

Selective Oxidation and Ammoxidation of
Propylene by Bismuth Molybdate Catalysts

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Introduction

Bismuth molybdates catalyzing selective oxidation (1) and ammoxidation (2) of propylene were discovered and developed at Sohio [1,2] in the early 1960's.

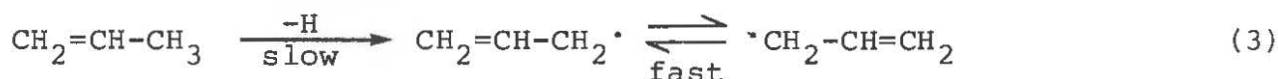


Since then, many fundamental studies have employed catalysts containing different bismuth to molybdenum atomic ratios. As a result of such studies, it is now known that bismuth molybdate catalysts display high activity and selectivity only if their Bi/Mo compositions lie within the range of 2/3 to 2/1 [3].

Depending on conditions such as the initial Bi/Mo ratio, pH value, reaction temperature, and interaction time, three major products can be isolated by co-precipitation from a mixed solution of bismuth nitrate and ammonium molybdate. The products are $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (2.3, α), $\text{Bi}_2\text{Mo}_2\text{O}_9$ (1:1, β) and Bi_2MoO_6 (2:1, γ) [4-7]. The structures α , β and γ differ in a number of ways: (1) the number of oxygens bound only to Bi (from 0 to 2); (2) the degree of clustering of MoO_4 (from 2 to layered); and (3) the number of Bi^{3+} vacancies (from 1 to 0) [8].

Mechanism

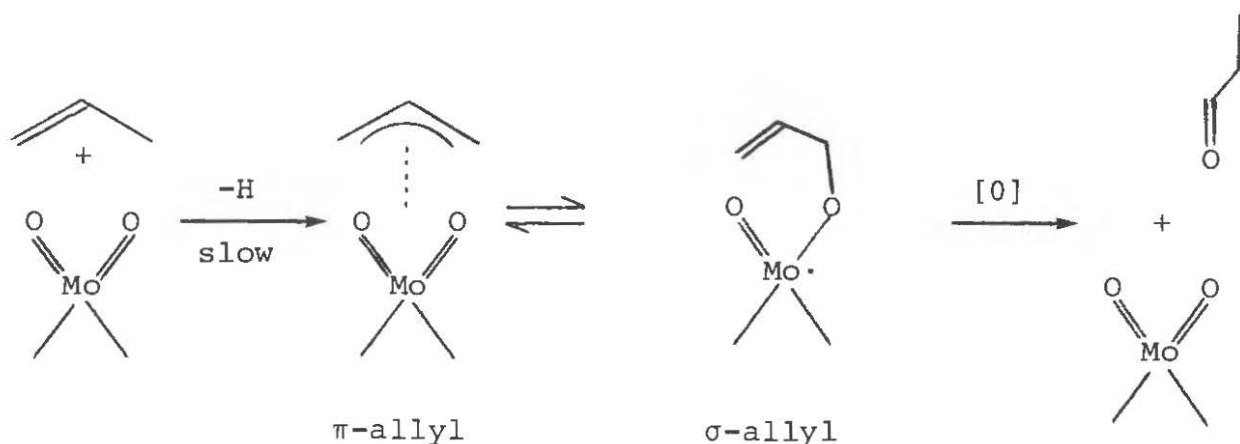
In a series of experiments using deuterium-labeled propylenes, Adams and Jennings [9] established the rate-determining nature of the α -hydrogen abstraction, in which a first order deuterium isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.82$, $T = 450^\circ\text{C}$) was observed. By studying the isotopic distributions of the oxidation products of ^{14}C - and ^{13}C -labeled propylenes, Sachtler [10] and McCain [11] concluded that equation (3) is the key step in the selective oxidation (ammoxidation)



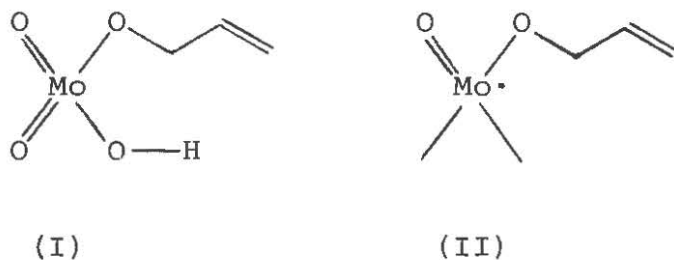
Grzybowska and Haber [12] in 1977 suggested that reactions with bismuth molybdate catalysts proceed via the association of allyl radicals with oxygens bound to bismuth. A number of factors led them to this conclusion. The isomerization of propylene to

1,5-hexadiene and benzene occurs only with Bi_2O_3 . Additionally, molybdenum polyhedra are oxygen inserters, and acrolein is known to be formed from the reaction of MoO_3 with "allyl radical" (from thermally decomposed allyl iodide). These experiments introduced the important multi-center (dual-site) concept [13], though there are still many different postulates about the roles of bismuth and molybdenum in α -H abstraction and olefin adsorption [12-15].

By comparing the product distributions of the reaction of azopropene over MoO_3 , the reaction of allyl iodide over MoO_3 , and the reaction of propylene over bismuth molybdates, Burrington and Grasselli [16] concluded that the general reaction route is:



In order to shed light on the details of the selective oxidation (ammoxidation) mechanism, in 1980 Grasselli and Burrington [15] studied the selective oxidation of d_0 , $1,1\text{-}d_2$ and $3,3\text{-}d_2$ allyl alcohol over MoO_3 and $\text{Bi}_2\text{O}_3 \cdot n\text{MoO}_3$ ($n=0, 1, 3$). From the product distributions and their similarities with the distributions obtained from analogous reactions with the well-studied Mo(VI) ester (I) [17] and Mo(V) ester (II) (which may be an intermediate in the selective oxidation of propylene), they proposed a more complete mechanism [15] for the selective oxidation (ammoxidation) of propylene over Bi-Mo catalysts.



Redox properties

Brazdil and Grasselli [18] utilized a pulse microreactor method to reduce the catalysts with propylene in the absence of oxygen and subsequently to reoxidize the partially reduced catalysts by gaseous oxygen. They found that the unit area rates of lattice oxygen participation decrease in the order: $\text{Bi}_2\text{Mo}_2\text{O}_9 > \text{Bi}_2\text{Mo}_3\text{O}_{12} > \text{Bi}_2\text{MoO}_6$ and the reoxidation rates decrease in the order: $\text{Bi}_2\text{MoO}_6 > \text{Bi}_2\text{Mo}_2\text{O}_9 > \text{Bi}_2\text{Mo}_3\text{O}_{12}$. They also found that the maximum selective utilization of reactive lattice oxygen occurs after partial reduction for $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and $\text{Bi}_2\text{Mo}_2\text{O}_9$. These results are consistent with a selective oxidation mechanism requiring coordinatively unsaturated metal ions in complex shear domains.

References

1. Idol, J. D. U.S. Patent 2,904,580 (to Standard Oil Co., Ohio) 1959.
2. Callahan, J. L.; Grasselli, R. K.; Milberger, E. C.; Strecker, H. A. Ind. Eng. Chem. Proc. Res. Dev. 1970, 9, 134-42.
3. Batist, P. A.; der Kinderen, A. H. W. M.; Leeuwenburgh, Y.; Metz, F. A. M. G.; Schuit, G. C. A. J. Catal. 1968, 12, 45.
4. Erman, L. Ya.; Gal'perin, E. L.; Kolchin, I. K.; Dobrzanski, G. F.; Chernyshev, K. S. Russ. J. Inorg. Chem. 1964, 9, 1174.
5. Gelbstein, A. J.; Stroeva, S. S.; Kulkoba, N. V.; Vanshkin, Yu. M.; Lapidus, V. L.; Sevast'yanov, N.; Nettichimiya 1964, 4, 909.
6. Bleyenbergh, A. C. A. M.; Lippens, B. C.; Schuit, G. C. A. J. Catal. 1965, 4, 581.
7. Blasse, G. J. Inorg. Nucl. Chem. 1966, 28, 1124.
8. a) Zemann, J. Heidelberger Beitr. Mineral Petrogr. 1956, 5, 139.
b) van den Elzen, A. F.; Rieck, G. D. Acta Crystallogr. 1973, B29, 2436-8.
c) van den Elzen, A. F.; Rieck, G. D. Acta Crystallogr. 1973, B29, 2433-6.
d) van den Elzen, A. F.; Rieck, G. D. Mat. Res. Bull. 1975, 10, 1163.
9. a) Adams, C. R.; Jennings, T. J. J. Catal. 1962, 2, 63-8.
b) Adams, C. R.; Jennings, T. J. J. Catal. 1964, 3, 549-58.
10. Sachtler, W. M. H. Rec. Trav. Chim. 1963, 82, 243-5.
11. McCain, C. C.; Gough, G.; Godin, G. W. Nature 1963, 989-90.

12. Grzybowska, B.; Haber, J.; Janas, J. J. Catal. 1977, 49, 150-63.
13. Keulks, G. W.; Krenzke, L. D.; Notermann, T. M. Adv. in Catal. 1978, 27, 210.
14. Matsuura, I. J. J. Catal. 1974, 35, 452; 33, 420.
15. Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. J. Catal. 1980, 63, 235-54.
16. Burrington, J. D.; Grasselli, R. K. J. Catal. 1979, 59, 79-99.
17. Iwasawa, Y.; Nakano, Y.; Ogasaware, S. J. Chem. Soc., Faraday Trans. 1978, 74, 2968.
18. Brazdil, J. F.; Suresh, D. D.; Grasselli, R. K. J. Catal. 1980, 66, 347-67.