

The Oxidative Dehydrodimerization of Propylene over Bi-Sn Oxide Catalysts

III. Reduction and Temperature-Programmed Reoxidation of the Catalyst

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A bismuth-tin oxide catalyst, which is active for the oxidative dehydrodimerization of propylene, was studied with the objective of characterizing its redox properties. The redox properties were investigated by kinetic methods and temperature-programmed reoxidation. The initial rate of reduction of the catalyst exhibited a first-order dependence on propylene partial pressure and an activation energy of 22 kcal/mol. The results of the temperature-programmed reoxidation investigation suggested a low-temperature reoxidation region and a high-temperature reoxidation region. The activation energy for the low-temperature reoxidation was 23 kcal/mol; the activation energy for the high-temperature reoxidation was 45 kcal/mol. Additional information regarding the physicochemical changes which occur in the catalyst in the two temperature regions was obtained from an examination of the catalyst by Auger and ESCA. The results obtained from these investigations suggested that the tin cations are more resistant to reduction than the bismuth cations. In addition, the low-temperature reoxidation appears to be associated with the transformation of Sn⁰ to Sn⁴⁺ and Bi⁰ to possibly an intermediate oxidation state. The high-temperature reoxidation appears to be associated with the full reoxidation of Bi to Bi³⁺. The redox properties and the physicochemical changes also correlated with the mechanism suggested for the oxidative dehydrodimerization of propylene in the earlier studies.

INTRODUCTION

Previous studies (1, 2) have established the kinetics and suggested a mechanism for the oxidative dehydrodimerization of propylene over bismuth-tin oxide catalyst. It was shown that 1,5-hexadiene was formed at comparable rates during the catalytic reaction and when propylene interacts with a catalyst which has reached steady state (1). This fact shows that the reaction occurs via a redox mechanism. The selectivity for the reaction is significantly determined by the degree of catalyst surface coverage by oxygen, and by the bond energy of surface oxygen (3). Similar results

have been reported for the oxidative dehydroaromatization of propylene to benzene (4).

The kinetics of the reaction can be adequately described by a scheme which involves the interaction of adsorbed propylene with gaseous propylene (2). However, this mechanism does not exclude the possibility of two adsorbed allyl radicals interacting on the surface as described by other workers (5, 6). It is conceivable that both of these mechanisms occur simultaneously with the relative importance of each one being determined by specific catalytic properties and the reaction conditions.

Under the experimental conditions reported (1) complete oxidation of propylene was found to occur partly via an associative (concerted) mechanism. It appears that 30% of the CO₂ formed via this route. The main pathway for CO₂ was a redox mecha-

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nism which occurred on sites other than those on which the oxidative dehydrodimerization reaction occurred. The main difference between the sites on which the oxidative dehydrodimerization reaction occurs and the sites which produce combustion is the bond energy of surface oxygen. This conclusion was reached as a result of studies utilizing pulse techniques (1), kinetic measurements (2), and calorimetric measurements (3).

The main purpose of the current work is to characterize the properties of surface oxygen on bismuth-tin oxide catalysts. We have utilized traditional reduction experiments coupled with reoxidation experiments to investigate the redox properties of the catalysts. In addition, we have utilized the technique of temperature-programmed reoxidation (TPR) (7, 8) to determine the various forms of oxygen on the catalysts.

EXPERIMENTAL

Bismuth-tin oxide catalysts of composition Bi/Sn = 1 were prepared by first precipitating bismuth hydroxide from an acidified solution of bismuth nitrate by adding ammonium hydroxide. Tin metal was dissolved in nitric acid. To this solution was added the bismuth hydroxide solution. The aqueous phase was evaporated and the solid precipitate was dried at 120°C. The final step involved calcining the material at 600°C for 6 h under ambient conditions. This preparation yielded predominantly Bi₂Sn₂O₇ with small amounts of bismuth oxide and tin dioxide (9). The surface area of the catalyst was 2.5 m²/g.

The reduction of the catalyst by propylene and reoxidation of the catalyst by oxygen were conducted under flow conditions in a RG Cahn electrobalance. Ultrapure nitrogen (99.999%) was used to prepare the desired mixtures for the reduction and reoxidation experiments.

The typical experimental conditions were as follows. Before reduction, the catalyst was treated in a flowing mixture (20% oxygen, 80% nitrogen) for 10 to 12 h at 450°C

until a constant weight was obtained. This state is taken as the completely oxidized state of the catalyst. Reduction was then accomplished by flowing a reducing mixture (propylene, nitrogen) over the catalyst until a certain predetermined weight was obtained. The degree of reduction was calculated on the basis of the catalyst's stoichiometry.

After reduction, the catalyst was cooled to room temperature under a flow of ultrapure nitrogen. No noticeable change in weight occurred during the cooling process. Temperature-programmed reoxidation was accomplished by flowing a mixture of oxygen and nitrogen over the catalyst while the temperature was increased linearly. The weight change was displayed in a derivative form utilizing a Cahn time derivative computer (Mark II).

Kinetics of reduction and reoxidation were investigated in various temperature regions under isothermal conditions. The rate of reduction or reoxidation was determined by evaluating the initial part of the weight versus time curve.

All experiments were conducted with a catalyst particle size of 0.5–1.0 mm. The amount of catalyst used was 0.3 g and the flow rate was 60 cm³/min.

The phase composition of finely ground samples was analyzed on a Norelco diffractometer equipped with a scintillation detector using CuK α radiation ($\lambda = 1.5405 \text{ \AA}$) at a scan rate of 0.5° (2 Θ)/min. A minimum of two scans per sample were taken, one at higher sensitivity to enable the detection of minor constituents.

The Auger electron spectroscopy (AES) data were obtained using a commercial (Varian) high-resolution cylindrical mirror analyzer (CMA) which has incorporated a normal-incidence electron gun as the excitation source. With this gun, sample areas of $\sim 10 \mu\text{m}$ diameter were analyzed. Beam energies were typically 3–5 KeV.

The ESCA spectra were obtained with a commercial (Physical Electronics) double-pass CMA using a magnesium X-ray

source. The analysis area for each sample was ~ 3 mm.

The samples were prepared for AES and ESCA analysis by partial grinding and subsequent embedding of the resultant granular powder into indium foil. The samples, mounted on the indium foil, were immediately placed inside the vacuum chamber which was quickly pumped to $\leq 1 \times 10^{-8}$ Torr. Sample preparation in this fashion produces samples which often do not pose serious charging problems, while at the same time minimizes extraneous contamination of the catalyst surface being analyzed.

RESULTS

1. Reduction and Reoxidation of Catalyst

The kinetic curves obtained for the reduction of the catalyst with propylene at various temperatures are shown in Fig. 1. Each of the reduction curves has two portions: an initial linear portion; and a nonlinear portion. The transition point from linear to nonlinear depends only on the temperature not on the propylene concentration. The initial rate of reduction obeys the Arrhenius equation and its plot is given in Fig. 2. The activation energy for the temperature region 380–455°C was determined to be 22 ± 2 kcal/mol.

The dependence of the rate on the propylene partial pressure was determined at 420°C at propylene partial pressures of 0.1–0.5 atm. The kinetic order was determined to be first order in propylene pressure as is shown in Fig. 3.

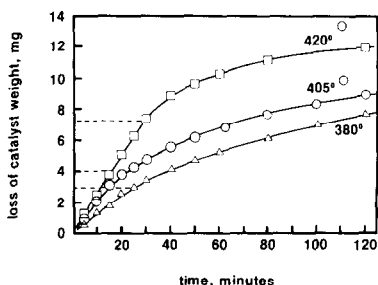


FIG. 1. Kinetic curves of catalyst reduction by propylene.

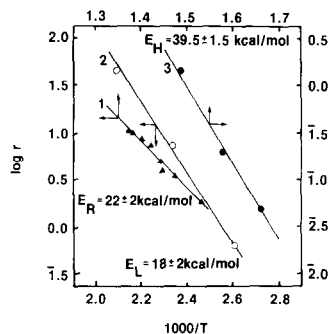


FIG. 2. Activation energies for processes of reduction (1), low-temperature oxidation (2), and high-temperature oxidation (3).

The typical temperature-programmed reoxidation curve for the bismuth-tin catalyst is given in Fig. 4. Two peaks were observed: the maximum of the low-temperature peak was in the region 185–200°C; and the maximum of the high-temperature peak was in the region 375–400°C. The activation energy of each peak was determined by the shift of the temperature maximum according to the following equation (8):

$$2 \log T_M - \log \beta = E/2.303RT + \log (E/RA),$$

where

T_M = temperature at peak maximum,

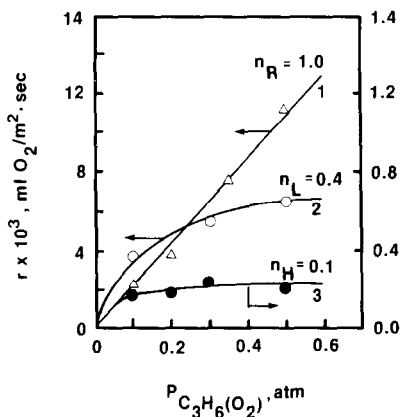


FIG. 3. Concentration dependencies for processes of reduction (1), low-temperature reoxidation (2), and high-temperature reoxidation (3).

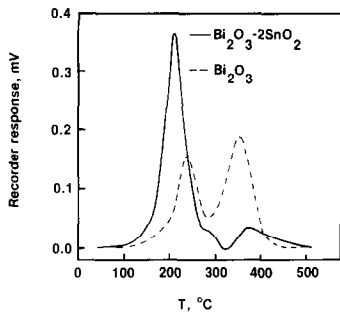


FIG. 4. TPR curves for 3% reduced Bi-Sn oxide catalyst (—) and Bi_2O_3 (---). Heating rate, $10^\circ\text{C}/\text{min}$.

β = heating rate in degree Celsius per minute,
 E = activation energy in kilocalorie per mole, and
 A = the temperature-independent constant.

The data plotted according to this equation are presented in Fig. 5. The activation energy of the low-temperature peak (E_L) is 23 ± 2 kcal/mol, and the activation energy for the high-temperature peak (E_H) is 45 ± 1 kcal/mol. For each of these peaks observed in the TPR experiments, we also conducted isothermal kinetic experiments in the same temperature region. The corresponding activation energies for isothermal reoxidation are given in Fig. 2 and the corresponding orders of reoxidation are given in Fig. 3.

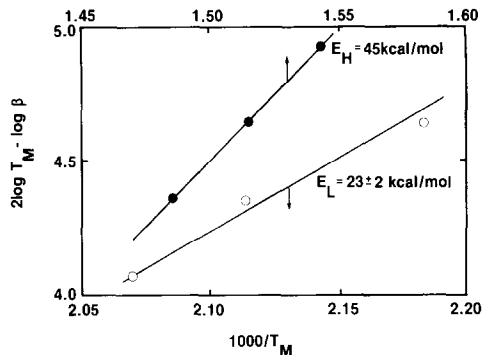


FIG. 5. Activation energies for two TPR peaks of reduced Bi-Sn oxide catalyst.

The reoxidation rate was found to also depend on the initial degree of catalyst reduction. This dependence is presented in Table 1. The activation energies determined for the reoxidation process by both the isothermal method and the temperature-programmed reoxidation method are similar (Figs. 2 and 5).

2. Phase Composition of Reduced and Reoxidized Catalysts

The results of X-ray diffraction analysis of variously treated bismuth-tin oxide catalysts are presented in Table 2. The observed d values and intensity of detected phases are in excellent agreement with the

TABLE I
Dependence of Reoxidation Rate on Degree of Catalyst Reduction

Low-temperature region ^a		High-temperature region ^b	
Reduction degree (%)	Reoxidation rate $r \times 10^3$ (ml O_2/m^2 sec)	Reduction degree (%)	Reoxidation rate $r \times 10^3$ (ml O_2/m^2 sec)
3.35	11.83	0.94	3.02
3.02	5.68	0.87	1.18
2.69	2.49	0.80	0.72
2.36	1.32	0.73	0.58
2.02	0.76	0.67	0.32
		0.60	0.17
		0.53	0.07

^a Temperature, 155°C ; partial pressure of oxygen, 0.2 atm.

^b Temperature, 400°C ; partial pressure of oxygen, 0.2 atm.

TABLE 2

Phase Composition of Various Treated Bismuth-Tin Oxide Catalysts

Catalyst state	Phases observed ^a
Fresh	$\text{Bi}_2\text{Sn}_2\text{O}_7 > \alpha\text{-Bi}_2\text{O}_3 \sim \text{SnO}_2 \gg \text{Bi}_2\text{O}_2\text{CO}_3$
Reduced	$\text{Bi} \sim \text{SnO}_2 > \alpha\text{-Bi}_2\text{O}_3 \gg \text{Bi}_2\text{Sn}_2\text{O}_7$
Low-temperature reoxidized	$\alpha\text{-Bi}_2\text{O}_3 \sim \text{SnO}_2 > \text{Bi}_2\text{Sn}_2\text{O}_7$
High-temperature reoxidized	$\text{Bi}_2\text{Sn}_2\text{O}_7 > \alpha\text{-Bi}_2\text{O}_3 \sim \text{SnO}_2$

^a Neither Sn nor SnO were observed in any of the samples.

following ASTM cards: $\alpha\text{-Bi}_2\text{O}_3$, No. 14-699; SnO_2 , No. 5-0467; $\text{Bi}_2\text{Sn}_2\text{O}_7$, No. 17-457; $\text{Bi}_2\text{O}_2\text{CO}_3$, No. 4-0666; and Bi, No. 5-0519.

The freshly prepared catalyst consists mainly of the $\text{Bi}_2\text{Sn}_2\text{O}_7$ phase and small amounts of bismuth oxide and tin dioxide. Traces of bismuthyl carbonate are also detected. It should be noted that when $\text{Bi}_2\text{Sn}_2\text{O}_7$ is present its peaks are broader than the peaks of the other components indicating that this phase has a poorer crystallinity and hence a higher surface area than other constituents.

The reduced catalyst shows that the bismuthyl carbonate was no longer present in the sample. It was also found that the main-phase $\text{Bi}_2\text{Sn}_2\text{O}_7$ was reduced with a concomitant increase in the amount of SnO_2 and appearance of bismuth metal.

When the reduced sample was reoxidized at low temperatures (up to 300°C), X-ray results indicated that the bismuth metal was no longer present in the sample and there was an increase in the amount of $\text{Bi}_2\text{Sn}_2\text{O}_7$.

When the sample was reoxidized at high temperatures (300–450°C), the main-phase $\text{Bi}_2\text{Sn}_2\text{O}_7$ was found to increase further with a resultant loss in the amount of $\alpha\text{-Bi}_2\text{O}_3$ and SnO . However, the amount of the main-phase $\text{Bi}_2\text{Sn}_2\text{O}_7$ was less than in the freshly prepared sample. In order to restore the amount equivalent to the fresh catalyst, the sample needed to be recalcined in air at 600°C.

3. ESCA and AES

The catalyst samples were analyzed using electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) in order to ascertain surface chemical composition.

For the ESCA data absolute binding energies were determined by using adventitious carbon referencing; chemical shifts were determined by comparison to standards run under the same conditions as well as handbook values (10). This data is presented in Table 3.

Binding energies for bismuth and tin in the fresh catalyst are close to the binding energies observed for bismuth in bismuth oxide and tin in SnO_2 . The small differences observed (0.4–0.6 eV) are probably caused by the differences in electronic configuration of the bismuth and tin cations in $\text{Bi}_2\text{Sn}_2\text{O}_7$ as compared to the pure oxides Bi_2O_3 and SnO_2 , respectively. It is known (10) that the binding energies for bismuth in the compounds $(\text{BiO})_2\text{Cr}_2\text{O}_7$, and $\text{Bi}_2\text{Ti}_2\text{O}_7$ are higher (0.3–0.5 eV) than the binding energy for bismuth in Bi_2O_3 . Thus, we can conclude that bismuth and tin exist on the surface as Bi^{3+} and Sn^{4+} , respectively.

When the catalyst is reduced, the binding energies are shifted to lower binding energies by 1.8–2.8 eV in comparison with the fresh sample. The binding energies ob-

TABLE 3

Parameters for the XPS Spectra of Bismuth- and Tin-Containing Samples

Catalyst	Bi binding energy (eV)		Sn binding energy (eV)	
	$4f_{7/2}$	$4f_{5/2}$	$3d_{5/2}$	$3d_{3/2}$
1 Bi_2O_3	161.6	166.9		
2 $\text{Bi}_2\text{O}_3\text{-}2\text{SnO}_2$, fresh	162.2	167.4	487.6	495.4
3 $\text{Bi}_2\text{O}_3\text{-}2\text{SnO}_2$, reduced	159.5	164.6	485.7	493.6
4 $\text{Bi}_2\text{O}_3\text{-}2\text{SnO}_2$, LT reoxidized	161.8	166.9	488.2	496.0
5 $\text{Bi}_2\text{O}_3\text{-}2\text{SnO}_2$, HT reoxidized	162.6	167.7	488.2	496.0
6 Bi metal	159.0	164.1		
7 SnO_2			487.6	495.9
8 SnO			487.6	495.9
9 Sn metal			486.2	494.3

served are very close to the binding energies observed for Bi metal and Sn metal.

Low-temperature reoxidation of the sample leads to a shift of the binding energies to higher energies. The binding energy for the bismuth line is between the binding energies observed for bismuth metal and Bi^{3+} . The binding energies for the tin line came very close to the binding energies observed for tin in the fresh sample.

Reoxidation of the catalyst at high temperatures leads to a further shift of the binding energies observed for the bismuth line to higher energies but does not influence further the binding energy for the tin line. After the high-temperature reoxidation, both the bismuth and tin binding energies are close to the bismuth and tin binding energies observed in the fresh sample.

The Auger spectra of the samples are presented in Fig. 6. As one can see, the ratio of the bismuth line intensity to the tin line intensity depends on the catalyst state. For the fresh and the reoxidized samples

(spectra 1, 3, and 4), the bismuth-to-tin ratios are approximately equal, while for the reduced catalyst (spectrum 2), the ratio is significantly lower.

DISCUSSION

The bismuth-tin oxide catalyst is relatively easily reduced by propylene. As noted earlier, the reduction curves have two portions: a linear portion and a nonlinear portion. The linear portion corresponds to easily removed oxygen. At 380°C , approximately 20 monolayers of oxygen are removable in the linear portion. This amount increases as the temperature increases and does not depend on the concentration of propylene in the reducing mixture. The kinetic parameters (activation energy, order with respect to propylene) determined for the linear portion are approximately equal to the kinetic parameters reported earlier (2) for the catalytic oxidation of propylene on the same catalyst. Thus, it appears that the oxygen removed in the early stages of reduction is also the oxygen that takes part in the catalytic reaction.

Information regarding the type of oxygen removed by a slight reduction can be obtained by temperature-programmed reoxidation. The temperature-programmed reoxidation results with a 2–3% prerduced sample indicate that there are two forms of oxygen, a low-temperature form with the activation energy of 23 ± 2 kcal/mol, and a high-temperature form with an activation energy of 45 ± 1 kcal/mol. Kinetic investigations in the temperature regions corresponding to these two forms of oxygen did not reveal any differences in their kinetic behavior. The order of the reoxidation, as well as the activation energy, is determined primarily by the degree of the catalyst reduction. We observed that as the latter decreases the activation energy increases, and the reoxidation rate becomes more critically dependent upon the degree of reduction (see high-temperature reoxida-

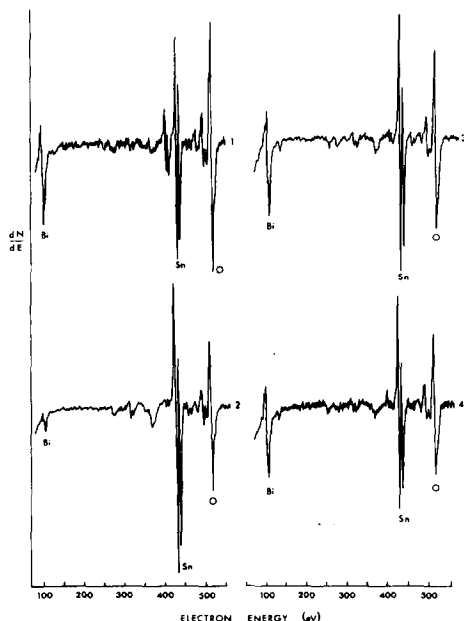


FIG. 6. Auger electron spectra for each catalyst treated: (1) fresh prepared; (2) 3% reduced; (3) oxidized at low temperatures; (4) oxidized at high temperatures.

tion dependence in Table 1). In addition, the decreasing order dependence of 0.4 in the low-temperature region to 0.1 in the high-temperature region reflects a decrease in the number of available oxygen vacancies in the catalyst.

Additional information regarding the nature of the two forms of oxygen is gained from the physicochemical changes which occur in the catalyst in the two temperature regions. Reduction of the catalyst by propylene to 3.2% indicates that the primary phase is unstable with respect to transformation into bismuth metal and tin dioxide. The formation of SnO as reported by Seiyama and co-workers (11) was not detected in our experiments. Surface analysis by ESCA indicates that the surface contains both bismuth and tin metal. The Auger results (Fig. 6) indicate that the relative concentration of tin to bismuth is greater in the reduced catalyst than in the fresh catalyst. This result may suggest diffusional effects which take place during the reduction process which allow the surface composition to undergo change.

Temperature-programmed reoxidation of the catalyst over the temperature range 50–300°C leads to the disappearance of bismuth in the bulk and tin metal on the surface. At the same time the concentration of $\text{Bi}_2\text{Sn}_2\text{O}_7$ in the bulk increases. Evidently, the oxidation of both Bi and Sn takes place in this temperature region. The ESCA data suggest that bismuth may exist on the surface in an intermediate state between 0 and 3+ (Table 3). The absence of stable oxides of bismuth having oxidation states of 1+ and 2+ prevents us from making a precise determination of the oxidation state.

A similar uncertainty exists when we consider the reoxidation of Sn^0 to Sn^{2+} on the surface of the catalyst. The ESCA binding energies of Sn^{2+} and Sn^{4+} are identical (Table 3) and are consistent with those reported in the literature (10). Thus, it is impossible to gain information regarding the oxidation state of tin in the catalyst

from ESCA measurements. However, when the catalyst was reduced, tin metal was detected on the surface while tin dioxide was present in the bulk. If tin oxide (SnO) had been present in the catalyst, it is conceivable that it should have been detected by X-ray. However, our X-ray results indicated that SnO was not present in the bulk. Therefore, it appears that during the low-temperature reoxidation, Sn^0 on the surface reoxidizes to Sn^{4+} . In addition to the changes noted above, we observed an increase in the amount of $\text{Bi}_2\text{Sn}_2\text{O}_7$ in the bulk apparently as a result of the interaction of Bi_2O_3 and SnO_2 . However, this interaction does not lead to an increase in the catalyst weight.

High-temperature reoxidation (300–450°C) leads to a further increase in the concentration of $\text{Bi}_2\text{Sn}_2\text{O}_7$ in the bulk. In the subsurface layers, the bismuth cations undergo further oxidation to 3+ (Table 3). In addition, the relative concentration of bismuth to tin on the surface increases during this reoxidation and becomes approximately equal to that observed in the fresh catalyst (see spectra 1 and 4, Fig. 6).

From these results, we can conclude the following:

1. Under the conditions reported herein, the tin cations appear to be more resistant to reduction than the bismuth cations;
2. the low-temperature reoxidation peak is associated with the transformation of Sn^0 to Sn^{4+} and Bi^0 to an intermediate oxidation state;
3. the high-temperature reoxidation peak is associated with the final reoxidation of bismuth to Bi^{3+} .

In order to relate the data obtained in these experiments to catalytic activity and selectivity we must note that the two forms of oxygen observed in the bismuth-tin oxide catalyst have different bond energies. It is reasonable to assume that the high-temperature form of oxygen is associated with the lower bond energy and, therefore, is weakly bound to the surface. By utilizing the peak area under the temperature-pro-

grammed reoxidation, as well as the weight change during the reoxidation, we can calculate that the loosely bound oxygen corresponds to 17–20% of all of the oxygen removed when the catalyst is reduced up to 3%. The remaining portion corresponds to the tightly bound oxygen (low-temperature reoxidation peak).

As we go from the bulk of the catalyst to the surface, we can expect a certain change in the ratio of the two forms of bound oxygen but qualitatively the picture must remain approximately the same. In support of this suggestion are the pulse results (1) and the kinetic results (2) which also assume that the catalyst contains on the surface sites associated with weakly bound oxygen and sites associated with strongly bound oxygen. According to these results, the interaction of propylene with weakly bound oxygen (bond energy 50–90 kcal/mol) leads to complete oxidation. This oxygen is readily removed from the catalyst surface, however, during the reaction, and it is essentially absent on the catalyst under steady-state behavior (3). Thus, it is reasonable to relate this form of oxygen to the high-temperature form of oxygen observed in this work.

Oxidative dehydrodimerization of propylene occurs selectively on a reduced catalyst on sites associated with tightly bound oxygen (1, 3). Therefore, it is also reasonable to relate the low-temperature form of oxygen observed in this work with the oxygen responsible for the selective oxidative dehydrodimerization reported earlier. In support of this conclusion, we can compare the temperature-programmed reoxidation spectrum for prereduced bismuth oxide (Fig. 4). As one can see, bismuth oxide contains much more (approximately 60%) of weakly bound oxygen and, therefore, is much less selective in the oxidative dehy-

drodimerization of propylene to 1,5-hexadiene (4, 9). These results are in agreement with the earlier suggestions (12, 13) that in order to obtain high selectivity catalysts should not contain weakly bound surface oxygen.

It is also interesting to note that the same qualitative behavior of the selective oxidation of propylene to acrolein was observed with the various phases of bismuth molybdate (14).

REFERENCES

1. Gamid-Zade, E. G., Mamedov, E. A., and Rizaev, R. G., *Kinet. Katal.* **20**, 405 (1979).
2. Mamedov, E. A., Gamid-Zade, E. G., Agaev, F. M., and Rizaev, R. G., *Kinet. Katal.* **20**, 410 (1979).
3. Mamedov, E. A., Gamid-Zade, E. G., Pankratiev, Yu. D., Kuliev, A. R., and Rizaev, R. G., *React. Kinet. Catal. Lett.* **10**, 19 (1979).
4. Solymosi, F., and Bozso, F., in "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bonds, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 365. The Chemical Society, London, 1977.
5. Trimm, D. L., and Doerr, L. A., *J. Catal.* **26**, 1 (1972).
6. Seiyama, T., Uda, T., Mochida, T., and Egashira, M., *J. Catal.* **34**, 29 (1974).
7. Miura, H., Morikawa, Y., and Shirasaki, T., *J. Catal.* **39**, 22 (1975).
8. Uda, T., Lin, T. T., and Keulks, G. W., *J. Catal.* **62**, 26 (1980).
9. Mamedov, E. A., Mekhtiev, K. M., Gamid-Zade, E. G., and Rizaev, R. G., *Kinet. Katal.* **18**, 914 (1977).
10. Muilenberg, G. E. (Ed.), "Handbook of X-Ray Photoelectron Spectroscopy." Perkin-Elmer Corporation, Eden-Prairie, Minn., 1979.
11. Egashira, M., Sunao, U., and Seiyama, T., *J. Chem. Soc. Japan Chem. Ind. Chem.*, 261 (1972).
12. Ilchenko, N. I., and Golodets, G. I., *J. Catal.* **39**, 73 (1975).
13. Borekov, G. K., Venyaminov, S. A., Sazonova, N. N., Pankratiev, Yu. D., and Pitaeva, A. P., *Kinet. Katal.* **16**, 1442 (1975).
14. Mamedov, E. A., unpublished results.