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Improvement of Furan Yield in Oxidation of Crotonaldehyde by Modifying 12-Molybdophosphoric Acid Catalysts

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12-Molybdophosphoric acid effective for oxidation of crotonaldehyde to furan was modified in two ways; by adding various cations and by replacing Mo with V or W. Among cations caesium was proved to be most effective in improving the furan yield, by decreasing reactivity of product furan relative to crotonaldehyde, thus minimizing the secondary oxidation of furan to maleic anhydride. The highest efficiency of caesium is associated with its high basicity, while the active catalyst species responsible for the furan formation is acidic in nature. The replacement of Mo by V or W gave rise to decreased activity, in contrast to other oxidations on the same catalyst. The unique character of crotonaldehyde oxidation is discussed.

It is known that acrylaldehyde and methacrylaldehyde are oxidized to acrylic acid and methacrylic acid, respectively, over V_2O_5- or MoO_3-based catalysts, while crotonaldehyde is oxidized to furan, instead of crotonic acid on the same catalyst.[1] Recently, it was found that heteropoly compounds such as 12-molybdophosphoric acid are effective as catalyst for the furan formation from crotonaldehyde and that an acidic caesium salt of 12-molybdophosphoric acid gives a higher yield than the 12-molybdophosphoric acid.[2]

It would be of interest to see how the yield of furan is affected by modification of the 12-molybdophosphoric acid catalyst. The present paper deals with the effect of partial relpacement of the catalyst protons by various cations and that of the catalyst molybdenum by vanadium or tungsten on the catalytic performance.

Experimental

Catalysts. Two series of supported heteropoly compounds were used: (i) The first series of catalysts are represented by a general equation of $M_{x/n}H_{3-x}PMo_{12}O_{40}$ where M represent an n valent cation and $0\leqslant x\leqslant 3$ is the extent of proton replacement. The cation M was introduced by adding carbonate (alkali, Ag, and Ba), acetate (Mn, Co, Cu, and Ni), or nitrate (Fe and Bi) to aqueous solution of $H_3PMo_{12}O_{40}$ followed by deposition on pumice by evaporation to dryness. Other procedures were the same as previously reported.[2] (ii) The second series of catalysts are $H_3PMo_6W_6O_{40}$, $H_4PMo_{11}VO_{40}$, and $H_5PMo_{10}V_2O_{40}$. The $H_3PMo_6W_6O_{40}$ catalyst was prepared by mixing aqueous solutions of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ (Kanto Chemical Co. Inc.). $H_5PMo_{10}V_2O_{40}$ was synthesized following a procedure reported by Tsigdinos.[3] The $H_4PMo_{11}VO_{40}$ catalyst was prepared by mixing aqueous solutions of $H_5PMo_{10}V_2O_{40}$ and $H_3PMo_{12}O_{40}$. Other procedures were the same as those for the series (i).

Reaction Procedures. The vapor-phase oxidation of crotonaldehyde was carried out in an ordinary continuous-flow system. The reactor and the experimental procedures were the same as those employed in the preceding work.[2]

Results

Effect of Cs+. The oxidation of crotonaldehyde was carried out over a series of $Cs_xH_{3-x}PMo_{12}O_{40}$ catalysts with x=0, 0.5, 1.0, 1.5, and 2.0 (amount of catalyst used=20 g), using a fixed concentration of reaction mixture: $C_4H_6O/O_2/H_2O/N_2=1.66/6.6/7.6/84.1$ mol% and a total flow rate of 1.0 l/min. Variation of furan yield with reaction temperature are shown for the Cs-exchanged catalysts in Fig. 1. The catalytic activity to give furan clearly decreases with increase in the caesium content at a fixed temperature, while the maximum yield of furan attained at a different temperatures increases with increase in caesium content up to $x=1.0$, and remains constant at about 40 mol% in the range of $x=1$ to 2.

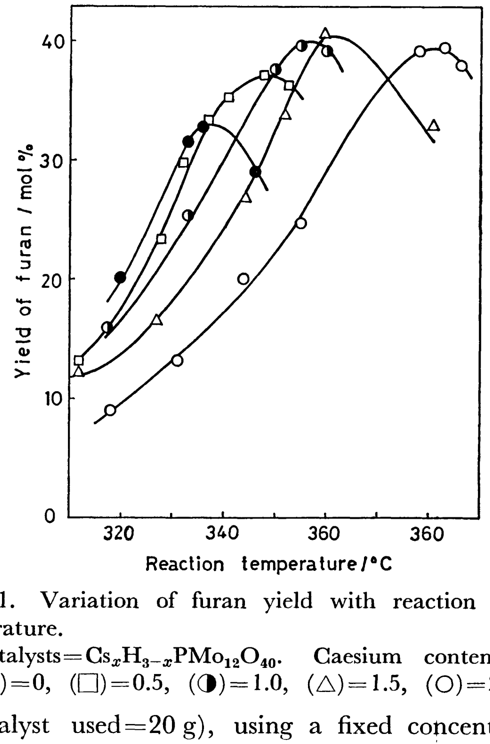


Fig. 1. Variation of furan yield with reaction temperature.
Catalysts=$Cs_xH_{3-x}PMo_{12}O_{40}$. Caesium content($x$): (●)=0, (□)=0.5, (◐)=1.0, (△)=1.5, (○)=2.0.

The yield of furan is plotted as a function of the overall conversion of crotonaldehyde in Fig. 2. The furan yield increases with increase in the conversion and passes a maximum. The conversion of crotonaldehyde to give the maximum yield of furan increases from 83 to 92% with the addition of caesium up to $x=1.0$ and remains almost constant at 92 to 95% in the range of $X=1.0$ to 2.0. As demonstrated in the preceding papers the product furan is consecutively oxidized to maleic anhydride on the heteropoly-acid catalyst so that the maximum yield of furan is determined by reactivity of furan relative to crotonaldehyde

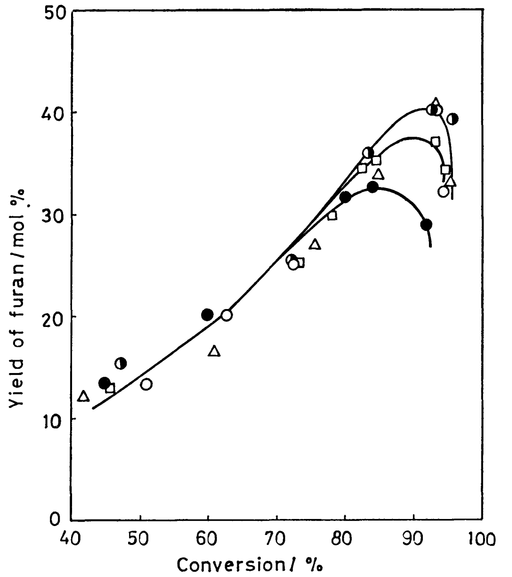


Fig. 2. Yield of furan as a function of the overall conversion of crotonaldehyde.
Catalysts = $Cs_xH_{3-x}PMo_{12}O_{40}$. Casesium content($x$): (●) = 0, (□) = 0.5, (◑) = 1.0, (△) = 1.5, (○) = 2.0.

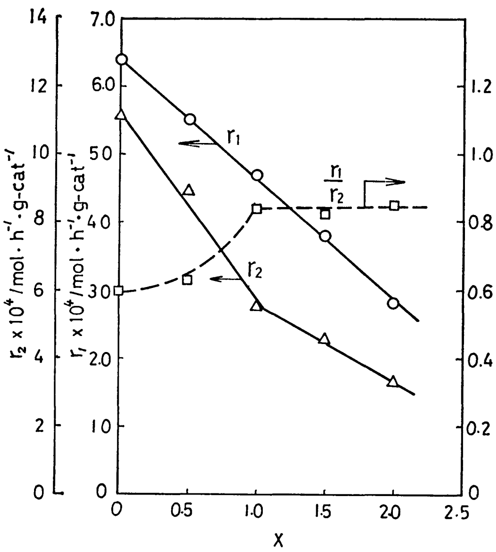


Fig. 3. Effect of the caesium content on the rate of furan formation and that of furan consumption. r_1 = Rate of furan formation from crotonaldehyde, r_2 = rate of furan consumption, catalysts = $Cs_xH_{3-x}PMo_{12}O_{40}$.

on the catalyst. The observed increase in the maximum yield of furan suggests that the reactivity ratio of furan to crotonaldehyde decreases with the caesium addition up to $x = 1.0$.

In order to examine the relative reactivity of furan, initial rate of furan formation from crotonaldehyde (concentration = 1.66 mol%), r_1, and that of furan consumption (concentration = 0.96 mol%), r_2, were determined at 330 °C over the Cs-exchanged catalysts. The results are shown in Fig. 3. The ratio r_1/r_2 really increases with x up to $x = 1.0$ and remains constant in the range of $x = 1.0$ to 2.0 in agreement with the above suggestion.

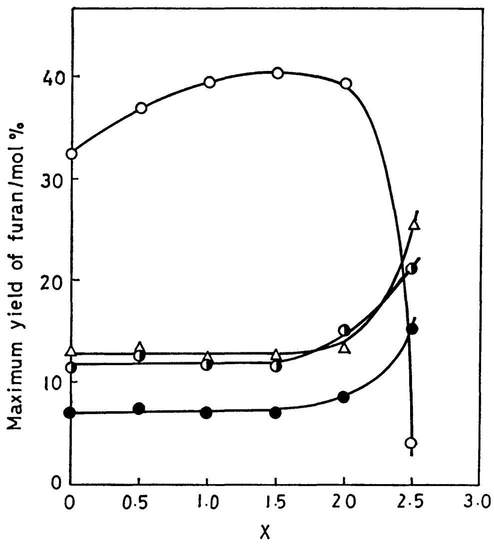


Fig. 4. Effect of caesium content on the yields of furan, maleic anhydride, CO, and CO_2 at a conversion of 85 to 90%.
(○) = Furan, (△) = maleic anhydride, (●) = 1/4 CO, (◑) = 1/4 CO_2, catalysts = $Cs_xH_{3-x}PMo_{12}O_{40}$.

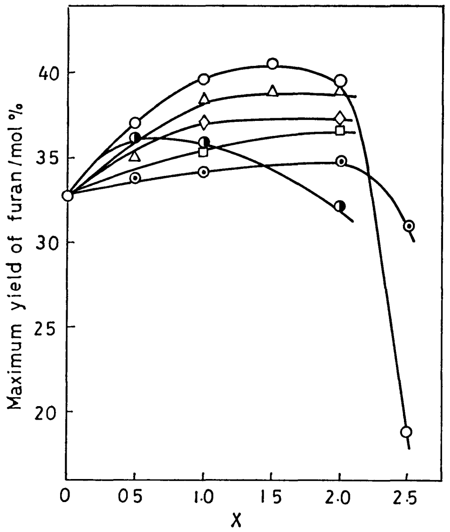


Fig. 5. Effect of the content of univalent cations on the maximum yield of furan.
Catalysts = $M_xH_{3-x}PMo_{12}O_{40}$, (○) = Cs^+, (◇) = Rb^+, (□) = K^+, (◎) = Na^+, (◑) = Li^+, (△) = NH_4^+.

The yield of furan, maleic anhydride, CO, and CO_2 obtained at a conversion of 85 to 90% are shown in Fig. 4 as a function of x. It is seen that the product distribution is much less affected by the caesium content up to $x = 2.0$ than in the range $x > 2$. It is clear that the x value should be kept below 2 to give higher yield of furan.

Effect of Univalent Cations. Analogous effect of other univalent cations was examined with Li^+, Na^+, K^+, Rb^+, and NH_4^+. Figure 5 shows variation of the maximum yield of furan as a function of x. The maximum yield was mostly attained at the aldehyde conversion of about 90 to 95%. It is seen that the maximum yield of furan generally increases with x

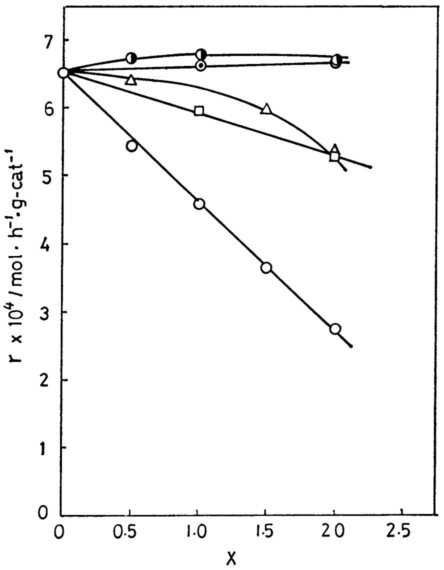


Fig. 6. Effect of the content of univalent cations on the rate of furan formation.
Temperature=330 °C. Catalysts=$M_xH_{3-x}PMo_{12}O_{40}$, (○)=Cs^+, (□)=K^+, (⊙)=Na^+, (◑)=Li^+, (△)=NH_4^+.

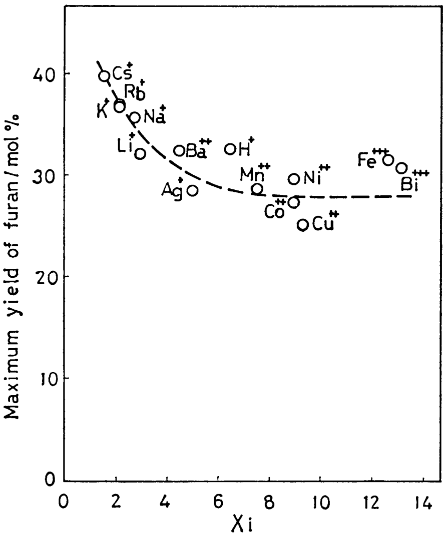


Fig. 7. Maximum yield of furan obtained with the $M_{2/n}HPMo_{12}O_{40}$ catalysts as a function of the electronegativity of metal cation, X_i.

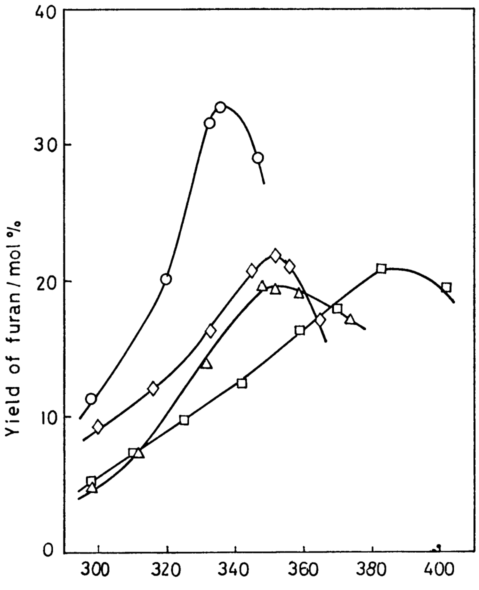


Fig. 8. Yield of furan obtained on $H_3PMo_{12}O_{40}$, $H_3PMo_6W_6O_{40}$, $H_4PMo_{11}VO_{40}$, and $H_5PMo_{10}V_2O_{40}$ catalysts.
(○)=$H_3PMo_{12}O_{40}$, (△)=$H_3PMo_6W_6O_{40}$, (◇)=$H_4PMo_{11}VO_{40}$, (□)=$H_5PMo_{10}V_2O_{40}$.

value up to respective maximum, while the yield of furan at the maximum decreases in the order of $Cs^+ > NH_4^+ > Rb^+ > K^+ > Na^+$. It is clear that caesium is the most effective in improving the furan yield.

Thus, the effect of alkali substitution on the initial rate of furan formation was examined at 330 °C. As shown in Fig. 6 as a function of x value, the inhibitive effect of cation is largest with Cs^+, less marked with K^+ and NH_4^+, and nondetectable with Li^+ and Na^+. The large inhibitive effect of Cs^+ seems to be associated with the favorable results on Cs-catalyst.

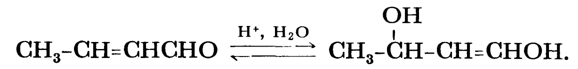
Effect of Other Cations. Analogous effect of other cations was studied with Fe^{3+}, Bi^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Ba^{2+}, and Ag^+. No clear improvement in the oxidation activity was observed by the addition of these cations up to $x=2$. Summarizing the effect of metal cations examined above, imporvement in furan yield is generally made by more basic elements. Thus, the maximum yield of furan obtained on the series (i) catalysts with $x=2$ are plotted against the electronegativity of metal cation, X_i, which can be regarded a parameter of acidity of cation. Although the reaction temperature to give the maximum yields were different from each other, it is apparent from Fig. 7 that the maximum furan yield decreases with increase in the acidity of metal cation added, in agreement with the above generalization.

Replacement of Mo Atom in $H_3PMo_{12}O_{40}$ by W or V. The oxidation of crotonaldehyde was carried out on the series (ii) catalysts under the same reaction conditions as adopted for the series (i) catalysts. The results obtained on $H_3PMo_6W_6O_{40}$, $H_4PMo_{11}VO_{40}$, and $H_5PMo_{10}V_2O_{40}$ catalysts are compared with those of $H_3PMo_{12}O_{40}$ catalyst in Fig. 8. It is clear that the replacement of Mo atom of $H_3PMo_{12}O_{40}$ by W or V results in decreases in the oxidation activity as well as in the maximum yield of furan.

Discussion

As demonstrated by the above results, the attainable furan yield in the oxidation of crotonaldehyde on the heteropoly acid catalysts is improved by adding basic element to the catalyst. Since complete replacement of the acidic proton results in loss of the catalytic activity, the improvement is likely caused by a partial neutralization of the acid. The result shown in Fig. 3 clearly demonstrated that the high furan yield is realized by increase in stability or decrease in reactivity of furan relative to crotonaldehyde on the catalyst surface. The reactivity decrease by the incorporation of caesium ion is associated with a decrease in acidity,[4] in conformity with the partial neutralization suggested above. The results shown in Fig. 7 suggest that the highest yield obtained with the Cs–HPA catalyst is ascribed to the highest basicity of caesium. Indeed other elements of less basicity are less efficient in reducing reactivity of crotonaldehyde as shown in Fig. 6.

On the other hand, the reactivity decrease caused by the incorporation of basic element indicates an active site acidic in nature. It is reported in the preceding paper that the rate of furan formation increases with partial pressure of water vapor.[2] In connection with this, it is known that enolization of crotonaldehyde requires water, *i.e.*[5]



$$CH_3\text{-}CH{=}CHCHO \overset{H^+,\ H_2O}{\rightleftharpoons} CH_3\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH{=}CHOH.$$

Since the trans-form predominates in crotonaldehyde, it is required to take a cis-form before cyclization to furan. The water-enhanced enolization would provide a chance for cyclization. Thus the water-promoted furan formation can be understood in terms of acid catalysis as suggested by the inhibitive effect of caesium. The enhancement of enolization would be another role of water in addition to the enhancement of furan desorption as suggested in the previous paper.[2]

The effect of caesium addition to heteropoly acid catalyst is also known with oxidation of methacrylaldehyde,[4] isobutyraldehyde,[6] butadiene,[7] and ethyl methyl ketone.[4] It is commonly observed that the catalytic activity increases with the caesium addition up to $x=2$, in a striking contrast to the present result. It is accordingly suggested that the nature of present oxidation of crotonaldehyde is quite different from others. Indeed, the oxidation of crotonaldehyde is unique in the kinetic behavior. The rate of furan formation is nearly zero order with respect to oxygen pressure,[2] whereas the rates of other oxidations are 0.5 to 1.0 order in oxygen.[4] This would be reasonable in view of the difference in the oxidation reaction to be undertaken. Methacryladehyde is oxidized to methacrylic acid, while crotonaldehyde is oxidized to furan, on the same catalyst. Since no furan formation was found in the oxidation of crotonic acid on the heteropoly-acid catalyst, crotonic acid cannot be the intermediate from crotonaldehyde to furan. Thus it is clear that the oxidation of crotonaldehyde is completely different from that of methacrylaldehyde although they are structural isomers. This difference in the nature of oxidation reaction should give rise to difference in the type of activation of reactant molecule.[4]

The last results shown in Fig. 8 may be understood on the ground of above concept. Partial replacement of Mo in $H_3PMo_{12}O_{40}$ with V is reported to enhance the oxidation of methacrylaldehyde[8] or isobutyraldehyde,[9] while it results in decrease in the activity to form furan from crotonaldehyde. It is likely that the replacement with V increases oxidizing activity which is essential for those oxidations, while modifies the acidic nature which is essential for the furan formation.

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