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USb_3O_{10} as a Catalyst for the Selective Oxidation of Propene

Dynamic Interaction of the Oxide Surface with the Gas Phase

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The dependence of catalytic performance on the surface dynamics of USb_3O_{10} has been studied. The sequential treatment of USb_3O_{10} with propene, oxygen and the reactant mixture under the experimental oxidation conditions has been studied using the pulse-microreactor method. The existence of two types of active site on the surface is proposed. Sites with highly coordinated oxygen are responsible for complete oxidation. On the other hand, unsaturated sites lead to a selective process. We also discuss the irreversible surface restructuring in relation to the observed low mobility of O^{2-} ions.

As described in our previous paper, propene is oxidized on USb_3O_{10} *via* a redox mechanism.[1] An X-ray photoelectron spectroscopic investigation of this mixed metal-oxide catalyst[2] has shown that the surface is irreversibly modified by the catalytic process. Previous studies have led us to consider four paths which may be held responsible for the surface dynamics. (i) Oxidation, hydroxylation[3] or coke deposition[4] can block some of the surface sites. (ii) The reversible or irreversible formation of surface structural phases (*e.g.* two- or three-dimensional clusters)[5] can occur. (iii) There can also be formation of surface polyhedric sites with high or low oxygen coordination.[6] (iv) Diffusion of different ions in the surface or in the bulk[7] can also occur. In this paper we report experiments performed to study these different assumptions by using a pulse microreactor.

EXPERIMENTAL

The preparation of the mixed oxide USb_3O_{10} has been described previously.[1] Surface treatments and catalytic-activity tests were carried out with a microcatalytic pulse reactor. The gas chromatograph was an Intersmat IGC 15. The two columns, each 2 m long, were made of 1/8 in. stainless-steel tubing packed with Porapack Q (100–200 mesh).

The carbon dioxide yield was determined at room temperature. Propene, water and other oxidation products (mainly C_3H_4O, C_3H_6O and C_2H_4O) were determined during programming from 20 to 180 °C. Pulses (1.6 cm^3) of reactant gases or of a reactant mixture were passed over 80 mg of the catalyst under a pressure of 3 atm in the reactor. Between each pulse the sample was kept under an He flow for 20 min, the time required for chromatographic analysis.

To ensure that the catalyst was completely oxidized at our experimental temperatures the sample was pretreated with an oxygen flow (30 cm^3 min^{-1}) at 400 °C for 16 h and then placed in an helium flow to reach the experimental temperature conditions.

Our experiments were carried out at 305 and 370 °C, temperatures for which propene oxidation with $C_3H_6+O_2$ reactant mixtures presents, respectively, 100% selectivity for allylic oxidation and a lower selectivity in the kinetic range.

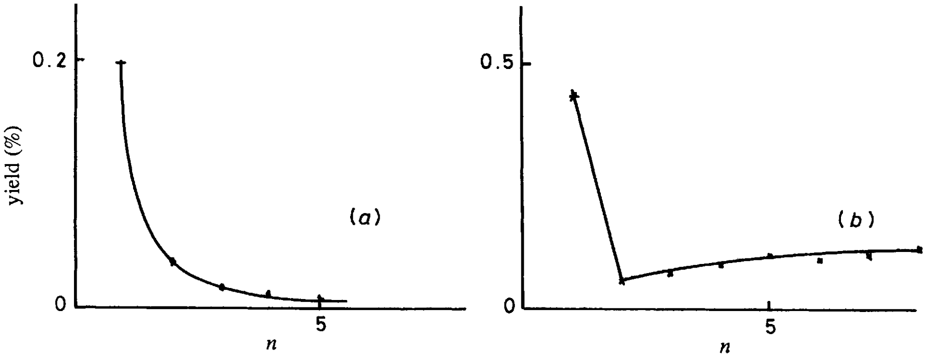

Fig. 1. Acrolein yields during propene oxidation in the absence of gaseous oxygen at (*a*) 305 and (*b*) 370 °C.

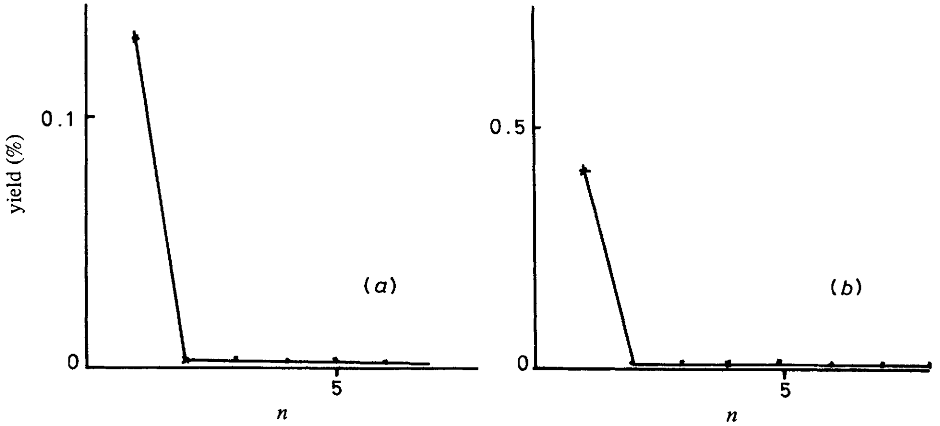

Fig. 2. CO_2 yields during propene oxidation in the absence of gaseous oxygen at (*a*) 305 and (*b*) 370 °C.

RESULTS

SURFACE RESTRUCTURING DURING PROPENE OXIDATION WITHOUT GASEOUS OXYGEN

The yield of propene oxidation as a function of the number of propene pulses is illustrated in fig. 1 and 2. The fresh catalyst, which is consequently in the higher oxidation state, has the higher activity. Whatever the temperature, a drop in activity is observed between the first and second pulses. The yield of acrolein, which is rapidly stabilized at 305 °C, is low. On the other hand, it increases after the third pulse at 370 °C. Whatever the experimental temperatures, selectivities for acrolein, lower at the first pulse, sharply increase to reach a high and constant value [fig. 3(*a*)].

Acetaldehyde and acetone are only found during the first pulse. As shown in a previous i.r. study,[8] the reaction proceeds through the removal of lattice oxygen from the catalyst. The amount of oxygen removed after 7 pulses is calculated from the quantity of oxygen transferred to the oxidation products and is related to one compact monolayer of O^{2-} ions, being 6 and 25% at 305 and 370 °C, respectively. The

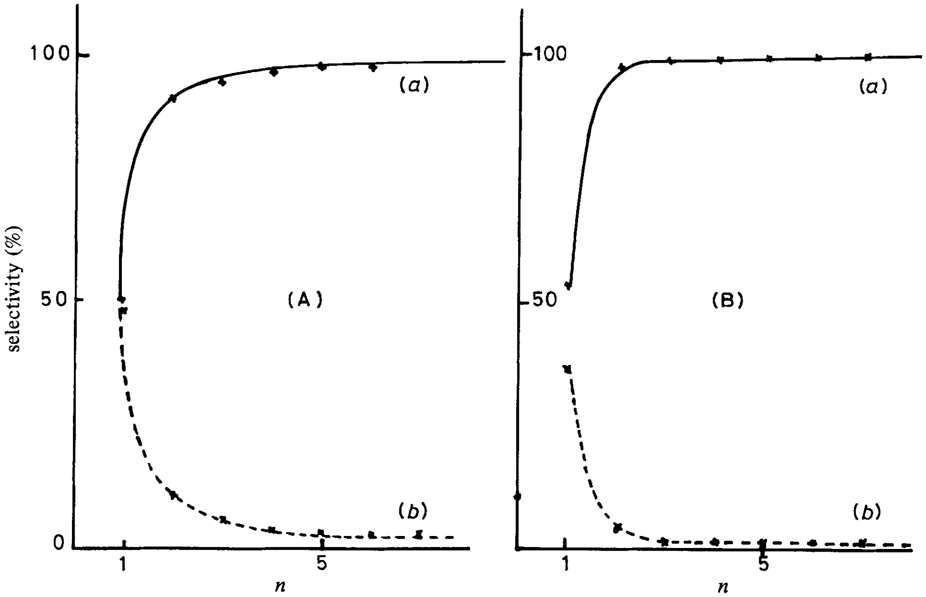

Fig. 3. Selectivities for (*a*) acrolein and (*b*) CO_2 during propene oxidation in the absence of gaseous oxygen at (A) 305 and (B) 370 °C as a function of the number of C_3H_6 pulses.

distributions of lattice oxygen among the products at both 305 and 370 °C were calculated on the assumption that a stoichiometric reaction takes place between the lattice oxygens and propene.

Fig. 4 shows that the interaction between hydrocarbon and surface atoms involves two different active sites, T and S, responsible for the complete and selective oxidation, respectively, of C_3H_6. The observed drop in activity may be related to coke formation on the surface of the catalyst. This has previously been observed under experimental conditions by Raman microprobe spectroscopy.[9] The change in the oxidation state of Sb surface ions, previously observed by X.p.s. studies[2] and which is connected with the observed low mobility of lattice oxygens from the bulk to the surface, may also explain the low activity. In order to characterize the phenomena more completely, the reduced catalyst was first treated for 2 h with a He flow to remove all the weakly fixed products. The formation of CO_2 following the first O_2 pulse at 305 or 370 °C corresponds to the oxidation of the coke or of a strongly chemisorbed species. A kinetic study of the reoxidation has not been carried out because the small amount of lattice oxygen removed during the next treatment, together with the oxidation of the fixed carbonaceous species, makes the measurement inaccurate. Nevertheless, qualitative analyses reveal that surface reoxidation is mainly achieved from the first pulse. Indeed, the analysed amount of unconsumed oxygen remains constant for each further pulse and is similar to the amount of oxygen in the pulse.

RELATION BETWEEN CATALYTIC PERFORMANCE AND SURFACE RESTRUCTURING

A comparison between the performances of (i) the initial USb_3O_{10} (catalyst α), (ii) a catalyst whose surface had been restructured by treatment comprising 15 C_3H_6 pulses (catalyst β) and (iii) a sample of catalyst β whose surface had been restructured by a reoxidative treatment (a flow of O_2 for 1 h) at 305 or 370 °C (catalyst γ) was

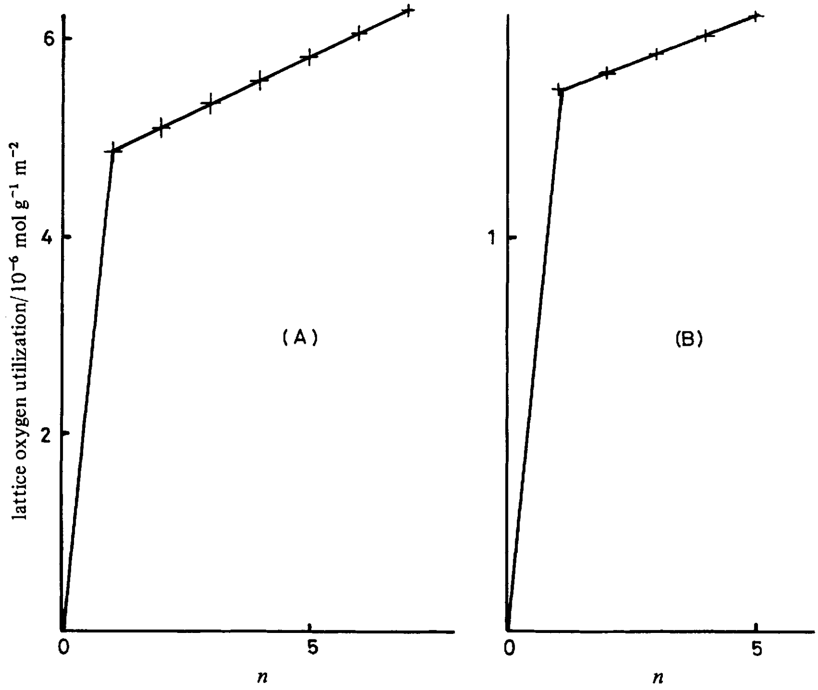

Fig. 4. Lattice-oxygen utilization during propene oxidation in the absence of gaseous oxygen at (A) 305 and (B) 370 °C.

carried out. The percentages of propene oxidized on these samples (fig. 5) and their selectivities for C_3H_4O and CO_2 (fig. 6 and 7) are shown as a function of the number of pulses. Acetaldehyde is always formed, so the values concerning CO_2 are corrected by taking its formation into account.

Whatever the temperatures of the catalytic tests, the action of the reactant mixture on β leads to an increase in activity as a function of the number of pulses. The activity remains nearly constant from the fifteenth pulse. Under steady-state conditions the amount of oxidized propene on β remains lower than that observed with α. Only incomplete reoxidation of the surface of β may be proposed. The same treatment on γ leads to a decrease in activity with the number of pulses. The steady-state value observed is always lower than the value obtained for α. For the first pulse the percentage of oxidized propene is highest on catalyst α. This percentage is never obtained again after oxidation treatment of the catalyst. Selectivities for C_3H_4O under these experimental conditions are always lowest for the first pulse and then quickly reach a high constant value.

These results lead us to formulate the following sequences of activity and selectivity. (i) At 305 °C activity follows the order $\alpha_i > \gamma_i > \alpha_{st} > \gamma_{st} > \beta_{st} > \beta_i$ while selectivity for C_3H_4O follows the order $\alpha_{st} > \beta_{st} > \gamma_{st} > \gamma_i > \alpha_i > \beta_i$.

(ii) At 370 °C activity follows the order $\alpha_i > \gamma_i > \alpha_{st} > \gamma_{st} = \beta_{st} > \beta_i$ while selectivity for C_3H_4O follows the order $\beta_{st} > \alpha_{st} > \gamma_{st} > \gamma_i > \beta_i > \alpha_i$. (The subscripts i and st indicate initial and steady-state values, respectively.)

The results reported here show that the catalyst surface is in dynamic interaction with the gas phase. The catalytic performance of the sample depends directly on the nature of the surface phase.

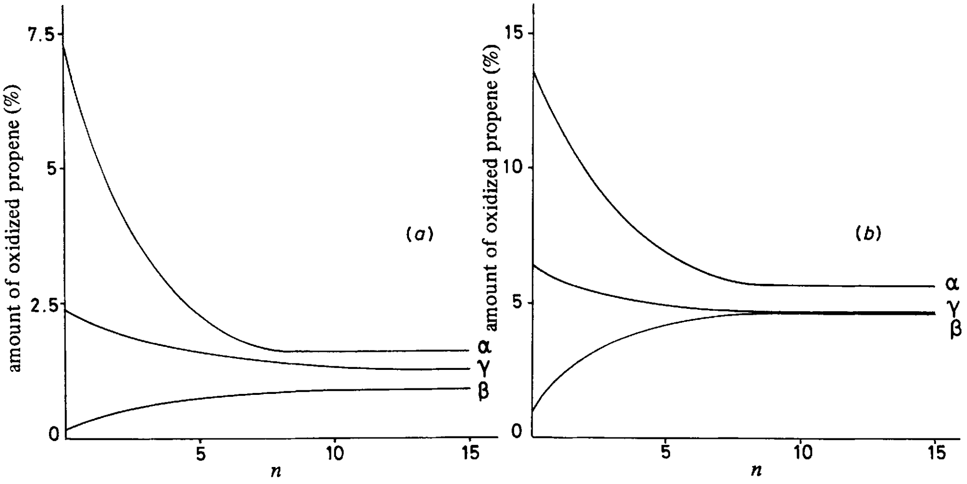

Fig. 5. Influence of the reactant-mixture treatment on the catalysts α, β and γ at (*a*) 305 and (*b*) 370 °C with $O_2/C_3H_6 = 1/1$.

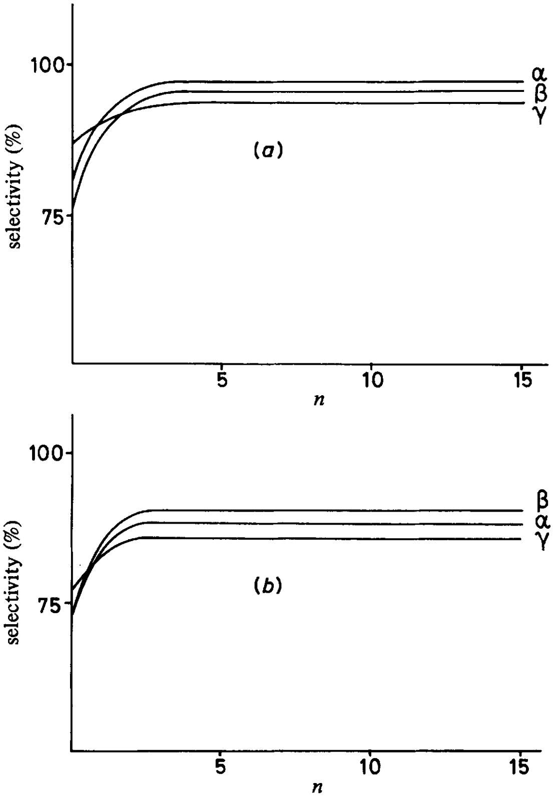

Fig. 6. Influence of the reactant-mixture treatment on selectivity for C_3H_4O of the catalysts α, β and γ at (*a*) 305 and (*b*) 370 °C with $O_2/C_3H_6 = 1/1$.

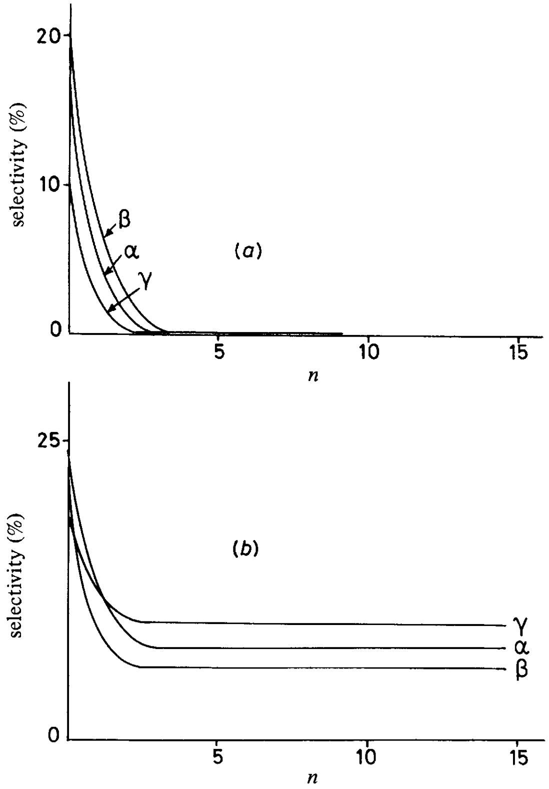

Fig. 7. Influence of the reactant-mixture treatment on selectivity for CO_2 of the catalysts α, β and γ at (*a*) 305 and (*b*) 370 °C with $O_2/C_3H_6 = 1/1$.

DISCUSSION

A change in the USb_3O_{10} surface is observed during propene oxidation without gaseous oxygen. In the steady state only one type of site, S, is seen at 305 °C; S seems to lead to allylic oxidation and the formation of C_3H_4O and C_2H_4O. At 370 °C a new type of site, T, responsible for complete oxidation coexists with S, the number of S sites being greater than those of T. The type of product obtained thus depends on the type and mutual proportions of these centres. At the first pulse S and T sites are both observed. The following pulses lead to a sharp decrease in the yield of T sites. These T sites may be considered as having highly coordinated oxygen: some of the oxygens in the lattice surrounding such a chemisorption site are activated in order to take part in the oxidation of C_3H_6 to CO_2. This oxygen depletion during the first pulse makes most of the sites inactive. Reactivity of the solid for complete oxidation is therefore directly dependent on the rate of regeneration of T sites occurring during the reoxidation step. It may be assumed that S possesses oxygen in low coordination, that propene activated on S reacts and that the products are then desorbed before unselective processes can occur. The metal–oxygen bonds on coordinatively unsaturated S sites are stronger than those on T sites, which have more highly coordinated oxygen than the S sites.[6] The presence of stronger bonds is characterized by unlabile oxygens which are expected to be more selective reactants for olefin oxidation. Such strong bonds are created when surface restructuring occurs. This surface change after the first propene pulse has been previously proved by an X.p.s. study[2] which characterized the depth profile of the catalyst. C_3H_6 treatment leads to a change into the antimony oxidation state: the initial Sb^{5+} is reduced to Sb^{3+}. Cation migration is never observed, so the formation of a defined surface structure cannot be proved. The hypothesis of the formation of unsaturated sites may be considered.

The evolution of sites and of the coke deposit on β is confirmed by examination of the structure of this catalyst during and after the action of gaseous oxygen. Raman studies show no coke at the surface of the catalyst, so we may assume that it is burnt off in the presence of gaseous oxygen. If coke is the only reactant responsible for β deactivation, the catalytic performance of γ should be identical to that of α. In so far as the selectivity of γ_i for acrolein is much greater than the selectivity of α_i, we must consider that S sites are not trapped by reoxidation. Moreover, since the initial catalytic performance of USb_3O_{10} is never recovered, we may reject the hypothesis that there is a reversible structural change to the surface. The T sites are not completely regenerated. The role of the reactant mixture on β may be analysed as follows. Initially the gaseous mixture reacts with a coked surface on which two types of active sites are present. At the first pulse, the oxygen of the mixture reacts with the coke, and C_3H_6 is activated on the sites. In this case CO_2 is the product of coke burning and of the complete catalytic oxidation of the hydrocarbon which takes place *via* the restructuring of T sites. This hypothesis explains the comparatively high selectivity for CO_2. During the following pulses the coke is completely removed and the restructuring of the surface occurs, resulting in the enhancement of selectivity for acrolein. In the steady state at 305 °C the restructured surface possesses essentially unsaturated S sites. At 370 °C two paths leading to complete oxidation may be proposed: a restructuring of the highly coordinated oxygen T sites or a reaction of acrolein or acetaldehyde with the catalyst surface. The latter mechanism involves successive oxidation reactions.

CONCLUSION

The present study permits the characterization of two types of active sites on the surface of USb_3O_{10}. It is proposed that the difference between these results from the difference in their degree of oxygen coordination. There is only a small amount of active oxygen available. The observed low mobility of oxygen ions from the bulk to the surface or from the surface to the bulk may explain the irreversible surface restructuring.

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