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Photocatalytic Oxidation of Propane by Oxygen on Supported Mo/SiO$_2$ Catalysts

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Propane photocatalytic oxidation on silica gel-supported molybdenum oxide catalysts has been investigated. The catalysts prepared via impregnation and Mo(π-C$_3$H$_5$)$_4$ fixation do not exhibit significant differences in their electronic spectra and photocatalytic behavior. The results indicate that photocatalytic activity cannot be related specifically to isolated Mo^{6+} ions in tetrahedral coordination and that other surface sites play an important role in photooxidation reactions. Depending on the molybdenum loading, two different domains of photocatalytic activity are observed. At molybdenum loadings below 2 wt% acetone predominates among the partial oxidation products whereas aldehydes are the most abundant at higher loadings. This change in product distribution has been attributed to a change in the nature of the radical intermediates formed in the initiating step depending on the nature and coordination symmetry of the participating Mo ions. The acetone dominating region may be related to the formation of propoxy ($C_3H_7\dot{O}$) radicals in contrast to the aldehyde region which is associated with the formation of propyl ($\dot{C}_3H_7$) radicals. The characteristics of the sites responsible for these two different behaviors have been suggested with reference to the electronic spectra of these catalysts. © 1984 Academic Press, Inc.

INTRODUCTION

In previous works from our laboratory photocatalytic oxidation of cyclohexane on supported catalysts V$_2$O$_5$/SiO$_2$ (*1*), Ta$_2$O$_5$/SiO$_2$ (*2*), and MoO$_3$/SiO$_2$ (*7*) prepared by pore volume impregnation was systematically investigated using a fixed-bed quartz reactor (*4*). The results obtained with MoO$_3$/SiO$_2$ systems were interpreted on the basis of two different types of surface species, namely tetrahedral isolated species that are active in photocatalysis and octahedral species in the surface polymer phase that may possess a certain mobility under photocatalytic reaction conditions. Possibly this mobility results in the formation of Mo–O–Mo bridges between photocatalytically inactive octahedral and active tetrahedral species and in partial loss of catalytic activity. In the case of Ta$_2$O$_5$/SiO$_2$ such a phenomenon was not observed.

From our previous investigations it was realized that photocatalytic properties could be used as a probe for surface species characterization. With the earlier large-scale reactor however only the total oxidation product (CO$_2$) was observed. Teichner *et al.* (*5*) were able to observe partial oxidation products of alkanes using a differential dynamic microreactor (*6*). A modified version of this reactor was constructed for the study of catalytic photooxidation of propane by oxygen on MoO$_3$/SiO$_2$ catalysts. The goal of this work was therefore to explore the use of partial oxidation of propane as a probe for the characterization of supported oxomolybdenum species.

The present state of the knowledge of photocatalytic phenomena on supported molybdenum catalysts indicates that possibly isolated superficial molybdenum species in tetrahedral coordination are active or at least possess greater activity than those of polymerized surface molybdenum species in various photocatalytic reactions (*7–15*). An unambiguous assignment however still seems to be premature. Accord-

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ingly, the present study is focused on elucidating the nature and activity of superficial molybdenum species participating in oxidation reactions.

The catalysts were prepared by two different procedures, namely by impregnation with ammonium paramolybdate and by fixation using the tetrakis-π-allyl–molybdenum complex. The latter preparative procedure is believed to enable one to control the coordination and nuclearity of the deposited elements contrary to the first procedure which is reported to result in a heterogeneous catalyst surface (*12–17*). It is hoped that a comparison of these catalysts may allow us to analyze the effect of the nature and the coordination symmetry of superficial molybdenum species. The uv source chosen is an ozone-free xenon lamp with practically no emission below 280 nm. The choice of this lamp is intended to avoid excitation of isolated tetrahedral species and to investigate the photoactivity of nonisolated species in different coordinative environments.

EXPERIMENTAL

Catalyst Preparation and Characterization

Two series of supported molybdena silica catalysts were prepared using different procedures (*18*). The silica gel used was commercial grade (Fisher, S-662) with 99.9% minimum purity. The particle size range and surface area were 60–200 mesh and 450 m^2/g, respectively.

The first series of catalysts was prepared by pore volume impregnation of the support with aqueous solutions of ammonium paramolybdate. This compound was of high purity (Anachemia, AC-630), its main impurities being Pb (0.001%) and Mg (0.02%). The pHs of the impregnation solutions were fixed around 5 to 6. The catalyst samples were dried at 120°C for 8 h and subsequently calcined at 500°C in air for 15 h before use.

The second series of catalysts was prepared by a facile reaction between the surface hydroxyl groups of the support with tetrakis-π-allyl–molybdenum complex in *n*-pentane (certified, Fisher, P-393) at ambient temperature (*19, 20*). Pentane was dried over sodium wire and distilled prior to use. The $Mo(\pi\text{-}C_3H_5)_4$ complex was synthesized under oxygen and humidity free conditions in a Pyrex-glass apparatus in an inert atmosphere of high-purity argon (Linde, 99.996%) according to the procedure reported by Wilke *et al.* (*21*). The product purity was verified by ir spectroscopy. The silica gel support was pretreated *in situ* at 200°C in a flow of argon for 8–10 h prior to Mo fixation. The silica was contacted for several hours with the π-allyl complex solution, filtered and washed several times with pure pentane until no π-allyl complex could be detected by ir spectroscopy in the pentane filtrate. The catalyst was then evacuated for several hours at room temperature and calcined in air for 15 h. This type of catalysts will be designated as fixed catalysts in the text.

The molybdenum content of all catalysts was determined by means of X-ray fluorescence (Ortec system) using a ^{241}Am–Ag source.

Ultraviolet diffuse reflectance spectra were measured with a double-beam Bausch & Lomb Spectronic 505 spectrophotometer in the range 200–500 nm. The catalyst samples were prepared in the form of disks by compressing the catalysts with MgO powder (Fisher, M-51), the reference being a sample prepared similarly, using pure silica gel with MgO.

Photocatalytic Activity Measurements

The photocatalytic activity for the partial oxidation of propane was studied using a differential dynamic reactor under atmospheric pressure in the presence of oxygen and helium (Fig. 1). Experiments were performed using 200 or 300 mg of catalyst evenly spread over a porous membrane made of glass fiber (Gelman). The tempera-

TABLE 1

Experimental Conditions

Mode	Parameter varied	$P_{C_3H_8}$ (Torr)	P_{O_2} (Torr)	P_{He} (Torr)	Total flow rate (cm³/min)	Mo loading (wt%)
I	Molybdenum loading	305	200	255	15	0.17–6.0
II	Oxygen partial pressure	305	2–355	453–100	15	2.0
III	Propane partial pressure	155–560	200	405–0	15	2.0
IV	Space–time	305	200	255	7.5–60	2.0

ture of the reactor was controlled using thermostated water circulating in a jacket, and measured by a thermocouple located beneath the membrane as shown on Fig. 1. The feed gases (oxygen, Inert, 99.6%, Linde; propane, Instrument Grade, 99.5%, Canadian Liquid Air and helium, Inert, 99.995%, Linde) were prepurified of CO_2 and H_2O traces by passing over gas purifiers containing Ascarite, Hopcalite, and Drierite. The ranges of experimental conditions utilized are given in Table 1.

During the photocatalytic activity measurements the catalyst layer was uv-irradiated using a 1000-W xenon lamp (Hanovia) equipped with an ozone-free envelope and a water filter (with emission above 280 nm).

The reactants and products were quantitatively analyzed using two gas chromatographs. The first one (Pye, Series 104, Model 44) was provided with a TC detector and a Porapak QS column (80/100 mesh, 1.5 m) which could separate O_2, CO_2, and C_3H_8. The second chromatograph (F & M, Model 810) was fitted with a FI detector and two columns in series: Chromosorb 102 (80/100 mesh, 2.1 m) and Chromosorb 108 (80/100, 6 m). The following compounds were detected and well separated; CH_4, C_3H_8, CH_3CHO, CH_3OH, C_2H_5OH, C_2H_5CHO, $(CH_3)_2CO$, i-C_3H_7OH, and n-C_3H_7OH.

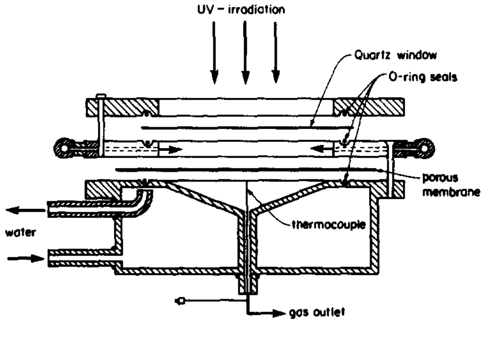


FIG. 1. Schematic diagram of the reactor.

RESULTS AND DISCUSSION

Catalyst Characterization

Ultraviolet diffuse reflectance spectra of the fixed catalysts are given in Fig. 2 and those for the impregnated catalysts can be found in Ref. (*7*). Impregnated catalysts show two major absorption bands centered around 250–260 and 320–340 nm. The band around 250–260 nm predominates at low loadings (below 1%), while the latter band predominates in the absorption spectra at higher loadings. The fixed catalysts calcined

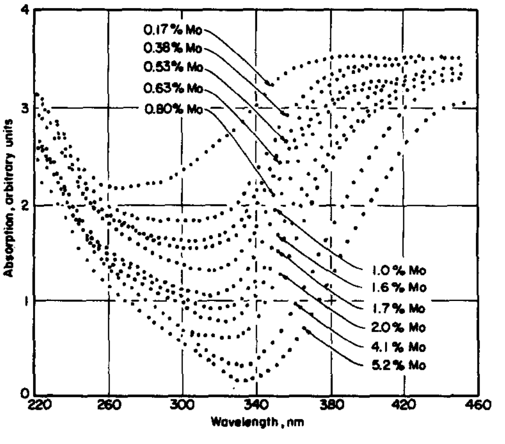


FIG. 2. Ultraviolet diffuse reflectance spectra of Mo-fixed catalysts calcined in air (15 h) at 500°C.

at 500°C show similar bands and similar behavior as a function of molybdenum loading compared to the impregnated catalysts, except for a band centered around 280–290 nm which becomes clearly discernible only at very low molybdenum content (Fig. 2). At higher loadings the presence of this band is less evident due to overlapping with the predominant band at 320–330 nm.

There is a general correlation between the absorption wavelength of the charge transfer spectra and the coordination symmetry of Mo ions. It is generally accepted that Mo^{6+} tetrahedral monomeric species absorb at 230–270 nm, while polymeric oxomolybdenum species with Mo in octahedral coordination are reported to absorb between 270 and 350 nm with the strongest most frequently found band between 320 and 340 nm (*7, 22–27*). However, the nature and the symmetry of the oxomolybdenum species responsible for the absorption band at 280–290 nm is not clear. Iwasawa (*17, 28*) observed a single band at 290 nm for the catalyst prepared by $Mo(\pi\text{-}C_3H_5)_4$ complex and attributed this band to a monomeric oxomolybdenum species with Mo in tetrahedral coordination. However, in view of the three absorption bands observed in our case and the evidence for the existence of a separate oxomolybdenum species responsible for the absorption band at 280–290 nm, we prefer to assign the band at 250–260 nm to monomeric species in tetrahedral coordination, at 320–330 nm to polymeric species in octahedral coordination, and at 280–290 nm to some polynuclear form, possibly an oxomolybdenum dimer in which the Mo coordination, although not clearly established, could be viewed as tetrahedral. This band could also be attributed to a tetrahedrally coordinated Mo in terminal position of a polymeric layer.

Propane Oxidation

(*a*) *Effect of molybdenum content.* The steady state rates of products formation for the experimental conditions specified in Table 1, line 1 (mode I) are given in Figs. 3 to 5.

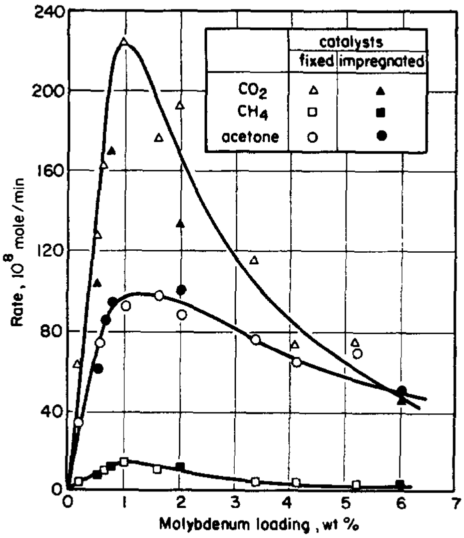


FIG. 3. Steady state rates of formation of CO_2, CH_4, and acetone as a function of molybdenum loading.

Rates of formation of CO_2, CH_4, acetone, methanol, and ethanol are characterized by curves that go through maxima as a function of molybdenum content. For the formation of CO_2, CH_4, and acetone (Fig. 3) maximum rate occurs in the vicinity of 1% Mo and no significant difference between the impregnated and fixed catalysts is observed. In the case of the two alcohols (Fig. 4) the maximum rate occurs around 1% Mo for fixed catalysts, while for impregnated catalysts the maximum is displaced toward slightly higher molybdenum content with significantly higher rates. The rates of formation of ethanal and propanal (Fig. 5) show a continuous increase with the Mo loading and are significantly higher for the impregnated catalysts. Figure 6 gives the steady state temperature measured in the vicinity of the catalyst; it parallels the aldehyde behavior. At Mo contents higher than 2 wt%, formaldehyde polymerizes at the outlet of the reactor. This product has been identified by mass spectrometry and elemental analysis but was not measured quantitatively.

The total conversion of propane (Fig. 7)

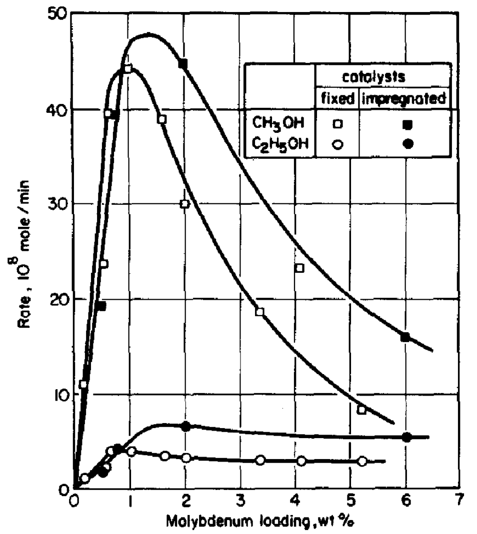


FIG. 4. Steady state rates of formation of CH_3OH and C_2H_5OH as a function of molybdenum loading.

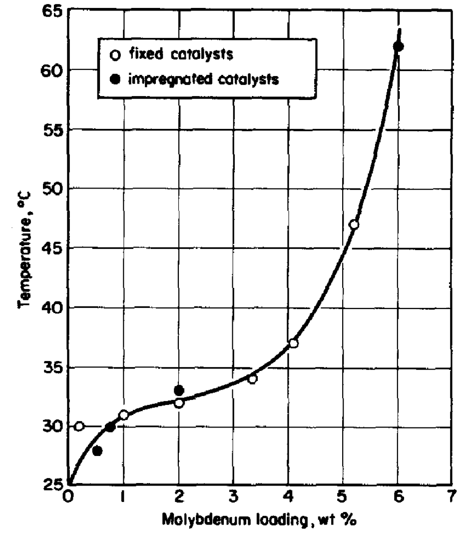


FIG. 6. Steady state temperature measured in the catalyst vicinity as a function of Mo content.

increases up to ~1% Mo content and stays relatively constant at higher Mo content. This is particularly true if account is made for the paraformaldehyde formed. However, at low Mo content (up to 2 wt% Mo) acetone appears as the major partial oxidation product, while at higher molybdenum content aldehydes become the major partial oxidation products. This variation in selectivity with the molybdenum loading suggests a change in the overall reaction mechanism of the photocatalytic partial oxidation of propane around 1 wt% Mo.

(*b*) *Effect of space–time and light inten-*

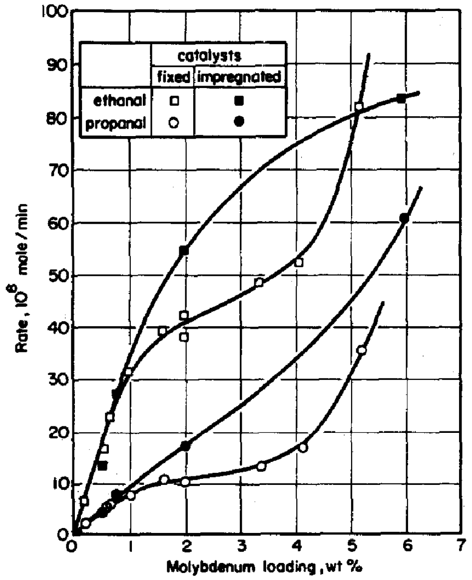


FIG. 5. Steady state rates of formation of ethanal and propanal as a function of molybdenum loading.

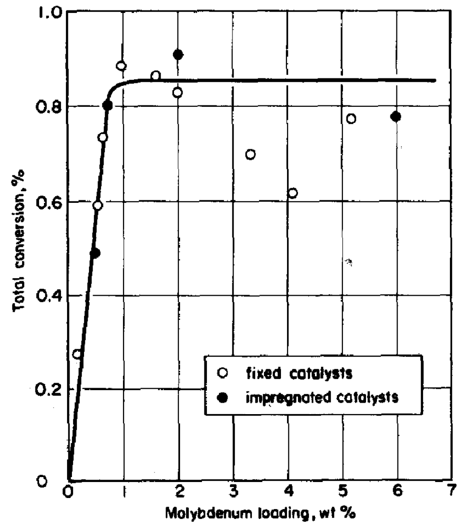


FIG. 7. Total conversion of propane as a function of Mo content (formaldehyde yields not included in this calculation).

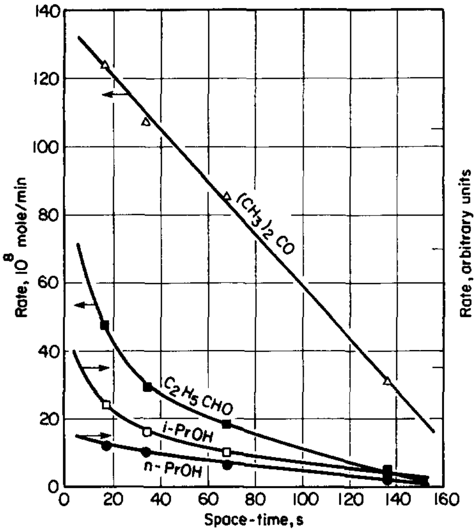


FIG. 8. Steady state rates of primary products formation as a function of space–time for the 2 wt% Mo/SiO_2 fixed catalyst.

TABLE 2

Light Intensity Effect upon the Rates of Formation of the Products

Product	n	Product	n
Methane	1.8	Propanal	0.9
Carbon dioxide	1.4	Acetone	0.9
Ethanal	1.5	i-Propanol	0.9
Methanol	1.6	n-Propanol	0.7
Ethanol	1.3		

Note. The intensity exponents (n) are obtained according to the formula $r = kI^n$ using the 2 wt% fixed Mo catalyst and conditions of mode I.

sity. The results obtained for the rates of formation of products as a function of space-time for the 2% Mo/SiO_2 fixed catalyst under the experimental conditions specified in Table 1, line 4 (mode IV) are summarized in Figs. 8 and 9. Two series of products can be clearly distinguished. Figure 8 shows that the primary partial oxidation products are acetone, propanal, iso- and n-propanol, their rates of formation being maximum at zero space-time. In contrast, Fig. 9 shows that all products with less than three carbon atoms are secondary products since their rates of formation tend toward zero at zero space–time. This classification of the products as primary and secondary is corroborated by the light intensity effect upon the rates of formation of the products. Table 2 gives rough estimates of the intensity exponents for the different products computed from the results obtained at two light intensities. To this end, the light beam was attenuated by passing through a grid (80 mesh) having a grid factor of ~2.6. The primary products have an exponent smaller but close to 1, while the secondary products show an exponent of nearly $\frac{3}{2}$ suggesting that the absorption of more than one photon is involved in their formation.

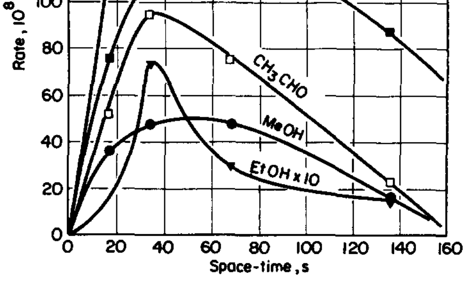


FIG. 9. Steady state rates of secondary products formation as a function of space–time for the 2 wt% Mo/SiO_2 fixed catalyst.

(*c*) *Effect of oxygen and propane partial pressures.* The effects of oxygen and propane partial pressures on the rates of primary products formation for the 2% Mo/SiO_2 fixed catalyst were investigated under the experimental conditions given in Table 1, lines 2 and 3 (modes II and III) and the results are shown in Figs. 10 and 11, respectively.

Variation of the oxygen partial pressure (Fig. 10) in the range 20–355 Torr does not show any influence on the rates of formation of most products, while a slight effect

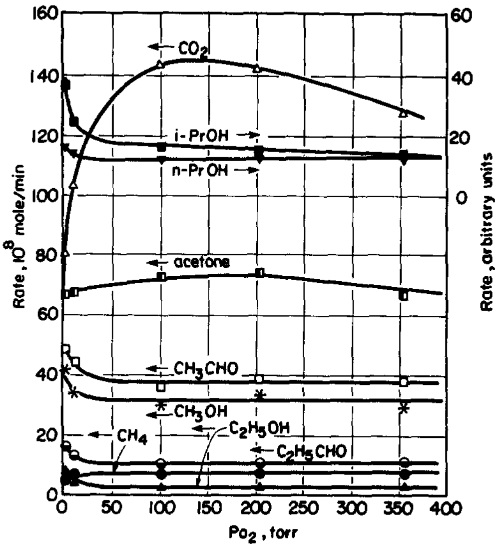


FIG. 10. Steady state rates of products formation as a function of oxygen partial pressure.

is often observed in the range 2–20 Torr.

On the other hand the rates of formation of all products show a strong dependence on the propane partial pressure (Fig. 11). At propane pressures lower than 300 mmHg, the rates of formation of the primary products are first-order with respect to propane. These observations suggest that the reaction of propane, either gaseous or very weakly adsorbed, with an excited surface complex bearing oxygen is the rate-limiting step in the partial oxidation of propane under the experimental conditions of mode I.

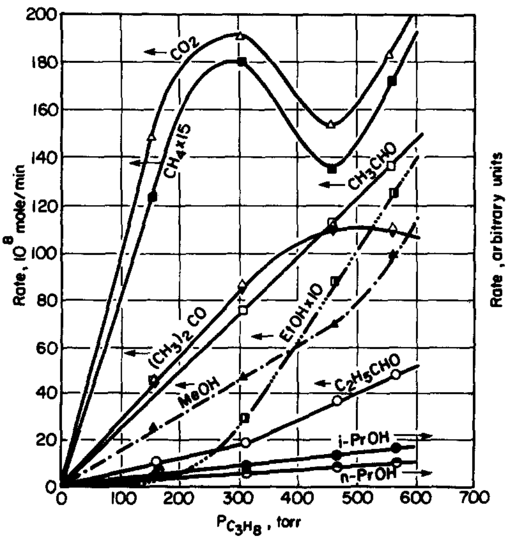


FIG. 11. Steady state rates of products formation as a function of propane partial pressure.

(*d*) *Photocatalytic behavior.* The rates of formation of the different oxidation products increase with the illumination time until they reach steady state after ½ to 3½ h, depending on the product. These steady state rates are maintained over irradiation periods at least 10 times longer than those which would correspond to photoassisted stoichiometric reactions involving preexisting nonrenewable species, assuming a maximum coverage of 10 nm^{-2} (~10^{-3} mol). This constitutes a very safe estimate since Mo^{6+}, the species which is the more liable to participate in such reactions, is only present at approximately 10^{-4} mol in the reactor at the highest Mo loading utilized.

Mechanistic Considerations

According to Teichner *et al.* (*5*) photocatalytic oxidation of propane on TiO$_2$ is supposed to occur in accordance with scheme

$$C_3H_8 + O_{ads} \rightarrow C_3H_7OH \xrightarrow{O_{ads}} (CH_3)_2CO + H_2O \quad (1)$$

According to the above scheme, acetone should appear as a secondary oxidation product. In our case such a reaction path can be excluded since acetone was shown to be a primary product.

Kazansky (*11*) suggested that the first step is hydrogen abstraction from an alkane molecule by photogenerated O$^-$ species, producing an alkyl radical in the absence of gas-phase oxygen

$$C_3H_8 + O^- \rightarrow \dot{C}_3H_7 + OH^- \quad (2)$$

while formation of peroxy radicals are suggested in the presence of gaseous oxygen

$$C_3H_8 + O^- + O_2 \rightarrow C_3H_7O\dot{O} + OH^- \quad (3)$$

The peroxy radicals would normally result in the formation of hydroperoxides at ambient temperature. Neither peroxy radicals nor hydroperoxides should however form acetone in important quantities at low temperature. It is indeed well accepted that they both lead to the formation of aldehydes (*29*). At low Mo content, our results indicate that acetone was the most abundant partial oxidation product. Therefore this mechanism can be ruled out at least at low Mo loading.

The predominance of acetone at low molybdenum contents could however well be explained by the reaction mechanism proposed by Roberge and Kaliaguine (*3*) which involves the formation of propoxy ($C_3H_7\dot{O}$) radicals in the initiating step

$$C_3H_8 + O^- + O^{2-} + Mo^{5+} \xrightarrow{O_2} C_3H_7\dot{O} + 2O^{2-} + Mo^{6+} \quad (4)$$

The formation of primary oxidation products involving the propoxy radicals for short space times can be represented as (*30*)

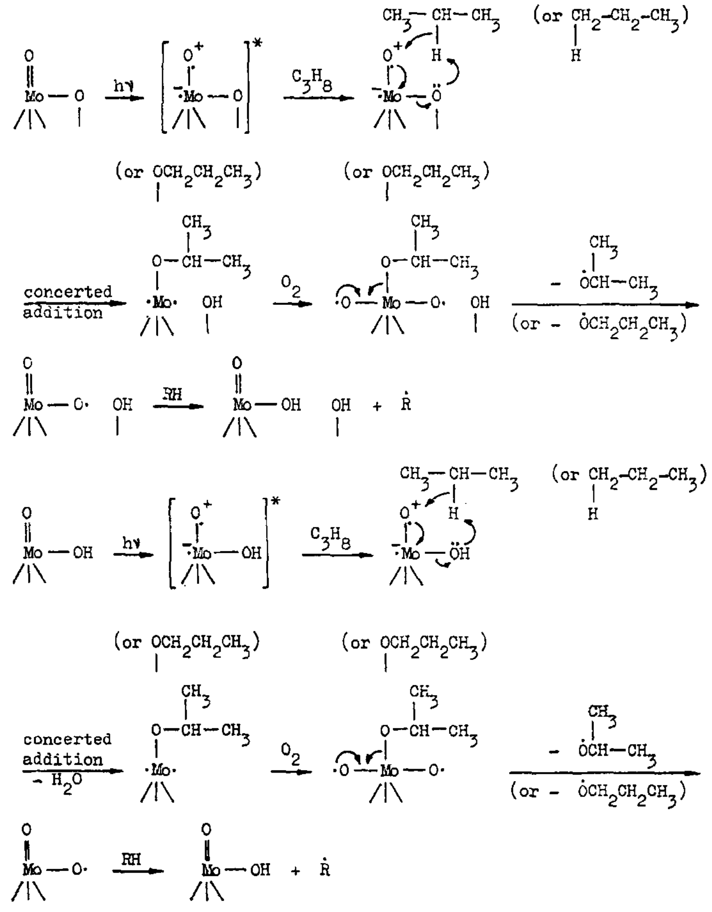
$$i\text{-}C_3H_7\dot{O} + O_2 \rightarrow (CH_3)_2CO + H\dot{O}_2 \quad (5)$$

$$i\text{-}C_3H_7\dot{O} + C_3H_8 \rightarrow (CH_3)_2CHOH + \dot{C}_3H_7 \quad (6)$$

$$n\text{-}C_3H_7\dot{O} + O_2 \rightarrow C_2H_5CHO + H\dot{O}_2 \quad (7)$$

$$n\text{-}C_3H_7\dot{O} + C_3H_8 \rightarrow n\text{-}C_3H_7OH + \dot{C}_3H_7 \quad (8)$$

This mechanism was initially proposed for the photocatalyst Ta/SiO_2. An adapted version for the Mo/SiO_2 system at low Mo contents is given in Scheme 1.



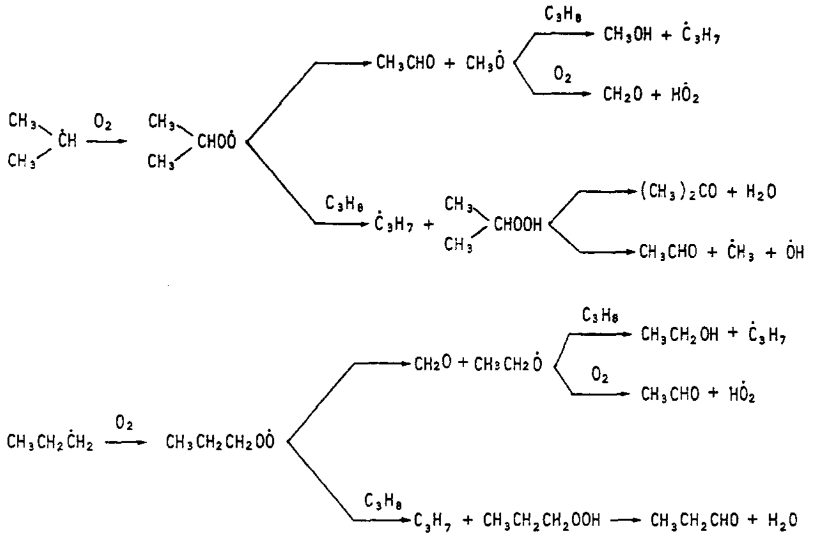
(9)

Scheme 1.

The only necessary characteristic of the oxomolybdenum species involved in mechanism (9) is the existence of a terminal M=O group. One such species with coordinatively unsaturated molybdenum would be the tetrahedral monomeric species. However, under our experimental conditions we know that this species which absorbs at 250–260 nm is not excited since our ozone-free xenon lamp has negligible emission below 280 nm. We believe therefore that at low Mo content where the intermediate species presenting an absorption band in the range 280–290 nm is present in large proportion, this species could be the site responsible for the formation of alkoxy radicals. Indeed at higher Mo contents, where the 330-nm band is predominant, the acetone and propyl alcohols formation decreases, which would mean that a mechanism of photocatalytic oxidation involving alkoxy radicals does not take place on octahedral polymeric species.

At higher molybdenum contents the dominance of aldehydes among the partial oxidation products signifies a change in the overall reaction mechanism. Since at these loadings the absorption at 320–330 nm (Fig. 2) predominates in the uv spectra of the catalysts, the photocatalytic activity in this region can be related to polynuclear species of surface Mo in octahedral coordination. The aldehydes domination may be related to the formation of alkyl radicals intermediates by a mechanism involving hydrogen abstraction by a photoexcited surface Mo species. This mechanism can be viewed in a manner similar to that proposed by Kazansky (*11*) [reaction (2)]. In the presence of gaseous oxygen the propyl radicals formed may undergo the transformations (Scheme 2) well established in the domain of combustion (*29*). This set of reactions can easily explain the increasing importance of ethanal and propanal among the partial oxidation products as Mo loading increases.

SCHEME 2.



(10)

CONCLUSION

On the basis of the experimental evidence presented here we suggest that at low levels of Mo loadings (<2%) the acetone dominance among the propane partial oxidation products may be related to the formation of propoxy radicals on coordinatively unsaturated surface molybdenum sites having an absorption maximum at 280–290 nm. The exact nature of these surface sites is however yet to be identified. At higher loadings the change in the distribution of partial oxidation products may be attributed to a change in the radical intermediates. The emergence of propyl radicals is very much consistent with the experimental data and the surface sites responsible for their occurrence may be related to the polynuclear forms of surface Mo species in octahedral coordination.

The fixed and impregnated catalysts show identical behavior at Mo content lower than 1 wt%. The main differences are observed for the rates of formation of aldehydes and alcohols at Mo content between 1 and 6%. This suggests that the two different methods of preparation yield different structures for the polymeric oxomolybdenum species.

REFERENCES

1. Nguyen, D. L., Roberge, P. C., and Kaliaguine, S., *Canad. J. Chem. Eng.* **57,** 288 (1979).

2. Kaliaguine, S., Gnakoury, M., and Roberge, P. C., *Canad. J. Chem. Eng.* **59,** 710 (1981).

3. Roberge, P. C., and Kaliaguine, S., *Canad. J. Chem. Eng.* **60,** 574 (1982).

4. Witier, P., Estaque, L., Roberge, P. C., and Kaliaguine, S., *Canad. J. Chem. Eng.* **55,** 352 (1977).

5. Djeghri, N., Formenti, M., Juillet, F., and Teichner, S. J., *Faraday Discuss. Chem. Soc.* **58,** 185 (1974).

6. Formenti, M., Juillet, F., Meriaudeau, P., and Teichner, S. J., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1101. North Holland, Amsterdam, 1973.

7. Mahay, A., Kaliaguine, S., and Roberge, P. C., *Canad. J. Chem.* **60,** 2719 (1982).

8. Surin, S. A., Shelimov, B. N., and Kazansky, V. B., *Khim. Vys. Energ.* **6,** 120 (1972).

9. Shuklov, A. D., Surin, S. A., Shelimov, B. N., and Kazansky, V. B., *Khim. Vys. Energ.* **7,** 550 (1973).

10. Gritskov, A. M., Shvets, V. A., and Kazansky, V. B., *Kinet. Katal.* **15,** 1257 (1974).

11. Kazansky, V. B., *Kinet. Katal.* **19,** 279 (1978).

12. Yermakov, Yu I., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 57. Elsevier, Amsterdam, 1981.

13. Kuznetsov, B. N., Startsev, A. N., and Yermakov, Yu I., *J. Mol. Catal.* **8,** 135 (1980).

14. Kuznetsov, B. N., and Yermakov, Yu I., *Kinet. Katal.* **23,** 519 (1982).

15. Iwasawa, Y., Ichinose, H., and Ogasawara, S., *J. Chem. Soc. Faraday Trans. 1* **77,** 1763 (1981).

16. Iwasawa, Y., Nakano, Y., and Ogasawara, S., *J. Chem. Soc. Faraday Trans. 1* **74,** 2968 (1978).

17. Iwasawa, Y., and Ogasawara, S., *J. Chem. Soc. Faraday Trans. 1* **75,** 1465 (1979).

18. Marcinkowska, K., thesis, Laval University, Quebec, 1983.

19. Candlin, J. P., and Thomas, H., *Advan. Chem. Ser.* **132,** 212 (1974).

20. Yermakov, Yu I., *Catal. Rev.-Sci. Eng.* **13,** 77 (1976).

21. Wilke, G., Bogdanovic, B., Hardt, P., Heimbach, P., Kein, W., Kröner, M., Oberkich, W., Tanaka, K., Steinrücke, E., Walter, D., and Zimmermann, H., *Angew. Chem. Int. Ed. Engl.* **5,** 151 (1966).

22. Wang, L., and Hall, W. K., *J. Catal.* **77,** 232 (1982).

23. Asmolov, G. N., and Krylov, O. V., *Kinet. Katal.* **11,** 1028 (1970).

24. Israeli, Y. J., *Bull. Soc. Chim. Fr.* 2692 (1964).

25. Bartecki, A., and Dembicka, D., *J. Inorg. Nucl. Chem.* **29,** 2907 (1967).

26. Ashley, J. H., and Mitchell, P. C. H., *J. Chem. Soc.* (*A*) 2821 (1968).

27. Praliaud, H., *J. Less-Common Met.* **54,** 387 (1977).

28. Iwasawa, Y., and Yamagishi, M., *J. Catal.* **82,** 373 (1983).

29. Shtern, V. Ya., "The Gas-phase Oxidation of Hydrocarbons." Pergamon, New York, 1964.

30. Batt, L., and Milne, R. T., *Int. J. Chem. Kinet.* **9,** 141 (1977).