CHEMISTRY LETTERS, pp. 53-56, 1982.

OXIDIZING POWER AS THE PRIME FACTOR CONTROLLING THE CATALYTIC ACTIVITY OF $H_3PW_xMo_{12-x}O_{40}$ FOR OXIDATION OF METHACROLEIN

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Oxidation of acrolein, methacrolein, and isobutyric acid by 12-heteropoly acids of Mo and W ($H_3PW_xMo_{12-x}O_{40}$: x = 0,2,6,10,12) was carried out with a pulse method. By the comparison of the pulse and flow experiments, it was concluded that the prime factor controlling the catalytic activity was the oxidizing power of catalyst (or reducibility of catalyst).

Heteropoly acids are superior catalysts for the oxidation of methacrolein to methacrylic acid. However, little is known about the reaction mechanism or primary factors controlling the catalytic activity. Structual factors, acidity, and oxidizing power of catalysts have been suggested as the factors.[1-4] We proposed a redox mechanism in which oxidizing power functions as the prime factor in the rate-determining step.[2,5] The evidence to support this idea is a fair relationship which was found between the oxidizing power (represented by reducibility with H_2) and the catalytic activity of several heteropoly acids and their salts. Both rate equation and oxidation state of catalyst also support the idea, but are circumstantial.

Therefore, we attempted to prove the idea by the comparison of pulse experiments and flow experiments. If the reduction of heteropoly acid is rate-determining in a redox mechanism, the reactivity of aldehyde observed in pulse experiments (non-catalytic reaction between catalyst and aldehyde), which reflects the oxidizing power, must be in parallel with the rate of catalytic oxidation.

To avoid complication, we confine the catalysts in this study to the acid from of 12-heteropoly acids of Mo and W. For comparison purpose, some additional experiments were performed with alkali salts. The effect of methyl substitution at α and ß position to carbonyl was also examined for acrolein and compared with the results of oxidative dehydrogenation of propionaldehyde.

Pulse experiments were carried out with a conventional method by using a microreactor, of which the outlet was directly connected to gas chromatographs (CO, CO_2 and propylene were analyzed by active carbon, molecular sieve and DMS columns, and aldehydes and carboxylic acids by Tenax or FFAP column). Carrier gas was He (10 or 30 cm^3 min^{-1}). Heteropoly acids were prepared as described previously following the literature.[6,7] Catalysts (ordinarily 100 mg in the form of unsupported powder) loaded in the microreactor was heated gradually in a He stream and kept at 300°C for 1 h in the He stream, prior to pulse experiments (this is regarded to be standard pretreatment). Reaction temperature was usually 300°C.

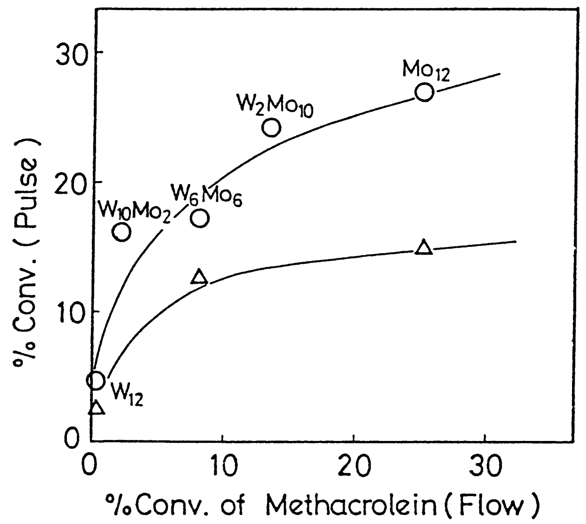


FIG. 1. COMPARISON BETWEEN PULSE EXPERIMENTS (1ST PULSE) AND FLOW EXPERIMENTS FOR OXIDATION OF UNSATURATED ALDEHYDES OVER $H_3PW_xMo_{12-x}O_{40}$ (W_xMo_{12-x}).

○:Acrolein , △:Methacrolein

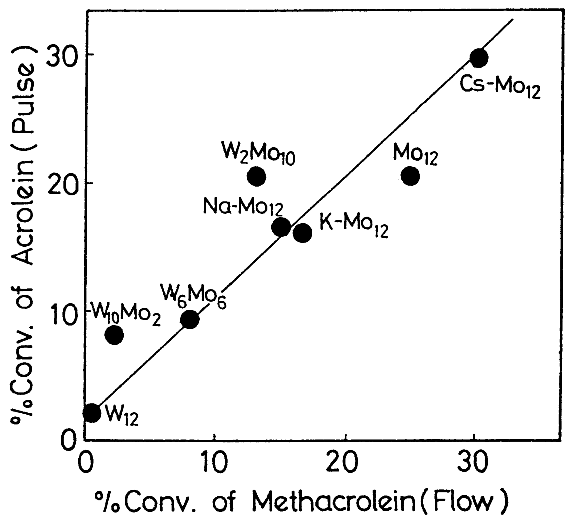


FIG. 2. COMPARISON BETWEEN PULSE EXPERIMENTS (CO-PULSE WITH O_2) AND FLOW EXPERIMENTS FOR OXIDATION OF UNSATURATED ALDEHYDES.

$Cs-Mo_{12}$, *etc.* are Cs salt of $H_3PMo_{12}O_{40}$, *etc.*.

Following results [(i) to (iv)] obtained for $H_3PMo_{12}O_{40}$ with acrolein may ensure the properness of the present pulse experiments. (i) % Conversion of the first acrolein pulse was fairly reproducible and increased proportionally to W/F upto 30% conversion, where both W, catalyst weight, and F, feed rate, were independently varied. (ii) Either O_2 (1ml), H_2O (1 - 5ml) or $O_2 + H_2O$ pulsed prior to the first acrolein pulse had only a small effect on the conversion of acrolein. (iii) When acrolein was pulsed with O_2 in the first pulse (co-pulse with O_2), the conversion increased by about 10%. Co-pulse with H_2O had a similar effect. However, the changes were not great so as to affect the reactivity order of heteropoly acids. (The effects was significant in the case of alkali salts, *vide infra*.) (iv) Carbon balance was close to 100% for each pulse of acrolein.

Then the following pulse experiments were performed for each $H_3PW_xMo_{12-x}O_{40}$ $(x = 0,2,6,10,12)$ after the standard pretreatment: 1st to 4th pulse--acrolein only (1μl), 5th pulse--acrolein (1μl) + H_2O(1ml), and 6th pulse--acrolein(1μl) + O_2(1ml). Before each 3th to 6th pulse, a $O_2 + H_2O$ pulse was injected. By the $O_2 + H_2O$ pulse, the decrease in reactivity from pulse to pulse was suppressed and nearly constant conversions were obtained (1/2 to 1/3 the initial value).

In Fig. 1, the % conversion of the first acrolein and methacrolein pulse was plotted against the conversion of methacrolein obtained previously at the stationary state of catalytic oxidation.[2,5] It is noted that the order among the catalysts was identical for the pulse experiments and the flow experiments. Selectivity for acrylic acid was 50 - 70% for $x = 0\text{-}10$ and 30% for $x = 12$. Data for alkali salts which are not given in Fig. 1 deviated downward from the curves. In Fig. 2, the conversion of 6th acrolein pulse (co-pulse with O_2) is compared with the flow experiment. Con-

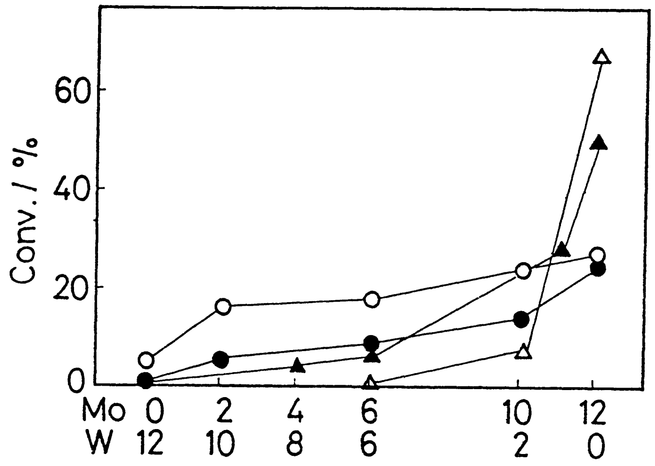
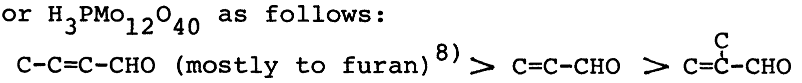


FIG. 3. OXIDATION REACTIONS OVER $H_3PW_xMo_{12-x}O_{40}$

○: Acrolein (Pulse), 300°C
●: Methacrolein (Flow), 300°C
△: Isobutyric Acid (Pulse), 250°C
▲: Isobutyric Acid (Flow), 280°C4)

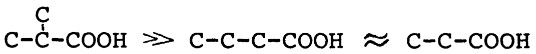
version over alkali salts increased by a factor of 2 to 4 when acrolein was pulsed with O_2, resulting in good correlation between pulse and flow experiments.

Relative reactivity of methyl-substituted and unsubstituted acrolein was determined for $H_3PMo_{12}O_{40}$ as follows:



$$\text{C-C=C-CHO (mostly to furan)}^{8)} > \text{C=C-CHO} > \text{C=}\overset{\text{C}}{\text{C}}\text{-CHO} \qquad (1)$$

Similar pulse experiments were performed for the oxidative dehydrogenation of isobutyric acid to methacrylic acid at 250 and 300°C (the rate of dehydrogenation was much greater than oxidation of acrolein). The oxidative dehydrogenation increased with increasing Mo/W ratio, while decarboxylation which is catalyzed by acids decreased with the Mo/W ratio as reported before.4) Methyl substitution gave a reactivity order (to oxidized products) of



$$\text{C-}\overset{\text{C}}{\text{C}}\text{-COOH} \gg \text{C-C-C-COOH} \approx \text{C-C-COOH} \qquad (2)$$

which is in contrast to Eq(1). Isobutyric acid was much more reactive than the others as already reported.4) Saturated aldehydes exhibited a similar trend: C-C(-C)-CHO $\gg$ C-C-CHO. In this case small amounts of unsaturated carboxylic acids were also formed, probably as a result of successive oxidation of unsaturated aldehydes. Under the same reaction conditions acetaldehyde produced acetic acid (it was noted that rate and selectivity increased markedly when co-pulsed with H_2O).

In Fig. 3, present data are plotted against the Mo/W ratio together with results of flow experiments. A general trend that the rates of four oxidation reactions increased monotonously with the Mo/W ratio may be noted, although the dependencies are not identical. Main differences are: (i) As for the oxidation of aldehydes to carboxylic acids the difference among the catalysts was considerably smaller in pulse experiments than in flow experiments, and (ii) the dependency on the Mo/W ratio was greater for oxidative dehydrogenation than for oxidation to carboxylic acids. Possible reasons which caused these differences are as follows. (a) Difference in the oxidation state of catalysts between pulse and flow experiments. It is suggestive that the yield of carboxylic acids increased by repeated pulses of aldehydes, particularly in the case of methacrolein over $H_3PMo_{12}O_{40}$. (b) Rate of oxygen supply: The amount of oxygen consumed in the first acrolein pulse amounted to about 1 atom per polyanion of 3 surface layers in the case of active catalysts, so that the rate of oxygen supply from the bulk may limit the reaction in this case. It is probable that the slow supply of oxygen from the bulk for alkali salts caused the large effect of O_2 co-pulsed. (c) Reaction intermediate is obviously different between the two types of oxidation and its stability may differently depend on the catalyst properties. See the reactivity sequences of Eqs.(1) and (2). (d) Deactivation due to polymerization of products was probably greater for pulse experiments in which H_2O or O_2 was only pulsed intermittently. However, these factors appear of secondary importance, although further investigation is required to confirm their roles.

Nonetheless, it is obvious that the rate of the oxidation of aldehydes to carboxylic acids increases with the Mo/W ratio both in pulse (non-catalytic) and flow (catalytic) experiments. Therefore, present results given in Figs. 1 to 3 demonstrate that the oxidizing power of heteropoly acids is the prime factor controlling their catalytic activity for the oxidation reactions and that the oxidation step of a reactant by catalysts (the reduction step of catalyst) is rate-determining. Different sequences of Eqs.(1) and (2) also support tha idea that the rate-determining step is not the step of catalyst re-oxidation but a step in which a reactant is directly involved. It was recently suggested as for the dehydrogenation of isobutyric acid over alkali salts that the oxidizing power was important.$^{9)}$ In the case of the oxidation of CO and H_2, it was shown that the reactivity was similar for non-catalytic and catalytic experiments.$^{10)}$

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8) Formation of furan from crotonaldehyde was reported (M. Ai, T.-H. Tsai, and A. Ozaki, Bull. Chem. Soc. Jpn., 53, 2647(1980)). The following mechanism which is analogous to the mechanism of acrolein or methacrolein oxidation may be possible.

$$CH_3\text{-}CH{=}CH\text{-}CHO \xrightarrow{+H_2O} CH_3\text{-}CH(OH)\text{-}CH{=}CHOH \xrightarrow{-H_2O} CH_2{=}CH\text{-}CH{=}CHOH \xrightarrow{-H_2} \text{Furan.}$$

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(Received November 7, 1981)