CHEMISTRY LETTERS, pp. 1177-1180, 1983.

ACTIVITY PATTERNS OF $H_3PMo_{12}O_{40}$ AND ITS ALKALI SALTS FOR OXIDATION REACTIONS

Takashi KOMAYA and Makoto MISONO*
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Bunkyo-ku, Tokyo 113

It has been demonstrated that oxidation reactions of organic compounds over $H_3PMo_{12}O_{40}$ and its alkali salts are classified into two prototypes. In the first type reactions, the surface redox properties of catalysts are important, and in the second type the bulk properties. Oxygen-addition reactions like methacrolein to methacrylic acid are an example of the former, and oxidative dehydrogenation is the latter example.

Heteropoly acids and their salts are selective catalysts for oxidation reactions of oxygen-containing organic compounds. These reactions usually proceed by redox mechanisms, and redox properties of these catalysts have been correlated with catalytic function.[1-3] However, in spite of extensive studies,[4-8] it is still difficult to find a general correlation between the structure (or composition) and catalytic functions. Particularly, as for the effects of counter cation of the salts, inconsistent results have been reported. Settlement of these apparent discrepancies is now eagerly needed for the proper understanding of the composition vs. catalysis relationships and for the catalyst design based on heteropoly compounds.

We have attempted to elucidate the above correlation by using alkali salts of $H_3PMo_{12}O_{40}$ which were prepared with attention to the structure and composition. We wish to report in this letter results which we believe very important for the understanding of the oxidation catalysis of heteropoly compounds. The reactions carried out are all stoichiometric (non-catalytic), but the results and concept presented here must be closely related to an essential aspect of catalytic oxidation over heteropoly compounds.

Alkali salts were prepared as before.[8] Water contents of the reagents were accurately determined for the calculation of the stoichiometry. Surface area was measured by N_2 adsorption (flow method) after various pretreatments. Methacrolein (Aldrich Chem. Co., Inc.) was stored in a cold place after distillation. Without distillation, oligomers present in the sample made the results unreliable. Isobutyric acid (Tokyo Kasei Chem. Co.) was used without further purification, but no impurities were detected by gas chromatography. Reactions were carried out by a microcatalytic pulse method as before.[8] The followings were confirmed in advance: (1) Conversion over $H_3PMo_{12}O_{40}$ was almost proportional to the catalyst weight. (2) Carbon balance was close to 100%. (3) Results were reproducible. Reaction temperature was 300°C for all reactions, pretreatment being 1 h at 300°C in a He stream.

Figure 1 shows the conversions (first pulse) of methacrolein and isobutyric acid. The selectivity to methacrylic acid from methacrolein was 40-70%, except for $H_3PMo_{12}O_{40}$ which showed 20%-selectivity in the first pulse and the selectivity increased by successive pulses. General trend observed in Fig. 1 did not change when the conversions of the 2nd or 3rd pulse are plotted. By-products were acetic acid, CO and CO_2. The selectivity to methacrylic acid and acetone from isobutyric acid was 95-100% among oxidation products, the former being 2/3 of them. Besides oxidation products, CO and propene were formed by acid catalysis in the case of isobutyric acid.[9)] These products are not included in the conversions in Fig. 1b. It is obvious in Fig. 1a and b that the reactivity varies markedly depending on the kind of counter cation (Cs vs. Na) and reaction (methacrolein vs. isobutyric acid). There is no simple or monotonous relationship between the reactivity and the amount of alkali. Furthermore, the reactivity of methacrolein was sensitive to pretreatment and varied from one catalyst lot to another in some cases, e.g., $Na_2HPMo_{12}O_{40}$ (Fig. 1a). Steam pretreatment gave a monotonous decrease with x even for Na salts. In contrast, the oxidation of isobutyric acid was not sensitive to these factors, showing monotonous variation with x. These irregular variations of reactivity must be the reason why the proper understanding of the composition vs. catalysis correlation has been difficult.

Table 1 summarizes the surface areas of catalysts after two different pretreatments. Acidity measured by irreversible absorption of pyridine[1)] is included in the table to indicate proper preparation of salts. The surface area changed signi-

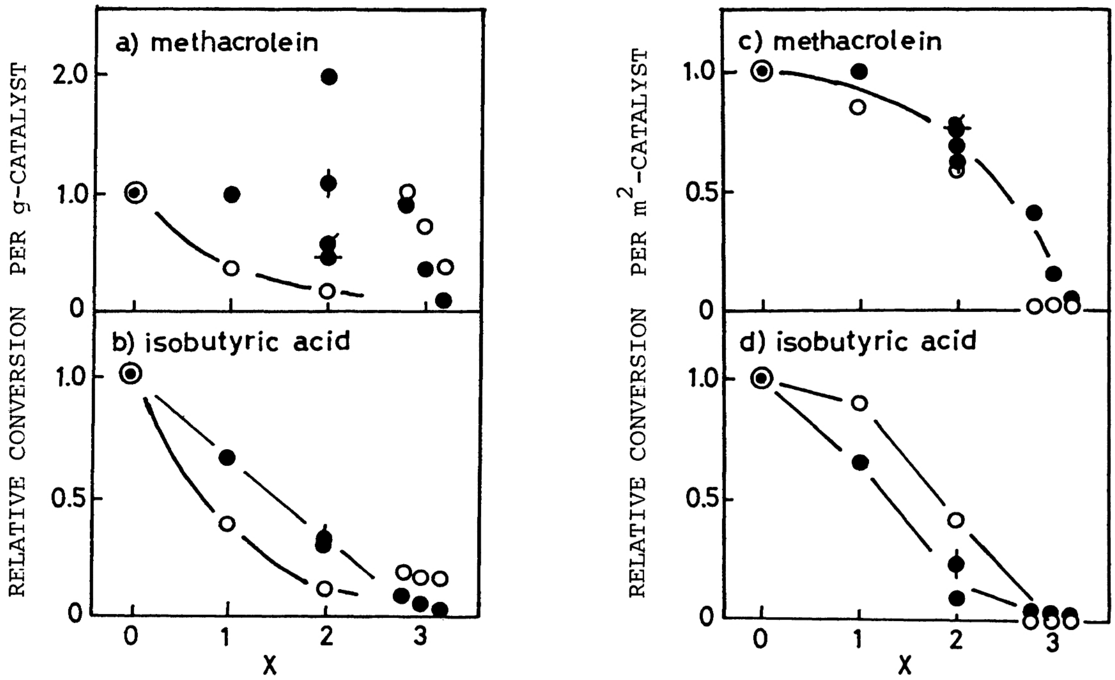


Fig. 1. Relative conversions of methacrolein and methacrylic acid over $Cs_xH_{3-x}PMo_{12}O_{40}$ (○) and $Na_xH_{3-x}PMo_{12}O_{40}$ (● ; flags attached indicate different lots or pretreatments) at 300°C.
Conversions over $H_3PMo_{12}O_{40}$ are taken as 1.0 [Methacrolein(1 μl): 16% over 400 mg-cat., isobutyric acid(1 μl): 75% over 50 mg-cat.].

Table 1. Surface Areas and Acidity of 12-Molybdophosphates.

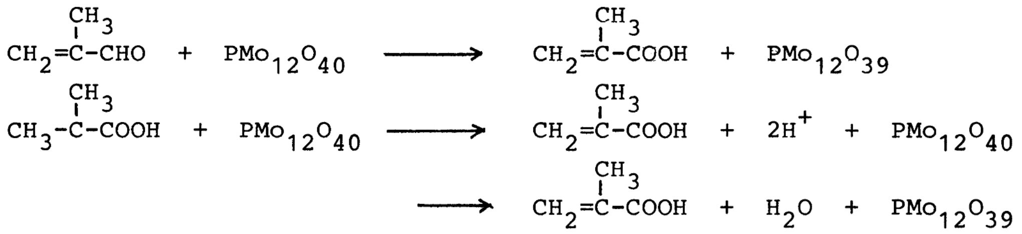
	Pretreatment	$Cs_xH_{3-x}PMo_{12}O_{40}$						$Na_xH_{3-x}PMo_{12}O_{40}$					
		x=0	1	2	2.85	3.0	3.15	0	1	2	2.85	3.0	3.15
Surface area (m^2/g)	150°C, 1h	4.7	5.0	10.0	162	165	159	4.7	4.1	3.9	-	2.0	-
	300°C, 1h	2.1	0.9	0.6[a]	146	133	125	2.1	2.0	5.3	4.5	4.4	4.3
Acidity[b]	150°c, 1h	3.0	1.8	0.8	-	0.1	-	3.0	2.2	1.6	-	0.2	-

a) Sensitive to pretreatments. b) Number of pyridine molecules/anion.

ficantly by pretreatments. Since a correlation was indicated between the change of surface area and reactivity, particularly in the case of $Na_2HPMo_{12}O_{40}$, the conversions given in Fig. 1 are normalized to the surface area which was measured after the same treatment as that prior to reaction, and replotted against x in Fig. 1c, d. The reactivity, which showed irregular variation in Fig. 1a, fell on a monotonous and smooth line in Fig. 1c. We reported previously that there is a fair correlation between the reducibility of several heteropoly compounds and catalytic activity for methacrolein oxidation.[1, 7, 8)] Therefore, monotonous decrease observed in Fig. 1c probably reflects the reducibility or the oxidation power of heteropoly compounds. In support of this idea, when the present catalysts were reduced by H_2 at 300-350°C, the rate of reduction decreased with the content of Na or Cs.[10)]

In contrast, in the case of isobutyric acid the reactivities normalized to surface area and weight both showed a nearly monotonous decrease. But the scatter was lesser in the latter case for the data of $Na_2HPMo_{12}O_{40}$.

Then, why do the two reactions behave so differently? One of the reasons may be whether the oxidation reaction involves oxygen addition or not.



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CHO + PMo_{12}O_{40} \longrightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}COOH + PMo_{12}O_{39} \qquad (1)$$

$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{-}COOH + PMo_{12}O_{40} \longrightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}COOH + 2H^+ + PMo_{12}O_{40} \qquad (2a)$$

$$\longrightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}COOH + H_2O + PMo_{12}O_{39} \qquad (2b)$$

In reaction (1), oxygen of $PMo_{12}O_{40}$ is incorporated into product, while only dehydrogenation takes place in reaction (2) and oxygen of $PMo_{12}O_{40}$ is not removed at least in the first step (2a). Second step (2b) and formation of acetone which was observed as a by-product require oxygen of catalyst. However, if one considers the selectivity described above, the amount of oxygen atoms consumed in one pulse was much greater for methacrolein than isobutyric acid.

The contrast between the two reactions as described above leads us to propose a postulate that there are two prototypes in the oxidation reactions over heteropoly compounds. In the first type of reactions, oxygen atoms are incorporated significantly into products. In the case of methacrolein over $M_xH_{3-x}PMo_{12}O_{40}$ (x=0-2), the number of oxygen atoms consumed in the first pulse was several times greater than the number of surface heteropoly anions. If the reaction proceeds on the surface, and the supply of oxygen from inside the bulk is not rapid enough, the oxidizing ability of catalyst must decrease rapidly during the passage of one pulse through catalyst bed. In fact, the conversion decreased rapidly when the methacrolein pulse was repeated. In this case, oxidation power of surface polyanion and its number become important, as demonstrated in Fig. 1c.

In the second class of reactions, dehydrogenation is the main process, so that oxygen supply is not always necessary. The diffusion of proton and electron into the bulk, which must be much faster than the diffusion of oxygen, restores the oxidation state of surface polyanions. In accordance with this idea, the conversion of isobutyric acid declined much more slowly than that of methacrolein when the conversions are plotted against the extent of reduction of $H_3PMo_{12}O_{40}$. Note that the number of isobutyric acid molecules which reacted in one pulse over $H_3PMo_{12}O_{40}$ was much greater than that of surface anions. In this case, the oxidizing ability of bulk anions may take part in the oxidation reactions as shown in Fig. 1b.

In order to confirm the above generalization, two additional reactions were examined, i.e., oxidation of acetaldehyde to acetic acid and oxidative dehydrogenation of cyclohexene to benzene as the examples of each type. Results of acetaldehyde closely resembled those of methacrolein (compare Fig. 2 and Fig. 1a, c); the reactivity per surface area is the good measure. On the other hand, cyclohexene which produced benzene very selectively behaved very like isobutyric acid. Thus, the classification of oxidation reactions into two protoypes seems widely applicable. In general, any reaction may fall between the two prototypes depending on the relative rate of oxygen or proton diffusion and oxidation reaction, and also on the relative amount of surface polyanions to the bulk polyanions.

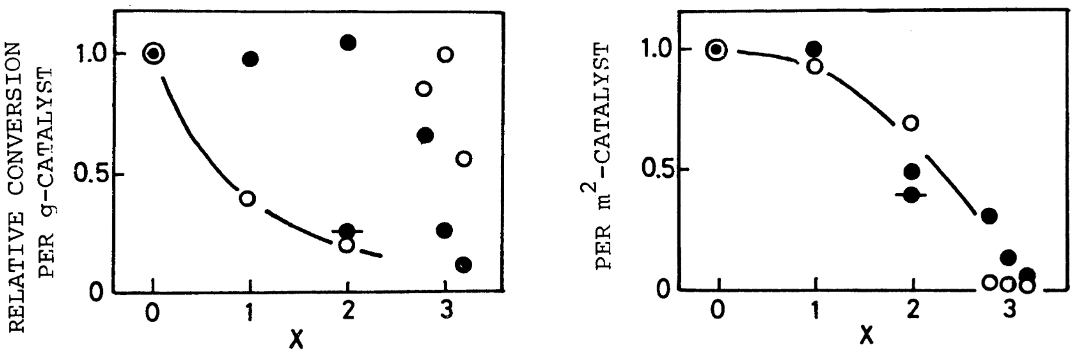


Fig. 2. Relative conversions of acetaldehyde over $Cs_xH_{3-x}PMo_{12}O_{40}$ (○) and $Na_xH_{3-x}PMo_{12}O_{40}$ (●,-●-; different pretreatments) at 300°C.

References

1) M. Misono, K. Sakata, Y. Yoneda, and W. Y. Lee, "Proc. 7th Intern. Congr. Catal., Tokyo, 1980," Kodansha-Elsevier (1981), p. 1047.
2) S. Yoshida, H. Niiyama, and E. Echigoya, J. Phys. Chem., 86, 3150 (1982).
3) K. Eguchi, Y. Toyozawa, K. Furuta, N. Yamazoe, and T. Seiyama, Chem. Lett., 1981, 1253.
4) K. Eguchi, I. Aso, N. Yamazoe, and T. Seiyama, Chem. Lett., 1979, 1345.
5) M. Akimoto,Y. Tsuchida, K. Sato, and E. Echigoya, J. Catal., 72, 83 (1981).
6) M. Ai, J. Catal., 71, 88 (1981).
7) Y. Konishi, K. Sakata, M. Misono, and Y. Yoneda, J. Catal., 77, 169 (1982).
8) M. Misono, T. Komaya, H. Sekiguchi, and Y. YOneda, Chem. Lett., 1982, 53.
9) M. Otake and T. Onoda, J. Catal., 38, 494 (1975).
10) N. Mizuno, T. Watanabe, and M. Misono, unpublished results.

(Received May 9, 1983)