Formation of Pyruvic Acid by Oxidative Dehydrogenation of Lactic Acid

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Lactic acid is converted to pyruvic acid with a high selectivity by a vapor-phase air oxidation over iron phosphate catalysts with a P/Fe atomic ratio of 1.2. The partially reduced iron phosphates show better catalyst performances than the fresh, fully reduced, or reoxidized iron phosphates.

Recently, attempts have been made to obtain alkyl pyruvates from corresponding lactates by a vapor-phase partial oxidation using V_2O_5-based mixed oxides[1,2] As an academic report, Hayashi. et. al.[3] have reported the catalytic performances of various MoO_3-based mixed oxides. However, it seemed still difficult to obtain free pyruvic acid from lactic acid by vapor phase oxidation, because lactic acid is easily converted to acetaldehyde and CO_2 by the oxidative C-C bond fission rather than to pyruvic acid by oxidative dehydrogenation.

It was found in our previous studies[4-6] that iron phosphate catalysts with a P/Fe atomic ratio of 1.0 to 1.3 are effective for oxidative dehydrogenation of a compound in which the carbon atom at the α-position of an electron-attracting group such as -COOH or -CHO is tertiary, but that they are inactive for oxygen insertion reactions. These findings led us to study the catalytic performance of iron phosphate catalysts in the oxidative dehydrogenation of lactic acid to pyruvic acid:

$$CH_3\text{-}CH(OH)\text{-}COOH + 0.5\,O_2 \longrightarrow CH_3\text{-}CO\text{-}COOH + H_2O.$$

An iron phosphate with a P/Fe atomic ratio of 1.2 was prepared according to the procedures described in the previous studies.[4-6] The freshly calcined catalyst samples were treated by the following four different manners. A) without futher treatment; B) partial reduction by isobutyric acid; C) ful reduction by isobutyric acid; D) ful reduction by isobutyric acid followed by reoxidation by air. The colors, oxidation states of iron ions, and structures obtained from XRD study for each sample are summrized in Table 1.

Table 1. Characters of P/Fe = 1.2 Catalysts

Catalyst sample	Color	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$	Structure
A	Pale yellow	0.0	$FePO_4$(T) + $FePO_4$(Q)
B	Blue	0.3	$Fe_3(P_2O_7)_2$
C	white	0.9	$Fe_2P_2O_7$
D	Red-brown	0.3	unknown phase*

$FePO_4$ (T): tridymite type, $FePO_4$ (Q): quartz type,
*characterized with a single XRD peak at $2\theta = 29.5°$.

The oxidation of lactic acid was carried out with a continuous flow system. The feed rates of lactic acid, water, and air were 19.2, 962, and 350 mmol/h, respectively, and the reaction temperature was kept at 230°C. The analysis was performed by gas chromatography.

Since the reaction temperature was low, the characters and activities of catalysts were remained almost unchanged during the use in the reaction for about 4 h.

The main products were pyruvic acid, acetaldehyde, acetic acid, and CO_2. The presence of a small amount of unidentified compound was detected when the conversion of lactic Acid was higer than about 50%. No other products were detected.

The obtained results are summarized in Table 2.

Table 2. Performance of P/Fe = 1.2 catalysts

Catalyst Sample	Catalyst used (g)	Conv. of LA (%)	Selectivity of LA (mol%) to PA	AcH	AcOH	CO2
A	5	21	71.6	23.3	3.7	1.4
	10	41	62.0	27.0	7.6	3.4
B	3	28	76.5	15.3	3.5	4.5
	5	38	72.8	16.8	5.2	5.0
	10	78	62.0	19.1	10.0	8.6
C	5	19	78.0	21.0	0.5	0.0
	10	42	75.0	20.8	4.5	0.0
D	3	27	64.4	24.5	1.5	9.5
	5	37	58.3	29.0	1.6	11.0
	10	67	52.8	31.0	5.6	10.6

LA:lactic acid, PA:pyruvic acid, AcH: acetaldehyde,
AcOH: acetic acid.

The results indicate that the selectivity to pyruvic acid falls gradually as increasing the conversion of lactic acid and that acetic acid is formed by the decomposition of pyruvic acid and the major part of acetaldehyde is formed from lactic acid in parallel with pyruvic acid. It is also found that the fresh and fully reduced samples are clearly less active than the partially reduced and reoxidized samples and that the reoxidized sample is markedly less selective than the other samples. It is therefore concluded that the best performances are obtained with the partially reduced sample with a $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio of about 0.3. The one-pass yield of pyruvic acid reaches 48.5 mol%.

References and Notes

1 Jpn. Patent, 56-19854 (1981).
2 Jpn. Patent, 57-24336 (1982).
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