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The Investigation of the Type of Active Oxygen for the Oxidation of Propylene over Bismuth Molybdate Catalysts Using Infrared and Raman Spectroscopy

INTRODUCTION

Investigations of the selective oxidation of propylene over bismuth molybdate catalysts have shown that there is extensive participation of lattice oxygen in the formation of acrolein and carbon dioxide (*1–3*). Recently, Keulks and Krenzke (*4*) have found that the amount of lattice oxygen involved in product formation is much greater for γ-Bi_2MoO_6 than for α-$Bi_2Mo_3O_{12}$. These data were obtained from a detailed mass spectrometric analysis of the oxygen-18 distribution in acrolein and CO_2 during the steady-state flow reaction of $^{18}O_2$, C_3H_6 and He over the above catalysts.

In this Note, we wish to report spectroscopic data which support the observations by Keulks and Krenzke. We have taken the ir and Raman spectra of α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6 oxidation catalysts after carrying out the following reaction in a recirculation reactor.

$$^{18}O_2 + C_3H_6 \xrightarrow{\text{catalyst}} \text{products}.$$

Those catalyst oxide ions (^{16}O) which are incorporated into the reaction products must be replaced during the catalytic oxidation by ^{18}O. Thus, by recirculating a predetermined $^{18}O_2$, C_3H_6, and He gas mixture over the catalyst at 425°C, it should be possible to replace with ^{18}O a significant portion of the lattice $^{16}O^{2-}$ which participate in propylene oxidation.

A comparison of ir and Raman spectra of a catalyst sample before and after propylene oxidation in the presence of ^{18}O should provide information concerning the types and to some extent the quantity of lattice O^{2-} participating in the reaction.

The reaction of propylene and ^{18}O in the recirculation loop was also conducted using USb_3O_{10} as the catalyst. Because it has been postulated that the oxidation of propylene over this catalyst proceeds via a surface hydroperoxide mechanism and no lattice O^{2-} are involved (*4*), then no change in the ir and Raman spectra before and after the reaction should be expected.

EXPERIMENTAL METHODS

The preparation of α-$Bi_2Mo_3O_{12}$ was taken from Keulks *et al.* (*5*), γ-Bi_2MoO_6 according to Batist *et al.* (*6*), and USb_3O_{10} from Grasselli and Suresh (*7*). The β-$Bi_2Mo_2O_9$ was prepared according to Grzybowska *et al.* (*8*) and was found to be pure and stable at these reaction conditions by using various spectroscopic techniques. The β-phase will be discussed in more detail in a later publication (*9*).

The amount of each catalyst placed in the recirculation reactor was 0.10 g and the oxygen content of each catalyst was then determined from the stoichiometry of the catalyst. The amount of propylene used in the recirculation loop was determined by calculating the amount of

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propylene (Linde, C.P. grade) necessary to remove a slight excess of 100% of the oxygen present in the catalyst as reaction products; only CO_2, H_2O, and C_3H_4O were considered as the oxygen-containing products. The selectivity of the reaction in the recirculation loop was assumed to be the same as for the single-pass flow reaction (85–90% for acrolein formation). This was a valid assumption since contact times were approximately the same for both reaction modes. The pumping speed of the recirculation pump was 105 ml (STP) min^{-1}. The amount of $^{18}O_2$ (99 atom% ^{18}O from Stohler Isotope Chemicals) in the gas mixture was equal to twice the amount of oxygen present in the catalyst. This was done to ensure oxidizing conditions over the catalyst at all stages of reaction. Helium (99.99%, prepurified from Airco) was used as a diluent, and the composition of gas mixtures before the reaction was 0.1 C_3H_6:0.2 $^{18}O_2$:0.7 He.

The gas mixture was circulated through the loop for 30 min prior to reaction to ensure homogeneous mixing. The reactions were conducted at 425°C at atmospheric pressure; a dry ice/acetone cold trap in the circulation loop removed all condensible products. The reaction was followed by monitoring the decrease of pressure within the loop by using a manometer attached to the loop. The reaction was stopped when there was no further pressure change.

The extent of lattice ^{16}O incorporation into acrolein and CO_2 during the steady-state oxidation of propylene was determined by flowing $^{18}O_2$, C_3H_6, and He [1:1:8; total flow = 20 ml (STP) min^{-1}] over the catalyst and analyzing the CO_2 and acrolein with a mass spectrometer connected directly to the reactor effluent. The quantity or dilution volume of reactive ^{16}O in the lattice of the catalyst with which the incoming $^{18}O_2$ equilibrates can be related to the oxygen-18 content of the products and the oxygen flux through the catalyst by assuming the catalyst acts as an exponential dilution volume.

The following modification of the exponential dilution volume equation developed by Ritter and Adams (*10*) was used to calculate the quantity of reactive bulk oxygen.

$$\frac{\%\ ^{18}\mathrm{O\ in\ product}}{\%\ ^{18}\mathrm{O\ in\ O_2}} = 1 - e^{-Ft/V}$$

where % ^{18}O in product/% ^{18}O in O_2 was determined mass spectrometrically at time, t; F was the total flow of oxygen through the catalyst which equals the flow of oxygen out of the catalyst as oxygenated products, in g-atoms/min, t = time of $^{18}O_2$ addition to flow stream in minutes, and V = reservoir of lattice oxygen, in g-atoms, participating in the formation of a particular product. This equation is more conveniently expressed as:

$$-\ln\left[1 - \frac{\%\ ^{18}\mathrm{O\ in\ products}}{\%\ ^{18}\mathrm{O\ in\ O_2}}\right] = \frac{F}{V}t.$$

Thus, a plot of the left-hand side of the equation versus t yields a straight line with slope F/V, from which V is calculated. By comparing V with the total quantity of oxygen present in the catalyst, the fraction of reactive oxygen for a given product formation was determined. It should be noted that the absence of $m/e = 34$ signal in the mass spectrum during the above experiments indicated that the heterophase exchange reaction between $^{18}O_2$ and $^{16}O^{2-}$ was not occurring at these conditions.

After the recirculation reactions were completed, KBr pellets containing the catalysts were made and the ir and Raman spectra of the pellets were taken. The ir spectra were taken with a Beckman ir 12 Spectrophotometer and the Raman spectra were taken with a Spex Ramalog Laser Raman system. Decomposition of the pellet was prevented by spinning the

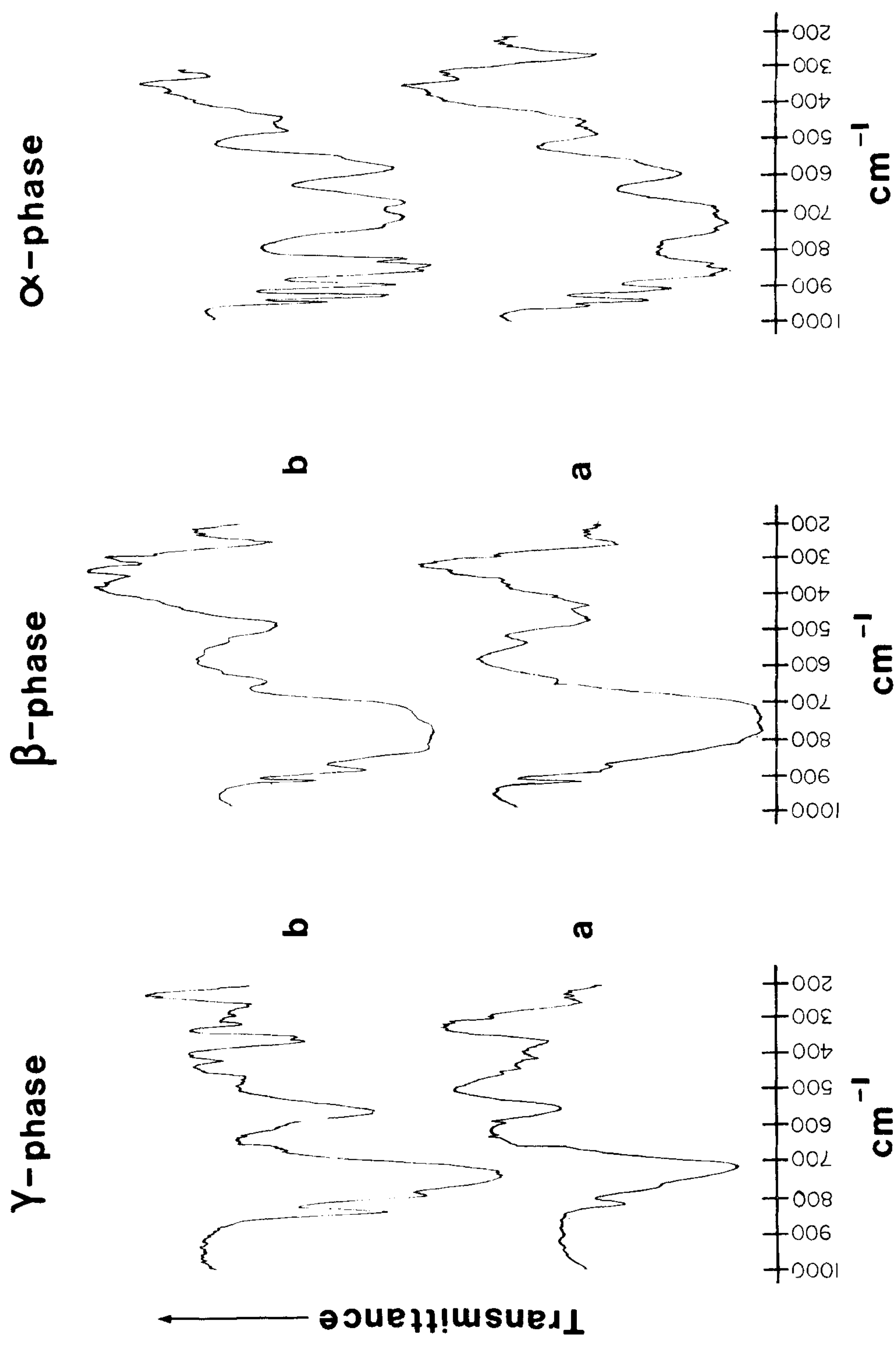


FIG. 1. ir Spectra of α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6 before (b) and after (a) propylene oxidation with $^{18}O_2$.

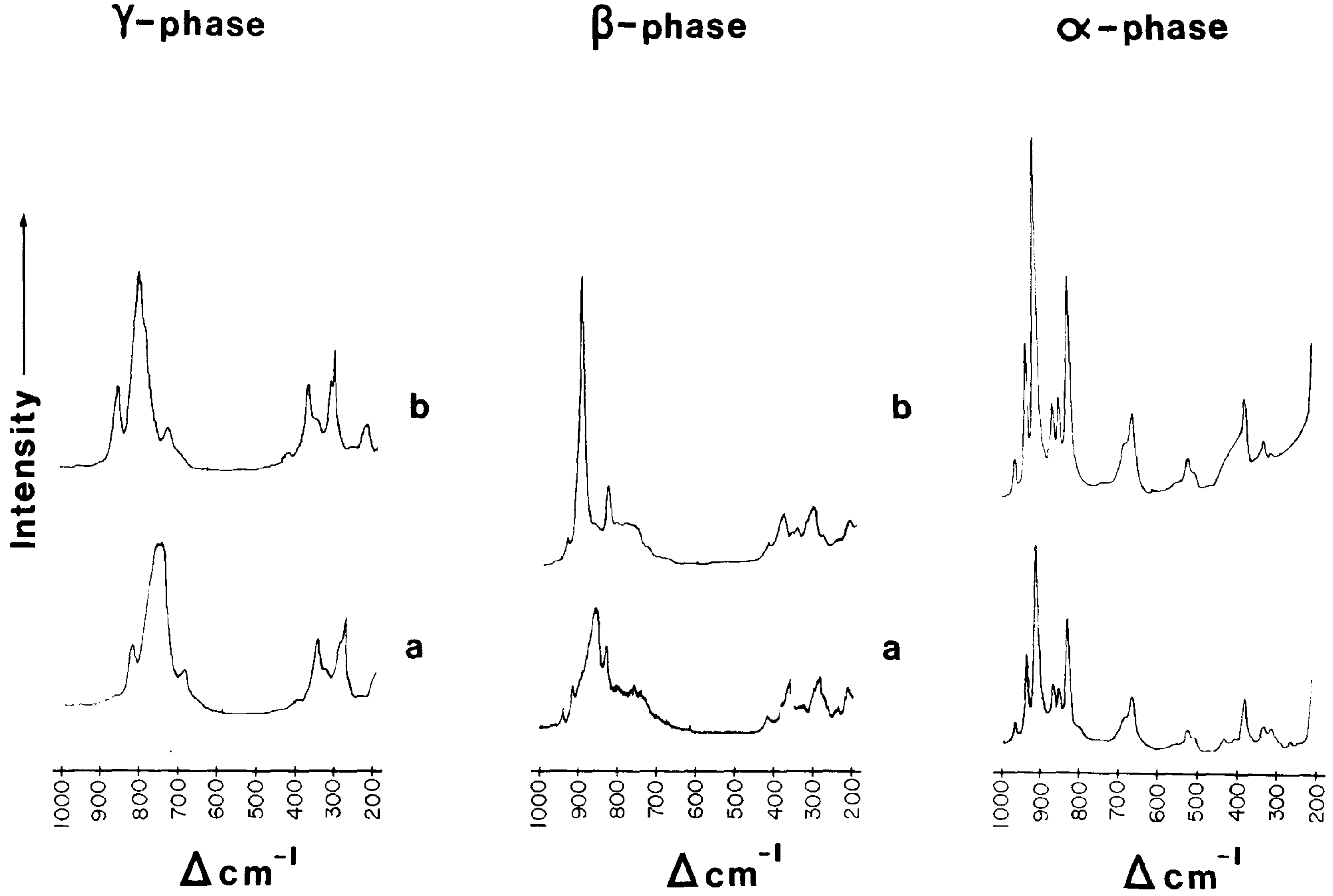


Fig. 2. Raman spectra of α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6 before (b) and after (a) propylene oxidation with $^{18}O_2$.

pellet while being irradiated with the laser beam.

RESULTS

The ir and Raman spectra of the α, β, and γ phase catalysts before and after the oxidation of propylene with $^{18}O_2$ in the gas phase are shown in Figs. 1 and 2. All of the bands in the ir and the Raman spectra of the γ-phase catalyst are shifted with respect to the bands of the γ-phase catalyst before the reaction. The ir and Raman spectra of the β-phase catalyst show similar changes after the reaction with the exception that in the ir spectrum the bands at 925 and 895 cm^{-1} still appear, and in the Raman spectra changes in lineshapes as well as in the frequencies of the band maxima appear. The band at 830 cm^{-1} is common to both spectra. It is not known whether this is due to a band not shifting or if this is due to the shifting of a different band. The ir spectrum of the α-phase after catalyzing the oxidation of propylene is only slightly different from that of the catalyst before the reaction. The greatest changes appear as a filling of the gap at 800 cm^{-1} and a broadening of the bands at 720 and 680 cm^{-1} into one band. The Raman spectrum of the α-phase catalyst after oxygen-18 oxidation of propylene shows only slight differences. These differences appear as a weak shoulder at 810 cm^{-1} and the appearance of a broad shoulder to the high frequency side of the band at 383 cm^{-1}. The positions of the band maxima are given in Table 1.

DISCUSSION

The absence of any unshifted bands in the ir and Raman spectra of the γ-phase after oxygen-18 oxidation of propylene suggests that all types of lattice oxygen ions participate in C_3H_6 oxidation and are thus exchanged during the reaction. The ir and Raman spectra of the β-phase catalyst show that most, but not all, types of lattice oxygen ions are exchanged during the oxidation of propylene.

Unfortunately, the assignments of the vibrational bands of the γ- and β-phases are not adequate to determine which

TABLE 1

The Band Positions (cm^{-1}) in the ir and Raman Spectra of the α-, β-, and γ-Phase Catalysts before (b) and after (a) the Oxidation of Propylene with $^{18}O_2$

α-ir		α-Raman		β-ir		β-Raman		γ-ir		γ-Raman	
(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)
951	952	965	965	925	925	940	(935) (915)	850	819	865	832
933	939	945	945	896	(895) (880)	898	863	805	770	812	770
906	908	916	914	800	760	830	830	750	720	728	700
865	870	872	872	645	640			565	543	367	355
850	855	850	850	—	533	376	362	(362) (348)	> 352	(310) (295)	> 285
836	—	830	830	480	< (463) (428)	300	285				
	800		810								
720	725										
680	—	665	665								
585	585										
475	475	383	382								
438	437	210	210								

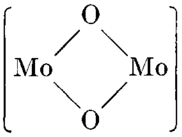
TABLE 2

Summary of Oxygen-18 Data

Catalyst	Temperature (°C)	Percentage of total lattice O^{2-} participating in product formation	
		C_3H_4O	CO_2
α-$Bi_2Mo_3O_{12}$[a]	450	9	9
	400	4	4
β-$Bi_2Mo_2O_9$	450	98	98
	400	56	60
γ-Bi_2MoO_6[a]	450	100	100
	400	45	45
USb_3O_{10}[a]	450	0.5	0.5
	400	0.6	0.6

[a] From Krenzke and Keulks (*J. Catal.*, in press).

lattice oxide ions are exchanged during the reaction. As stated above, the ir and Raman spectra of the α-phase catalysts after the reaction show very little change with respect to the spectra of the catalysts before the reaction. This permits us to suggest that only a few types of lattice oxygen ions in the α-phase are involved in the reaction. The bands at 955, 940, 910, 870, 850, and 840 cm^{-1} have been assigned to the ν_1 and ν_3 group vibrations of the edge sharing disordered $Mo_2O_8^{4-}$ tetrahedra (*11*). In addition we suggest that the bands at 720 and 680 cm^{-1} might be due to the dioxo bridge



vibrational modes because of the similarity of the band positions to these found in oxo-molybdenum complexes (*12*). Because the bands are altered by the reaction involving ^{18}O, this implies that the bridged oxide ions are involved in the exchange during the reaction. In all three phases studied, the magnitude of the isotopic shifts of the high-frequency bands are similar to those found for Mo–O bands in oxo-molybdenum complexes (*12*).

The dilution volume experiments were not carried out at 420°C, but at 400 and 450°C. Nevertheless, the results in Table 2 show that the quantity of lattice O^{2-} involved in CO_2 and C_3H_4O formation for γ-phase ~ β-phase > α-phase at all reaction temperatures. When considering the slight difference between the spectroscopic and dilution volume results for β-$Bi_2Mo_2O_9$, it must be remembered that the extinction coefficients of the individual band are not known. Thus, it is not possible from spectroscopic data to quantitatively determine the amount of oxide ions exchanged during propylene oxidation.

To test the hypothesis that propylene oxidation over USb_3O_{10} proceeds via a hydroperoxide mechanism (*4*), we carried out the oxidation of propylene with $^{18}O_2$ over USb_3O_{10}. There were no differences in the ir and Raman spectra before and after reaction, indicating that there was no lattice O^{2-} participation during propylene oxidation. This is in excellent agreement with the dilution volume data for USb_3O_{10} in Table 2.

On a more general basis, these results illustrate the utility and sensitivity of this relatively simple, spectroscopic technique in determining the type of active oxygen involved in oxidation reactions.

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