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Mechanism of Promoter Action in Catalytic Oxidation of Propylene to Acrolein*

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Addition of gaseous methylbromide at low concentrations causes a marked increase in specificity for acrolein during propylene oxidation catalyzed by cuprous oxide. The role of the alkyl-halide promoter is investigated with a cuprous oxide crystal at 350°C by simultaneous measurements of product distribution and electrical conductivity at different ratios of propylene to oxygen. Helium was employed as a carrier gas. Based on the electrical measurements it is noted that the promoter prevents the oxidation of Cu^+ to Cu^{2+} at high O_2/C_3H_6 ratios. The results emphasize previous observations of the catalytic properties of cuprous oxide for acrolein formation. The mechanism of promoter action is interpreted in terms of a solid-state model with charge exchange between adsorbates and catalyst surface controlled by electronic surface-state energy levels.

INTRODUCTION

The oxidation of olefins on metal-oxide catalysts has been the subject of a number of investigations as reviewed in two recent publications (*1*, *2*). In a preceding paper we described the results obtained for the oxidation of propylene catalyzed by a single crystal of cuprous oxide (*3*). In this system the specificity for acrolein formation was related to the defect structure of the cuprous oxide. The interpretation of the experimental data was based on a model involving the relative distribution of occupied and empty surface-state energy levels at the catalyst/gas interface.

An interesting aspect of the oxidation of propylene to acrolein over copper catalysts is the pronounced enhancement of specificity brought about by the addition of gaseous additives (*1*, *2*) such as halogens, halogenated compounds, and selenium compounds. A striking feature of all these promoters is the fact that they contain atoms which are electron acceptors and which on adsorption could provide populated surface states on the catalytic surface. The degree of occupancy of these surface-state levels could result in anchoring of the barrier height in the space-charge region and thereby control of the Fermi level at the surface of the catalyst. In the present study, we have attempted to investigate the electronic role of a promoter additive in catalyst specificity.

APPARATUS

The apparatus employed was identical to that described in Ref. (*3*). The single crystal of cuprous oxide was grown in situ inside the quartz reaction vessel in accordance with the procedure given by Triuich and co-workers (*4*). For electrical conductivity measurements during catalytic reaction, the crystal was provided with suitable connections (four-point probe) shielded from the gas mixture by means of ceramic coatings. For quantitative chemical analysis of propylene and acrolein, a gas-chromatographic column was employed containing 15 wt % UCON 300 on Chromosorb P at 60°C. The total quantity of CO and CO_2 formed in the reaction was calculated from the difference in the mass of propylene lost and the mass of acrolein formed on the assumption that

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CO, CO_2, H_2O, and C_3H_4O are the only products of reaction. The degree of conversion was kept at a sufficiently low level that no condensation of products occurred during their sojourn from the reactor (kept at 350°C) to the gas-chromatographic column. Propylene, oxygen, and helium were metered and mixed before entering the reactor at a total flow rate of 65 to 75 cm^3/min and a total gas pressure of 1 atm. In view of the small amounts of gaseous additive (CH_3Br) required for enhancement of the specific activity of the catalyst for acrolein formation, the additive was added to the reactant stream by displacement from a gas-tight syringe at a prescribed rate of flow. The piston of the syringe was advanced with the aid of a servocontrolled drive mechanism. By this means flow rates from 5 to 100×10^{-3} cm^3/min could readily be achieved. In a given set of experiments the electrical and chemical measurements were carried out simultaneously. Thus the product distribution and conductivity in the presence of CH_3Br could be compared with those in the absence of CH_3Br for a range of mixture ratios of C_3H_6/O_2. Under our experimental conditions no measurable conversion of propylene was detected in the absence of the catalyst.

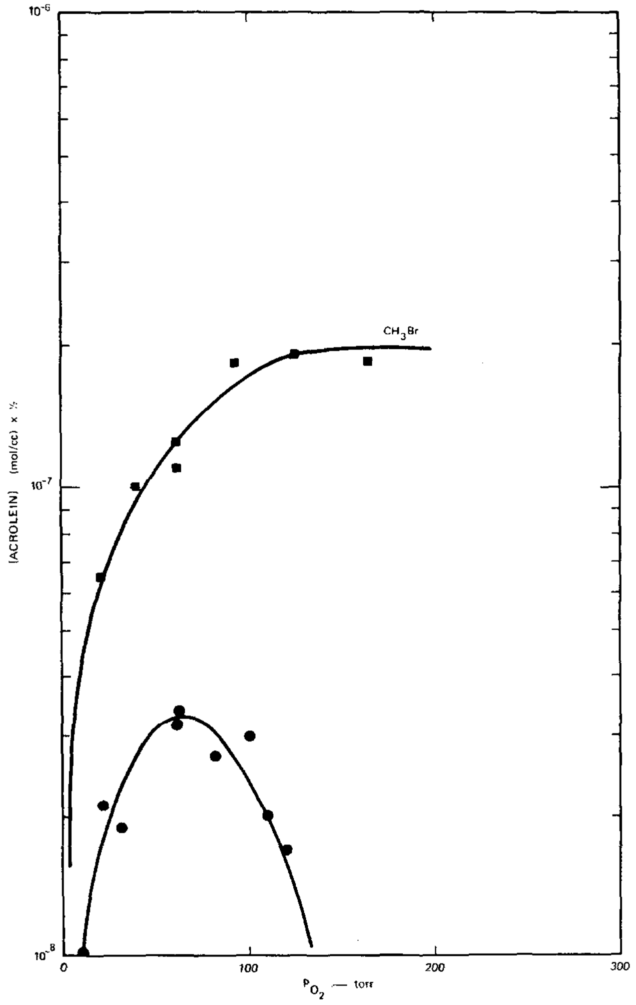

FIG. 1. Acrolein formation at 350°C with and without methylbromide (partial pressure of C_3H_6 = 130 ± 5 Torr; $CH_3Br/C_3H_6 = 4.5 \times 10^{-2}$ vol %).

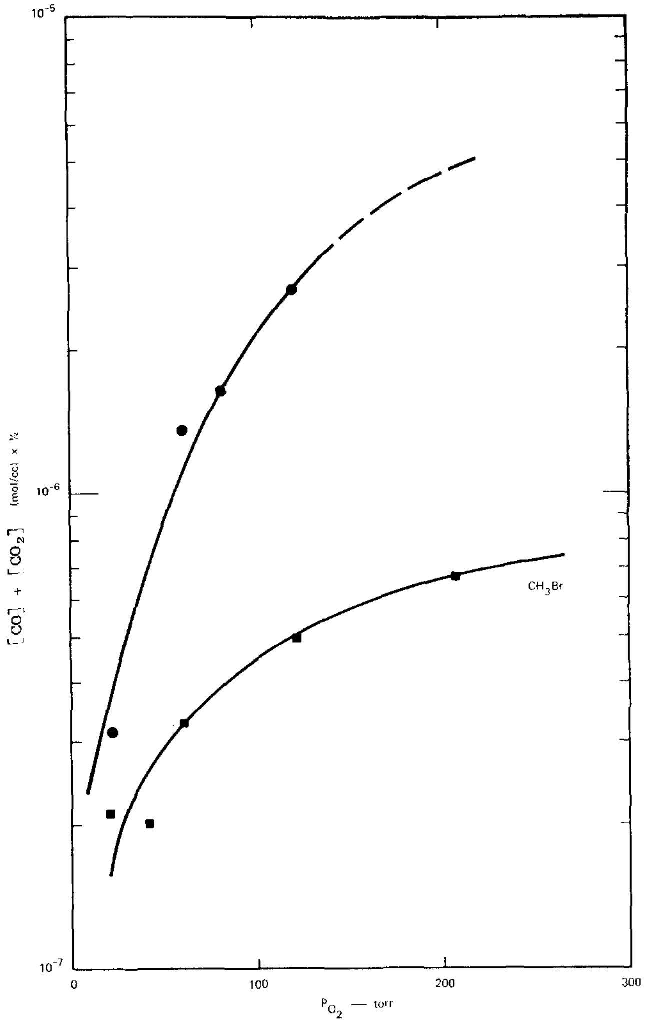

FIG. 2. Carbon monoxide and dioxide formation at 350°C with and without methylbromide (partial pressure of $C_3H_6 = 130 \pm 5$ Torr; $CH_3Br/C_3H_6 = 4.5 \times 10^{-2}$ vol %).

EXPERIMENTAL RESULTS

As reported earlier (*3*) the formation of acrolein catalyzed by cuprous oxide is a sensitive function of the partial pressures of oxygen and propylene. The specificity of the catalyst for acrolein formation is favored by copper-rich cuprous oxide and attains a maximum (Fig. 1) under conditions which, on the basis of electrical conductivity data, suggest a catalyst composition of nearly stoichiometric cuprous oxide (*3*). On the other hand, the production of carbon monoxide and dioxide, CO_x, (Fig. 2) exhibits a monotonic increase as the oxygen partial pressure is raised.

The addition of methylbromide to the reactant stream in relatively small concentrations (volume ratio $CH_3Br/C_3H_6 = 4.5 \times 10^{-4}$) completely alters the specificity pattern observed at various oxygen concentrations. For a given partial pressure of oxygen the formation of acrolein is increased and that of CO_x reduced in the presence of methylbromide. In addition, the maximum noted in the acrolein formation curve is completely eliminated. The results suggest that the catalyst is now capable of producing acrolein under conditions which, in the absence of CH_3Br, would have led to complete oxidation of the propylene and conversion of the catalyst to cupric oxide. The data listed in Table 1 show the change in the product ratio of C_3H_4O/CO_x effected by the addition of CH_3Br at different oxygen pressures. While in the absence of CH_3Br this ratio is relatively small and decreasing, it remains high and practically constant in the presence of CH_3Br. These results confirm the profound promoting effect (*1*, *2*) of methylbromide when added in small quantities to the reactant stream.

TABLE 1
EFFECT OF METHYLBROMIDE ON PRODUCT DISTRIBUTION FROM PROPYLENE[a] OXIDATION AT 350°C

Partial pressure O_2 (Torr)	$C_3H_4O/[CO_2 + CO]$	
	without CH_3Br	with CH_3Br[b]
25	0.042	0.37
50	0.035	0.38
65	0.027	0.40
100	0.011	0.39
125	0.005	0.37
150	—	0.34

[a] Partial pressure of propylene = 130 ± 5 Torr.
[b] Vol ratio $CH_3Br/C_3H_6 = 4.5 \times 10^{-4}$.

Similarly the electrical conductivity of the catalyst shows an entirely different response to oxygen in the presence of CH_3Br. Without CH_3Br, the transition from a nonstoichiometric copper-rich to an oxygen-rich cuprous oxide is demonstrable by the change from $\frac{1}{2}$ to $\frac{1}{7}$ in the exponent of the electrical conductivity curve with oxygen pressure (*3*). On addition of CH_3Br the exponential conductivity factor in the copper-rich region is markedly reduced from the value of 0.5 observed in the absence of CH_3Br (Table 2). Also, the slope of the electrical conductivity curve remains constant up to much higher partial pressures of oxygen in the presence of methylbromide.

DISCUSSION

An interpretation of the experimental result may be sought in a phenomenological examination of the model previously employed in the analysis of catalyst specificity for acrolein formation in the absence of a promoter. It was suggested (*3*) that variations in the density of different oxygen species on the surface of cuprous oxide are reflected in the observed reaction kinetics. The surface density of these species, both charged and uncharged, is governed by the location of the surface-state energy levels of the adsorbates relative to the Fermi level of the catalyst. In terms of this model the action of a promoter such as methylbromide is to be found in a mechanism by means of which the Fermi level of the catalyst becomes anchored as the concentration of such reactants as propylene and oxygen is altered. This interpretation is based on a concept developed by Morrison (*5*, *6*) according to which nonreactive surface additives can be used to provide surface states, which adjust the Fermi level and control the electronic properties of a catalyst.

TABLE 2
VARIATION OF ELECTRICAL CONDUCTIVITY EXPONENT OF CUPROUS OXIDE IN THE PRESENCE OF METHYLBROMIDE AT 350°C

CH_3Br/C_3H_6 (vol ratio)	Exponential factor
0	0.50
0.9×10^{-3}	0.42
2.1×10^{-3}	0.30
5.8×10^{-3}	0.23
$>10^{-2}$	0

In the presence of empty acceptor-like surface states below the Fermi level of the cuprous oxide catalyst, a transfer of electronic carriers will take place, i.e., the injection of holes into the valence band (Fig. 3). Due to this process the surface acquires a negative charge and a positive space charge region is formed, i.e., the energy bands near the surface bend upwards with respect to the Fermi level. The surface-state energy levels in the band-gap region are governed by short-range atomic forces and are relatively unaffected by the space charge. As a result they change their position in such a way that the relative distances between the edge of the valence-band level, of the con-

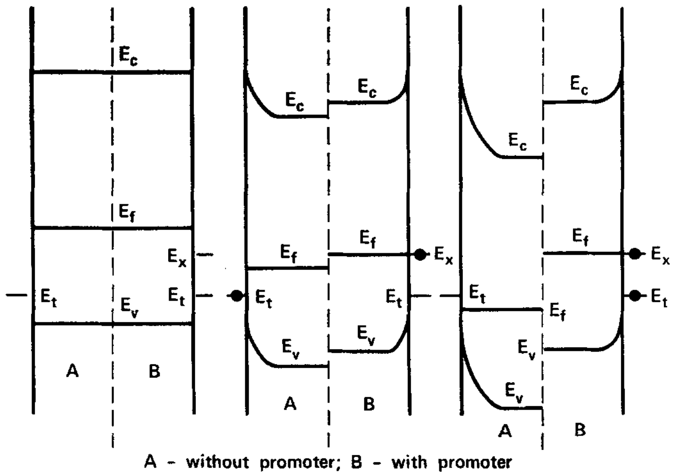

FIG. 3. Energy-level diagram (energy levels: E_v, valence band; E_c, conduction band; E_F, Fermi level; E_t, surface-state level of oxidizing species; E_x, surface-state level of promoter).

duction-band level, and of the surface-state level remain unaffected. Due to the requirement of overall electrical neutrality, the degree of band bending at the surface is in direct proportion to the density of the occupied electronic energy levels of the surface states in the absence of an external electric field. It is possible therefore that the surface-state energy levels may be only partially occupied due to the fact that the band bending has caused these levels to lie above the Fermi level (Fig. 3, Model A).

The location of the Fermi level relative to the surface-state level for a given degree of occupation of the surface states can be deduced from the equilibrium distribution of filled n_t to unfilled p_t levels (*7*):

$$n_t = N_t f_n(E_t) \text{ and } p_t = N_t f_p(E_t), \quad (1)$$

where $f(E_t)$ represents the Fermi distribution function and N_t the total number of surface centers, $N_t = n_t + p_t$. For a single-charge surface state the ratio of filled to unfilled levels is found to be:

$$n_t/p_t = \left\{\frac{1}{1 + \exp[(E_t - E_F)/kT]}\right\} \Big/ \left\{\frac{1}{1 + \exp[-(E_t - E_F)/kT]}\right\} = \exp[-(E_t - E_F)/kT], \quad (2)$$

so that

$$E_F = E_t - kT \ln (n_t/p_t). \quad (3)$$

It is apparent (Eq. 3) that by suitable adjustment of the ratio of filled to unfilled surface-state centers (n_t/p_t), adjustment of the Fermi level of the catalyst is feasible (*5*).

In general, the surface potential v_s is determined by the density and energy distribution of various surface-state levels associated with different adsorbates so that $n_t = \Sigma_i N_{ti} f(E_{ti})$. Two such levels are shown in Fig. 3 (Model B), with E_x, assigned to the catalytic promoter species, located closer to the Fermi level than E_t, assigned to a reactant species such as oxygen, for example. It is of interest to examine the change in surface potential due to filling of these individual levels. Electrical neutrality conditions specify that the space charge density Q_{sc} must be equal to the charge density in the surface states. Thus for acceptor-like states of energy E_t and E_x

$$Q_{sc}/q = -(n_t + n_x). \quad (4)$$

If we allow the surface-state level E_x to be filled by exposure of the catalyst to the promoter X, a space charge will build up as shown diagrammatically in Fig. 3 (B). Addition of the other species having a surface-state level at E_t may result in further charge transfer. The change of the barrier height with electron occupation of the level E_t is found to be

$$dv_s/dn_t = -1/[(1/q)(dQ_{sc}/dv_s) + (N_x df(E_x)/dv_s)]. \quad (5)$$

The second term in the denominator of Eq. (5) suggests that the space-charge region may become relatively protected from the effect of electron occupancy of E_t because the derivative $df(E_x)/dv_s$ goes through a maximum as E_x passes through the Fermi level E_f (*7*). In addition, a high density of surface-state centers N_x will also tend to anchor the barrier height. In essence, a surface state E_x present at high surface density and close to the Fermi level will tend to protect the space-charge region from the influence of other charge-transferring adsorbed species.

An indication of the control of the Fermi level of cuprous oxide in the presence of small quantities of CH_3Br at the solid/gas interface is to be found in the variation of the electrical conductance measurements. In the absence of the promoter additive, the conductivity change as a function of partial pressure of oxygen exhibits the characteristics deduced from the defect structure of cuprous oxide. Thus the conductivity exponent of $\frac{1}{2}$ in the copper-rich cuprous-oxide regime corresponds to the theoretical value of $\frac{3}{8}$ calculated by Bloem (*8*). However, the addition of CH_3Br causes a marked decrease in the exponent (Table 2). This result suggests that the Fermi level is being anchored so that hole injection associated with oxygen sorption is becoming more difficult. It may be concluded that the cuprous-oxide phase has become resistant to further oxidation due to the presence of the bromine-containing additive. From a catalytic viewpoint the stabilization of the cuprous oxide Fermi level at a value leading to high acrolein formation allows selective oxidation of propylene at much higher partial pressures of oxygen. As shown in Fig. 1, the addition of methylbromide at a vol ratio of $CH_3Br/C_3H_6 = 4.5 \times 10^{-4}$ stabilizes the catalyst to such an extent that even at an oxygen partial pressure of 200 torr, the products contain a very high proportion of acrolein. In the absence of CH_3Br under a comparable condition of O_2/C_3H_6, the catalyst would have been oxidized to cupric oxide and would have produced predominantly carbon dioxide. Yet the addition of the halogen compound results in an almost constant specificity for acrolein formation with increasing oxygen concentration (Table 1).

The mechanistic model proposed for the action of bromine-containing additives is expected to apply as well to other promoters, all of which appear to have electron-acceptor properties (compounds containing halogens, sulfur, selenium). As yet the chemical nature of the surface-state species responsible for the promoter action cannot be identified with certainty. However, the observed decrease in the absolute value of electrical conductance associated with the promoter's presence suggests that the species of interest does not inject holes directly into the valence band of cuprous oxide. A process such as the following could be proposed:

$$O^{2-}(s) + Br(s) + p \rightleftarrows BrO^-(s), \quad (4)$$

where (s) refers to surface-adsorbed species, and p to the hole carriers. Therefore, the surface-state energy level associated with BrO would be filled with electrons due to depletion of hole carriers. The anchoring of the Fermi level in accordance with Eq. (3) could therefore be associated with reaction (4) involving a BrO^-/BrO localized surface-state.

At very high concentrations of methylbromide in the reactant stream ($CH_3Br/C_3H_6 > 10^{-1.5}$ by volume) we observed increases in conductivity, undoubtedly due to the reaction:

$$Br(s) \rightleftarrows Br^-(s) + p,$$

with the formation of a space charge layer and a negative surface charge. However, under these conditions complete loss of catalytic activity was noted. The solid had become inert for the oxidation of propylene to acrolein and carbon dioxide.

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