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The Catalytic Oxidation of Propylene

VII. The Use of Temperature Programmed Reoxidation to Characterize γ-Bismuth Molybdate

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Temperature programmed reoxidation (TPR) was used to characterize the redox properties of γ-Bi_2MoO_6. Reoxidation of a prereduced catalyst by this technique yielded two well-defined temperature ranges for reoxidation. When the catalyst was prereduced by propylene, the maximum of a low-temperature peak occurred at 158°C and the maximum of a high-temperature peak occurred at 340°C. The physicochemical changes associated with these reoxidation temperatures were further investigated by X-ray diffraction, Auger spectroscopy, and kinetic measurements. The low-temperature reoxidation peak was found to be a result of the reoxidation of Mo^{4+} to Mo^{6+} and Bi^0 to Bi^{m+}, where $0 < m < 3$. The high-temperature reoxidation peak was found to be a result of the reoxidation of Bi^{m+} to Bi^{3+}. The high-temperature reoxidation may involve the direct oxidation of bismuth by gas phase oxidation or may involve shear structures. The high-temperature reoxidation process also appears to be related to the rate-limiting step for propylene oxidation to acrolein at temperatures below 400°C.

INTRODUCTION

It has been demonstrated that several phases of bismuth molybdate exhibit excellent activity and selectivity for the oxidation of propylene. The mechanism of the reaction has been investigated by numerous workers. Keulks (*1*) and Wragg *et al.* (*2*) have demonstrated that gas phase oxygen is incorporated into the lattice, and the lattice oxygen, in turn, participates in the production of acrolein from propylene. Matsuura, *et al.* (*3*) proposed the existence of two sites (Site A and Site B) on Bi_2MoO_6 and suggested that the oxygens associated with these two sites exhibit different catalytic behavior.

The possibility of more than one active site on the catalyst surface has led to investigations which have attempted to correlate the active oxygen species for selective oxidation with one of the active sites. Seiyama *et al.* (*4*) suggested that the molybdenum of bismuth molybdate catalysts serves as the carrier of oxygen. Otsubo *et al.* (*5*) utilized bismuth molybdate catalysts containing ^{18}O in the Bi_2O_2 layer and in the MoO_2 layer. Their results suggested that the oxygen of the Bi_2O_2 layer is incorporated into acrolein, while the MoO_2 layer serves as the site for reoxidation and incorporation of gas phase oxygen into the lattice. Their work also suggested the diffusion of oxygen from the MoO_2 layer to the Bi_2O_2 layer.

The present investigation was undertaken with the objective of examining in more detail the redox properties of γ-Bi_2MoO_6 utilizing temperature programmed reoxidation (TPR), X-ray diffraction, and Auger spectroscopy.

EXPERIMENTAL

The γ-Bi_2MoO_6 was prepared according to Batist *et al.* (*6*). X-Ray diffraction and

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spectroscopic measurements indicated it was the pure phase.

The γ-Bi_2MoO_6 was further characterized by utilizing temperature programmed reoxidation (TPR). This technique consists of reducing the catalysts to a predetermined degree of reduction in an RG Cahn microbalance with a reducing agent. In the experiments reported herein, propylene (20% in ultrapure nitrogen) was used as the reducing agent. After reduction at elevated temperature, the catalyst was cooled to room temperature while continuing to flow the reducing agent though the microbalance.

Varying the flow rate of the reducing agent or varying the catalyst weight had a minimal effect on the TPR curves. When the catalyst was reduced above 400°C by propylene, no decrease of the catalyst weight was observed in the reoxidation process. Therefore, it appears that the surface residues do not affect the reoxidation as reported (*3*).

Pure nitrogen was then allowed to flow through the microbalance until all of the reducing agent was flushed from the microbalance. The reoxidation of the catalyst was investigated by flowing dry air through the microbalance while increasing the temperature linearly. A Cahn Time Derivative Computer (Mark II) was used to display the weight change in a differential form.

The catalyst samples were examined by Auger electron spectroscopy utilizing a Varian Auger analysis system equipped with a cylindrical mirror analyzer having resolution of better than 1%. Normal incidence for the primary beam was used in all measurements. The spectrometer was operated at beam energy, 3 keV; beam current, 10 μA; lock-in amplifier sensitivity, 0.2 mV; time constant, 100 msec; modulation voltage, 2 V (peak to peak). Special care was taken to avoid the possible charging effects which are usually associated with an insulator specimen. The sample was prepared by pressing a thin layer of powder between indium foil (Martz grade, Materials Research Corporation). For the purpose of comparison, clean Bi, Bi_2O_3, MoO_2, and MoO_3 powder specimens were also included in the measurements. In order to reduce beam effects, both incident beam current density and beam exposure time were carefully controlled and minimized. Also, to reduce the sweep time of each run, only $BiN_5N_{6,7}N_{6,7}$, $N_{6,7}O_{4,5}O_{4,5}$, and $MoM_{4,5}N_{2,3}N_{4,5}$ Auger transition peaks were monitored in most measurements.

Reduction and reoxidation of the catalyst were also investigated under isothermal conditions in the microbalance. The kinetics of the reduction and reoxidation were calculated on the basis of initial weight changes.

RESULTS AND DISCUSSION

1. Temperature Programmed Reoxidation (TPR) of γ-Bi_2MoO_6

A typical TPR curve of the γ-phase catalyst prereduced by propylene is shown in Fig. 1. Two peaks are observed. The maximum of the low-temperature peak occurs at 158°C and the maximum of the high-temperature peak occurs at 340°C.

The activation energy of the reoxidation for each peak was calculated from the shift of the temperature maximum (T_M) as a function of the heating rate by using the following equation:

$$2 \ln T_M - \ln \beta = E_a/RT + \ln E_a \cdot V_m/[2RkP_{O_2} \cdot (1 - \theta_M)]. \quad (1)$$

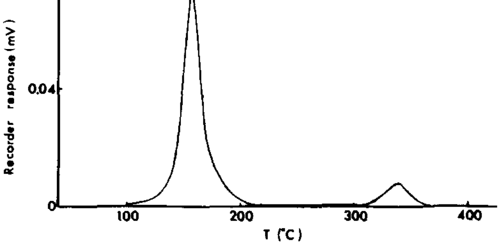

FIG. 1. TPR chromatogram for 3% reduced γ-phase by C_3H_6 at 420°C (heating rate = 6.0°C/min).

This equation is based on the assumption that the reoxidation process involves a homogeneous surface, is not controlled by diffusion, and the adsorption of oxygen is dissociative. These assumptions lead to the following equation for the reoxidation process:

$$V_{\mathrm{M}} \frac{d\theta}{dt} = K \cdot P_{\mathrm{O}_2} \cdot (1 - \theta)^2 \exp(-E_{\mathrm{a}}/RT) \quad (2)$$

where V_{M} is the amount of adsorbate at the full adsorption, θ_{M} the surface coverage at peak maximum, P_{O_2} the partial pressure of oxygen, and k and R are constants. Equation (1) can be derived from Eq. (2) using the method of Cvetanovic and Amenomiya (*7*). We also assume that θ_{M} in Eq. (1) is independent of the heating rate, β. Utilizing Eq. (1), the activation energy for the low-temperature peak was determined to be 29 kcal/mole and the activation energy for the high-temperature peak was determined to be 63 kcal/mole (Fig. 2). There are a number of inherent difficulties in determining activation energies by this method. Therefore, as discussed later, we utilized more traditional isothermal methods to also determine activation energies for reoxidation.

2. *X-Ray Diffraction*

The X-ray diffraction patterns are shown in Fig. 3. Figure 3a shows the pattern of γ-$\mathrm{Bi_2MoO_6}$ which was reduced 3.5% by propylene. Figure 3b shows the pattern of γ-$\mathrm{Bi_2MoO_6}$ with only the low-temperature peak reoxidized. Figure 3c shows the pattern when both peaks are reoxidized. Figure 3a shows that a small amount of bismuth metal but no $\mathrm{MoO_2}$ is detected at 3.5% reduction. Seiyama *et al.* (*4*), Shirasaki *et al.* (*8*), Fattore *et al.* (*9*), and Grzybowska *et al.* (*10*) have detected bismuth metal and $\mathrm{MoO_2}$ present in γ-$\mathrm{Bi_2MoO_6}$ which has been extensively reduced. However, $\mathrm{Mo^{6+}}$ is reduced to $\mathrm{Mo^{4+}}$ but is not reduced from $\mathrm{Mo^{4+}}$ to $\mathrm{Mo^0}$ upon further reduction. Seiyama *et al.* (*4*) also suggested the reduction from $\mathrm{Mo^{6+}}$ to $\mathrm{Mo^{4+}}$ was favored over the reduction of $\mathrm{Bi^{3+}}$ to $\mathrm{Bi^0}$ based on thermodynamic considerations and reduction experiments. Consequently, it is reasonable that in our samples both $\mathrm{Bi^0}$ and $\mathrm{MoO_2}$ are formed on the catalyst surface when the catalyst is reduced by propylene. In Fig. 3b, the X-ray peaks of bismuth metal have disappeared, and the X-ray pattern is almost identical to that

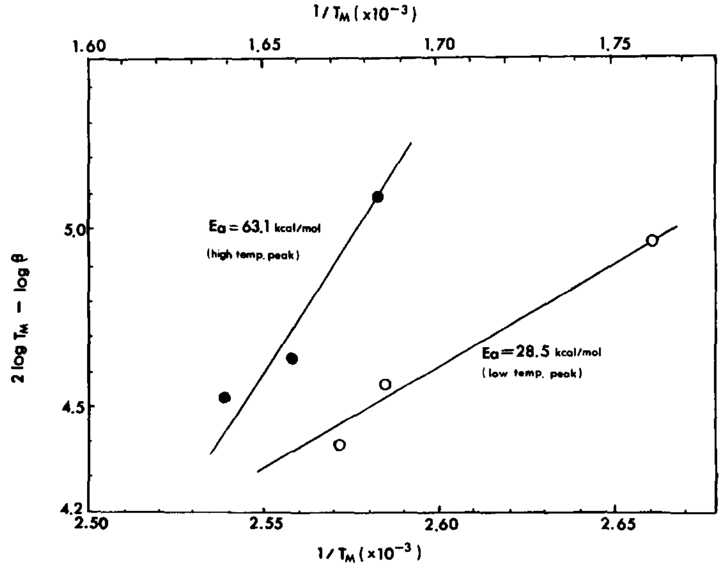

FIG. 2. Activation energies for two TPR peaks of γ-phase reduced by propylene at 420°C.

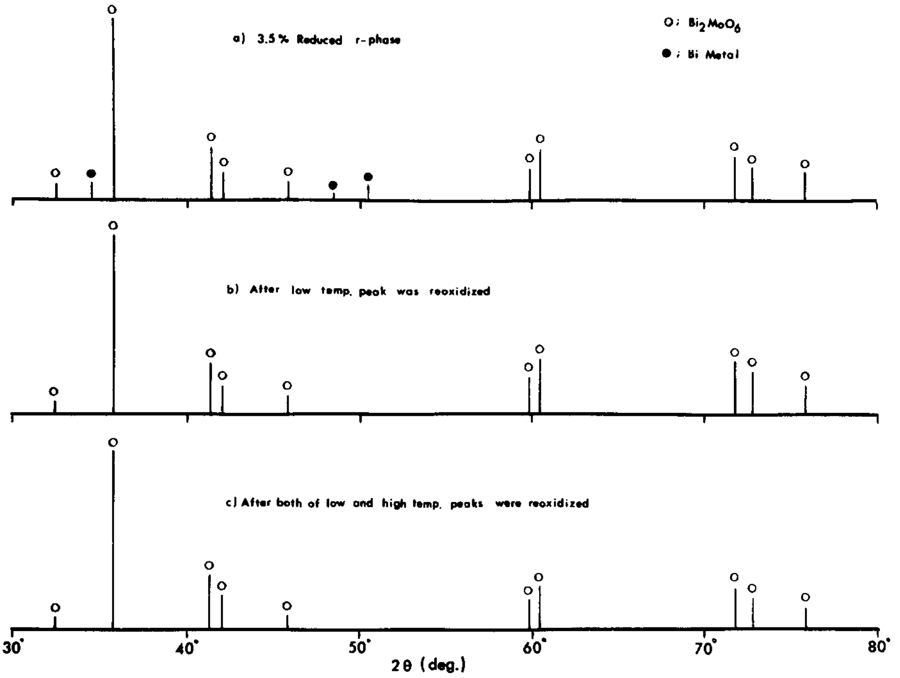

FIG. 3. X-Ray diffraction pattern for each catalyst treated.

obtained when both peaks are reoxidized (Fig. 3c). It is possible that bismuth metal is reoxidized and reincorporated into the catalyst bulk at reoxidization temperatures characteristic of the low-temperature reoxidation peak. However, the X-ray diffraction technique is limited and we were not able to obtain definitive information regarding the nature of the reoxidation of the high-temperature peak.

3. *Auger Electron Spectroscopy (AES)*

A change in the chemical environment can result in core-level energy shifts and variations in valence-band density of states which can lead to a change of the position and shape of Auger peaks. Therefore, the catalysts were investigated by AES, since the oxidation state in both Bi and Mo in either the reduction process or the reoxidation process might be revealed from chemical shift measurements. Figure 4 summarizes the profile spectrum for Bi, Bi_2O_3, MoO_2, MoO_3 and the corresponding spectrum for each catalyst. The change in the bismuth $N_5N_{6,7}N_{6,7}$ and $N_{6,7}O_{4,5}O_{4,5}$ Auger transition spectrum as a function of oxidation state can be obtained by comparing spectrum 1 of Bi^0 with spectrum 5 of Bi^{3+}. This is also possible for the molybdenum $M_{4,5}N_{2,3}N_{4,5}$ Auger transition spectrum between Mo^{4+} (spectrum 6) and Mo^{6+} (spectrum 10). By comparing the spectrum of each catalyst with the spectra of Bi^0, Bi^{3+}, Mo^{4+}, and Mo^{6+}, one is able to obtain some idea of the oxidation state of Bi and Mo for each catalyst.

For the 6% prereduced catalyst, the bismuth spectrum (spectrum 2) closely resembles that obtained with bismuth metal (spectrum 1). This is consistent with the results obtained in the X-ray diffraction studies. For the same catalyst, the Mo spectrum (spectrum 7) reflects the typical spectrum of Mo^{4+} (spectrum 6). This suggests that Mo^{6+} is reduced to a lower valence state, Mo^{4+}, as has been reported in the literature. Therefore, we have concluded that extensive reduction of this catalyst results in the reduction of Bi^{3+} to Bi^0 and Mo^{6+} to Mo^{4+}.

Spectra 3 and 8 were obtained on a

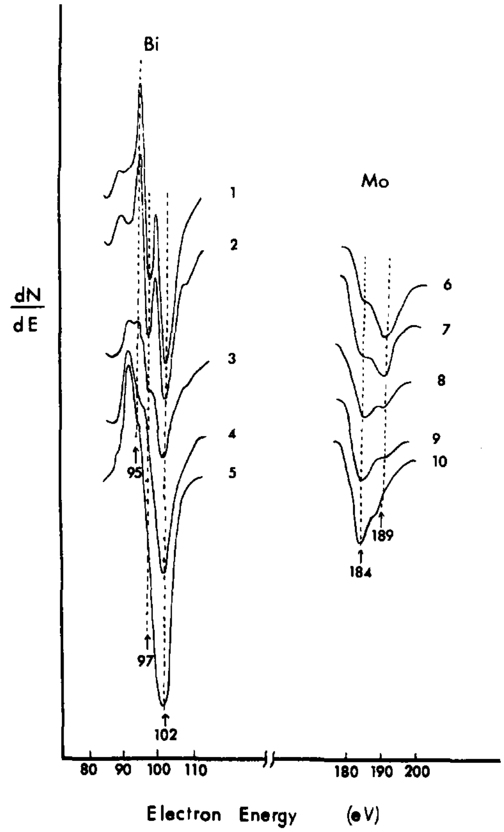

FIG. 4. Auger electron spectrum for each catalyst. 1, Bi metal; 2 and 7, 6% reduced γ-phase; 3 and 8, reoxidized at 200°C (only low-temperature site is reoxidized); 4 and 9, reoxidized at 400°C (both the low-temperature and the high-temperature sites are reoxidized); 5, Bi_2O_3; 6, MoO_2; 10, MoO_3.

catalyst with the low-temperature site reoxidized. Significant changes are observed from spectrum 2 and 7, respectively. Furthermore, spectrum 3 is not similar to either Bi^0 or Bi^{3+}. Therefore, we have assumed the oxidation state for Bi in spectrum 3 as Bi^{m+}, $0 < m < 3$. On the other hand, we have assigned the oxidization state of Mo (spectrum 8) as Mo^{6+} due to the similarity between the spectrum 8 and 10. This result suggests that during the low-temperature reoxidation, Bi is oxidized to Bi^{m+} and molybdenum to Mo^{6+}.

Spectra 4 and 9 were obtained after complete reoxidation of the reduced catalyst at 400°C. They resemble the spectra obtained from the original, fresh catalyst (which has good activity for acrolein formation) before the reduction. The similarity of spectra 4 and 9 with spectra 5 and 10 also confirms the existence of Bi^{3+} and Mo^{6+} as expected. This result also suggests that the high-temperature reoxidation process produces the complete reoxidation of Bi^{m+} to Bi^{3+}. Thus, the reoxidation of bismuth is not complete until the high-temperature site is reoxidized, even though the reoxidation of Mo^{4+} to Mo^{6+} is accomplished during low-temperature reoxidation.

The chemical shift observed in AES is a resultant shift of the three levels involved in a particular Auger transition. The situation is even more complicated when there is a possibility of overlapping of several Auger transition peaks. It is, therefore, difficult to assign an exact value of m without the aid of appropriate profile spectra. In summary, the results obtained from AES suggest that the low-temperature TPR peak is related to the reoxidation of Mo^{4+} to Mo^{6+} and the reoxidation of Bi to an intermediate state, possibly Bi^{1+}. The high-temperature TPR peak is related to the reoxidation of Bi^{m+} to Bi^{3+}.

4. *Reactivity of the TPR Peaks*

We have attempted to relate the peaks obtained by the TPR technique to the activity and selectivity of γ-Bi_2MoO_6 by examining the reactivity of representative catalyst samples. The results are summarized in Table 1.

The activity tests were done in the microbalance so we could monitor the degree of reduction of the catalyst. To determine the reactivity of a catalyst with only the low-temperature site reoxidized, we utilized a 6% prereduced γ-Bi_2MoO_6 catalyst which had been reoxidized at 200°C. According to the results obtained in the TPR study, only the low-temperature site is reoxidized under these conditions. The temperature of the microbalance was then increased to 420°C under flowing nitrogen. The nitrogen was replaced with a propylene–nitrogen mixture and the effluent passed through a

TABLE 1

Reactivity of Each Site[a]

Initial state[b]	Extent reduced[c] (%)	Products collected	
		Acrolein ($\times 10^{-3}$ mmole)	CO_2 ($\times 10^{-3}$ mmole)
Low-temperature site reoxidized	2.3	1.08	39.1
Both sites reoxidized	2.3	7.9	47.1
Low-temperature site reoxidized	0.6	0.14	20.5
Both sites reoxidized	0.6	4.8	8.3

[a] Reaction conditions: T = 420°C; total flow = 100 cm^3/min (20% C_3H_6, 80% N_2); catalyst weight = 615 mg.

[b] Indicates the level of reoxidation of γ-Bi_2MoO_6 prereduced 6%.

[c] Weight loss from the initial state; 2.3% reduction required 4 min, 0.6% reduction required 30 sec.

liquid nitrogen trap. The products of the reduction were trapped until the sample was reduced 0.6 to 2.3% from the reoxidized level. The liquid nitrogen trap was allowed to warm to room temperature and the trapped products were allowed to expand into an evacuated gas-sampling bulb for gas chromatographic analyses.

To determine the reactivity of a catalyst with both the low-temperature and the high-temperature sites reoxidized, a prereduced catalyst was reoxidized at 420°C. After reoxidation, the microbalance was purged with nitrogen, and the reactivity with propylene was determined as described above.

It is clear from these experiments that when the high-temperature site is not reoxidized, the formation of acrolein is significantly reduced. Thus, the incorporation of oxygen into acrolein is enhanced by the full reoxidation of the high-temperature site.

5. *Redox Kinetics under Isothermal Conditions*

The kinetic parameters of reduction and reoxidation of γ-Bi_2MoO_6 were studied independently utilizing the microbalance. The kinetics were determined from the initial slopes of the weight vs time plots.

The activation energy for the reduction by propylene was calculated to be 14.0 kcal/mole (Fig. 5). This value is similar to that for the formation of acrolein in propylene oxidation reported by Haber and Grzybowska (*11*) and Krenzke and Keulks (*12*). Seiyama *et al.* (*4*) has reported an activation energy of 15.8 kcal/mole for the initial reduction of γ-Bi_2MoO_6 with propylene which is quite close to the value obtained in this work.

It is reasonably well accepted that an activation energy in this range is indicative of a rate-limiting abstraction of an allylic

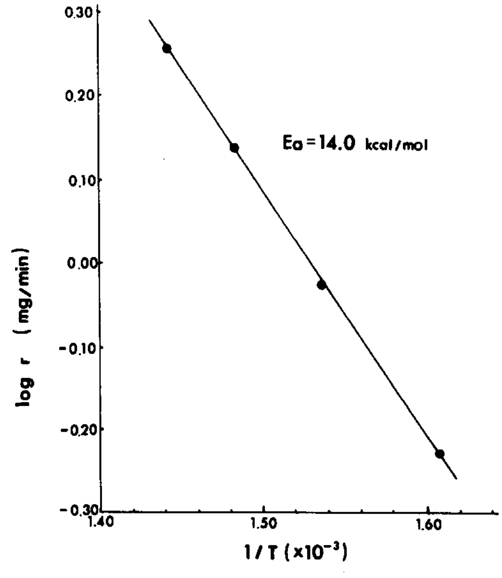

FIG. 5. Arrhenius plot for the reduction of γ-phase by propylene. Temperature range: 350–422°C.

hydrogen from propylene. For our reduction experiments, this value is obtained over a rather broad temperature range, 350 to 420°C. In contrast to this result, however, are the reports of a break in the activation energy of the oxidation of propylene and butene in the temperature range 350 to 450°C. Batist *et al.* (*13*) and Linn and Sleight (*14*) have reported a break in the activation energy around 400°C for butene oxidation. They suggest that the break is due to inhibition caused by the strong adsorption of butadiene at lower temperatures. Morimoto (*15*) also observed a break in the activation energy for the formation of acrolein from propylene. He suggested however, that the break may be due to a change in the rate-determining step from abstraction of an allylic hydrogen at high temperatures (>400°C) to reoxidation of the catalysts at low temperatures (400°C). More recent work by Krenzke (*16*) and Monnier (*17*) have confirmed this suggestion.

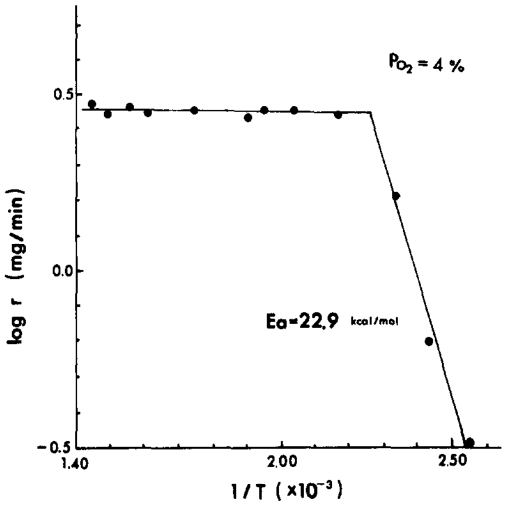

FIG. 6. Arrhenius plot for the reoxidation of low-temperature peak. Temperature range: 120–423°C. Cat., 3% reduced γ-phase by C_3H_6 at 420°C.

Because the reduction process does not exhibit a break in the activation energy over the temperature range 350 to 420°C, we decided to examine the kinetics of the reoxidation of the low-temperature and the high-temperature TPR peaks in the microbalance under isothermal conditions. The Arrhenius plot for the reoxidation of the catalyst under conditions corresponding to the low-temperature peak is given in Fig. 6. The Arrhenius plot has a break at 170°C. The activation energy is approximately 0 above 170°C and 22.9 kcal/mole below 170°C. Thus, the low temperature site can be expected to be fully reoxidized even at low temperatures.

This is consistent with the observation of Batist *et al.* (*18*) that reoxidation of a reduced bismuth molybdate (γ-phase) catalyst at temperatures below 225°C is extremely fast. However, complete reoxidation of the catalyst was possible only at higher temperatures. Moreover, the reoxidation which occurred at higher temperatures exhibited a high activation energy and appeared to occur on surface plane other than that from which oxygen had been removed by reduction (3). Thus, this high-temperature reoxidation process may be related to the high-temperature site detected by TPR.

The Arrhenius plot for the reoxidation of the catalyst under conditions corresponding to the high-temperature peak is given in Fig. 7. As in the case of the low-temperature site, the Arrhenius plot also shows a break, but at 400°C rather than 170°C. The activation energy for the reoxidation at temperatures below 400°C is 46 kcal/mole. The 400°C break point for the high-temperature site activation energy is in good agreement with the reported break in activation energy for the oxidation of propylene and butene (*13, 14, 16*). The activation energy for acrolein formation below 400°C was reported by Krenzke (*14*) to be 44 kcal/mole. The close correspondence between the activation energy for acrolein formation at temperatures below 400°C and the activation energy for full reoxidation at the high-temperature site suggests that the rate-limiting step for propylene oxidation below 400°C can be related to the process which occurs when the catalyst becomes

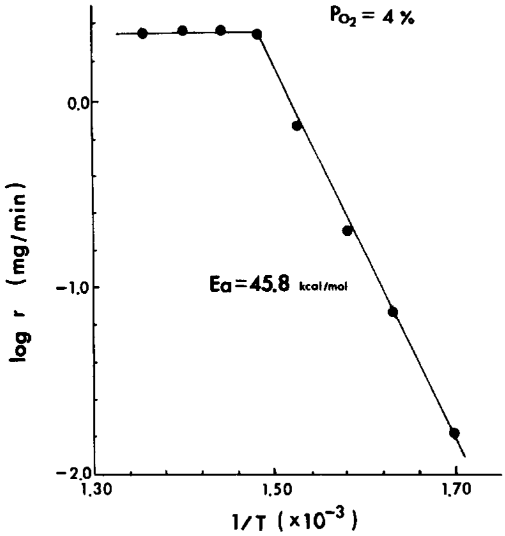

FIG. 7. Arrhenius plot for the reoxidation of high-temperature peak. Temperature range: 315–462°C. Cat., 3% reduced γ-phase by C_3H_6 at 420°C.

fully reoxidized at the high temperature site. At temperatures above 400°C, the reoxidation processes become fast, and the reaction kinetics become those of the abstraction of the allylic hydrogen from propylene by the catalyst, i.e., first order in propylene pressure and zero order in oxygen pressure.

The results of Auger spectroscopy indicate that the full reoxidation of the bismuth molybdate catalyst involves primarily the reoxidation of bismuth. This is consistent with the mechanistic schemes suggested by Matsuura and Schuit (*3*), Haber and Grzybowska (*11*), Peacock *et al.* (*19*), and Sleight (*20*). Each of these schemes suggests that reoxidation of the bismuth molybdate catalyst occurs at a site associated with bismuth. Two possible processes seem the most reasonable. First, the reoxidation may simply involve the reoxidation of Bi^{m+} $(0 < m < +3)$ to Bi^{3+} by gas phase oxygen. The activation energy for the incorporation of the oxygen into the bulk would, therefore, include both the dissociation energy of oxygen as well as the activation energy for diffusion into the bulk.

A second possibility may be a result of the interaction of Mo^{4+} and Bi^{3+}. (Some Mo^{4+} may still be present in the catalyst even though the Auger results suggest that the Mo exists as Mo^{6+} after the low-temperature reoxidation.) The Mo^{4+} ions may be associated with shear structures which have been proposed to be responsible for the fast diffusion of oxygen through the γ-phase bismuth molybdate (*10*). The Mo^{4+} ions could be reoxidized to Mo^{6+} by bismuth according to the following equation,

$$3Mo^{4+} + 2Bi^{3+} \rightarrow 3Mo^{6+} + 2Bi^{0}.$$

It is conceivable that this reaction would take place at temperatures near the high-temperature reoxidation peak. However, in the presence of oxygen the bismuth would be reoxidized to Bi^{3+} with a concomitant increase in oxygen uptake. The low-temperature activation energy for propylene oxidation would, therefore, involve the activation energy for the shear structure rearrangement as well as the dissociation energy to oxygen. At the present time we are unable to decide between these two possibilities for the high-temperature reoxidation peak.

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