JOURNAL OF CATALYSIS **106**, 16–22 (1987)

Acrolein Oxidation over 12-Molybdophosphates

II. Catalytic Testing

J. B. BLACK,* J. D. SCOTT,† E. M. SERWICKA,* AND J. B. GOODENOUGH*

**Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom; and †I.C.I. PLC Mond Division, The Heath, Runcorn, Cheshire WA7 4QF, United Kingdom*

Received April 17, 1986; revised January 27, 1987

Continuous-flow microreactor techniques have been used to investigate the catalytic properties in acrolein oxidation of catalysts from the system $K_xH_{3-x}PMo_{12}O_{40}$ ($0 \leq x \leq 3$). At 623 K all catalysts were highly selective to acrylic acid, with selectivity maximized near $x = 2.5$. The specific activity was found to fall with increasing x. The properties of the catalysts studied were rationalized in terms of the characterization scheme presented in Part I (preceding paper), which showed them to be complex mixtures of $K_3PMo_{12}O_{40}$ and phases derived from the thermally unstable $H_3PMo_{12}O_{40}$ nH_2O. Highest selectivity for the $x = 2.5$ composition was attributed to the presence of undecomposed $H_3PMo_{12}O_{40}$ stabilized in an epitaxial, isostructural layer at the surface of the $K_3PMo_{12}O_{40}$ particles and providing a Brønsted acidity required for the efficient selective oxidation to acrylic acid. A drop in selectivity at lower values of x is associated with an increasing concentration of decomposition products from the thermally unstable $H_3PMo_{12}O_{40}$ component.

INTRODUCTION

The application of polymolybdophosphates as catalysts in the oxidation of unsaturated aldehydes to corresponding acids appeared almost a decade ago (*1*), but only in the last few years have commercial and scientific interest in these catalysts been intensified. This interest is due to the increasing demand for polyacrylate and polymethacrylate resins. Of these, the most important is polymethylmethacrylate, known in its sheet form as "Perspex" (I.C.I.) or "Lucite" (Du Pont). A schematic route leading to this product through a two-step isobutene oxidation is shown in Fig. 1; the polymolybdophosphate catalyst is used in the second step.

The oxidation of acrolein and methacrolein over phosphopolymolybdates is known to be remarkably selective; only carbon oxides and traces of acetic acid are produced in addition to acrylic and methacrylic acid (*2, 3*). Commercially, selectivities of 87 at 97% conversion have been claimed (*3*) for complex heteropolymolybdate-based catalysts, and high selectivities (e.g., 60 at 60% conversion) were found for the free acid $H_3PMo_{12}O_{40}$ (*4*).

Most of the basic research in this field has been done in Japan. A range of neutral salts of composition $M^{n+}_{3/n}PMo_{12}O_{40}$ was investigated by Ai (*4, 5*) and Eguchi *et al.* (*6*). Their attempts to correlate the catalytic activity with cation ionic potential or cation electronegativity were only partially successful, and no satisfactory correlation was found for the whole range of investigated catalysts. Ai (*5*), Nakamura and Ichihashi (*2*), and Komaya and Misono (*7*) have studied the influence of proton substitution in the free acid by different cations. The formation of the corresponding solid solutions was generally assumed. These studies showed interesting trends in the catalytic performance of the alkali-metal acid salts of general formal formula $M_xH_{3-x}PMo_{12}O_{40}$, but these trends proved difficult to rationalize. For instance, in the particularly promising case of cesium-based catalysts, the

0021-9517/87 $3.00

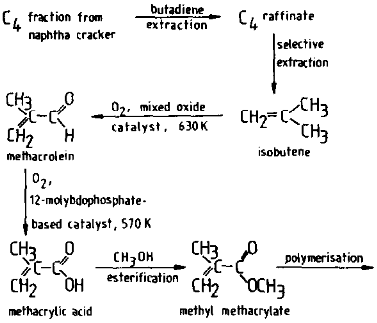

FIG. 1. Schematic route to polymethylmethacrylate formation via a direct two-step oxidation of isobutene.

selectivity was found to pass through a maximum for $x \cong 2.5$. Attempts to interpret this result in terms of changes in cation content within a solid-solution region do not appear convincing and must be treated with caution in view of a lack of full catalyst characterization in the range $0 \leq x \leq 3$.

No detailed study of acrolein oxidation over catalysts from the $K_xH_{3-x}PMo_{12}O_{40}$ series (referred to below as K_x) has previously been reported, but similarities to the cesium-based catalysts might be expected. The extensive characterization of working catalysts presented in Part I (*8*) showed them to be complex, multiphase mixtures of the neutral salt and partially decomposed free-acid component. In particular, no formation of a solid solution was observed. In the present paper we shall use the structural information acquired in Part I to rationalize the observed catalytic behavior of the K_x series.

EXPERIMENTAL

Catalysts

Samples of the K_x series were prepared as described in Part I (*8*), and the calcination was carried out at 673 K for 5 h. One catalyst with excess potassium content, $K_{3.25}$, was also prepared. X-ray examination of this sample revealed only the presence of the K_3 (i.e., $K_3PMo_{12}O_{40}$) structure.

A number of "supported" catalysts were prepared: they were designed to model two-phase mixtures for some of the members of the K_x series and to further investigate the effects of increased MoO_3 content associated with decomposition of the free-acid component. These samples were prepared by impregnation of the insoluble K_3 phase with solutions of K_0 or ammonium paramolybdate (e.x., BDH, AnalaR grade), followed by evaporation to dryness and calcination at 673 K for 5 h. In the latter case, elemental analysis for nitrogen showed that these conditions were sufficient to decompose all of the paramolybdate to MoO_3. Two supported catalysts, designed to model K_1 and $K_{2.5}$, and two MoO_3-containing catalysts with $MoO_3 : K_3$ ratios 5 : 1 and 1 : 1, corresponding to 0.3 and 1.5 monolayer coverage, respectively, were tested under catalytic conditions for comparison with tests on normally prepared catalysts.

Catalytic Testing

Catalytic oxidation of acrolein was carried out under continuous-flow conditions in a glass tubular reactor (6.4 mm inner diameter). Catalyst charges of 0.1–0.2 and 0.5–1.2 g for activity and selectivity measurements, respectively, were placed between quartz-wool plugs. The reactor tube was mounted in a "hot block"; its temperature could be set between room temperature and 673 K. The feed stream was made up from nitrogen and air (I.C.I. laboratory supply). Acrolein (e.x., BDH, General Purpose Reagent grade) was introduced into the feed stream by bubbling nitrogen through the liquid reagent contained in a sealed vessel. The use of a second nitrogen line enabled a feed gas of any desired composition to be made up. The average feed composition was 4.5% acrolein, 10.5% oxygen, and 85% nitrogen.

For analysis of organic products, exhaust gases from a sampling loop were introduced into a helium flow. Products were separated on a 2-m-long column consisting of 10% tritolyl phosphate and 2% orthophosphoric acid supported on acid-washed Celite

(44/60 mesh); they were then detected with a flame-ionization detector (FID).

For the analysis of carbon oxides (CO and CO_2), a sample of feed gas was introduced into a helium flow and carried through a 60-mm-long silica-gel column to remove water and organic acids. Then CO_2 was resolved over a 1-m-long column of Poropak-T and CO over a 1-m-long column of molecular sieve 5A. The products were detected with a katharometer.

The outputs from the FID and the katharometer were analyzed by a Perkin-Elmer Sigma 10 gas chromatography data station.

RESULTS

Experiments were designed to measure both the rate of reaction and the product distribution so as to give information about the activities and selectivities of the catalysts tested. The results are presented below in the form of:

(a) selectivity–conversion profiles, which include the primary selectivity data obtained by extrapolation of the selectivity–conversion plots back to zero conversion;

(b) activity vs composition data, where the rate of acrolein consumption at 623 K after the reaction had been run for one hour was taken as the basic measure of catalytic activity.

Figure 2 shows the dependence of the selectivity to acrylic acid as a function of acrolein conversion for various catalysts from the K_x series. The acrolein conversion was adjusted by changing the contact time with the catalyst. In addition to acrylic acid, the nonselective by-products carbon monoxide, carbon dioxide, and acetic acid were detected.

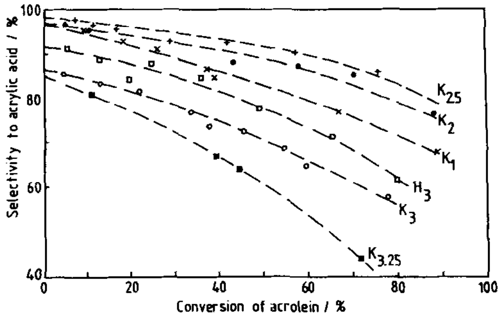

FIG. 2. Selectivity–conversion curves for calcined catalysts from the K_x series. H_3 refers to $H_3PMo_{12}O_{40}$, designated K_0 in the text.

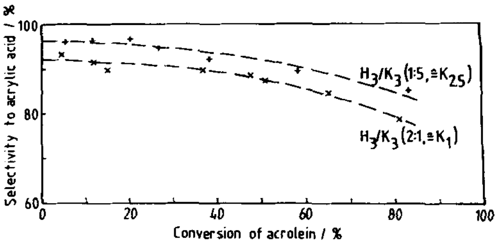

FIG. 3. Selectivity–conversion curves for supported catalysts K_0/K_3 (ratio 1 : 5 modeling $K_{2.5}$, ratio 2 : 1 modeling K_1). H_3 signifies K_0.

The selectivity–conversion plots show clearly that the catalytic performance improves as x increases in the range $0 \leq x \leq 2.5$, but falls abruptly at higher x as the neutral-salt composition is reached. The catalyst with $x = 2.5$ is the most selective, which is in good agreement with the results reported previously for the cesium-based series (*5*). The slight excess of potassium in the $K_{3.25}$ sample leads to a further drop in selectivity. The primary selectivity is high for all the catalysts (>85%) and very high (>97%) for $1 \leq x \leq 2.5$.

Selectivity–conversion curves for supported catalysts with K_0 to K_3 ratios of 2 : 1 and 1 : 5, designed to model K_1 and $K_{2.5}$, respectively, are shown in Fig. 3. An exceptionally good match to the $K_{2.5}$ performance of Fig. 2 was obtained for the $K_{2.5}$ model. This sample was also found to be the more selective of the two supported catalysts, as expected. The primary selectivities of these two catalysts fall close to those of the samples they were intended to model, the catalyst modeling $K_{2.5}$ being the more selective.

In Part I (*8*) it has been demonstrated that calcination results in partial decomposition of the K_0 component in the K_x series, and MoO_3 was found to be one of the decomposition products. MoO_3 is known to display catalytic properties of its own in many oxidation processes. Other decomposition products may be catalytically active as well. Therefore it seemed important to find out how the presence of those phases affects the catalytic performance of the K_x series.

Figure 4 shows the selectivity–conversion profiles for uncalcined K_1 and K_2 catalysts, both of which contain substantial amounts of undecomposed K_0 phase. It may be seen that the uncalcined catalysts are more selective than their calcined counterparts in which, according to our structural analysis, part of the K_0 phase has undergone thermal decomposition.

The effect of calcination was next investigated for the supported K_0/K_3 (2 : 1) catalyst (modeling K_1) by heating it, after the standard calcination, for a further 24 h in air. Selectivity–conversion curves for the catalyst after 5 and 29 h of calcination are compared in Fig. 5. The sample calcined for 29 h is less selective, especially at higher conversions.

Interesting results were obtained for the catalysts where different amounts of MoO_3 were intentionally supported on K_3. Two catalysts, formally corresponding to 0.3 and 1.5 monolayer coverage, were tested. Their primary selectivity data are shown in Fig. 6. The catalyst with lower MoO_3 content has a primary selectivity of around 88%, similar to that of K_3. Increasing the amount of MoO_3 lowers the primary selectivity to around 77%, indicating that an increasing coverage of the catalyst surface by MoO_3 leads to a poorer catalytic performance.

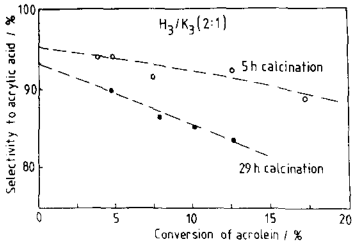

FIG. 5. Selectivity–conversion curves for supported K_0/K_3 (2 : 1) catalyst calcined for different periods of time. H_3 signifies K_0.

The results of activity measurements are presented in Fig. 7. The plots of activity per unit mass and specific activity for the catalysts of the K_x series show that the increase in the activity of the catalysts as x approaches 3 is due solely to increasing surface area. The actual activity of the catalyst surface decreases gradually from K_0 to K_3, but K_3 is still significantly active. A slight excess of potassium in the $K_{3.25}$ sample results in an abrupt drop in activity.

The activity of the K_0/K_3 (1 : 5) supported sample, which models $K_{2.5}$, corresponds exactly to that of the $K_{2.5}$ catalyst; the activity of the K_0/K_3 (2 : 1) catalyst is lower than the activity of the K_1 sample it was designed to model. Nevertheless it may be seen that the catalyst modeling K_1 is the more active of the two, in agreement with the trend observed for the unsupported samples. This (2 : 1) sample, after calcination for 29 h, has only one-third of the activity shown in Fig. 7, which was measured after 5 h of calcination.

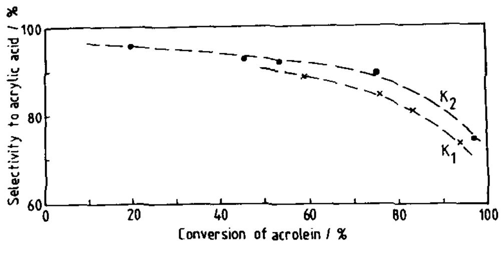

FIG. 4. Selectivity–conversion curves for uncalcined K_1 and K_2 catalysts.

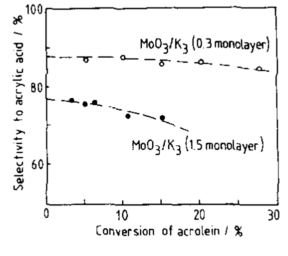

FIG. 6. Selectivity–conversion curves for supported MoO_3/K_3 catalysts (0.3 and 1.5 monolayer coverage).

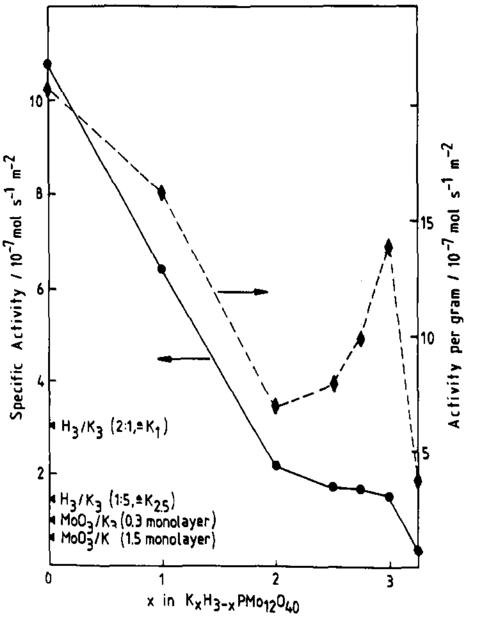

FIG. 7. Variation of catalytic activity per gram and specific activity across the K_x series. H_3 signifies the potassium-free solid, $H_3PMo_{12}O_{40}$, i.e., K_0 in the text.

Specific activities of catalysts containing different amounts of MoO_3 impregnated on K_3 are also included in Fig. 7. It is obvious that the MoO_3 phase is less active than the K_3 support. Where the coverage with MoO_3 exceeds 1 monolayer, the activity drops to ca. 30% that of K_3.

DISCUSSION

Detailed characterization of the K_x series, presented in Part I (*8*), revealed that the "fresh" catalyst is a two-phase mixture of K_0 and K_3 phases and that on calcination at 673 K for 5 h the K_0 phase is partially decomposed. The extent of irreversible decomposition to MoO_3 increases with calcination time. Evidence was also given for stabilization of a K_0-phase coating on K_3 particles, presumably due to proton transfer from the coat to the underlying K_3 phase. The importance of this stabilized K_0-phase coat is particularly pronounced for higher values of x, where it corresponds to the majority of the K_0 component present in the catalyst. Scanning electron microscopy showed that for compositions of larger x ($x \geq 2.5$), well-formed crystallites with clean surfaces were found, and no significant amount of decomposition products of the K_0-phase component was observed. Finally, it was also demonstrated by diffuse-reflectance IR spectroscopy that undecomposed Keggin units are present at the surface of the catalyst.

In view of this structural characterization of the operational catalyst, it is now argued that the catalyst testing presented in this paper shows that selective oxidation of acrolein to acrylic acid occurs on an undecomposed Keggin unit and that the selectivity of this reaction is enhanced if associated with a stabilized K_0 component on the surface of a K_3 phase.

Selective oxidation of acrolein to acrylic acid by uncalcined samples (Fig. 4) provides direct evidence that the selective oxidation occurs on Keggin units; the fresh samples contain only H_2O, H_3O^+, and K^+ species in addition to the Keggin unit. Moreover, identification of these units by diffuse-reflectance IR spectroscopy at the surface of the most selective composition studied, $K_{2.5}$, provides additional direct evidence. If these units are the seat of the selective oxidation, it follows that a reduction in selectivity must be correlated with an increasing concentration of Keggin-unit decomposition products.

Figure 6 provides direct evidence that the presence of MoO_3, a final decomposition product of the calcined K_0 phase, reduces the selectivity. The presence of this phase could only just be detected (in the form of a single crystallite) in the calcined $K_{2.5}$ sample, but it was evident in both X-ray diffraction and ^{31}P solid-state NMR for samples with lower values of x (Part I). We may conclude that the MoO_3 phase is not selective in the oxidation of acrolein.

These findings provide a direct interpretation of Fig. 5, which shows a decrease in selectivity on increasing the calcination time from 5 to 29 h for a supported K_0/K_3 (2 : 1) catalyst, which models K_1. From the

DTA/TGA data of Part I, increasing the calcination time of a K_1 sample increases the irreversible decomposition of the K_0 component to MoO_3.

The supported catalyst K_0/K_3 (1 : 5) has performance curves (Figs. 3 and 7) strikingly similar to those of the $K_{2.5}$ catalyst that it models. This similarity is in full accord with the characterization studies, which show that the $K_{2.5}$ catalyst is indeed a two-phase mixture, but with a K_0 component that is not decomposed by a 5-h calcination at 673 K. We may conclude that the K_0 phase of the model system is similarly stabilized by its interaction with the K_3 phase. The improved selectivity of the supported K_0/K_3 (2 : 1) system relative to the K_1 catalyst (Figs. 3 and 7) would seem to imply a smaller degree of decomposition in the model system, especially if Figs. 2 and 3 are compared with the selectivity of the "fresh" K_1 given in Fig. 4.

These conclusions permit an immediate qualitative rationalization of the catalytic tests shown in Fig. 2 for the compositional range $0 \leq x \leq 2.5$. The lower selectivity of the catalysts with lower x is associated with a higher concentration of MoO_3, as well as other partial decomposition products. However, the marked reduction in selectivity for the neutral salt K_3 indicates that, although selective oxidation occurs at the Keggin unit, the selectivity of the reaction on these units is enhanced by the Brønsted acidity associated with the stabilized K_0 component on the surface of the catalyst. The significance of this last observation is discussed in detail in Part III (*9*), which is concerned with the reaction mechanism.

In addition, the very high primary selectivities (close to 100% for most of the catalysts) indicate that at low conversion a unique reaction mechanism is operative and suffers little competition from nonselective oxidation pathways. At higher conversion, a loss in selectivity is observed with all catalysts. Two types of nonselective pathways can be distinguished: one involves further oxidation of the desorbed product, acrylic acid; the other is a deeper oxidation of the chemisorbed species. Ai (*10*) has shown that acrylic acid can be oxidized by polymolybdophosphate catalysts above 550 K. Nonselective oxidation of the chemisorbed species would appear to be due to deeper oxidation by dioxygen, either gaseous or chemisorbed. Chemisorbed dioxygen would occur at an oxygen vacancy as a peroxide anion, which would create an active, mobile surface-oxygen species

$$(O_2)^{2-} + O^{2-} \rightleftharpoons O^{2-} + (O_2)^{2-}$$

In the latter case the chemisorbed acrolein species and/or the chemisorbed active oxygen must be mobile on the surface of the catalyst, perhaps even transferring from one Keggin unit to another. If the latter step is slow compared to the reaction step responsible for desorption of acrylic acid, the primary selectivity should be high.

At low conversion, any chemisorbed acrolein species tend to be well separated from oxygen vacancies created by desorbed acrylic acid, so the probability that the chemisorbed species is attacked by active oxygen during the residence time at the surface is low; consequently the primary selectivity is high.

Finally, the fact that the interaction of acrolein with the Keggin anion leads almost exclusively to acrylic acid formation at low conversion signals that the K_x system with $2.5 \leq x \leq 3$ provides an excellent opportunity for a detailed mechanistic study of the catalytic reaction itself. The results of such an investigation are presented in Part III (*9*).

REFERENCES

1. Otake, M., and Onoda, T., *Shokubai* (*Catalyst*) **18,** 169 (1976).
2. Nakamura, S., and Ichihashi, H., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 755. Kodansha (Tokyo)/Elsevier (Amsterdam), 1981.
3. Uloe Industries Ltd., Japan Patent 59 69 148 (1984).

4. Ai, M., *J. Catal.* **71,** 88 (1981).

5. Ai, M., *Appl. Catal.* **4,** 245 (1982).

6. Eguchi, K., Aso, I., Yamazoe, Y., and Seiyama, T., *Chem. Lett.*, 1345 (1979).

7. Komaya, T., and Misono, M., *Chem. Lett.,* 1177 (1983).

8. Black, J. B., Clayden, N. J., Gai, P. L., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106,** 1–15 (1987) [Part I].

9. Serwicka, E. M., Black, J. B., and Goodenough, J. B., *J. Catal.* **106,** 23–37 (1987) [Part III].

10. Ai, M., *J. Catal.* **85,** 324 (1984).