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The Oxidation of Propene over Bismuth Oxide, Molybdenum Oxide, and Bismuth Molybdate Catalysts

II. ESR Studies of Bismuth Molybdate and MoO_3 Catalysts

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The ESR signals ascribed to Mo^{5+} have been found when bismuth molybdate or molybdenum oxide catalysts were exposed to propene at temperatures between 225 and 500°C. With molybdenum oxide the signal intensities increase steadily with time; with bismuth molybdates they increase continuously at lower temperatures, but increase and then decay rapidly at higher temperatures. When 1:1 mixtures of propene and oxygen contact the catalysts, no Mo^{5+} signals are seen while gaseous oxygen is still present. With bismuth molybdate and 1-butene, the Mo^{5+} signals behave as with propene, but with hydrogen the Mo^{5+} signals increase continuously. These changes are discussed in relation to the reduction of the catalysts, as revealed in parts III and IV, and some deductions are made about the possible bonding of the hydrocarbon radicals to the molybdenum ions and the effects of oxygen gas and bismuth ions on that bonding.

A correlation has been reported between the intensity of an ESR signal attributed to Mo^{5+} in a supported MoO_3 catalyst and the activity of the catalyst in polymerization reactions (*1*). Cornaz *et al.* (*2*) reported that in MoO_3 which had been degassed at 500°C, or partially reduced by 1-butene at 350°C, a number of ESR lines were visible at −196°C, including one at $g = 1.94$ attributed to Mo^{5+}, although they found no signals when the spectrum was recorded at room temperature. On exposure of the sample to oxygen at −195°C, the Mo^{5+} signal diminished, but no new lines appeared. With bismuth molybdate, first activated in oxygen or air at 500°C and subsequently degassed at 400°C for 4 hr, no Mo^{5+} lines were observed. Nevertheless, there seems little doubt that bismuth molybdate is extensively reduced by 1-butene (*3*) and also by propene (other parts of this paper). It was expected that Mo^{5+} and Mo^{4+} would be produced, possibly in states that show paramagnetism, and it seemed worth looking for ESR signals from bismuth molybdate and MoO_3 catalysts, reduced by propene and by propene–oxygen mixtures for differing times and at different temperatures.

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Equipment and Experimental Procedure

The ESR spectrometer. This was a Decca Type X1 spectrometer with 100 kcps field modulation and phase-sensitive detection. The klystron supplied about 30 mW to the cavity and was phase-locked at a frequency of 9270 Mcps, and a correction signal was applied for changes in the resonant frequency of the cavity. Full microwave power was used and no signal saturation was observed at room temperature. For initial scans of the spectrum, the field was swept from zero to about 5000 G in about 1000 sec, and for measurements of the Mo^{5+} signals at about 1 G/sec around the value corresponding to $g = 2$.

A Decca variable-temperature cavity insert was used for some studies at ca. 77°K. Unfortunately, the highest temperature attainable, 300°C, is well below the normal operating range of the catalysts (450–550°C). Consequently, it was necessary to record the spectra at room temperature after treatment of the catalysts. The catalyst samples were contained in an 8-mm quartz tube which could be located accurately in the ESR cavity (a Decca Mw 232) and also transferred to a conventional vacuum system for evacuation and admission of gases. The sample tube was attached by a graded seal to a 20 ml Pyrex vessel, to provide ample gas space, and the whole sample vessel could be surrounded by an accurately regulated furnace to attain the temperature of activation or reduction. It was necessary to standardize the activation, reaction, and transfer procedures rigorously to obtain reproducible results.

Experimental Procedure

With the procedures described below, the results were reproducible to better than 10%.

After activation of the catalysts *in situ* for 1 hr in oxygen at 150 torr and 500°C, the sample tube was rapidly removed from the furnace and immersed in a slush bath at 195°K to stop the reaction. The quenching time necessary to attain a temperature low enough for this purpose was estimated to be only a few seconds. The sample was then evacuated to 5×10^{-4} torr.

Vapors from tap grease and the laboratory air reduced the hot catalysts, giving rise to large Mo^{5+} signals (*4*). To investigate nonreduced catalysts, vapors were excluded from the sample by liquid nitrogen traps and the samples were sealed after the evacuation prior to the recording of the ESR spectrum. However, when reduction by propene, 1-butene, or hydrogen was investigated, it was not so necessary to exclude grease vapors, so transfer of the samples to the ESR spectrometer was greatly facilitated.

For the reductions, the hydrocarbon vapor at a measured pressure was admitted to the catalyst maintained at the required temperature, and after reduction for a measured time the sample was quenched rapidly to 195°K without removing the gases. Earlier procedures, where the gases were removed by evacuation before quenching, proved unsatisfactory. For each point obtained at short times in a series at a particular reaction temperature, repeated activations and reductions were carried out until reproducible results were obtained. Most spectra were taken at room temperature, but a few examinations were made at 77°K.

An internal reference signal from a ruby crystal fixed in the ESR cavity was used to compare the signal intensities obtained from different samples and to enable corrections to be applied for the slight variations found in the spectrometer's gain. By comparison with a sample of $CuSO_4 \cdot 5H_2O$, it was estimated that a relative intensity of unity corresponds to about 5×10^{15} Mo^{5+} ions in the cavity.

The Spectra

Our preliminary studies showed that "Syton P" supported catalysts SBM-1 and SM-1 gave large signals caused by the presence of iron and manganese, some of which would obscure any small Mo^{5+} lines. Reduction of UBM-2 often produced a large broad line extending from 0 to 5000 G, with a maximum about $g = 2$ which greatly distorted the Mo^{5+} signals. A similar line was often observed on reducing SB-2 and UBM-4. The signal persisted after reoxidizing the samples. No satisfactory explanation of this persistent but rather irreproducible signal can be given. The ultrapure supported catalysts SBM-3 and SM-2, which did not show the broad signal, were therefore used for the present investigation.

The ultrapure supported catalysts showed well-defined signals that varied systematically and reproducibly with the conditions and the duration of reduction with propene, 1-butene, and hydrogen. Figure 1 shows two ESR signals. The broader one, with $g_{\parallel} = 1.865$ and $g_{\perp} = 1.933$, is typical of lines observed under reducing conditions, and is ascribed to Mo^{5+} (*5*). This signal was asymmetric as expected for a polycrystalline

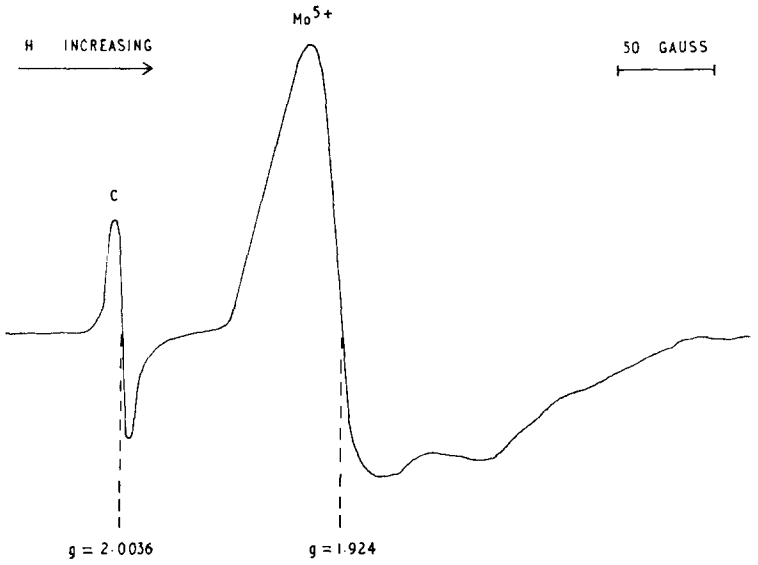

FIG. 1. A typical ESR spectrum, containing a Mo^{5+} signal and a signal assigned to carbon.

sample. The general line shape remained fairly constant with an overall width of about 140 G which varied by less than ±5% for all observed Mo^{5+} lines. The doubly integrated areas under a number of these signals were calculated by a numerical integration method (*6*) and were found to be proportional to the corresponding peak–peak heights of the derivative curves. These "heights" were therefore used as measures of the number of Mo^{5+} species present after correcting for changes in spectrometer gain and sensitivity.

The signal at $g = 2.0036$ appeared on the SBM-3 and SM-2 samples reduced by propene. It was fairly symmetric, with line width of 9 G, and its relative peak height was usually small compared with the Mo^{5+} signal for all observed reductions. Its intensity did not change on evacuation; it decreased on exposure to oxygen, but returned to the original value when the oxygen was removed. It is therefore more likely to be due to carbon than a free hydrocarbon radical, but it was not investigated systematically. (It did not appear on reduction of the catalysts by hydrogen.)

Examination of various reduced ultrapure samples at 103°K showed the expected increase in size of the Mo^{5+} signals, but no new signals of the type reported by Cornaz *et al.* (*2*) were found from these or from activated or reoxidized samples of SBM-3, UBM-4, SM-2, and SB-2.

Variation of Mo^{5+} Signals with Reaction Conditions

Prolonged evacuation of SBM-3 at 500° C, in a vessel free from grease, did not produce any Mo^{5+} signals. Evacuation of SM-2 did produce small Mo^{5+} signals. These results agree with those reported by Cornaz *et al.* (*2*) and suggest that there is little free MoO_3 in the bismuth molybdate catalyst.

The behaviors of SBM-3 and SM-2 on exposure to propene differed greatly. The Mo^{5+} signal obtained with SM-2 continued to increase with time whereas the mixed oxide exhibited an initial increase in Mo^{5+} signal intensity followed by a decrease which in turn (at the highest temperatures studied) led into a region where the Mo^{5+} concentration increased once more. Figure 2 shows the steady increase with time of the Mo^{5+} signal on exposure of SM-2 to 20 torr C_3H_6 at 375°C, and the much steeper initial rise at 500°C. Figure 3 shows that with SBM-3 and 20 torr C_3H_6 at the lower temperatures used (225 and 275°C), the mixed oxide resembles the "low temperature" supported molybdenum oxide in its behavior.

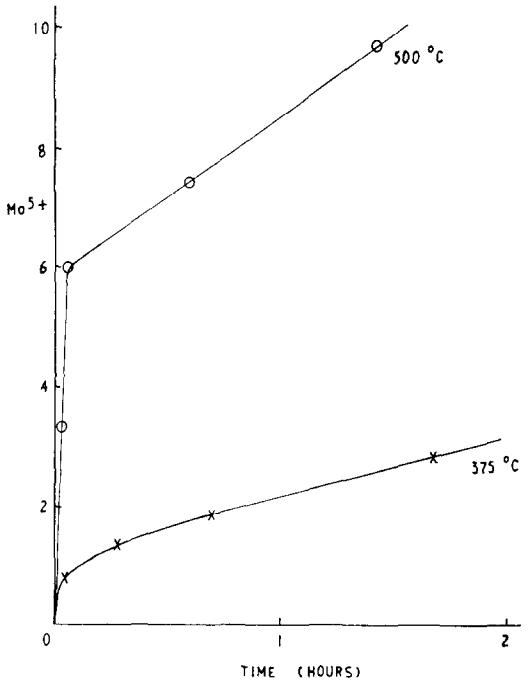

FIG. 2. Relative Mo^{5+} signal with time for 20 torr C_3H_6 over SM-2 at 375 and 500°C.

At the intermediate temperatures, 325–475°C, a further process, whose efficiency increased with increasing temperature, occurred and reduced the Mo^{5+} intensities thus causing them to pass through maxima which occur at shorter times for higher temperatures. At the highest temperatures studied (475 and 500°C) the first and second processes are very rapid, and are followed by a third process such that at 475°C the Mo^{5+} signal shows both a maximum and a minimum value. At 500°C the three processes are so rapid that no maximum or minimum is observed and the SM-2 and SBM-3 curves at 500°C are closely similar in appearance, though not in magnitude of signal.

As the results presented in Part IV indicate, only the first two of these processes are related to the initial catalytic reaction since the final continually-increasing Mo^{5+} signal intensity occurs during a period in which all the propene in the system has been oxidized. It is possible that the third process corresponds only to reactions within the catalyst itself; unfortunately other possible reactions, such as those with products like CO, have not yet been investigated.

Increasing the propene pressure at fixed temperatures (Fig. 4) on SBM-3 increased both the initial (Mo^{5+} increasing) and secondary (Mo^{5+} decreasing) processes in such a way that the maxima corresponded to a greater Mo^{5+} signal intensity and occurred

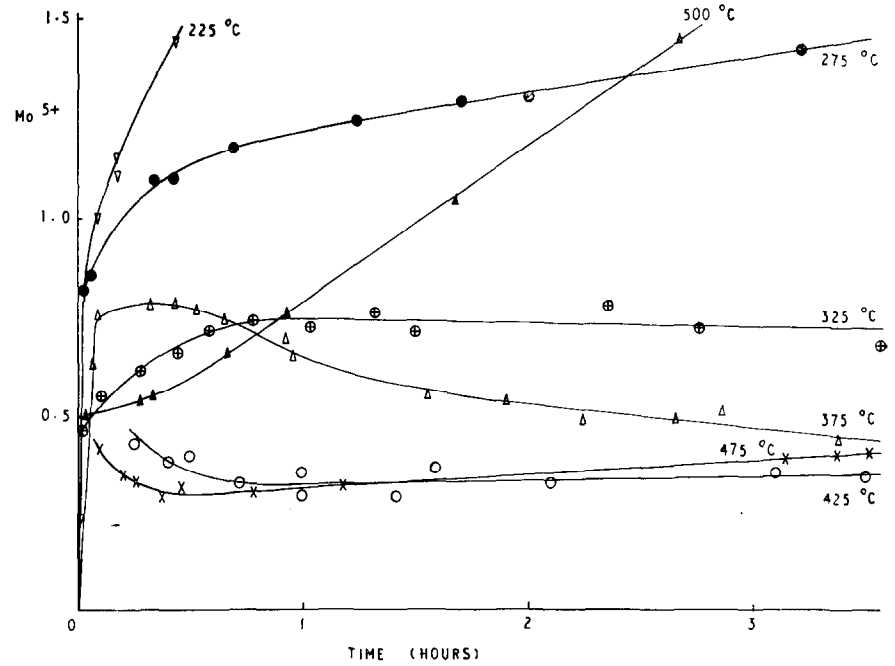

FIG. 3. Relative Mo^{5+} signal with time for 20 torr C_3H_6 over SBM-3 at various temperatures.

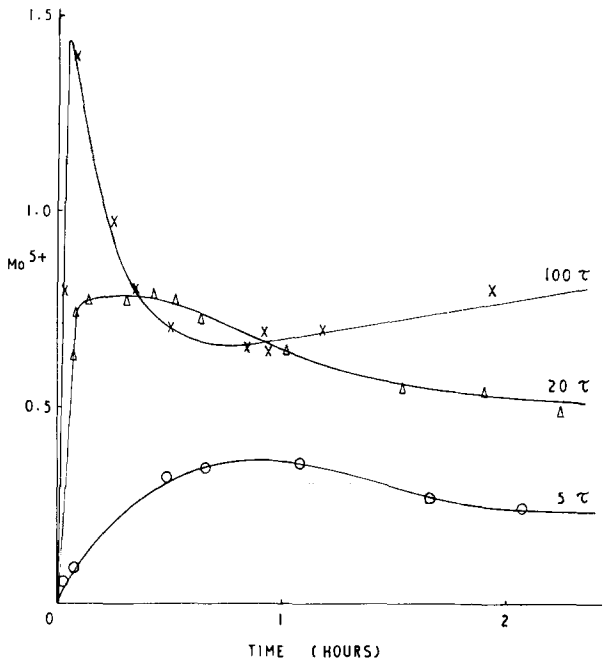

FIG. 4. Relative Mo^{5+} signal with time for 5, 20, and 100 torr C_3H_6 over SBM-3 at 375°C.

after a shorter time. At high pressures and high temperatures it was impossible to follow these processes by the quenching technique. Even at 425° the pattern of the pressure effects is relatively unclear as the maxima occur so clearly, although, as Fig. 5 shows, the maxima are still present at a propene pressure of 100 torr, which is close

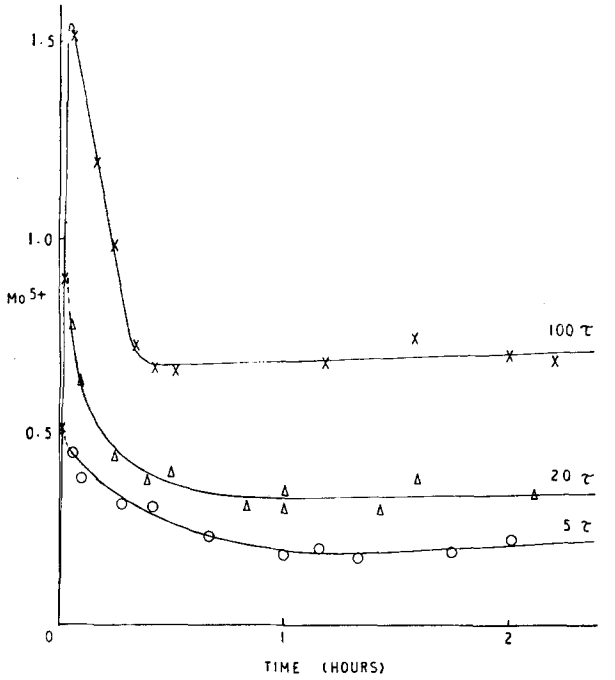

FIG. 5. Relative Mo^{5+} signal with time for 5, 20, and 100 torr C_3H_6 over SBM-3 at 425°C.

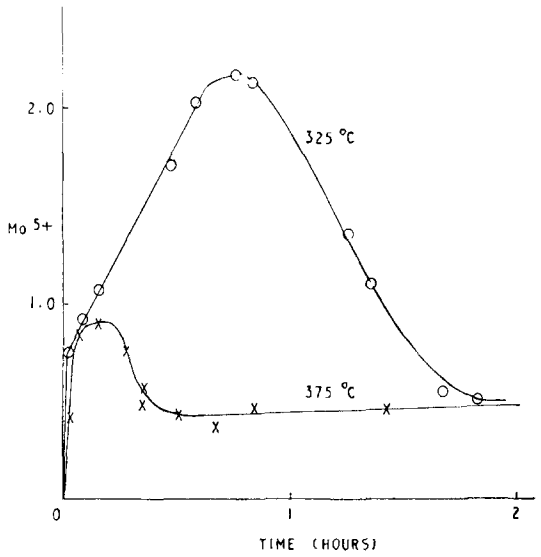

FIG. 6. Relative Mo^{5+} signal with time for 20 torr 1-butene over SBM-3 at 325 and 375°C.

to that used in the catalytic reaction system employing a stoichiometric propene–air feed at atmospheric pressure.

Some comparative studies (Fig. 6) of the reduction of SBM-3 with 1-butene show clearly that Mo^{5+} is formed and removed just as with propene. Figure 6 shows that the initial buildup of signal strength is roughly the same at 325 and 375°C but, as with propene, the decay is faster at the higher temperature. The maximum signal intensities are somewhat higher than with propene.

Figure 7 shows that on reduction with hydrogen Mo^{5+} signals also appear, building up more slowly at comparable temperatures. There is no decay, however; the signals increased for 4 hr under the conditions investigated.

Finally, experiments were carried out to look for Mo^{5+} signals from SBM-3 and SM-2 exposed to 1:1 mixtures of propene and oxygen. 20 torr of C_3H_6 and 20 torr of O_2 were admitted to samples of the catalysts at 425, 475, or 500°C. After selected reaction times, the sample tube was quenched as before and the spectra were examined at room temperature. The results obtained with SM-2 and SBM-3 were closely similar. In each case no Mo^{5+} appeared in the catalysts until all the gas-phase oxygen had been consumed by the oxidation (4). Thus Mo^{5+} signals appeared only after a finite period of time which was of course shorter at the higher temperatures. The absence of the Mo^{5+} signals early in the runs is not due to paramagnetic interactions of these centers with oxygen since the evacuated catalysts yield results similar to those obtained from samples studied in the presence of gas phase oxygen.

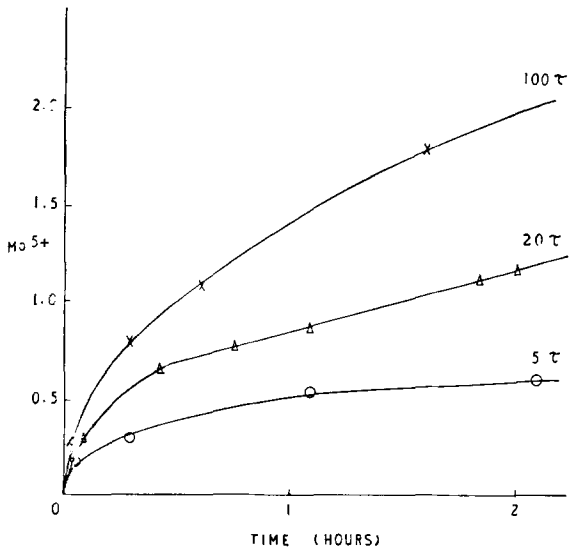

FIG. 7. Relative Mo^{5+} signal with time for 5, 20, 100 torr H_2 over SBM-3 at 425°C.

Discussion

The results establish quite clearly that Mo^{5+} species are produced in the reduction of bismuth molybdates or molybdenum oxide by propene over wide ranges of temperature and propene pressures, and also by reduction of bismuth molybdates by 1-butene and by hydrogen.

There are substantial differences in the behavior of Mo^{5+} signals from SBM-3 and from SM-3, however. The signals on SM-2 increase with time at all temperatures investigated (Fig. 2), whereas on SBM-3 the signals increase with time at low temperatures (e.g., 225°C), but at higher temperatures a second process causing Mo^{5+} to disappear becomes increasingly important Fig. 3).

It seems very probable that the first process on both catalysts is the irreversible dissociative chemisorption of propene. As indicated in Part I, it is generally accepted that the chemisorption leads to a symmetrical allylic intermediate, probably bonded to a molybdenum ion. We shall write

$$C_3H_6 + Mo^{6+} + O^{2-} \rightarrow [C_3H_5^{\cdot}\text{-}Mo]^{6+} + OH^- + e^-, \quad (I)$$

where the electron may be localized on a further metal ion. The bonding between the allylic species and the molybdenum cation is likely to be $\sigma\pi$ bonding. The four-centered σ-bonding molecular orbital is formed from the filled π-bonding orbital of the allylic species and the initially empty $4d_{z^2}$ atomic orbital of the molybdenum cation. The three-centered π-bonding molecular orbital is formed from the empty d_{xz} atomic orbital of the molybdenum cation and the nonbonding orbital of the allylic ligand. Of these two molecular orbitals, the σ orbital is filled, whereas the π ligand–cation bonding orbital contains only one electron. This system of bonding would result in a partial positive charge on the chemisorbed allyl species and also allows for reduction of a neighboring Mo^{6+} cation to Mo^{5+} by the electron set free in reaction (I).

Full occupation of both the σ and π molecular orbitals [i.e., with the electron in Eq. (I) localized in the complex], allows for no paramagnetism associated with the complex. Bonding the allyl species to the molybdenum cation by the σ orbital alone, with accompanying electron transfer from the ligand to the molybdenum ion, leads to the species

$$(C_3H_5)^{+\cdot}\text{-}Mo^{5+}$$

which, although accounting for the production of Mo^{5+}, leaves the ligand as a carbonium ion. If the latter were the case, then the relative oxidation rates of alkenes with different structures would span many more orders of magnitude than is observed in practice. This point has been presented in detail by Adams (*7*) and, noting his comments, we prefer the first bonding system proposed here since this produces an allyl species with only a partial positive charge.

It is assumed that the ESR signals reported in the present paper arise from the Mo^{5+} ions formed at sites adjacent to the chemisorption complex by reduction of Mo^{6+} ions by electrons from reaction (I); it is significant that identical signals are observed after reduction with hydrogen. No signals were observed under our experimental conditions which could be attributed unambiguously to the complex itself. It would be interesting to observe ESR spectra from the same samples at liquid helium temperatures in order to determine whether signals from the complex appear as the relaxation times are increased.

Further oxidation of the allylic species, or chemisorption of propene on Mo^{5+}, may lead to reduction of Mo^{5+} to Mo^{4+}, and hence to a diminution of the initial rate of rise of the Mo^{5+} signal as seen in Figs. 2 and 3. At the higher temperatures, this is augmented by depletion of gas-phase propene. However, it is very difficult to see how the second process on SBM-3 can be solely due to further coupled oxidation of the allyl radical and reduction of only molybdenum; the second process must involve bismuth. Now bismuth oxide by itself is not an active catalyst (see Fig. 3 of Part I), nor is it reduced rapidly by propene (*4*). Consequently it appears that reduction of Bi^{3+} occurs after, or is linked with, the

reduction of Mo^{6+}. If this is so, the disappearance of Mo^{5+} in the second process over SBM-3 could be attributed to reactions like Eq. (II), rather than to further reduction of Mo^{5+} to Mo^{4+}.

$$Mo^{5+} + Bi^{3+} \rightarrow Mo^{6+} + Bi^{2+}. \quad \text{(II)}$$

Thus further oxidation of the allyl radical can be associated with reduction of Bi^{3+} by coupled reactions, leading to net processes like Eq. (III) (alternatively, lower oxidation states of bismuth may be formed).

$$[C_3H_5\text{-}Mo]^{6+} + OH^- + O^{2-} + 3Bi^{3+} \rightarrow C_3H_4O + Mo^{6+} + H_2O + 3Bi^{2+}. \quad \text{(III)}$$

The increase in electrical conductivity of SBM-3 on reduction (Part III) could be attributed to the release of electrons to the conduction bands from the lower oxidation states of bismuth, as well as from those of molybdenum. The conductivity studies show that SBM-3 is more readily reduced than SM-2, but do not reveal whether the conduction electrons are released directly from oxide ions or via lower oxidation states of molybdenum or bismuth.

The absence of Mo^{5+} signals from either catalyst when propene *and* oxygen are present strongly suggest the ready reoxidation of Mo^{5+} to Mo^{6+}, presumably by release of electrons to chemisorbing oxygen molecules or atoms. The action of bismuth in SBM-3 is similarly regarded as a reoxidizing function.

It is pertinent to note here that the lower oxidation states of molybdenum provide for an increased possibility of back donation from filled cation *d*-orbitals into the π-bonding molecular orbital system. Such increased back donation leads to strengthening of the ligand–cation bonding and also to a relative weakening of the carbon–carbon bonds in the ligand skeleton, resulting in lower selectivity, since the selective oxidation to acrolein arises only as a result of selective carbon–hydrogen bond scission. Thus one may expect that the selectivity to acrolein will fall as the catalyst surface becomes more reduced. As the results in Part IV demonstrate, this was observed in practice. It is also interesting to note that the bonding scheme proposed allows for relatively rapid desorption of the 1–3 conjugated oxidation products (e.g., acrolein, acrylonitrile, butadiene) obtained in general over these catalysts. Essentially, 1–3 conjugation in the ligand increases the delocalization in the π-bonding ligand orbital and hence reduces the overlap between this and the atomic orbitals of the ssurface cations.

It seems likely that 1-butene behaves in a very similar way to propene in causing the observed patterns of Mo^{5+} signals. On the other hand, the chemisorption of hydrogen almost certainly occurs on oxide ions, not on Mo^{6+} ions, and the whole sequence and rates of reactions are different; there is no intermediate other than OH^- ions. The absence of the second process with hydrogen suggests that the chemisorbed hydrocarbon intermediate is intimately involved in electron-transfer processes between molybdenum and bismuth ions as in Eq. (III).

It would clearly be desirable to examine other oxide-pairs that form active, selective catalysts and where *both* cations show oxidation states with known ESR spectra. At present the absence of any signals clearly identifiable with lower oxidation states of bismuth is a great handicap to attempts to interpret in detail the behavior of the signals from bismuth molybdate catalysts.

Acknowledgments

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