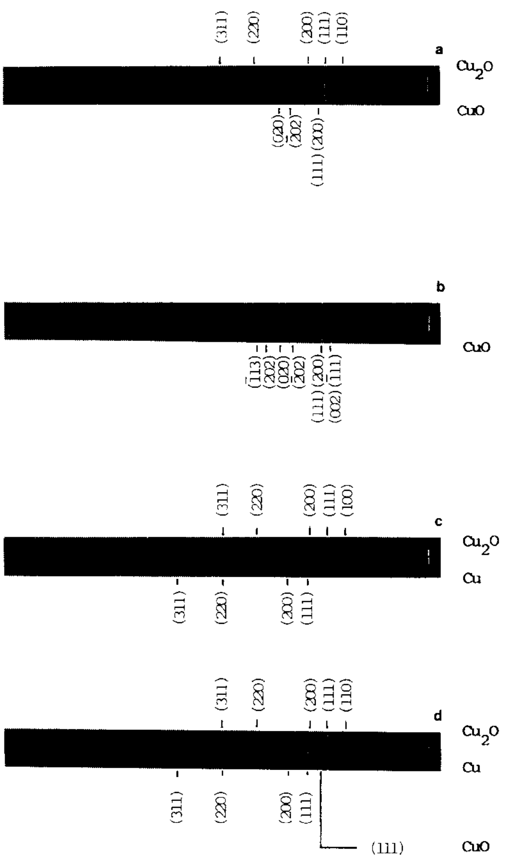

FIG. 1. X-ray diffraction lines of catalysts after various experiments. (a) and (b): Initial state CuO, see text. (c) and (d): Initial state Cu, see text.

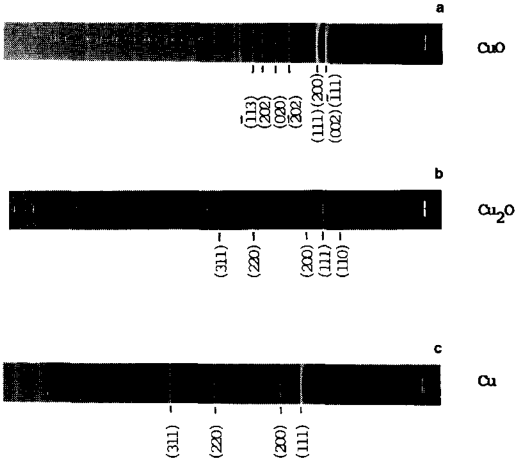

FIG. 2. X-ray diffraction lines of the reference compounds. (a) CuO; (b) Cu_2O (Alfa-Ventron 89014); (c) Cu obtained by reduction of CuO (see text).

tance heater (Thermocoax from Philips Industry) was coiled against the internal wall of the silica tube so that the catalyst bed, which was situated at the lower part of one side of the U-tube and placed between two plugs of silica wool, could easily be observed and photographed while being heated.

Heating of this resistance was achieved using a linear programmer which could also be used as a simple controller if the reference temperature were kept constant. A control thermocouple was situated against the electric resistance and a measurement thermocouple was situated against the other side of the reactor wall at midheight of the catalyst bed. In some experiments, another thermocouple was introduced into the catalyst bed itself and gave the same signal as the measurement thermocouple except during the temperature spikes. In this last case, there was no visible delay between the spikes of the inside and outside temperatures though they could differ by as much as a few tens of degrees Kelvin. The temperature profile along the axis of the catalyst bed was also estimated by setting a second thermocouple on the outer side of the reactor just at the level of the entrance of the bed and a third one at the exit. No significant differences were indicated by the three thermocouples except in the case of a temperature spike. In this latter case each thermocouple was reached in turn by the heat wave and the spike was accordingly detected at clearly distinct, though very close, times (time lag less than 1 s). The difference between the three temperatures jumps did not exceed 7 to 8 K.

Through the use of a number of four-port valves, the reactor could be fed either with a reactant mixture (He, C_3H_6, O_2) of appropriate composition or any of its three usual components, or with pure H_2. The reactant mixture was made by using thermal mass flow meters (Brooks). Gases were from Air Liquide (He, N_{45}; H_2, U; O_2, N_{45}; C_3H_6, G_{32}). O_2 and C_3H_6 were used without further purification. H_2 and He were purified as previously described (*4*).

At the exit of the reactor, the gases were analyzed chromatographically (FID for C_3H_6 and C_3H_4O; TCD for CO, CO_2, and O_2). Before being analyzed, C_3H_6 and C_3H_4O were separated on a Porapak QS column (150 cm; $\phi_i = 1.6$ mm; $T = 138°C$). A suitable separation of O_2, CO, and O_2 was achieved by using two parallel columns displaying equal resistances to the gas flow and filled with carbosphere. The shorter one allowed CO_2 to be quickly eluted after He, CO, and O_2 had appeared in one unresolved peak. The longer one separated O_2 from CO. These elutions were achieved within 90 s. The gases remaining inside each column were then back-flushed. The injection and back-flush valves were actuated automatically by means of an integrator Intersmat ICR-1B. The characteristics of the columns were as follows:

(1) $L = 75$ cm; $\phi_i = 1.6$ mm
(2) $L = 200$ cm; $\phi_i = 2.1$ mm
$T = 110°C$.

The O_2 content could also be continuously monitored by a paramagnetic analyzer (BECKMAN).

III. RESULTS

The oxidation of propene produced mainly CO_2 and C_3H_4O and little CO, according to the following equations:

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O + 337\ \text{kJ}$$
$$(C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O + 1056\ \text{kJ})$$
$$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O + 1906\ \text{kJ}.$$

Since the CO production rate was insignificant compared to that of CO_2, it was ignored and the selectivity relative to acrolein, S, was calculated according to

$$S = \frac{F_{\text{Acro}}}{F_{\text{Acro}} + \frac{1}{3} F_{CO_2}},$$

where F_{Acro} and F_{CO_2} are respectively the production rates of acrolein and CO_2.

III.1. Bistability and Hysteresis Loops

Riekert *et al.* (*3*) have shown that when CuO (dispersed on alumina) is used in propene oxidation, at 645 K and under constant partial pressure of propene but different partial pressures of O_2, the variations of acrolein and CO_2 production rates show hysteresis loops. Either one or the other branch of the loop is obtained, according to the way the O_2 concentration is changed (increased or decreased). In agreement with Wagner, the authors suggested this phenomenon was due to a hysteresis in the phase transition between CuO and Cu_2O under nonequilibrium conditions. The amount of O_2 in the catalyst was determined *in situ* by H_2 titration at 713 K.

In our experiments, the catalyst was *bulk* CuO, which allowed easy and direct determination of the chemical nature of the solid to be obtained by X-ray diffraction for various steady states of the reacting system. This advantage was counterbalanced by the fact that it was difficult to avoid thermal effects and ignition of the solid, unless we used a very small quantity of catalyst and worked at moderate temperatures.

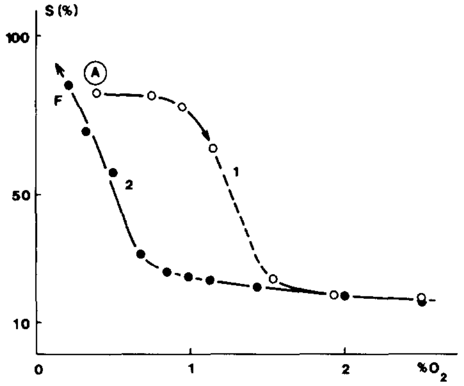

FIG. 3. Variation of the selectivity relative to acrolein as a function of the O_2 content of the reactant mixture (steady state). Catalyst: initially 9 mg CuO (see text); 315 < CuO particle size < 400 μm. Reactant mixture: 3% C_3H_6, O_2, He. Flow rate: 123 $cm^3\ min^{-1}$. Temperature: 278°C.

We could however confirm the preceding results as shown in Fig. 3, deduced from steady-state measurements performed at 278°C and giving the variations of the selectivity, S, as a function of the oxygen content of the reactant mixture. (The catalyst—initially 9 mg CuO—was previously used at 300°C for a similar experiment performed by decreasing the O_2 content of the reacting mixture, so that its initial state, point A, was Cu_2O.) All the measurements were done at conversions lower than 1% of the limiting reactant (O_2).

At the beginning of the experiment (point A), the catalyst was orange-brown. It remained so when the oxygen content of the reactant mixture was increased (branch 1) until a content of ca. 1.2%, at which point it became black. It remained so for higher oxygen contents. When the O_2 content was decreased (branch 2), it remained black until a content of ca. 0.5% was reached, at which point it became orange-brown. X-ray diffraction confirmed the presence of a substantial amount of Cu_2O in the solid submitted to the reactant mixture containing the smallest O_2 concentration (Fig. 1a) whereas only CuO could be detected after the sample had been submitted to the O_2-rich mixture (Fig. 1b).

Similar experiments were conducted on a sample reduced to Cu with H_2 at 400°C and similar kinetic results were obtained. The presence of Cu_2O and CuO was correspondingly evidenced by XRD but in this case metallic Cu remained always abundantly present. This resulted from the fact that only a superficial region of the copper underwent the phase transitions. Figure 1c shows the diffractogram obtained after the O_2 content was increased up to 3% and then decreased again to 2000 ppm at 300°C (in a reactant mixture containing 3% C_3H_6). Formation of Cu_2O is clearly evidenced. On the other hand the (111) diffraction line of CuO is clearly visible in Fig. 1d obtained after the sample had been fed at 300°C with the reactant mixture containing 3% O_2 and 3% C_3H_6.

III.2. Oscillating Regimes

Oscillating regimes could be observed when one started from the metallic state obtained by reduction of CuO under H_2 (400°C; 2 h) but not when one started from CuO. These different behaviors will be interpreted later.

III.2.1. Preliminary experiment. Feeding the Cu powder with the reactant mixture while submitting it to a linear ramp of temperatures (4 K min^{-1}) from room temperature resulted in a superficial oxidation of the metal, in agreement with the result of XRD observations (X-ray diffraction lines similar to those of Figs. 1c and 1d). Before the amount of Cu_2O was sufficient to give rise to X-ray diffraction lines, the oxidation was made visible at $T \geq 200°C$ through a succession of various colors due to light interference in the thin oxide film. The reaction occurred therefore on the oxidized surface.

As clearly evidenced in Fig. 4, at about 280°C the rates of production of CO_2 and acrolein increased suddenly, which corresponded to a departure from linear heating. The temperature reached a maximum (ca. 360°C) followed by a sharp and unexpected decrease followed by another increase. After the ignition, the catalyst was red and the X-ray diffractogram showed only Cu radiation lines.

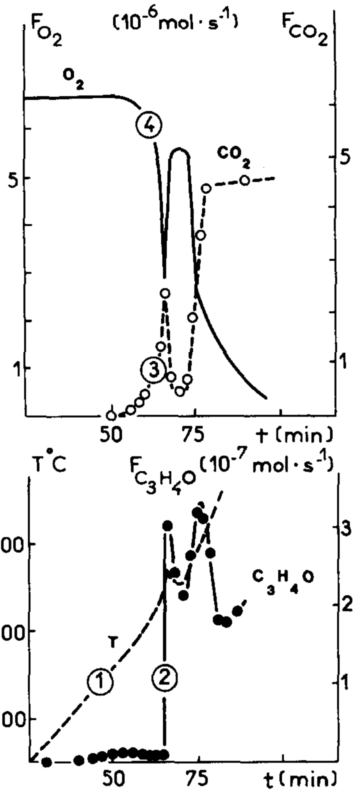

FIG. 4. Simultaneous variations of the catalyst temperature and of the molar flow rates of O_2, CO_2, C_3H_4O at the exit of the reactor, as a function of time-on-stream during the application of a linear ramp of heating. Catalyst: 240 mg of Cu obtained by H_2 reduction (1 atm; 400°C; 2 h) from 300 mg CuO; 315 < CuO particle size < 400 μm. Reactant mixture: 9% C_3H_6, 9% O_2, He. Flow rate: 110 cm^3 min^{-1}. Rate of heating: 4 K min^{-1}.

III.2.2. Obtainment of oscillations. The experiment was therefore repeated but the ramp of temperatures assigned to the oven was stopped just after the maximum temperature was reached (as soon as the temperature decrease became evident), so that the system should have maintained an isothermal state in the absence of reaction. Its evolution was then followed against time and the oscillating regime depicted in Fig. 5 established itself. The regularity of the oscillations was checked over 15 h.

The variations of rates and temperature were accompanied by meaningful color changes of the catalyst. Before each rise of

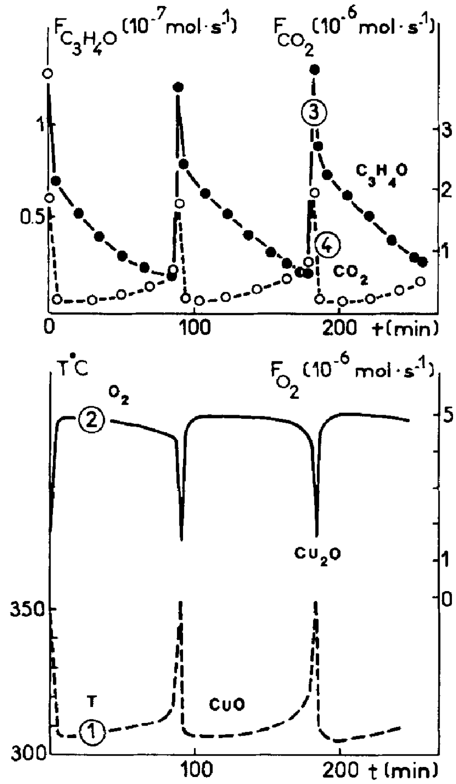

FIG. 5. Oscillating regime in the catalytic oxidation of propene. Catalyst: Cu obtained through the reduction of 300 mg CuO by H_2 (see text); CuO particle size <315 μm. Reactant mixture: 7.2% O_2; 9% C_3H_6; He. Flow rate: 120 cm^3 min^{-1}.

temperature the solid was black (superficial CuO; same X-ray diffractogram as in Fig. 1d) and became orange-brown (superficial Cu_2O; same X-ray diffractogram as in Fig. 1c) as the temperature reached its maximum. It remained so during and after cooling of the catalyst but darkened progressively as the temperature began to increase again and turned black again about 10 min later. The selectivity reached its best level (ca. 50%) just after the maximum (Cu_2O) and its lowest level (ca. 10%) just before (CuO).

It was then in order to examine the influence of every factor to which the system could be expected to be responsive.

III.2.3. Influence of the flow rate. Figure 5 is related to a flow rate of 120 cm^3/min. Figures 6 and 7 show the oscillations which were displayed with lower values of the flow rate. The system behaved in the same qualitative way. The amplitudes of the oscillations decreased and the shapes of the peaks became smoother, thus making visible that the variations of CO_2 and acrolein were out of phase.

Increasing the flow rate to 200 cm^3/min made the temperature rise above 400°C with complete conversion of oxygen and no oscillation. The solid was completely reduced.

III.2.4. Influence of the O_2 content. The O_2 content was varied from 8 to 3% at a constant flow rate (120 cm^3/min) and propene concentration (9%).

The highest content (8%) caused immediate ignition and reduction of the solid with complete reaction of O_2.

At 6.3% O_2 the oscillating regime was similar to that in Fig. 5 (obtained for 7.2%

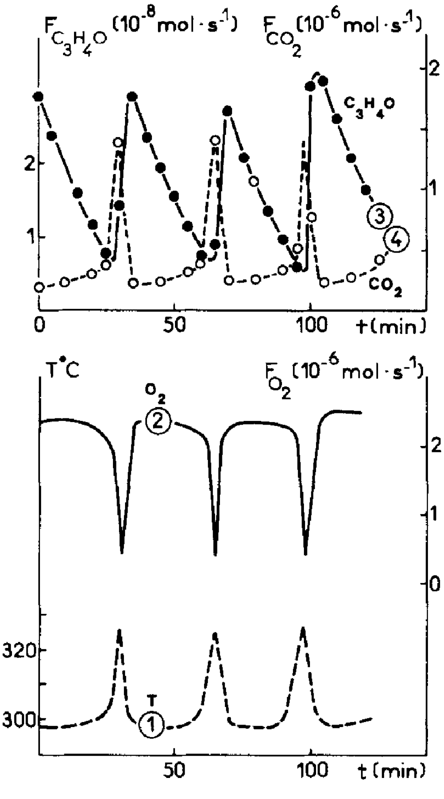

FIG. 6. Influence of the flow rate upon the oscillations. Same conditions as those in Fig. 5 except flow rate (63 cm^3 min^{-1}).

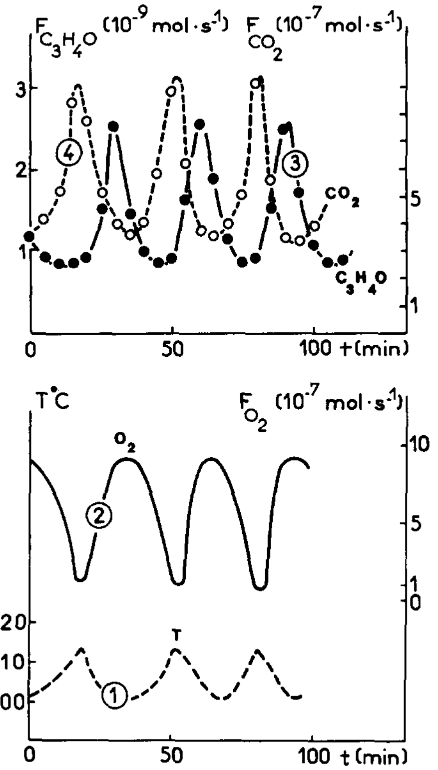

FIG. 7. Influence of the flow rate upon the oscillations. Same conditions as those in Fig. 5 except flow rate (30 cm^3 min^{-1}).

O_2) but the extent of temperature variations was more limited (290–330°C).

At 5.5% each oscillation was double as shown in Fig. 8. The first and smaller temperature peak corresponded to a brownish color of the catalyst, due to a probable incomplete reduction, whereas the second and higher one corresponded to the usual state of reduction.

At 4.3% O_2 erratic oscillations were observed. It was checked that reverting to 7% O_2 resulted in the usual and regular oscillating regime.

When the O_2 content was decreased to 3%, no oscillation occurred.

III.2.5. Influence of the amount of catalyst. Diminishing the mass of catalyst at a constant flow rate is in principle equivalent to decreasing the contact time and therefore to increasing the flow rate through a constant mass. However, as this statement may be misleading, due to the interference of strong thermal effects and of the modification of surface area due to phase transitions, new experiments were carried out with samples of lower masses (respectively 150 and 70 mg instead of 300 mg) submitted to the same conditions as those in Fig. 5.

The first sample (150 mg) caused oscillations with a longer period (140 instead of 90 min) and temperature extremes 10 K higher than those in Fig. 5.

The second sample gave rise to an irreversible ignition (420°C) followed by reduction, all the gaseous O_2 being consumed. When the O_2 content of the reacting gas was lowered from 7 to 6%, the thermal effect was lowered and the oscillations were restored, but with a period varying between 185 and 200 min.

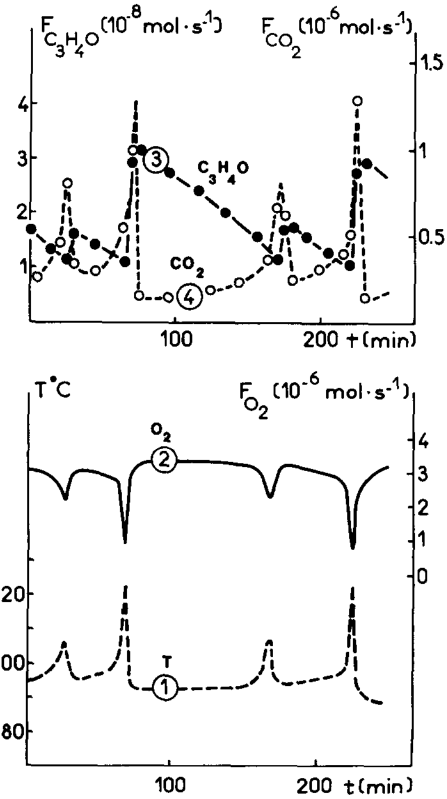

FIG. 8. Splitting of peaks obtained by decreasing the O_2 content. Same conditions as those in Fig. 5 except O_2 content (5.5%).

III.2.6. Influence of the particle size. When the mean size of the particles in their initial oxidized state ranged from 315 to 400 μm little difference occurred with respect to Fig. 5 (related to particles smaller than 315 μm) except for a slight increase in the extreme temperatures.

With broader particles (500–800 μm) no oscillation took place and after the ramp was stopped, the temperature decreased to 340°C, thus leading to steady state.

III.2.7. Influence of the conditions of initial reduction of the oxide. All the experiments described previously were carried out after initial reduction of the copper oxide under H_2 at 400°C for 2 h. When this initial reduction was effected during the same time but at 300°C a more active surface resulted (even giving rise to a transient formation of acrolein at room temperature). Because of this higher activity the catalyst so prepared led to a quick ignition and no oscillation when heated at about 280°C.

IV. DISCUSSION

It was on CuO that the first example of temperature and rate oscillations in heterogeneous catalysis was obtained in the decomposition of N_2O (*5*, *6*). This oxide was also shown to display the kind of oscillations in the oxidation of CO (*7*). However, the possible reduction of CuO under certain reacting conditions was overlooked. The number of oscillatory heterogeneous catalytic reactions reported since then has been continuously increasing. Most cases refer to oxidations proceeding on metallic surfaces, such as CO and H_2 oxidations. Some examples refer to organic molecules (*8–12*). Lintz *et al.* (*13*) reported a case where interferences with physical effects were excluded. More recently, Ertl *et al.* (*14–16*) demonstrated that the CO-induced reconstruction of Pt single-crystal surfaces, together with the different catalytic activities of the involved structures, caused the oscillating CO oxidation, conducted isothermally and at very low extents of reaction.

Such is not the case here since thermal effects originating in (and causing) high extents of reaction play an important part in the oscillations. The various factors examined here may be thought to influence the oscillation amplitude and period through the increase or decrease of heat supplied to the catalyst from the reactions. However, when the heat supply was sufficient to raise the temperature of the catalyst above 400°C the solid remained in a reduced state since the O_2 was completely exhausted. This helps us to understand why bulk CuO does not give rise to oscillations: the heat evolved by its own reduction is an additional and noticeable supply to the heat of reaction and so contributes significantly to the irreversible ignition of the catalyst (*17*).

However, the catalyst behavior is not entirely governed by physical factors. It is worth noting that within every period there is an exact coincidence between maximum heating of the solid, maximum production rate of CO_2, and quick and visible reduction of the superficial oxide. The latter is due to the consumption of O_2 by the thermally accelerated oxidation of C_3H_6 into CO_2 and the consequent exposure of the solid to the C_3H_6-rich reaction mixture. The reduced phase (Cu_2O) favors the much less exothermic oxidation of propene into acrolein ($\Delta H^\circ = -337$ kJ per C_3H_6, instead of -1906 for CO_2) but this reaction is unable to maintain the solid at the temperature just attained, which leads to a maximum. The resulting cooling of the solid as well as the lower stoichiometric amount of O_2 required for the mild oxidation of C_3H_6 entail a fast increase of the O_2 content in the gas which therefore ends up reoxidizing the catalyst. Oxidation of propene into CO_2 is again favored, which leads to the repetition of the preceding events and consequently to oscillations. There remains no doubt in our minds that the oscillations observed in these experiments have a thermochemical origin.

The period of the oscillations is much higher than the time needed for the reaction of one monolayer of adspecies, which is in accord with the fact that the phenomena underlying the periodic behavior are dependent upon bulk changes in the solid and are therefore much more time consuming. The period is accordingly partly determined by the kinetics of deep chemical modifications of the solid. In addition, the solid is probably maintained in a more or less disordered state by the repeated oxidations and reductions. The defective state of the solid can reasonably be thought to influence not only the kinetics of its own transformations but its catalytic activity as well. This has recently been proposed by Sadykov *et al.* (*18*) in a work devoted to the oxidation of CO on CuO which had been progressively activated by an increasing number of defects generated by the reaction itself. In the present work, the same notion of structural quality sensitive to chemical actions can be used to account for two other aspects of the oscillations:

(i) In several cases reoxidation of the solid, although made visible by its complete blackening, was not immediately sufficient to trigger strong self-heating and reduction of the catalyst. Instead the CO_2 rate began to increase slowly (Fig. 5). This behavior is not expected to result from a variation of the surface area of the sample since most of this variation must parallel the formation of the CuO layer which occurs quickly after the temperature spike. Furthermore oxidation causes a decrease in the surface area and if it is assumed to be going on slowly during the preignition period the surface area would go on decreasing, which would make the ignition less and less possible. The ignition delay could result, as assumed above, from an increase in the defective state of the surface which accordingly would display an increasing activity in the total oxidation of propene.

(ii) What was noticeable when the O_2 content of the reactant mixture was depressed was the splitting of the peaks into two. The first effect expected from a decreased O_2 content would be a corresponding decrease in the height of the temperature spike as a result of a lower heating rate from the reactions and that was the case for the first peak of each pair. On the other hand, the fast reduction of CuO which occurs at the moment of maximum self-heating can easily be supposed to cause a number of defects to develop. Roughly speaking, the state of the resulting Cu_2O is expected to be more defective when the amount of oxide having reacted is greater and when the maximum heating is lower since thermal restructuring is strongly activated by heat. However, it is reasonable to assume that the number of defects originating in the reduction process and situated at the surface and in the near-surface region should approach a limiting value as soon as the thickness of the oxide exceeds a few atomic layers. The situation is obviously different regarding the contribution to the heating rate due to the reduction of the superficial oxide which is lower when the oxide layer is thinner. We can therefore understand that the reduction of a thinner CuO layer may eventually result in a more defective Cu_2O. The latter can reasonably be assumed to react faster and deeper with O_2 under recovered oxidizing conditions, which should in turn become the origin of an increased thermal effect. Thereafter the surface region of the catalyst recovers a state proper to the repetition of the same events.

This peak splitting may be viewed as a step toward the chaotic oscillations which took place at still lower O_2 concentrations. These oscillations may have resulted from the increasingly difficult synchronization of the processes occurring on the different regions of the catalyst.

The possible relationship between kinetic oscillations and changes in the oxidation state of the solid used as a catalyst has already been considered not only on a theoretical basis (*19*) but also in several experimental situations (*8–11, 20–26*). One advantage of the present system is that little doubt remains that the oscillating behavior of the solid reveals its oscillating oxidation state. Clear evidence of such a situation results from the deep and visible modification of the solid. Conversely, a drawback of this same system is that the essential chemical part of the phenomenon is confused with elevated extents of reaction and related heat effects. Riekert has shown (*19*) that Wagner's views (*2*) can be extended to the interpretation of kinetic oscillations involving solid catalysts under isothermal conditions and at negligible extents of reaction. The main assumption of this approach is that the solid may undergo a phase transition under nonequilibrium conditions and that the two phases involved display different catalytic activities. Such conceptions can be applied equally well to chemical changes or to restructurings limited to the surface (*14–16, 27*). However, heterogeneous catalysts such as the one used in the present work are not expected to be able to bring about observable oscillations without some kind of synchronizing action. Heat effects and large extents of reaction can be the synchronizing agents required.

V. CONCLUSIONS

The experiments reported in this work clearly show that the contribution of the lattice oxygen of an oxide used as a catalyst in a reaction of the redox type may result in phase changes involving the bulk of the catalyst and occurring very far from equilibrium.

In the case reported, a powder of Cu fed with an appropriate mixture of C_3H_6 and O_2 under certain operating conditions was unable to reach a steady state and was led to an oscillating regime. The periphery of each grain displayed a chemical composition oscillating between CuO and Cu_2O. The depth involved could not be determined but extended over thousands of atomic layers. This behavior was fundamentally related to the difference between the catalytic activities of each oxide in the mild oxidation of propene into acrolein and in the total oxidation of propene into CO_2, and to the large difference between the heats of the two reactions involved. The whole phenomena appeared accordingly to have a thermochemical origin.

An advantage of the system is that the easily visible color changes of the solid make it look very much like an indicator of its own cyclic transformation.

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