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Formation of Glyoxylic Acid by Oxidative Dehydrogenation of Glycolic Acid

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Iron phosphates with a P/Fe atomic ratio of 1.2 were found to be effective as catalysts for a vapor-phase oxidative dehydrogenation of glycolic acid to glyoxylic acid. The effects of the reaction variables on the conversion and selectivity were studied. The optimum reaction temperature was around 240 °C and the optimum feed rate of oxygen was in the range of 10 to 25 $\text{mmol}\,\text{h}^{-1}$ when the feed rate of glycolic acid was 12.3 $\text{mmol}\,\text{h}^{-1}$. The reaction was not affected by a variation in the feed rate of water vapor in the range of 86 to 480 $\text{mmol}\,\text{h}^{-1}$. The selectivity to glyoxylic acid remained unchanged at 74 mol% with an increase in the conversion of glycolic acid up to 70%; the highest yield of glyoxylic acid was 56.5 mol% at the conversion of 80%.

In the preceding studies,[1—3] it was found that iron phosphate catalysts show a high selectivity in the oxidative dehydrogenation of compounds in which the carbon atom at the α-position of an electron-attracting group (X), such as –COOH, –CHO, or CN, is tertiary, for example, isobutyric acid, isobutyraldehyde, and isobutyronitrile,

$$\text{R–CH}_2\text{–CHR}'\text{–X} + 0.5\ \text{O}_2 \rightarrow \text{R–CH=CR}'\text{–X} + \text{H}_2\text{O},$$

while they are inactive for oxygen insertion reactions.

Recently, it was also found that iron phosphate catalysts show high selectivity in both the oxidative dehydrogenation of lactic acid to pyruvic acid and the oxidative decarboxy-condensation of pyruvic acid to citraconic anhydride (3-methyl-2,5-furanfione) [$C_5H_4O_3$].[4—6]

$$\text{CH}_3\text{–CH(OH)–COOH} + 0.5\ \text{O}_2 \rightarrow \text{CH}_3\text{–CO–COOH} + \text{H}_2\text{O}$$

$$2\text{CH}_3\text{–CO–COOH} + 0.5\ \text{O}_2 \rightarrow \text{C}_5\text{H}_4\text{O}_3 + \text{CO}_2 + 2\text{H}_2\text{O}$$

These findings led us to study the catalytic performance of iron phosphates in the oxidative dehydrogenation of glycolic acid to glyoxylic acid,

$$\text{HOCH}_2\text{–COOH} + 0.5\ \text{O}_2 \rightarrow \text{OHC–COOH} + \text{H}_2\text{O}$$

Glyoxylic acid is a raw material of various chemicals. It is generally produced by the enzymatic or nitric acid oxidation of glyoxal, or the electrolytic reduction of oxalic acid. It is also known that alkyl esters of glyoxylic acid are obtained by a vapor-phase oxidation of the corresponding alkyl esters of glycolic acid.[7] The yield of the ester reached 69 mol% at a conversion of 94%. However, it has still seemed difficult to obtain glyoxylic acid directly from glycolic acid in a vapor-phase process.

Experimental

1. Catalysts. Iron phosphate catalysts with a P/Fe atomic ratio of 1.2 were prepared according to the "Method C" procedures described in previous studies.[8] Iron(III) nitrate [$\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}$] (122 g, 0.3 mol) was dissolved in about 5 dm^3 of water, and a dilute ammonia solution was added to precipitate iron(III) hydroxide gel. The precipitate was filtered and the obtained wet gel was mixed with 41.5 g of 85% orthophosphoric acid [H_3PO_4]. The mixture was then slowly boiled for 1 to 2 h, yielding a slightly brownish-white precipitate. Excess water was evaporated by means of a hot air current; the obtained paste-like compound was dried in an oven at 120 °C for 6 h. The resulting solid was broken up and sieved to a 7—20 mesh size. Finally, it was calcined in a stream of air at 450 °C for 4 h. From the XRD study, the catalyst was found to consist of tridymite-type iron phosphate containing a small amount of quartz-type iron phosphate.

A V–P oxide catalyst with a P/V atomic ratio of 1.06 consisting of divanadium(IV) dioxide diphosphate [$\text{V}_2\text{O}_2(\text{P}_2\text{O}_7)$] was prepared according to a patent.[9] $H_3PMo_{12}O_{40}$ and $H_5PMo_{10}V_2O_{40}$ catalysts were prepared by supporting molybdovanadophosphoric acid and molybdovanadophosphoric acid, respectively, on an equal weight of natural pumice between 10 to 20 in mesh size.[10]

2. Reaction Procedures. The vapor-phase oxidation of glycolic acid was done with a continuous-flow system at atmospheric pressure. The reactor was made of a stainless-steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. The catalyst was placed near to the bottom of the reactor and porcelain cylinders (3 mm long and 1.5 mm i.d./3.0 mm o.d.) were placed both under and above the catalyst bed. Air, or a mixture of nitrogen and oxygen, was fed in from the top of the reactor; an aqueous solution containing 100 g of glycolic acid in 1000 ml was introduced into the preheating section of the reactor with a syringe pump. Unless otherwise indicated, the feed rates of glycolic acid, oxygen, water, and nitrogen were 12.3, 10.0, 480, and 500 mmol h^{-1}, respectively, and the reaction temperature was 240 °C. The amount of catalyst used was 10 g; the contact time was 2.5 s. The extent of the reaction was varied by changing the amount of catalyst used from 0.7 to 20 g, while fixing the feed rates. The effluent gas from the reactor was led successively into four chilled scrubbers to recover the water-soluble compounds. The products were analyzed by GC and LC. The definitions of the contact time, conversion, yield, and selectivity were the same as those in a previous study.[11]

Results

1. Comparison of the Performances of Metal Phosphate Catalysts. Since the reaction is an "acid-to-acid type" transformation, it is predictable that the catalysts should be acidic.[12] Together with an iron phosphate catalyst, the V–P oxide and heteropoly compound catalysts, which show a good performance in oxidation reactions producing acidic compounds, such as maleic anhydride and methacrylic acid, were tested for the oxidation of glycolic acid. The results are summarized in Table 1. It is clear that the iron phosphate catalyst is much more effective than the V–P oxide and heteropoly compound catalysts.

2. Characteristics of the Reaction. We then attempted to clarify in more detail the characteristic features of the reaction using an iron phosphate catalyst freshly calcined at 450 °C.

2.1. Product Distribution: The reaction was performed under the fixed reaction conditions described in the Experimental section, while changing the contact time from 0.3 to 5.0 s. The main products detected were glyoxylic acid, formaldehyde, formic acid, and carbon oxides. The yields of these products are plotted as a function of the conversion of glycolic acid in Fig. 1. The slope of lines from the origin indicate the selectivities to each product.

The selectivity of glycolic acid to glyoxylic acid remains unchanged at about 74 mol% with an increases in the conversion of glycolic acid up to 70%. With a further increase in the conversion, the yield of glyoxylic acid levels off; the maximum yield is 56.5 mol% at the conversion of 80%. The consecutive decomposition of produced glyoxylic acid is small at the conversion below 70% suggesting that glyoxylic acid is relatively stable under the reaction conditions used. The side reactions are the formation of formaldehyde and formic acid, that is, C–C bond fission by oxygen insertion.

2.2. Effect of the Reaction Temperature: The reaction was performed by changing both the reaction temperature from 200 to 300 °C and the contact time from 0.3 to 5 s, while fixing the feed rates, as described in the Experimental section. The conversions of glycolic acid obtained at different temperatures are plotted in Fig. 2 as a function of the contact time. The results indicate that the rate of the reaction becomes about double as the temperature is raised by 20 °C.

The yield of glyoxylic acid obtained at different temperatures is plotted as a function of the conversion of glycolic acid in Fig. 3. As the temperature is raised, the selectivity to glyoxylic acid decreases, especially at higher conversion regions. However, it should be noted that vaporization of glycolic acid becomes difficult at temperatures below 230 °C, because the boiling point of glycolic acid is high. It is therefore concluded that the optimum temperature is about 240 °C under the reaction conditions used.

2.3. Effect of the Oxygen Feed Rate: The reaction was performed by changing the feed rate of oxygen from 1.5 to 100 mmol h^{-1} and the amount of catalyst used, while fixing the temperature and the feed rates of glycolic acid, water, and nitrogen as described in the Experimental section.

The conversions of glycolic acid obtained at a short contact time of 0.62 s (amount of catalyst used=2.5 g) are plotted as a function of the feed rate of oxygen in Fig. 4. Although the rate of reaction increases along with an increase in the feed

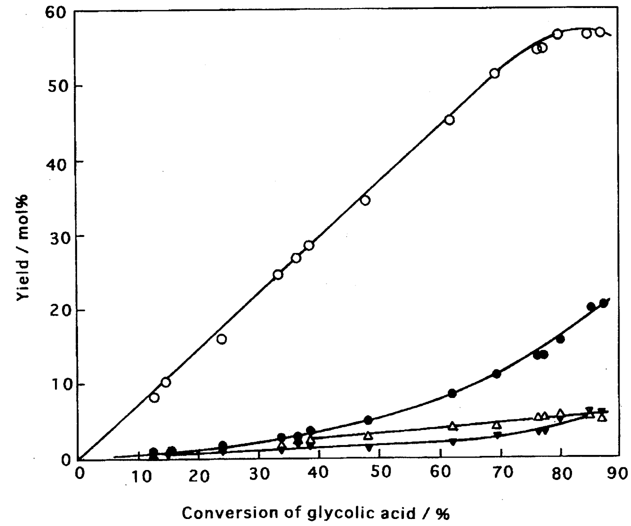

Fig. 1. Yields as a function of the conversion of glycolic acid over iron phosphate. (○) glyoxylic acid; (△) HCHO; (▼) HCOOH; (●) CO_x.

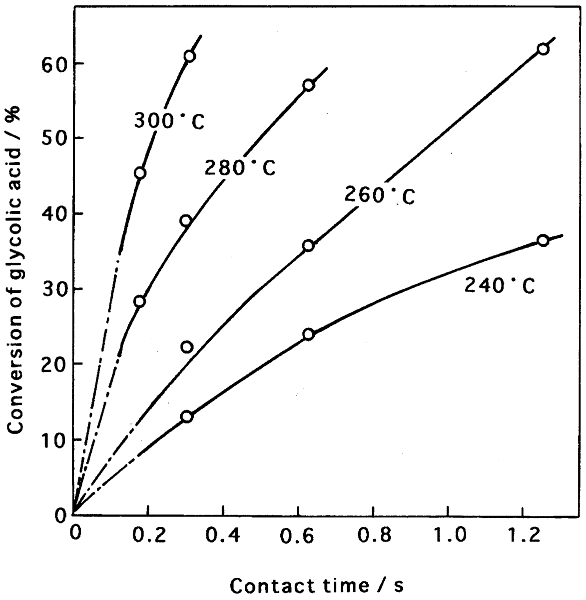

Fig. 2. Effect of the reaction temperature on the rate over iron phosphate.

Table 1. Performances of Metal Phosphate Catalysts

Catalyst	Temp	O_2 feed	Conv.	Yield/mol%				S
	°C	mmol h^{-1}	%	GXAD	HCHO	HCOOH	CO_x	mol%
Fe–P	240	11.3	53.0	40.0	3.9	0.7	7.4	77
	240	12.5	59.0	45.0	4.0	0.9	6.7	76
	240	16.2	70.4	53.8	4.1	1.6	10.7	76
V–P	240	7.5	54.4	15.1	10.0	2.0	15.2	28
	265	7.5	93.7	16.0	30.0	4.5	45.1	18
Mo–P	240	11.0	66.0	16.6	9.1	10.0	32.4	25
	250	11.0	83.7	15.5	10.6	10.9	38.0	19
Mo–V–P	240	10.0	70.5	19.5	2.5	5.7	15.2	27
	270	10.0	86.9	24.4	11.2	11.0	42.1	28

Conv. : conversion of glycolic acid, GXAD: glyoxylic acid, S: selectivity to glyoxylic acid, Fe–P: iron phosphate, V–P: $(VO)_2P_2O_7$, Mo–P: $H_3PMo_{12}O_{40}$, Mo–V–P: $H_5PMo_{10}V_2O_{40}$.

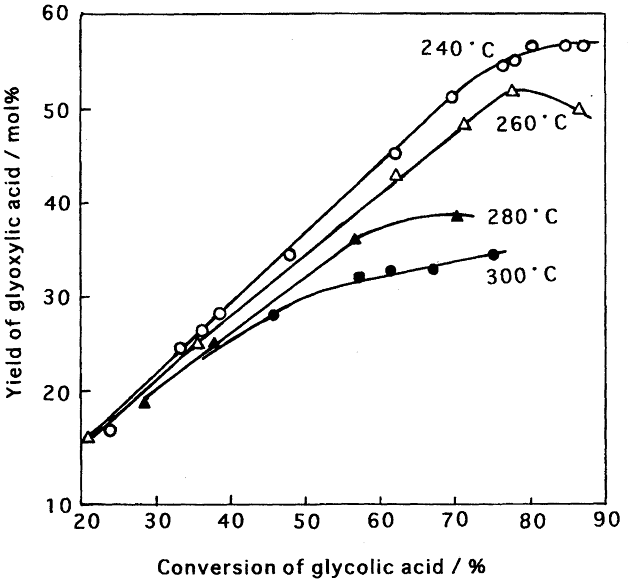

Fig. 3. Effect of the reaction temperature on the yield of glyoxylic acid over iron phosphate.

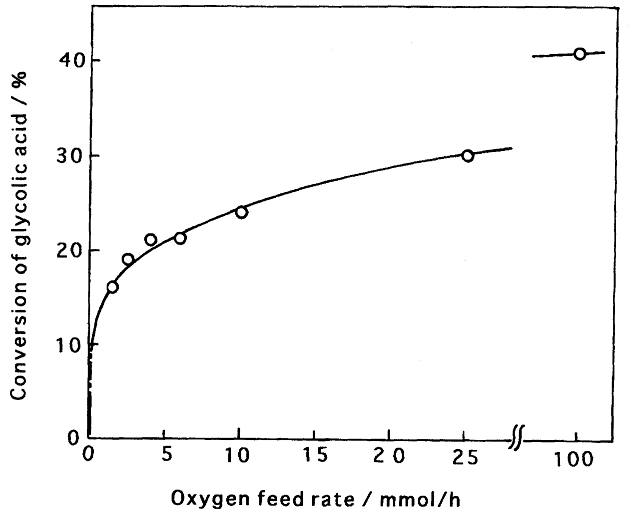

Fig. 4. Effect of the oxygen feed rate on the reaction rate over iron phosphate. The feed rate of glycolic acid is fixed at 12.3 mmol h^{-1}

rate of oxygen, the oxygen dependency is very low, far from first-order dependency.

The yields of glyoxylic acid obtained with different oxygen feed rates and at different contact times are plotted as a function of the conversion of glycolic acid in Fig. 5.

When the conversion is not high, less than 60%, the selectivity to glyoxylic acid is almost independent of the oxygen feed rate. However, with a further increases in the conversion, the selectivity decreases along with an increase in the feed rate of oxygen. It is therefore concluded that the optimum oxygen feed rate is in the range of 10 to 25 mmol h^{-1} under the reaction conditions used.

2.4. Effect of the Water Vapor: It is difficult to charge glycolic acid free from water, because it is a nonvolatile solid. The effects of feed rate of water vapor was studied by changing the concentration of glycolic acid in the aqueous solution introduced into the reactor from about 10 to 40 wt%, while fixing constant the feed rates of both glycolic acid and the sum of water vapor plus nitrogen at 12.3 and 980 mmol h^{-1}, respectively. The results obtained at 250 °C are summarized in Table 2.

It is clear that both the reaction rate and selectivity are independent of the variation in the feed rate of water vapor in the range from 86 to 480 mmol h^{-1}. However, it was observed that vaporization of glycolic acid at 240 °C becomes incomplete as the feed rate of water vapor decreases.

2.5. Stability and Regeneration of the Catalytic Activity: The stability of catalytic activity was checked at 240 °C using a 5 g portion of catalyst (contact time=1.25 s) with an oxygen feed rate of 25 mmol h^{-1}. The variation in the yield of glyoxylic acid is shown in Fig. 6 as a function of the elapsed time-on-stream.

The yield increased a little in the beginning, passed through a broad maximum, and then decreased slowly as the time-on-stream increased. On the other hand, the selectivity to glyoxylic acid remained in the range of 70 to 74

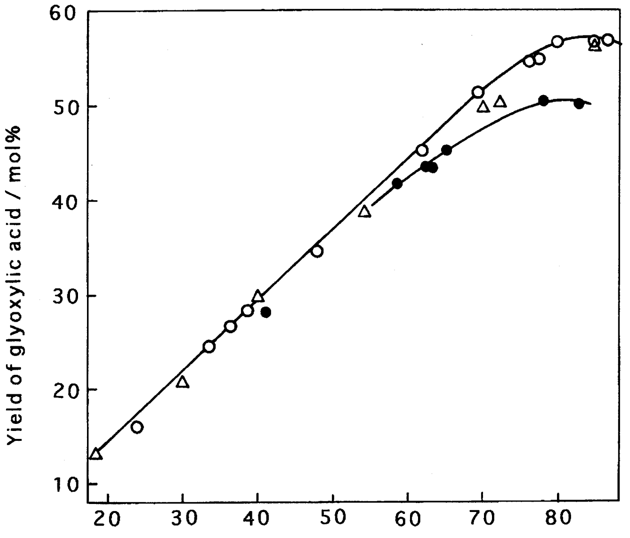

Fig. 5. Effect of the oxygen feed rate on the yield of glyoxylic acid over iron phosphate. Oxygen feed rate (mmol h^{-1}): (○) 10; (△) 25; (●) 100.

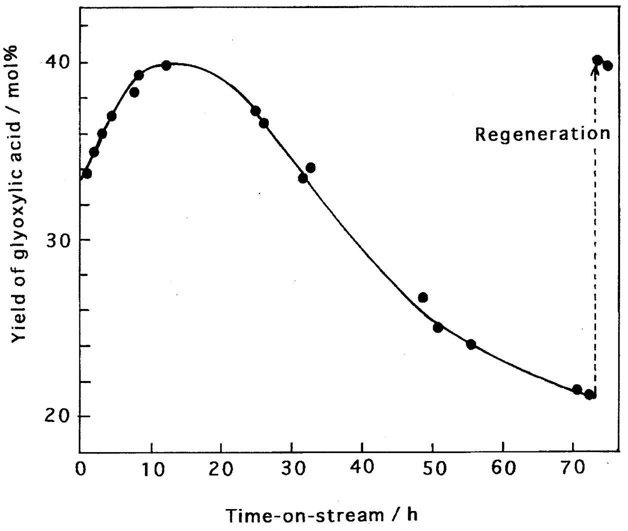

Fig. 6. Stability of catalytic activity of iron phosphate. Temperature=250 °C; contact time=1.25 s. The conditions of catalyst regeneration: temperature=420 °C; feed rate of air=500 mmol h^{-1}; period=4 h.

Table 2. Effect of the Feed Rate of Water Vapor on the Reaction Rate and Selectivity over Iron Phosphate

Contact time	H_2O feed	Conversion	Yield	Selectivity
s	mmol h^{-1}	%	mol%	mol%
	86	21	15	72
0.12	214	22	16	73
	480	22	16	73
	86	62.2	44.6	72
1.25	214	68.9	48.6	71
	480	65.8	46.8	71
	86	83.2	56.5	68
1.89	214	85.0	56.3	66
	480	82.1	56.3	68

Reaction temperature=250°C. Feed rates (mmol h^{-1}): glycolic acid=12.3, oxygen=25, sum of water plus nitrogen=980. Conversion: conversion of glycolic acid, selectivity: selectivity to glyoxylic acid.

mol%.

It was found that, after 10 to 70 h on stream, the catalyst was partially reduced; the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios in the bulk measured by the redox titration method[12] were in the range of 0.25 to 0.29, and that the structure of catalyst was transformed from tridymite-phase to an unknown phase.

Then, air was introduced into the reactor at 420 °C for 4 h in order to regenerate the catalyst which had been deactivated during the reaction. It was found that the catalytic activity is completely regenerated by the treatment.

Discussion

Three reactions of glycolic acid may take place in parallel, as follows:

$$HOCH_2\text{–}COOH + 0.5O_2 \rightarrow OHC\text{–}COOH + H_2O$$

$$HOCH_2\text{–}COOH + O_2 \rightarrow HCHO + CO_2 + H_2O$$

$$HOCH_2\text{–}COOH + O_2 \rightarrow HCOOH + CO + H_2O$$

Mo and V based oxides and phosphates possess both acidic and redox functions. Indeed, they show good performance as catalysts in many partial oxidations for producing especially acidic compounds.[13] It is generally believed that they possess double-bond species in the metal–oxygen bonding, that is, Mo=O or V=O species, which promote oxygen-insertion reactions as well as dehydrogenation. In the reaction of glycolic acid, they preferentially promote C–C bond fission by oxygen insertion.

On the other hand, iron phosphate possesses both acidic and redox functions like those of Mo and V oxides and phosphates. However, it possesses no double-bond species in the iron–oxygen bond, unlike the Mo and V compounds. Therefore, its function to promote oxygen-insertion processes is very weak. As a result, in the reaction of glycolic acid, the formation of formaldehyde and formic acid is suppressed, to a certain extent, and a relatively good performance for production of glyoxylic acid is obtained.

As can be seen in Fig. 3, the use of a low temperature of 240 °C is beneficial to avoid the consecutive degradation of glyoxylic acid. It should be noted that the iron phosphate catalyst shows a relatively high oxidation activity, even at a low temperature of 240 °C. This finding strongly suggests that the redox cycles on the catalyst surface takes place rapidly at 240 °C. This is also supported by the finding that the oxygen dependency of the reaction is low (Fig. 4). Interestingly, the rates of reduction and reoxidation in the bulk of iron phosphate are very slow at 240 °C.[14]

It is considered that the increase in the catalytic activity in the beginning of reaction is related to the change in the structure of catalyst due to the partial reduction of iron ions and that the deactivation of catalyst observed after more than 15 h on stream is ascribable to the accumulation of nonvolatile reaction products on the surface of catalyst during the reaction. Possibly, the oxidizing function of iron phosphate should be too low to burn off the nonvolatile products at a low temperature of 240 °C. As a result, the regeneration of catalyst may be performed by removing of the nonvolatile products at a higher temperature.

References

1) M. Ai, E. Muneyama, A. Kunishige, and K. Ohdan, *Bull. Chem. Soc. Jpn.*, **67**, 551 (1994).

2) M. Ai, E. Muneyama, A. Kunishige, and K. Ohdan, *Catal. Lett.*, **24**, 362 (1994).

3) E. Muneyama, A. Kunishige, K. Ohdan, and M. Ai, *J. Mol. Catal.*, **89**, 371 (1994).

4) M. Ai and K. Ohdan, *Chem. Lett.*, **1995**, 405.

5) M. Ai and K. Ohdan, *Chem. Lett.*, **1996**, 247.

6) M. Ai and K. Ohdan, *Stud. Surf. Sci. Catal.*, **101**, 201 (1996).

7) P. R. Anantaneni and T. P. Li, U. S. Patent No. 4900864 (1990).

8) M. Ai, E. Muneyama, A. Kunishige, and K. Ohdan, *J. Catal.*, **144**, 632 (1993).

9) M. Katsumoto and D. M. Marquis, U. S. Patent 4132670 (1979).

10) M. Ai, *J. Catal.*, **116**, 23 (1989).

11) M. Ai, E. Muneyama, A. Kunishige, and K. Ohdan, *Appl. Catal. A*, **109**, 135 (1994).

12) R. A. J. Day and A. L. Underwood, "Quantitative Analysis," 4th ed, Prentice-Hall, Englewood-Cliffs, New Jersey (1980).

13) M. Ai, "Proceedings, 7th International Congress on Catalysis," Tokyo, 1980, Abstr., p. 1060 (1981).

14) E. Muneyama, A. Kunishige, K. Ohdan, and M. Ai, *Bull. Chem. Soc. Jpn.*, **69**, 509 (1996).