Oxidative Dehydrogenation of Glycolic Acid to Glyoxylic Acid over Fe-P-O Catalyst

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Glyoxylic acid was obtained by a vapor phase oxidative dehydrogenation of glycolic acid over an iron phosphate catalyst with a P/Fe atomic ratio of 1.2. The one-pass yield reached 59 mol% at the glycolic acid conversion of 78%; the selectivity of 76 mol%.

Glyoxylic acid is used as a raw material of various chemicals. It is generally produced by enzymatic or nitric acid oxidation of glyoxal, or electrolytic reduction of oxalic acid. It is also known that alkyl esters of glyoxylic acid are obtained by a vapor-phase oxidation of corresponding alkyl esters of glycolic acid.[1] The yield of ester reached 69 mol% at the conversion of 94%. However, it seemed still difficult to obtain glyoxylic acid directly from glycolic acid in a vapor phase process:

$$HOCH_2\text{-}COOH + 0.5\ O_2 \longrightarrow OHC\text{-}COOH + H_2O.$$

In the preceding studies,[2,3] it was found that the iron phosphate catalysts show a high selectivity in the oxdative dehydrogenation of lactic acid to pyruvic acid and also in the oxidative decarboxy-condensation of pyruvic acid to citraconic anhydrtide. These findings led us to study on the catalytic performance in the oxidative dehydrogenation of glycolic acid to glyoxylic acid.

An iron phosphate with a P/Fe atomic ratio of 1.2 was prepared according to the procedures described in the previous studies.[2,3] As for the structure, the freshly prepared catalyst consisited of tridimite-type $FePO_4$ with a small amount of quartz-type $FePO_4$. A V-P oxide catalyst with a P/V atomic ratio of 1.06 consisting of divanadium(IV) dioxide diphosphate $[(VO)_2P_2O_7]$, was prepaed according to a patent.[4] $H_3PMo_{12}O_{40}$ and $H_5PMo_{10}V_2O_{40}$ catalysts were prepared by supporting molybdophosphoric acid and molybdovanadophosphoric acid, respectively, on an equal weight of natural pumice between 10 to 20 in mesh size.[5]

The oxidation of glycolic acid was carried out with a continuous-flow system. A mixture of oxygen and nitrogen was fed in from the top of the reactor and 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. The feed rates of glycolic acid, oxygen, and nitrogen, and water vapor were 12.3, 7 to 20, 500, and 480 mmol/h, respectively. The amount of catalyst used was 10 g; the contact time was about 2.5 s. 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 reaction temperature was in the range of 240 to 270 °C.

The main products were glyoxylic acid, formaldehyde, formic acid, CO_2, and CO. A small amount of unidentified compound was detected by LC. The catalytic activity was stable enough for the use of more than 10 days. The performances obtained over the iron phosphate catalyst are shown in Table 1.

Table 1. Performance of iron phosphate catalyst at 240 °C

O_2 feed mmol/h	Conv %	Yield (mol%) GXAD	HCHO	HCOOH	CO_x	S mol%
7.5	50.2	39.6	3.9	0.7	6.0	79
11.3	53.0	40.0	3.9	0.7	7.4	77
12.5	59.0	45.0	4.0	0.9	6.7	76
16.2	70.4	53.8	4.1	1.6	10.7	76
18.6	78.0	59.0	4.0	2.1	14.4	76

Conv: conversion of glycolic acid, GXAD: glyoxylic acid, S: selectivity to glyoxylic acid.

It is clear that the iron phosphate shows a good catalytic performance. The one-pass yield of glyoxylic acid reaches 59 mol% at the conversion of 78%; the selectivity to is 76 mol%. The selectivity is almost unchanged with a variation in the conversion from 53 to 78%. This finding suggests that the produced glyoxylic acid is relatively stable under the conditions used, that is, the four products are formed in parallel.

Table 2. Performances of V-P and heteropoly compounds

Temp °C	Conv %	Yield (mol%) GXAD	HCHO	HCOOH	CO_x	S mol%
V-P oxide catalyst; O_2 feed rate = 7.5 mmol/h						
240	54.4	15.1	10.0	2.0	15.2	28
265	93.7	16.0	30.0	4.5	45.1	18
$H_3PMo_{12}O_{40}$ Catalyst; O_2 feed rate = 11. mmol/h						
240	66.0	16.6	9.1	10.0	32.4	25
250	83.7	15.5	10.6	10.9	38.0	19
$H_5PMo_{10}V_2O_{40}$ Catalyst; O_2 feed rate = 10. mmol/h						
240	70.5	19.5	2.5	5.7	15.2	27
270	86.9	24.4	11.2	11.0	42.1	28

For a purpose of comparison, the performances obtained over the V-P oxide and heteropoly compound catalysts, which show a good performance in oxidation producing acidic compounds such as maleic anhydride and methacrylic acid, were also studied (Table 2). It is clear that the catalysts consisting of V-P oxide and heteropoly compound are not effective.

Iron phosphate has no double bond oxygen species connected with iron atoms, unlike V- and Mo-based catalysts. This may relate to the high selectivity in oxidative dehydrogenations.

References

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