September, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **53**, *2647—2650 (1980)*

Production of Furan by Vapor-phase Oxidation of Crotonaldehyde Using Heteropoly Compounds as Catalysts

Mamoru Ai,* Tian-hsi Tsai, and Atsumu Ozaki
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Nagatsuta, Midori-ku, Yokohama 227

(Received February 19, 1980)

The synthesis of furan by direct vapor-phase oxidation of crotonaldehyde has been studied. It was found that heteropoly compounds such as 12-molybdophosphoric acid are more effective than the mixed oxide (MoO_3–P_2O_5, P/Mo=1/12) as catalyst for furan formation, and that the cesium salt of 12-molybdophosphoric acid with a Cs/Mo atomic ratio of 1/12 is more effective than the 12-molybdophosphoric acid catalyst. The rate of furan formation increases with increase in steam concentration in the feed, but is nearly independent of oxygen and crotonaldehyde concentrations. The yield of furan increases by decreasing the crotonaldehyde concentration, attaining 60 mol% at a concentration of 0.17 vol% in the feed. The conversion of crotonaldehyde at maximum yield is 90—95%.

Furan is a raw material for tetrahydrofuran which is in great demand as a solvent and a starting material for polymer compounds. Tetrahydrofuran has been manufactured by three methods: the furfural process, hydrolysis of 1,4-dichloro-2-butene, and hydrogenation of maleic anhydride. Attempts were also made to obtain furan by direct oxidation of butadiene.[1] Several reports have appeared on the oxidation of crotonaldehyde, but they deal exclusively with the formation of maleic anhydride.[2-5]

One of us (M.A.) reported that furan is an intermediate in the oxidation of butene, butadiene, or crotonaldehyde to form maleic anhydride,[6] and found that the MoO_3–P_2O_5 (P/Mo atomic ratio=*ca.* 1/10) catalyst is effective for furan synthesis from butadiene or crotonaldehyde.[7,8] The effects of reaction variables on the yield of furan were studied using the MoO_3–P_2O_5 catalysts, where the best result for furan yield is 30—35 mol % in the oxidation of crotonaldehyde.[8]

Recently, heteropoly compounds were found to be effective for furan formation from butadiene,[9] suggesting that the heteropoly compounds are also effective for the oxidation of crotonaldehyde to furan.

In this study, we have directed our attention to furan formation in the oxidation of crotonaldehyde and attempted to clarify the effects of catalyst and reaction variables, since no detailed information is available on the oxidation reaction.

Experimental

Catalysts. The following three catalysts were used. (A) Heteropoly acid (HPA) catalyst: 136 g of 12-molybdophosphoric acid (Kanto Chemical Co. Inc.) was dissolved in water and 0.50 l (*ca.* 190 g) of 10—20 mesh pumice from volcanic rocks was mixed with the solution, the mixture then being evaporated with vigorous stirring below 200 °C. (B) MoO_3–P_2O_5 catalyst: 80 g of $(NH_4)_6Mo_7O_{24}\cdot 2H_2O$ and 4.6 g of 85 wt% H_3PO_4 were dissolved in hot water (P/Mo atomic ratio=1/12), and 0.30 l of the pumice was added: the mixture was then evaporated. (C) Cs-HPA catalyst: 9.75 g of Cs_2CO_3 was added to the 12-molybdophosphoric acid solution (Cs/Mo atomic ratio=1/12), the subsequent procedure being the same as that for (A). All the catalysts were calcined at 380 °C for 4—5 h in a stream of oxygen. The surface areas measured by the BET method using nitrogen at −196 °C, were (A) 2.1, (B) 9.5, and (C) 3.4 m^2/g.

Reaction Procedures. Oxidation of crotonaldehyde was carried out in the conventional continuous-flow system under atmospheric pressure. The reactor, made of a steel tube lined with aluminum, length 50 cm, i.d. 1.8 cm, was mounted vertically and immersed in a molten lead bath. The oxygen–nitrogen mixed gas was fed from the top of the reactor, liquid crotonaldehyde and water being introduced into the preheater section by means of two injection syringe pumps (micro feeders). The total flow rate was kept constant at 1.0 l/min. The amount of catalyst used was 20 g and the concentration of crotonaldehyde, oxygen, steam, and nitrogen 1.66, 6.6, 7.6, and 84.1 vol%, respectively. The effluent gas from the reactor was led successively into four chilled water-scrubbers in order to recover the water soluble compounds. The contents (*ca.* 300 ml) of the water-scrubbers were collected every 1 h. Maleic anhydride was analyzed by titration with 0.10 mol dm^{-3} NaOH, and the other compounds by gas chromatography. The inlet and exit gases were intermittently analyzed. In order to measure the catalytic activity in stationary state, the data were taken more than 7 h after the start of each run.

Results

Comparison of Performance of Catalysts. Since the Cs–HPA catalyst gives a good yield of furan in the oxidation of butadiene,[9] the actions of the HPA, MoO_3–P_2O_5, and Cs–HPA catalysts in the oxidation of crotonaldehyde were examined at different temperatures. The results are summarized in Fig. 1.

The heteropoly compound, HPA catalyst, is effective for furan formation to a greater extent than the mixed oxide, the MoO_3–P_2O_5 catalyst. Addition of a small amount of Cs^+ to the heteropoly acid promotes furan formation. The results are in line with those obtained in the oxidation of butadiene to give furan.[9]

Since a good result is obtained with the Cs–HPA catalyst, the effects of reaction variable on the reaction rates and the furan yield were studied using only the Cs–HPA catalyst.

Effect of Temperature on the Reaction Products. The main products were furan, maleic anhydride, CO, CO_2, and unidentifiable polymer compounds. The amounts of other products were negligibly small. The yields of the main products are plotted as a function

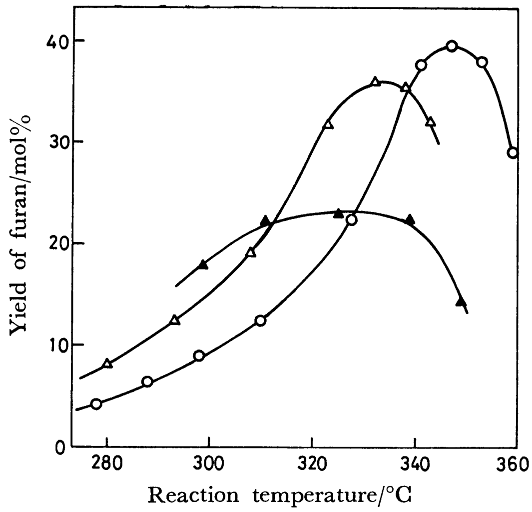
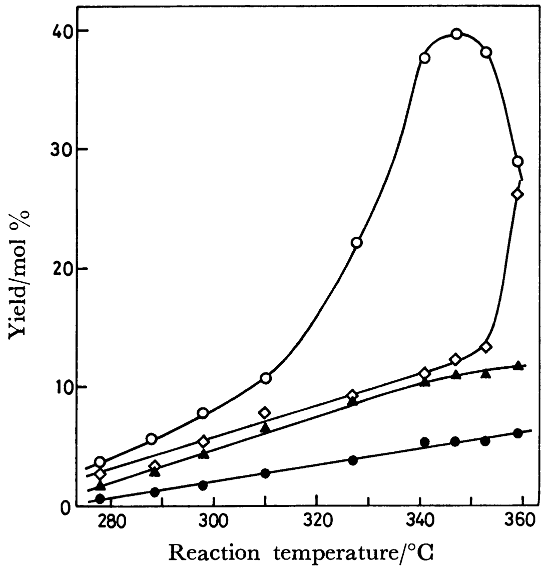


Fig. 1. Comparison of the performances of the catalysts.
Catalyst: (△)=HPA, (▲)=MoO_3-P_2O_5, (○)=Cs-HPA.



Fif. 2. Product distribution in the oxidation of crotonaldehyde over the Cs-HPA catalyst.
(○)=furan, (◇)=maleic anhydride, (●)=1/4 CO, (▲)=1/4 CO_2.

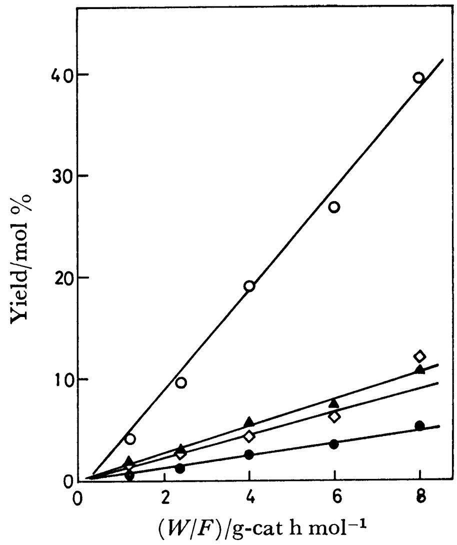


Fig. 3. Yields of products as a function of the contact time (W/F).
Temperature=346 °C, (○)=furan, (◇)=maleic anhydride, (●)=1/4 CO, (▲)=1/4 CO_2.

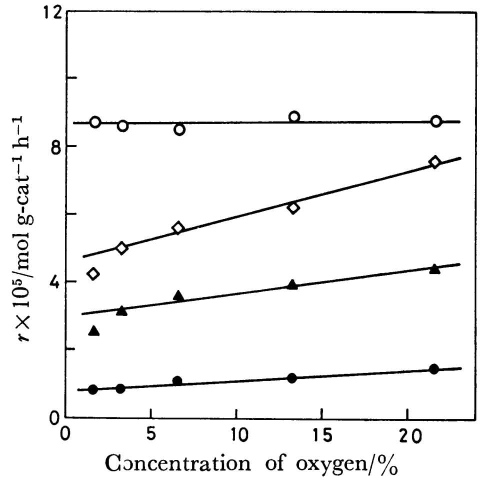


Fig. 4. Effect of oxygen concentration on the reaction rates.
Temperature=278 °C, (○)=furan, (◇)=maleic anhydride, (●)=1/4 CO, (▲)=1/4 CO_2.

of the raction temperature in Fig. 2.

Below 310 °C, the yield of each product increases in proportion to temperature rise, indicating that the products are formed competitively but not consecutively. However, at *ca.* 347 °C, the yield of furan attains a maximum value of 40 mol % when the conversion is estimated to be *ca.* 90—95%. The yield decreases above this temperature accompanied by a sharp increase in the yield of maleic anhydride. The results suggest that maleic anhydride is formed also by the oxidation of the produced furan. The yield of maleic anhydride attains *ca.* 55 mol% at 98—100% conversion

Effect of Contact-time on the Yields of Products. The change in the yields of products with the progress of reaction was studied at 346 °C by changing the amounts of catalyst from 3 to 20 g (Fig. 3). Furan, maleic anhydride, CO, and CO_2 are produced in line with the results shown in Fig. 2, suggesting zero order dependence on the crotonaldehyde concentration.

Effect of Oxygen Concentration on the Reaction Rates. The reaction was carried out by changing the oxygen concentration in the feed gas from 1.6 to 21.6 vol%. Following the principle of the differential reactor, the conversion was held at a low level. The rates of furan, maleic anhydride, CO, and CO_2 formation measured at 278 °C are plotted as a function of oxygen concentration in Fig. 4.

The rate of furan formation is independent of oxygen concentration, the rates of maleic anhydride, CO, and CO_2 formation increasing slightly with increase in the oxygen concentration.

Effect of Crotonaldehyde Concentration on the Reaction Rates. The concentration of crotonaldehyde was varied in the range 0.34—1.66 vol%. The initial rates of formation for the main products are shown in Fig. 5. All the rates increases slightly with increase in the crotonaldehyde concentration.

Effect of Crotonaldehyde Concentration on the Furan Yield. The yield of furan was measured at five different crotonaldehyde concentrations at various temperatures. The results are shown in Fig. 6. Since the reaction order with respect to the crotonaldehyde concentration is very low (Fig. 5), it is reasonable to assume that the higher the initial crotonaldehyde concentration, the higher the temperature required to achieve sufficient conversion. The maximum yield of furan decreases with increase in the crotonaldehyde concentration. The yield of furan attains 60 mol% when the crotonaldehyde concentration is very low (0.17 vol%), becoming 40 mol% at a 1.66 vol% concentration.

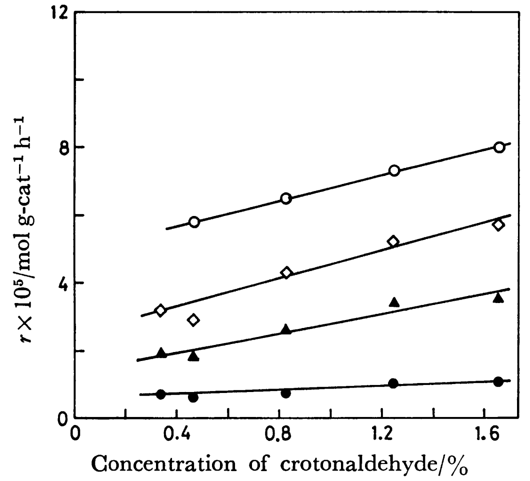


Fig. 5. Effect of crotonaldehyde concentration on the reaction rates.
Temperature=278 °C, (○)=furan, (◇)=maleic anhydride, (●)=1/4 CO, (▲)=1/4 CO_2.

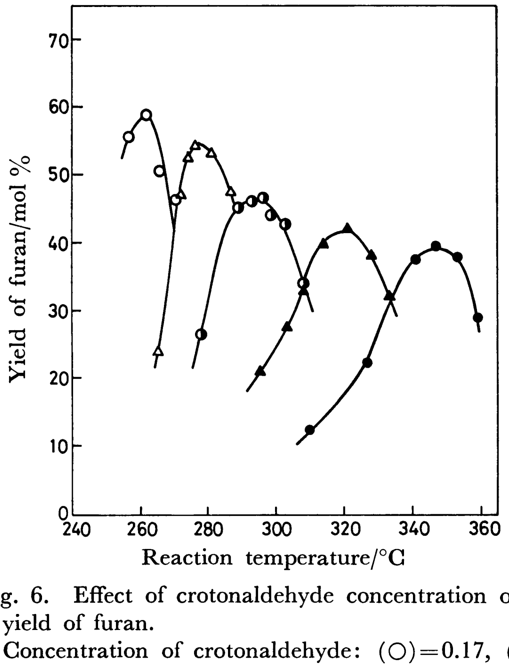


Fig. 6. Effect of crotonaldehyde concentration on the yield of furan.
Concentration of crotonaldehyde: (○)=0.17, (△)=0.25, (◑)=0.46, (▲)=0.83, (●)=1.66% in the feed.

Effect of Steam Concentration on the Reaction Rates. The effect of steam concentration on the initial rate for each product is shown in Fig. 7. The rates increase almost linearly with steam concentration, the slopes becoming more gentle at higher steam concentrations. The results are in line with those obtained in the oxidation of olefins as well as of furan over 12-molybdophosphoric acid catalyst.[10]

Effect of Steam on the Yield of Furan. The effect of steam concentration on the yield of furan was also examined. The presence of steam increases the yield of furan as well as the catalytic activity. (Fig. 8).

Discussion

The Cs–HPA catalyst as well as the HPA and MoO_3–P_2O_5 catalysts are acidic. Thus, they are active for

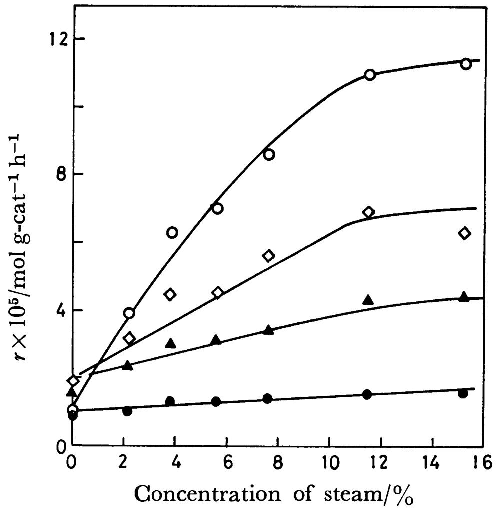


Fig. 7. Effect of steam concentration on the reaction rates.
Temperature=278 °C, (○)=furan, (◇)=maleic anhydride, (●)=1/4 CO, (▲)=1/4 CO_2.

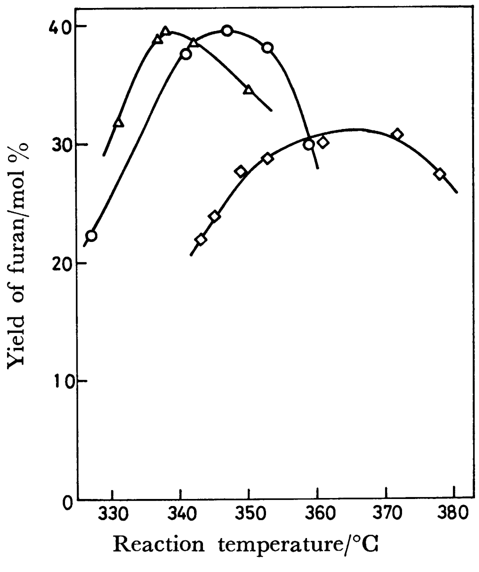


Fig. 8. Effect of steam on the yield of furan.
Concentration of steam: (◇)=3.8, (○)=7.6, (△)=15.1% in the feed.

oxidation of such basic compounds as butadiene, crotonaldehyde and furan but inactive for acidic compounds such as maleic anhydride. Their selectivity to maleic anhydride from the basic reactants at high conversion attains *ca.* 50—60 mol%.

Since furan is an intermediate product, the yield is affected by two factors:[6,11] (i) relative reactivity of furan to crotonaldehyde, and (ii) affinity of the catalyst for furan; this indicates that the stronger the furan adsorption, the larger the portion of the adsorbed furan species which goes to the next oxidation, without being desorbed to the gas phase.

The yield of furan attains a maximum at a 90—95% crotonaldehyde conversion, the catalysts being markedly more active for the oxidation of crotonaldehyde than that of furan.

On the other hand, the results indicate that the reaction rate markedly increases with increase in the steam concentration but is almost independent of the concentration of both oxygen and crotonaldehyde. This suggests that the reaction is mainly restricted by the desorption of oxidation products to gas phase, in contrast with the oxidation of butadiene which is of first order with respect to oxygen concentration.[10] The effect of steam addition on the yield of furan can be explained by assuming that the steam acts to remove the adsorbed furan.[10]

The effect of cesium addition to the heteropoly acid actalyst can also be understood on the same assumption. The addition of a basic compound such as cesium ion reduces the acidic property of catalyst and the affinity for furan, facilitating the desorption of adsorbed furan and increasing the yield of furan.

Since the character of mixed oxide has not yet been defined, it is difficult to understand the difference in catalytic behavior between the heteropoly compounds and the MoO_3–P_2O_5 mixed oxide catalyst.

Conclusion

The cesium salt of 12-molybdophosphoric acid with a Cs/Mo atomic ratio of 1/12 is an excellent catalyst for furan production by direct oxidation of crotonaldehyde as in the case of furan formation from butadiene. Reaction conditions favorable for furan formation are higher steam concentration and lower crotonaldehyde concentration. The maximum furan yield is attained at a 90—95% crotonaldehyde conversion.

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