

Structure and Catalytic Activity of $\text{MoO}_3 \cdot \text{Al}_2\text{O}_3$ Systems

IV. Nature of Sites for Oxyhydration of Propylene to Acetone

N. GIORDANO,¹ A. VAGHI, J. C. J. BART²
AND A. CASTELLAN

Montedison, Research Centre of Bollate (Milano), Italy

Received January 18, 1974

Alumina based catalysts containing up to 30 wt% MoO_3 have been studied in depletive and heterogeneous conditions in the oxyhydration reaction of propylene to acetone. In this process, confined to the 10-30 wt% MoO_3 region, water greatly enhances catalytic activity and promotes selectivity to acetone, whereas gaseous oxygen promotes only the catalytic activity. Results strongly indicate that active sites should have a mixed Mo(V)/Mo(VI) character, originating from reduction of octahedral oxomolybdenum species, either polymeric or incorporated in the lattice. The origin of acidity is connected with Mo(V), whereas Mo(VI) rather than gaseous oxygen is involved in the oxidation of the reaction intermediate. It is suggested that the essential features of catalysts active in oxyhydration are proper acidity and mobility of OH-groups together with a site for oxidation of the reaction intermediate. $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ or reduced heteropolyacids appear to satisfy these conditions.

INTRODUCTION

During the last decade, increasing attention has been paid to the catalytic oxidation of olefins to ketones. The reaction, first discovered by Smidt *et al.* (1), using $\text{PdCl}_2\text{-CuCl}_2$ catalysts in aqueous solution, has later been reported to occur also over heterogeneous catalysts (2-4). A reaction mechanism involving alkoxy groups has been first proposed by Buiten (5,6) for oxidation of propylene over $\text{SnO}_2 \cdot \text{MoO}_3$. More recently, extensive work by Moro-oka *et al.* (7-11) has outlined some essential factors for acetone formation over various molybdates: a mechanism involving hydration of olefin to an alcoholic intermediate followed by oxydehydrogenation has been suggested. The mechanism was further supported by the evidence, using H_2^{18}O tracer, that the ox-

xygen atom in the ketone is incorporated from the water molecule and not from molecular oxygen (12,13).

In the present work, results of catalytic oxidation of propylene over $\text{MoO}_3 \cdot \text{Al}_2\text{O}_3$ catalysts are presented and correlated with previous studies on solid state properties reported in Part I (14) and Part II (15). Disclosure of two composition regions, characterized by different physicochemical properties, has been confirmed now also in the catalytic activities. The differentiation entails disproportionation activity in the low MoO_3 region, as discussed in Part III (16), and oxyhydration to acetone at higher MoO_3 concentrations. The aim of the present paper, which is devoted to the latter reaction, is to show which active sites are most probably involved in the specific reaction.

EXPERIMENTAL METHODS

Experimental apparatus and procedures, samples, conditions of experiments and

¹ Present address: Montedison Research Laboratories, Priolo (Sicily).

² Present address: Montedison Corporate Research Laboratories, Novara, Italy.

analytical methods were the same as in Part III (16), except for minor modifications of the microreactor to allow for addition of water vapor and air in tail experiments. Reactants were fed in the ratio C_3 (propylene)/air/water vapor = 1/2.6/7.7, at total flow rates of 3 l/hr and contact times of 2.2 sec. Spent catalysts were analyzed by EPR and optical reflectance techniques, as described elsewhere (14-16).

Reference will be made to the various samples as indicated previously (14-16): thus, MoO_3 -20 indicates a $MoO_3 \cdot Al_2O_3$ catalyst containing 20 wt% MoO_3 .

RESULTS

Pulse Experiments

Results of pulse experiments, extensively discussed elsewhere (16), have indicated acetone formation to start at MoO_3 -20, and to increase remarkably at higher MoO_3 concentrations. Striking differences were observed by use of water, injected as a pulse simultaneously with propylene: presence of water causes suppression of disproportionation activity and enhancement of acetone formation. Specific effects of water are shown in Fig. 1A and B in terms of conversion and selectivities, as a function of the composition, for runs at 300°C. Comparison with previous results (16) emphasizes the dissimilarity in behavior of the two regions with acetone as the main reaction product throughout the high MoO_3 region. Even more evidence for ketone formation may be added by noting that isobutene, a by-product in the reaction (Fig. 1), is formed via aldolic condensation of acetone and consecutive cracking of the intermediate mesityl oxide, as demonstrated from independent experiments (17). We may thus consider acetone to be a primary product and the highly selective catalyst to provide for sites active in the main and the consecutive reaction; details of this behavior in

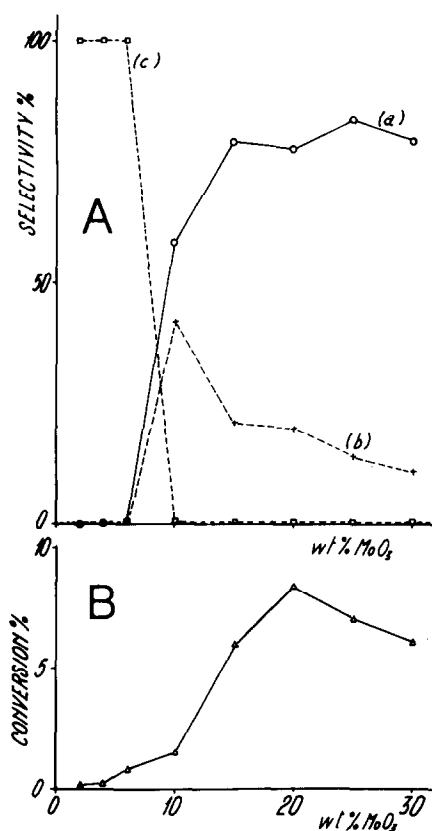


FIG. 1A. Selectivities for products in the presence of water (Mode 2): curve (a) acetone, curve (b) isobutene; curve (c) products of disproportionation. (B) Conversion of propylene, expressed as total sum of yields to various products, as a function of catalyst composition (runs in the presence of water).

the reaction of acetone will be given elsewhere (17).

The different performance of the high MoO_3 region is further proven by results of propylene chemisorption or coking, as shown in Fig. 2. The chemisorbed fraction is always small below MoO_3 -10, but steeply increases to a maximum at MoO_3 -25. Comparison with acetone (Fig. 1) suggests for both reactions similar sites, most probably of an acidic type.

As to the effect of degree of reduction (number of pulses) on catalytic performance, results shown in Table 1 indicate that selectivities to acetone do not vary with the degree of reduction, if the reaction is performed in the presence of water

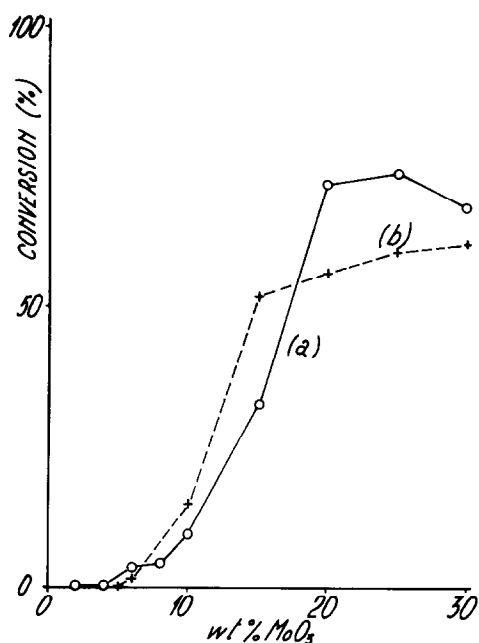


FIG. 2. Conversion of propylene to coke or chemisorbed species: curve (a) for runs in absence of water, curve (b) for runs in presence of water.

(Mode 2); on the contrary, in the absence of water, disproportionation largely surpasses acetone formation, as reduction is increased.

TABLE I
CONVERSION OF PROPYLENE AND SELECTIVITIES TO PRODUCTS IN CATALYTIC EXPERIMENTS AT 300°C OVER MoO₃ · Al₂O₃ SAMPLES OUTGASSED IN HE AT 500°C FOR 2 HR^a

Catalyst	Pulse no.	Mode 1			Mode 2			
		Conv.	S _D	S _A	Conv.	S _D	S _A	S _I
MoO ₃ -10-500	1	10.5	96.7	—	1.5	—	58.2	41.8
	2	5.8	99.7	—	0.8	—	100	—
	3	2.0	99.0	—	0.6	—	100	—
MoO ₃ -20-500	1	0.6	44.0	56.0	8.4	—	77.5	19.9
	2	1.4	90.7	9.3	4.7	—	71.1	26.6
	3	1.2	96.4	3.6	2.8	—	77.0	23.0
MoO ₃ -25-500	1	1.8	2.3	97.7	7.1	—	83.9	13.8
	2	0.8	54.5	31.6	3.3	—	78.7	14.9
	3	1.1	92.6	3.7	2.5	—	72.6	24.2
MoO ₃ -30-500	1	1.8	4.6	85.1	6.1	—	79.1	11.1
	2	1.2	86.5	13.5	3.0	—	75.8	20.5
	3	1.7	100	—	2.0	—	73.1	24.0

^a S_D = selectivity to products of disproportionation; S_A = selectivity to acetone; S_I = selectivity to isobutene; Mode 1: injection of 1.09 cc C₃; Mode 2: injection of 1.09 cc C₃ and 2 μl H₂O.

Tail Experiments

The general behavior disclosed by pulse experiments was further confirmed by results in tail conditions. Figure 3 shows that, other conditions being constant (*T*, *t_c*, ratio of reactants), conversion of propylene and yields to acetone increase with increasing MoO₃ concentration. The lowest activity is again a property of the low MoO₃ region; maximum activity is displayed by MoO₃-20, beyond which it decreases smoothly. The selectivity to acetone is maximum at MoO₃-15 (80%) and minimum at the extremes (MoO₃-10 and MoO₃-30). Besides acetone and CO_x, some acetaldehyde (4–6%) was also formed; acrolein and isopropyl alcohol could not be detected at any MoO₃ composition level. No marked variations were observed as a function of time on stream

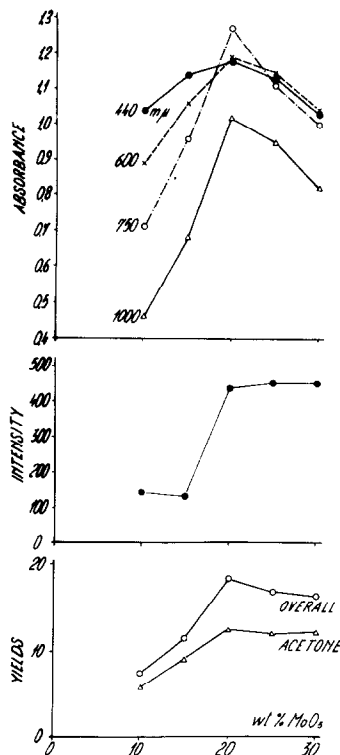


FIG. 3. Catalytic activity, Mo(V) EPR intensity and optical reflectance data in oxyhydration of propylene to acetone at 250°C, contact time = 2.2 sec. C₃/air/H₂O = 1/2.6/7.7.

as conversions and selectivities read after the first hour scattered to within $\pm 5\%$ only.

To disclose the nature of active sites for acetone formation, spent catalysts were analyzed by EPR and diffuse reflectance spectroscopy. Spectra are shown in Fig. 4 (upper part) against those of fresh catalysts (lower part), i.e., activated in air at 500°C for 8 hr (14). Absorbances at a few selected positions (see below), as derived from Fig. 4, are replotted in Fig. 3 against catalytic activity; spin densities are also given, for measurements at room temperature (rt). The comparison suggests that formation of acetone is related to some reduced species of molybdenum as proven by the differences between fresh and spent catalysts, indicating for the latter samples: (a) lower absorbance in the uv region, in which Mo(VI) is known to absorb (b) parallel increase of the absorbance in the visible characteristic of reduced molybdenum, (c) existence of an EPR signal ($g = 1.93$)

characteristic of Mo(V). Closer appraisal of spectra in this region reveals also some shifts as a function of the composition. In the case of MoO₃-10 we observe that maximum absorbance occurs at 400 nm with a shoulder at 500 nm. On the MoO₃-15 sample the 500 nm band is comparable with the 400 nm; in the MoO₃-20 and MoO₃-25 samples a broad band is observed ranging from 400 to 600 nm. Reversal of the trend occurs for MoO₃-30 which displays a maximum at 520 nm. In addition, in the whole range of compositions a broad band above 700 nm is found, its intensity increasing towards higher MoO₃ concentrations.

Interpretation of spectra on the basis of the literature (18-20) and our previous work (14-16) suggests: (a) prevalence, in the MoO₃-10 sample, of Mo(V) in C_{4v} coordination, in accordance with the assignment of the 400-450 nm band (18); (b) for compositions comprised between 10 and 30 wt% MoO₃, the characteristic ab-

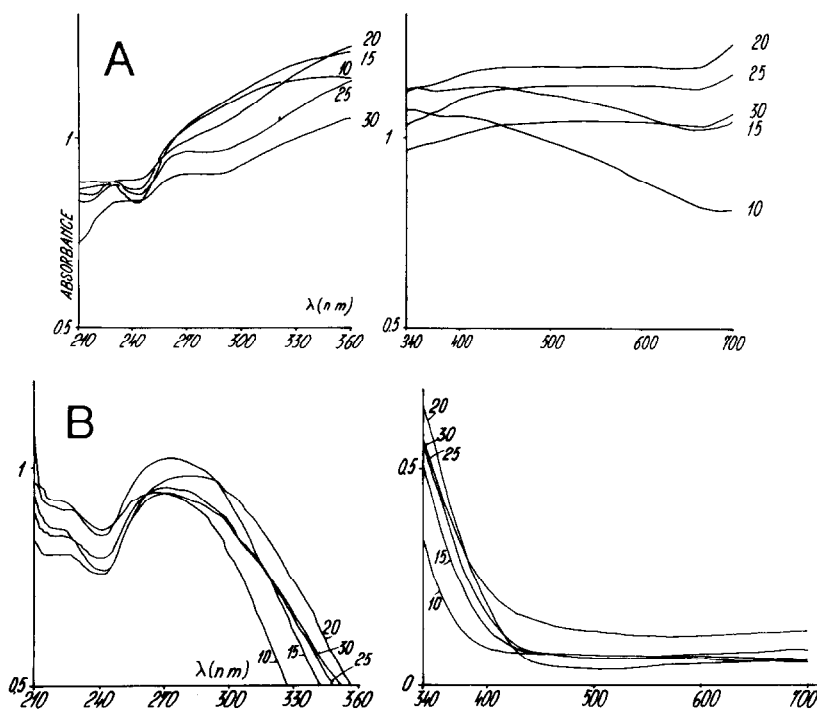


FIG. 4. Diffuse reflectance spectra of: (A) spent catalysts (upper part), for runs as in Fig. 3; (B) fresh catalysts (lower part), i.e., activated at 500°C for 8 hr.

sorption at 400 nm and 700–750 nm (19) indicates prevalence of Mo(V) in a square-pyramidal configuration, as well as some Mo(IV); absorbance above 700 nm presages Mo(V), as in reduced heteropoly acids (15); (c) on MoO₃-30, mainly Mo(IV) is present, as evident from absorption at 500 nm (20), and possibly some Mo(V).

To establish which species is most likely in the acetone formation, consider catalytic activity vs spectral intensities (Fig. 3): if Mo(V) in *C_{4v}* coordination or Mo(IV) were the seats of catalytic activity one would expect a maximum at MoO₃-10 or MoO₃-30, respectively. Instead, the observed broad maximum of catalytic activity spanning from MoO₃-15 to MoO₃-25 may be looked upon as a proof in favor of Mo(V) which, as already discussed (14,15), can be related to compounds such as Mo₄O₁₀(OH)₂ or reduced heteropoly acids.

General features outlined above were confirmed by results of experiments at 300°C over a MoO₃-20 sample when varying the O₂/C₃ ratio between 0.1 and 1 at a contact time of 2.1 sec (Table 2); variations in *p_{C₃}* and *p_{H₂O}* were assumed not to influence the course of the reaction. Comparison of catalytic activities with EPR and reflectance intensities (Table 2) show only a small influence of the O₂/C₃ ratios on the solid state properties. In fact, notwithstanding the 10-fold variations in the O₂/C₃ ratios, EPR and reflectance inten-

sities undergo only a moderate decrease, also parallel to the selectivities to acetone. On the contrary, total conversion more than doubles, obeying a kinetic rate law dependent upon *p_{O₂}*^{0.2}.

DISCUSSION

The formation of acetone in the high MoO₃ region proves undoubtedly that unique characteristics of the solid are involved, differing from those causing disproportionation in the low MoO₃ region (16). As to their identification, consider first the role of each reactant. With regard to H₂O, pulse experiments prove that it constitutes a necessary partner in the reaction, as it greatly enhances catalytic activity and yields to acetone [cf. Fig. 1 and Figs. 1, 2 of Part III (16)]. Moreover, selectivity to acetone is unaffected by surface reduction, in contrast to runs in the absence of water (Table 1). In the latter case, activity is probably related to the fact that MoO₃ impregnated alumina presents Brønsted sites after activation, with a site concentration increasing with the MoO₃ content (21); water then serves mainly to regenerate those sites, maintaining the selectivity to acetone almost constant in successive pulses. With regard to oxygen, we notice the strong dependence of catalytic activity, in tail experiments, on the O₂/olefin ratio and its compliance to a *p_{O₂}*^{0.2} rate law (Table 2). From the above, it appears that formation of ketone requires both H₂O and O₂. A survey of results of previous investigations proves undoubtedly the correctness of the assumption. Thus besides the already cited results using H₂O¹⁸ tracer (12,13), we recall kinetic experiments over various molybdates (22) which show a rate proportional to *p_{H₂O}*^{0.5}, and the observation of a rapid H₂-D₂ exchange between propylene and water on SnO₂ · MoO₃ catalysts (5,6). Accordingly, acidic OH-groups were assumed to effect the exchange and to constitute the intermediate species in the oxidation to acetone

TABLE 2
SPECTRAL DATA FOR MoO₃-20 AND CATALYTIC
ACTIVITY FOR RUNS AT 300°C^a

O ₂ /C ₃	Diffuse reflectance intensities at (nm):				EPR ^b intensities	Total conversion of C ₃ (%)	Selectivity to acetone (%)	Selectivity to Co ₂ (%)
	440	600	750	1000				
0.1	1.23	1.18	1.28	1.00	565	12.4	83	17
0.3	1.22	1.21	1.25	1.08	520	18.1	60	40
0.5	1.27	1.26	1.30	1.09	420	22.3	55	45
1.0	1.20	1.19	1.15	0.93	335	28.0	52.5	47.5

^a Reflectance and EPR intensities are referred to arbitrary units.

^b Referred to the *g₁* signal.

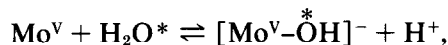
and acetic acid; similar conclusions have been drawn (23) for the role of OH-groups in governing selectivities to various by-products (acetone, acetaldehyde, etc.) in the allylic oxidation of propylene to acrolein.

The present results concerning oxygen (rate of acetone proportional to $p_{O_2}^{0.2}$ at 300°C on a 20 wt% MoO₃ sample) agree well with those reported by Moro-oka *et al.* (8) for SnO₂ · MoO₃ ($p_{O_2}^{0.2}$ on a 10MoO₃ · 90SnO₂ catalyst) or those derivable from results of Ogasawara *et al.* (24) for coprecipitated MoO₃ · Al₂O₃ ($p_{O_2}^{0.2}$ for a 30% MoO₃ sample). In view of this common feature, i.e., reaction rates over various molybdates somehow dependent upon p_{O_2} , we thus envisage a primary role of gaseous oxygen (in whatever form it may react) in sustaining and promoting catalytic activity. Moreover, it is important to note that increasing p_{O_2} , while causing a great enhancement of catalytic activity, leads to a decrease in the selectivity to acetone, although to a lesser extent. We are thus confronted with the remarkable phenomenon of a different role of each reactant, namely, H₂O promoting both the selectivity and the conversion (Table 1), O₂ promoting catalytic activity (Table 2); this suggests a polyfunctional catalyst or a consecutive reaction.

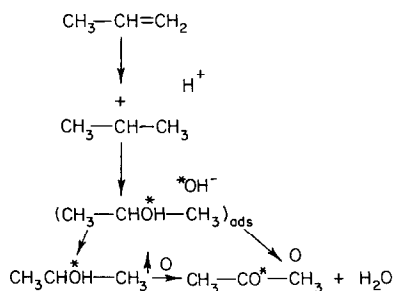
To clear up these aspects, it is imperative to consider the nature of active sites for the reaction: according to Buiten (5,6), they can be identified with MoO₂(OH)₂ formed as a monolayer from MoO₃ sorbed over the SnO₂ surface. Recent results of Takita *et al.* (11) point to the primary role of acidic sites as proven by the close relationship between catalytic activity and butylamine titration: acidic sites are said to be formed by combination of MoO₃ and SnO₂ or any other specific oxide. The present results, while still confirming the role of acidity, suggest their association with some reduced Mo-species: this stems from the close correlation between EPR and reflectance spectra and the formation

of acetone, and it holds for pulse [cf. Fig. 3 in Part II (15) and Fig. 1 in Part III (16)] and tail experiments (Fig. 3). The essential features of these relationships can be rationalized starting from the already established structure of oxidized samples (14). Active sites are then to be identified primarily with octahedral oxomolybdenum species, either polymeric or incorporated in the lattice. In the course of the reaction, some reduction of the catalyst is assumed to occur, involving bridged oxygens, as in the case of H₂-reduction or outgassing (15): structures containing Mo(V)/Mo(VI) are thus formed, such as Mo₄O₁₀(OH)₂ or reduced heteropolyacids. Even though under steady state conditions of the reaction the equilibrium between Mo(VI) and Mo(V) is greatly dependent upon the experimental conditions, it is plausible that Mo(V) is favored on account of large differences in the electronegativities of Mo and Al.

The origin of the acidity appears now to be connected with an acid-base equilibrium of the type



thus creating hydroxylated reduced sites similar to those in Mo₄O₁₀(OH)₂. In the reaction with olefin, the proton generated is transferred from the surface to the gaseous molecule. Oxyhydration occurs through participation of oxygen from H₂O or from an OH-group of the solid (Mo^V-OH⁻) and it is followed by oxidation of the intermediate thus formed, with oxygen being derived from air or vicinal Mo(VI).



Although our present knowledge does not permit definite deductions to be made on the nature of the intermediate and the way oxygen enters into the reaction scheme, some tentative suggestions may be made. Thus, we notice failure to detect isopropyl alcohol in our experiments. Apparently, this observation points to intermediate isopropoxy groups, in accordance with Buiten (5,6) and in contrast to Moro-oka *et al.* (7-11). However, isopropyl alcohol as an intermediate cannot be excluded either, as this product might not have been detected in the reaction mixture because of very fast oxidation to acetone (isopropyl alcohol is more easily oxidized than propylene) or the extremely unfavorable equilibrium conditions at the experimental temperature (300°C). With regard to oxygen, the opposite variations of Mo(V) and of the catalytic activity (Table 2) tend to exclude oxygen interacting directly from the gas phase: on the other hand, Mo(VI) seems to be involved, acting by a redox mechanism as the true oxidizing agent of the intermediate.

It is useful now to compare the observed catalytic behavior with the properties of the proposed active sites: the main features of Mo₄O₁₀(OH)₂ are its relationship with MoO₃ (25-26), the presence of Mo(V) and Mo(VI) and of OH-groups stable at temperatures as high as 400°C. Considering that changes in the O²⁻/OH⁻ ratio accompanying the reduction from Mo(VI) to Mo(V) are likely to cause only a slight decrease of acid strength (27) according to general arguments on acid strength of oxyacids MO_m(OH)_n, it appears that in Mo₄O₁₀(OH)₂ sufficient acidity is still left on Mo(V) to sustain the rate determining step (formation of a carbonium ion). As to the OH-groups, which supply oxygen, general considerations on the heat of hydration of metal cations suggest an increasing rate of dissociation with decreasing charge of the cation. Mo(V) should therefore dissociate its water ligand faster than Mo(VI), thus determining a

higher mobility of OH-groups. In this connection, it is of interest to note the analogy with the hydration of olefins to alcohols over MoO₃ or WO₃, a reaction which is known to be highly favored by a reduced state of the catalysts (tungsten blue). On the basis of the arguments above, we suggest that the unique features of catalysts active in oxyhydration are a combination of a proper acidity [Mo(V) less acidic than Mo(VI)] together with mobility of OH-groups [Mo(V)-OH looser than Mo(VI)-OH]; Mo(VI) is also essential as it serves to oxidize the intermediate.

A final remark on the role of the second oxide appears necessary: using as a reference the work of Moro-oka (7-11) which indicates preference of SnO₂-, TiO₂-, Fe₂O₃-, Cr₂O₃- and Co₃O₄-MoO₃ in the formation of acetone, we suggest as a guideline the combination of Mo(V) concepts and coordination state as suggested above for the MoO₃ · Al₂O₃ system. In fact, as neither the chemical properties of the second oxide nor its intrinsic reactivity have so far indicated a criterion for an effective catalyst (10), we may consider reactivity of mixed oxide systems as depending upon the degree of stabilization of Mo(V) and as a consequence of the degree of acidity and mobility of OH-groups.

CONCLUSIONS

Correlation of results of catalytic oxidation of propylene over MoO₃ · Al₂O₃ catalysts with studies in solid state properties have permitted us to confirm the role of acidity in the oxyhydration reaction and to associate active sites with some reduced Mo-species. Apart from the requirements imposed upon the solid, the role of the two reactants, H₂O and O₂, is assessed. While water greatly enhances catalytic activity and promotes selectivity to acetone, gaseous oxygen promotes the catalytic activity, but negatively influences the yields to the ketone. Acidity appears to be connected with Mo(V), while Mo(VI) rather than gaseous oxygen seems to be involved

in the oxidation of the reaction intermediates, either isopropoxy species or isopropyl alcohol. The mechanistic requirements of the oxyhydration reaction are best reflected in compounds such as $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ or reduced heteropolyacids, which therefore are indicated as the most likely active species.

REFERENCES

1. Smidt, J., Hafner, W., Jira, R., Sedlmeier, J., Sieber, R., Ruttinger, R., and Koier, H., *Angew. Chem.* **71**, 176 (1959).
2. Soc. Edison, *Ital. Pat.* 631,868 (Jan. 17, 1962); 640,456 (May 29, 1962).
3. Farbwerke Hoechst A. G., *Germ. Pat.* 1,123,310 (Feb. 8, 1962); 1,135,880 (Sept. 6, 1962).
4. Ruhrchemie, A. G., *Fr. Pat.* 1,395,378 (Apr. 9, 1965).
5. Buiten, J., *J. Catal.* **10**, 188 (1969).
6. Buiten, J., *J. Catal.* **13**, 373 (1969).
7. Moro-oka, Y., Tan, S., and Ozaki, A., *J. Catal.* **12**, 291 (1968).
8. Moro-oka, Y., Tan, S., and Ozaki, A., *J. Catal.* **17**, 125 (1970).
9. Tan, S., Moro-oka, Y., and Ozaki, A., *J. Catal.* **17**, 132 (1970).
10. Moro-oka, Y., Takita, Y., and Ozaki, A., *J. Catal.* **23**, 183 (1971).
11. Takita, Y., Ozaki, A., and Moro-oka, Y., *J. Catal.* **27**, 185 (1972).
12. Moro-oka, Y., Takita, Y., and Ozaki, A., *Bull. Chem. Soc. Jap.* **44**, 293 (1971).
13. Moro-oka, Y., Takita, Y., and Ozaki, A., *J. Catal.* **27**, 177 (1972).
14. Giordano, N., Bart, J. C. J., Vaghi, A., Castellan, A., and Martinotti, G., *J. Catal.* **36**, 81 (1975).
15. Giordano, N., Castellan, A., Bart, J. C. J., Vaghi, A., and Campadelli, F., *J. Catal.* **37**, 204 (1975).
16. Giordano, N., Padovan, M., Vaghi, A., Bart, J. C. J., and Castellan, A., *J. Catal.* **38**, 1 (1975).
17. Santoro, E., and Vaghi, A., unpublished data.
18. Asmolov, G. N., and Krylov, O. V., *Kinet. Katal.* **13**, 188 (1972).
19. Mitchell, P. C. H., and Trifirò, F., *J. Chem. Soc. A* 3183 (1970).
20. Porter, V. R., White, W. B., and Roy, R., *J. Solid State Chem.* **4**, 250 (1972).
21. Kiviat, F. E., and Petrakis, L., *J. Phys. Chem.* **77**, 1232 (1973).
22. Buiten, J., Symposium on Oxidation in Organic Chemistry, Manchester, Jul. 8-9, 1969.
23. Giordano, N., Int. Symposium on Heterogeneous Catalysis, Roermond, Jul. 5-10, 1970.
24. Ogasawara, S., Nakada, Y., Iwata, Y., and Sato, H., *Kogyo Kagaku Zasshi* **73**, 509 (1970).
25. Rode, E. Y., and Lysanova, G. V., *Dokl. Akad. Nauk SSSR* **145**, 573 (1962).
26. Glemser, O., and Lutz, G., *Z. Allg. Anorg. Chem.* **264**, 17 (1951).
27. Parks, A. G., *Chem. Rev.* 177 (1965).