JOURNAL OF CATALYSIS **39**, 22–28 (1975)

Studies on the Reduction–Reoxidation of Bismuth Molybdate Catalysts by Temperature Programmed Reoxidation Method

HIROSHI MIURA, YUTAKA MORIKAWA AND TAKAYASU SHIRASAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguroku, Tokyo, Japan

Received October 2, 1974

A new method of temperature programmed reoxidation (TPR) which gives a correlation of reoxidation rates with temperature in curved lines was devised and applied to slightly reduced MoO_3, Bi_2O_3 and bismuth molybdate catalysts. Those oxide catalysts are found to be characterized by peaks in TPR. That is, MoO_3 and Bi_2O_3 give TPR peaks at 410 and 180°C, respectively. An increase in the extent of prereduction results in another peak with both oxides, indicating that reoxidation takes place in two steps. Bismuth molybdate catalysts of different compositions give different peaks which may be identified as composites of three TPR peaks. Every bismuth molybdate catalyst which gives the TPR peak at 320°C is invariably active for selective oxidation of propylene to acrolein. The addition of phosphoric acid to bismuth molybdate catalysts increases the peak area at 320°C and consistently enhances the formation of acrolein from propylene.

The activation energies were determined for reduction of bismuth molybdate catalysts, reoxidation of slightly reduced catalysts and catalytic oxidation of propylene to acrolein. Those values are correlated to the TPR peak.

INTRODUCTION

Many papers have been published on the oxidation of olefins over bismuth molybdate catalysts, some of which were directed to its reaction mechanism. Adams and Jennings (*1,2*) clarified through their tracer studies that the propylene oxidation reaction proceeds by way of an allylic intermediate, the formation of which is rate determining in the overall reaction. However, the mechanism of oxygen incorporation is not very clear yet. Some investigators (*3,4*) suppose that the oxygen atoms in the products are derived from the oxide lattice, standing on the experimental results that acrolein is obtained by the oxidation of propylene with the catalyst oxide. Keulks (*5*) and Wragg *et al.* (*6*) confirmed this mechanism, using $^{36}O_2$ as a tracer.

It is also known that the properties of bismuth molybdate catalyst remarkably depend on the atomic ratio of Bi and Mo (Bi/Mo ratio) (*7*). Catalysts of higher activity and selectivity are found in the Bi/Mo ratio of 2/1 to 2/3. Since it is generally assumed that bismuth molybdate catalyst is in a slightly reduced state under the working condition and is subjected to repeated reduction and oxidation, the bismuth molybdates of different composition may be expected to exhibit different behaviors in the reduction and oxidation. In this respect the temperature programmed desorption as devised by Cvetanovic and Amenomiya (*8*) may be useful when some modifications are made to meet the present problem. Thus the temperature programmed reoxidation method was devised and applied for the slightly reduced samples of bismuth molybdate catalysts.

EXPERIMENTAL PROCEDURES

a. Preparation of Catalysts

Oxides of bismuth and molybdenum were prepared by decomposition of bismuth nitrate and ammonium paramolybdate in air at 550°C for 5 hr, respectively. Bismuth molybdate catalysts were prepared as follows; to the solution of bismuth nitrate in 4 *N* HNO_3, aqueous solution of ammonium paramolybdate was added under vigorous stirring and in some cases, 1 *N* phosphoric acid was further added up to the atomic ratio of $P/Bi + Mo = 0.075$. To this solution, dilute ammonia solution was added slowly and final pH of the mixture was adjusted to 7 ± 0.5. The solution containing precipitate was dried up and heated at about 80°C for 12 hr, and calcined in air at 550°C for 5 hr. The catalysts thus obtained were designated, according to the Bi/Mo ratio, as 2/1 cat. and 1/1P cat., where "P" denotes the catalysts containing phosphoric acid.

The X-ray diffraction patterns of the catalyst powder were in agreement with literature (*9,10*), i.e., 2/1 cat. showed only the diffraction lines of γ-phase (Bi_2MoO_6), and 2/3 cat. only those of α-phase ($Bi_2Mo_3O_{12}$). 1/1 cat. was the mixture of α-, β- and γ-phases. 1/2 cat. showed the lines of α-phase and MoO_3. 3/1 cat. had the form of $Bi_{2x}Mo_{(1-x)}O_3$, $x = 0.645$, which was reported by Kohlmuller and Badaud (*11*); whereas several unknown diffraction lines were also found. 2/1P cat. exhibited, in addition to γ-phase, α-phase. 1/1P cat. mainly consisted of β-phase and contents of α- and γ-phases were smaller than 1/1 cat. 2/3P cat. showed only the diffraction lines of α-phase.

b. Experimental Method

The oxidation of propylene was carried out using a flow reactor immersed in a heated fluidized bath. Two to 5 g of catalyst were packed in a glass tube 20 mm in diameter. The temperature of catalyst bed was determined *in situ* thermowell. Reaction products were analyzed by gas chromatography with three columns; molecular sieve 5A (for N_2, O_2 and CO), silica gel (for CO_2 and C_3H_6) and DOP + PEG (for acrolein and acetaldehyde). Small amount of acetaldehyde was detected only when the conversion exceeded 20%.

c. Catalytic Activity and Selectivity

The conversion of propylene was determined at a fixed reaction temperature of 450°C with a fixed composition of feed mixture varying space velocity and the rate of reaction and selectivity to acrolein were estimated and summarized in Table 1. There is a big difference among the catalytic activities of catalysts, while the surface area does not change so much. The catalysts are divided into two groups, A and B, according to the activity level. The selectivities are obtained at different conversion, 15% for A and 1% for B. The type A catalysts of higher activity give higher selectivities to acrolein, which increase with decreasing conversion up to 100% at 0% conversion. This fact indicates that the intermediate product, acrolein, is consecutively oxidized to CO and CO_2. On the other hand, the inactive type B catalysts give low selectivities even at the low conversion of 1%. It may be accordingly inferred that the type B catalysts are inferior to the type A in their intrinsic selectivity. It may be conceived that the composition of type A catalysts is in the range of 2/1 to 2/3 Bi/Mo ratio, and that addition of phosphoric acid increases activity, while gives little change in selectivity. The best catalyst found was 1/1P catalyst.

d. Reoxidation of the Catalysts and TPR Curves

At first, the partial reduction of catalyst was conducted in a closed ciruclating

TABLE 1

COMPONENTS IDENTIFIED BY X-RAY DIFFRACTION, CATALYTIC ACTIVITY AND SELECTIVITY OF BISMUTH MOLYBDATE CATALYSTS

Catalyst	Atomic ratio Bi:Mo:P	Component	Surface area (m/g)	Type	Rate of reaction[a] (mmol/hr)	Selectivity to acrolein at conv. 15%	Selectivity to acrolein at conv. 1%
Bi_2O_3	1:0:0	Bi_2O_3	1.1	B	0.54		2
MoO_3	0:1:0	MoO_3	1.0	B	0.07[b]		33
3/1	3:1:0	—[c]	1.4	B	0.31		13
2/1	2:1:0	γ[d]	1.3	A	6.48	70	
1/1	1:1:0	α, β, γ	0.7	A	4.53	87	
2/3	2:3:0	α	0.8	A	3.51	80	
1/2	1:2:0	α, MoO_3	1.8	B	0.70		75
2/1P	2:1:0.225	γ, α	1.0	A	3.70	75	
1/1P	1:1:0.15	β, γ, α	1.0	A	13.9	87	
2/3P	2:3:0.375	α	0.8	A	9.76	78	

[a] Catalyst charged 2 g (type A) or 5 g (type B). Reaction temp, 450°C; composition of reactant gas, $C_3H_6:O_2:N_2 = 1:1:4$ (molar ratio).

[b] Activity of MoO_3 was so low that the run was made at 500°C.

[c] $Bi_{2x}Mo_{(1-x)}O_3$, $x = 0.645$.

[d] $\alpha = Bi_2Mo_3O_{12}$, $\beta = Bi_2Mo_2O_9$, $\gamma = Bi_2MoO_6$.

system. The catalyst bed was heated up to the desired temperature in circulating air, followed by evacuation and introduction of measured quantity of hydrogen, which was circulated through the catalyst bed with dry ice–methanol trap. The rate of reduction was measured by the decrease in hydrogen pressure. When the reduction reached the desired extent, hydrogen was evacuated, and oxygen of 300 mm Hg was introduced at room temperature. The catalyst temperature was raised at a constant rate of 2°C/min, circulating oxygen. The rate of reoxidation was determined by the rate of decrease in oxygen pressure.

Assuming that the rate of reoxidation r is proportional to both the number of oxygen defects in the catalyst and nth power of oxygen pressure P, the rate r is expressed by

$$r = dN/dt$$
$$= k(N_0 - N)P^n \exp(-E_r/RT), \quad (1)$$

where N_0 is the number of oxygen atoms which are required to complete the reoxidation of the partially reduced catalyst, N the number of oxygen atoms consumed for reoxidation in time t, E_r the activation energy of reoxidation and k the rate constant. From the expression (1), it is expected that raising the temperature T results in an increase in the rate r due to the exponential term followed by a decrease due to $(N_0 - N)$ term, thus giving a peak in the TPR. TPR measurement defined above gave well reproducible peaks. When N is small, i.e., in the first part of peak, the terms $(N_0 - N)$ and P^n may be regarded to be constant, and thus E_r may be obtained from Arrhenius plot of r.

RESULTS AND DISCUSSION

a. *Reoxidation of Molybdenum Oxide*

The TPR curves of molybdenum oxide (MoO_3) of different degree of reduction are shown in Fig. 1. In the case of 1% reduction, TPR curve gives a single peak at 410°C (Fig. 1a). Separate experiments showed that the peak temperature T_{max} is practically unaffected by the reduction temperature in the range of 400–470°C.

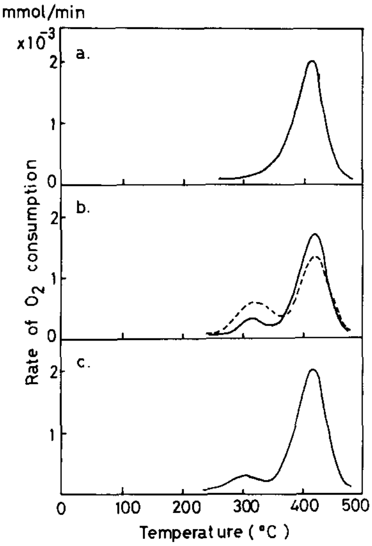

FIG. 1. TPR curves of MoO_3 prereduced at 450°C. (a) 1.0% prereduced; (b) 3.8% (—); and 9.5% (----) prereduced; (c) temperature programmed oxidation of MoO_2 prepared from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

Even in the case of a higher degree of reduction (3.8, 9.5%), the T_{max} does not shift, whereas a second peak appears at 300–320°C (Fig. 1b). This fact indicates that the deep reduction of molybdenum oxide produces another oxygen defect which can be reoxidized at lower temperature, giving rise to the second peak. Temperature programmed oxidation was applied to molybdenum dioxide (MoO_2) prepared by decomposition of ammonium paramolybdate in an atmosphere of hydrogen at 450°C, the structure of which was confirmed by X-ray diffraction. As shown in Fig. 1c, the TPR peak of MoO_2 at 410°C is much larger than that at 300°C as was the case in Fig. 1b. Hence the peak at 410°C may be attributed to the following reaction,

$$2MoO_2 + O_2 \longrightarrow 2MoO_3. \quad (2)$$

b. Reoxidation of Bismuth Oxide

TPR curves for bismuth oxide are shown in Fig. 2a and b. The sample prereduced at 350°C by 4.9% gives a single peak at 180°C (Fig. 2a); whereas the sample prereduced at 450°C gives another peak at 230°C in addition to the one at 180°C, in spite of the lower degree of reduction (3%) (Fig. 2b). The T_{max} of second peak shifts to higher temperature, while the first peak is unaffected, by increasing the degree of reduction. The reduction of bismuth oxide reportedly produces metallic bismuth only and no other oxide (*12*). Hence the reoxidation is expressed as (3):

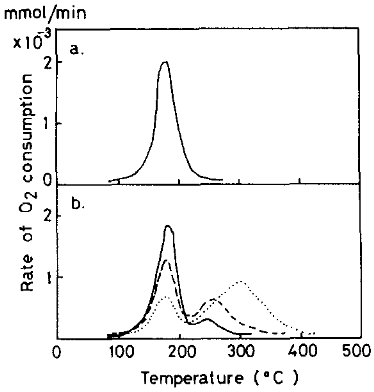

FIG. 2. TPR curves of Bi_2O_3. (a) 4.9% prereduced at 350°C; (b) 3% prereduced at 450°C (—); 12.5% prereduced at 400°C (----) and 25% prereduced at 400°C (····).

$$4Bi + 3O_2 \longrightarrow 2Bi_2O_3. \quad (3)$$

The metallic bismuth formed at lower temperature may be more finely dispersed so that it may be more readily oxidized. This readier reoxidation is likely to correspond to the first peak at 180°C in Fig. 2. Another peak at higher temperatures (230–300°C) may be ascribed to the oxidation of agglomerated particles of metallic bismuth, thus depending on the degree of reduction.

c. Reoxidation of Bismuth Molybdate Catalysts

All the samples of bismuth molybdate including those containing phosphoric acid were prereduced at 400°C up to 2 to 3%. Their TPR curves are shown in Fig. 3a–d. 3/1 cat. and 1/2 cat. show only one peak at 160 and 370°C, respectively (Fig. 3a).

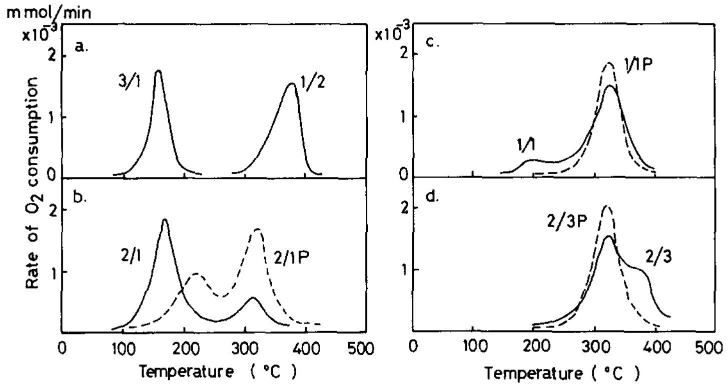

FIG. 3. TPR curves of bismuth molybdate catalysts prereduced at 400°C. Amount of hydrogen for reduction: 0.71 mmol H_2/2.5 g cat. (a) 3/1 cat. (degree of reduction: 3.2%) and 1/2 cat. (2.1%); (b) 2/1 cat. and 2/1P cat. (2.9%); (c) 1/1 cat. and 1/1P cat. (2.4%); (d) 2/3 cat. and 2/3P cat. (2.1%).

Both 2/1 cat. and 2/1P cat. give two peaks as shown in Fig. 3b, the former at 170 and 320°C. 1/1 cat. shows one large peak at 320°C preluded by a small broad peak at 200°C, while the latter one disappears from the curve for 1/1P cat. (Fig. 3c). 2/3 cat. also gives the 320°C peak although it is followed by a shoulder at 380°C, which disappears from 2/3P cat. (Fig. 3d).

The peak temperatures, except the 170°C peak in Fig. 3b, were reproducible within ±10°C, even though the degree of reduction at 400°C was changed from 3 to 10% and reduction temperature was changed from 350 to 430°C, keeping the degree of reduction at 3%. Matsuura and Schuit (*13*) studied the behavior of 2/1 catalyst and reported that the starting temperature of reoxidation of fully reduced catalyst markedly depends on the reduction temperature and also on the condition of sintering treatment after reduction. In their fully reduced catalyst, considerable amount of metallic bismuth must be formed and agglomerated, giving rise to the different starting temperature of reoxidation.

The TPR curve of 2/1 cat. shows interestingly two peaks, although the catalyst is exclusively made up of γ-phase bismuth molybdate (Bi_2MoO_6). The fact suggests that the reduced γ-phase is reoxidized in two steps. The first step suggested by the first peak at 170°C is likely to be the oxidation of metallic bismuth since the T_{max} is close to that of Bi_2O_3. The second step suggested by the peak at 320°C may be the reoxidation of MoO_2. The presence of metallic bismuth and MoO_2 was confirmed by X-ray diffraction, and the final product of reoxidation proved to be the γ-phase, suggesting that the reaction of reoxidation products, MoO_3 and Bi_2O_3, is very fast.

TPR curves of bismuth molybdates shown in Fig. 3 do not apparently correspond to the catalyst component identified by X-ray diffraction. For example 1/2 cat. is a mixture of α-phase and MoO_3 but its TPR curve is quite different from either of 2/3 cat. (α-phase) or MoO_3. However the TPR curve appears to reflect the catalytic activity for selective oxidation of propylene. Referring to the data in Table 1, it is found that every catalyst of higher selectivity to acrolein does not contain any phase other than α, β or γ, and gives the characteristic TPR peak at 320°C. For example, 1/2 cat. contains MoO_3 in addition to α-phase, giving no peak at 320°C and a very poor selectivity to acrolein. In addition to the catalysts shown in Fig. 3, 3/2 cat. which proved to be a mixture of 2/1 and 1/1 on X-ray diffraction, consistently gave two TPR peaks at 200 and 320°C and showed high activity and selectivity. Thus the oxygen defect responsible to the 320°C peak seems to play an important role in the selective oxidation of propylene.

In conformity with the above inference, addition of phosphoric acid to 1/1 and 2/3 cat. results in the intensification of 320°C peak accompanied by disappearance of other peaks as well as the enhancement of selective oxidation. In the case of 2/1 cat. which contains only γ-phase and gives another peak at 170°C, the effect of phosphoric acid addition is somewhat different from 1/1 and 2/3 cat. Although the addition intensifies the 320° peak, another peak appears at 210°C and the catalytic activity is reduced one half accompanying a slight increase in selectivity. In addition, 3/1 cat. which gives a single peak at 160°C is little active.

Some of bismuth molybdate catalysts were prereduced by ethylene and propylene instead of hydrogen and subjected to the TPR measurements. It was confirmed that the change of reductant does not affect the TPR curve. It is accordingly concluded that the same oxygen species are involved in the oxidation of olefin by the catalyst.

The nature of bismuth molybdate surface was investigated by Matsuura and Schuit (*13,14*) analyzing isotherms of variety of compounds. It was claimed that bismuth molybdate acts as a bifunctional catalyst with two types of adsorption center, A and B, where A and B on γ-phase were supposed to be made up, respectively, of Bi_2O_2 and the interconnecting oxygen between Bi_2O_2 and MoO_2 planes. In fact the γ-phase (2/1 cat.) gives two TPR peaks (170 and 320°C). The 170°C peak is close to that of Bi_2O_3 (180°C), and the 320°C peak is also observed with MoO_2 and with MoO_3 prereduced to more than 3.8%. Thus the two peaks observed with γ-phase might correspond to the two types of oxygen proposed by Matsuura and Schuit. However, as described above the selective oxidation is likely to be associated with the 320°C peak.

d. Kinetic Correlation Between the Reduction and Catalytic Oxidation

The activation energies were determined for catalytic oxidation of propylene (E_p), partial reduction of the catalysts by hydrogen (E_h), and reoxidation of the reduced catalysts (E_o), and are plotted against T_{max} of main TPR peak of the catalysts in Fig. 4. It may be natural that E_o increases with T_{max}. It is to be noted, however, that the three values substantially run parallel regardless of the difference in the reaction involved. This seems to imply that a common factor controls the activation energy of three reactions. In this respect it would be relevant to recall that the lattice oxygen is responsible for the propylene oxidation over bismuth molybdate as shown by Keulks (5) and Wragg *et al.* (6). If a migration of lattice oxygen is commonly involved in those three reactions, the result as shown in Fig. 4 may be understood.

In order to examine the above correlation, the activation energies were determined for the reduction of bismuth molyb-

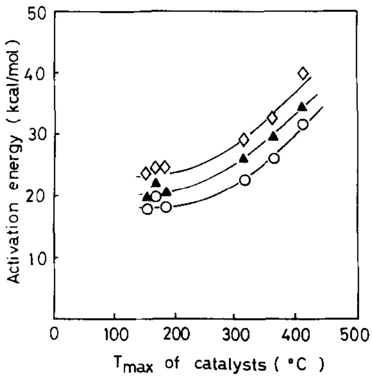

FIG. 4. Activation energies as functions of T_{max}. (▲) E_p (catalytic oxidation of C_3H_6); (○) E_h (H_2 reduction of the catalysts); (◇) E_o (reoxidation of the partially reduced catalysts).

TABLE 2
COMPARISON OF ACTIVATION ENERGIES BETWEEN THE REDUCTION OF CATALYST BY H_2 OR C_2H_4 AND THE CATALYTIC OXIDATION OF H_2 OR C_2H_4

Reaction	Activation energy (kcal/mol) 2/1 cat.	1/1 cat.	2/3 cat.
Reduction of catalyst with H_2	21	26	
Catalytic oxidation of H_2	22	26	
Reduction of catalyst with C_2H_4		35	38
Catalytic oxidation of C_2H_4		34	39

date catalysts with hydrogen or ethylene, and compared with those for the catalytic oxidation of hydrogen or ethylene over the same catalysts as shown in Table 2. It is clearly indicated that both values for the reduction and catalytic oxidation are in agreement over three catalysts tested. These results demonstrate that the reduction and the reoxidation of bismuth molybdate catalysts is closely correlated with the catalytic oxidation of olefins.

In this way the temperature programmed reoxidation method seems promising in offering information about the oxidation mechanism. Temperature programmed reduction of bismuth molybdate catalysts was also examined. The reduction peak appears at a higher degree of reduction, where the structure of bismuth molybdate catalyst is largely destroyed. Accordingly, the reduction method is less suitable for the investigation of working state than the reoxidation method in which the destruction of oxide lattice is minimized.

REFERENCES

1. Adams, C. R., and Jennings, T. J., *J. Catal.* **2,** 63 (1963).
2. Adams, C. R., and Jennings, T. J., *J. Catal.* **3,** 549 (1964).
3. Batist, P. A., Kapteijins, C. J., Lippens, B. C., and Schuit, G. C. A., *J. Catal.* **7,** 33 (1967).
4. Peakock, J. M., Parker, A. J., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **15,** 398 (1969).
5. Keulks, G. W., *J. Catal.* **19,** 232 (1971).
6. Wragg, R. D., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **22,** 49 (1971).
7. Batist, P. A., Lippens, B. C., and Schuit, G. C. A., *J. Catal.* **5,** 55 (1966).
8. Cvetanovic, R. J., and Amenomiya, Y., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 17, p. 103. Academic Press, New York, 1967.
9. Batist, P. A., Der Kindern, A. H. W. M., Leeuwenburgh, Y., Mets, F. A. M. G., and Schuit, G. C. A., *J. Catal.* **12,** 45 (1968).
10. Aykan, K., *J. Catal.* **12,** 281 (1968).
11. Kohlmuller, P. R., and Badaud, J. P., *Bull. Soc. Chim. Fr.* 3434 (1969).
12. Egashira, M., Sumie, H., Sakamoto, T., and Seiyama, T., *Kogyo Kagaku Zasshi* **75,** 860 (1970).
13. Matsuura, I., and Schuit, G. C. A., *J. Catal.* **25,** 314 (1972).
14. Matsuura, I., and Schuit, G. C. A., *J. Catal.* **20,** 19 (1971).