Formation of Glyoxal by Oxidative Dehydrogenation of Ethylene Glycol

Mamoru Ai

Department of Applied Chemistry and Biotechnology, Niigata Institute of Technology, 1719 Fujihashi, Kashiwazaki 945-1195

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Iron(III) phosphates doped with a very small amount of molybdenum(VI) were found to be effective as catalysts for a vapor-phase oxidative dehydrogenation of ethylene glycol to glyoxal. The effects of the molybdenum(VI) content and of the reaction variables on the conversion of ethylene glycol and selectivity to glyoxal were studied. The optimum Mo/ Fe atomic ratio was in the range from 0.002 to 0.01. The highest selectivity to glyoxal was obtained in the temperature range of 290 to 310 °C. The rate of ethylene glycol consumption increased almost in proportion to the oxygen concentration, while the selectivity to glyoxal increased only slightly as the oxygen concentration was increased. The selectivity to glyoxal increased markedly as the concentration of water was increased. It reached 37 and 32 mol% at ethylene glycol conversions of 60 and 80%, respectively. The one-pass yield of glyoxal reached 26.5 mol%.

Iron(III) phosphates have been claimed to be effective as catalysts for oxidative dehydrogenation of isobutyric acid to form methacrylic acid.¹ There have been a number of scientific studies on iron(III) phosphate as catalysts for production of methacrylic acid.^{2–13}

 $\begin{array}{l} CH_3-CH(CH_3)-COOH\,+\,0.5\ O_2\rightarrow\\ CH_2=\!C(CH_3)-\!COOH\,+\,H_2O \end{array}$

Recently, it was found that iron(III) phosphate catalysts show a uniquely high selectivity for several other oxidative dehydrogenation reactions, such as formation of pyruvic acid from lactic acid,¹⁴ glyoxylic acid from glycolic acid,¹⁵ and pyruvaldehyde (2-oxopropanal) from hydroxyacetone (acetol).¹⁶

$$\begin{array}{l} \text{CH}_3\text{-}\text{CH}(\text{OH})\text{-}\text{COOH} + 0.5\text{O}_2 \rightarrow \text{CH}_3\text{-}\text{CO}\text{-}\text{COOH} + \text{H}_2\text{O} \\ \text{HOCH}_2\text{-}\text{COOH} + 0.5\text{O}_2 \rightarrow \text{OCH}\text{-}\text{COOH} + \text{H}_2\text{O} \\ \text{CH}_3\text{-}\text{CO}\text{-}\text{CH}_2\text{OH} + 0.5\text{O}_2 \rightarrow \text{CH}_3\text{-}\text{CO}\text{-}\text{CHO} + \text{H}_2\text{O} \end{array}$$

Iron(III) phosphate possesses both acidic and redox functions, as do phosphates of vanadium(V) and molybdenum(VI). However, it is interesting to note that iron(III) phosphate catalysts are effective only for the oxidative dehydrogenation, but not for oxygen insertion reaction, unlike phosphates of vanadium(V) and molybdenum(VI).^{15,17,18} It is believed that C–C bond fission, which is one of the main side-reactions in an oxidative dehydrogenation, is promoted by the oxygen insertion. This may be the reason why iron(III) phosphate shows a uniquely high selectivity for several oxidative dehydrogenation reactions.

More recently, it was also found that both the catalytic activity and the selectivity of iron(III) phosphate in the oxidative dehydrogenation of lactic acid to pyruvic acid are improved dramatically by a doping of very small amounts of molybdenum(VI) compounds.¹⁹ These findings led us to examine the catalytic performances for a more difficult reaction, that is, oxidative dehydrogenation of ethylene glycol to glyoxal (ethandial).

$$HOCH_2-CH_2OH + O_2 \rightarrow OHC-CHO + 2H_2O$$

Glyoxal is a raw material of various chemicals. It is generally produced by a vapor phase oxidation of ethylene glycol using Ag or Cu catalysts at a high temperature of above 600 °C in a manner similar to the oxidative dehydrogenation of methanol to formaldehyde. An academic study has been reported by Gallezot et al.²⁰ It should be noted that formaldehyde is produced also by another oxidative dehydrogenation of methanol using mixed metal-oxide catalysts such as MoO_3 – Fe_2O_3 at a low temperature of around 350 °C, while glyoxal is not produced in the oxidative dehydrogenation of ethylene glycol over such mixed metal-oxide catalysts. Recently, Chumbhable and Awasarkar reported that the yield of glyoxal in the oxidation of ethylene glycol is enhanced by an addition of a small amount (2.5 wt%) of phosphorus into Fe(MoO₄)3.²¹

Experimental

1. Catalysts. The original iron(III) phosphate catalyst sample with a P/Fe atomic ratio of 1.0 was prepared according to procedures similar to those described previously.¹¹ Iron(III) nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ (122 g, 0.3 mol) was dissolved in about 5 dm³ of water, and a dilute ammonia solution was added to precipitate iron(III) hydroxide gel. Most of the water was removed by decantation; then the obtained precipitate was mixed with a 41.5 g portion of 85% orthophosphoric acid [0.36 mol of H₃PO₄]. Next, the mixture was slowly boiled for 3 to 5 h, yielding a slightly brownish-white precipitate. The precipitate was filtered and washed by water to remove axcess phosphoric acid. The obtained cake was dried in an oven at 120 °C for 6 h. The resulting fine powder of precursor was pressed under a pressure of 200 Kg/cm² to make tablets with a diameter of 20 mm. The tablets were then broken

Table 1. Comparison of Performances of Catalysts

Catalyst	Т	Conv	Yield/mol%								$S_{\rm G total}$
(atomic ratio)	°C	%	GX	GALD	GXAD	HCHO	HCOOH	AcH	CO_x	others	mol%
Fe–Mo	260	64.6	4.9	2.0	0.4	25.9	0.0	2.6	6.7	22.0	11.3
(3–7)	270	85.4	5.5	1.5	0.5	47.6	0.0	2.0	4.0	24.5	8.7
	280	91.9	6.4	1.3	0.0	61.8	0.0	3.2	4.3	14.9	8.4
	240	28.6	4.0	1.5	0.1	6.3	4.9	4.2	2.1	5.4	19.8
$H_3PMo_{12}O_{40}$	250	48.7	6.7	2.0	0.5	10.4	5.1	4.8	2.0	17.1	19.1
	260	63.3	9.1	2.0	0.8	15.0	5.9	7.1	3.2	20.2	18.8
	270	76.3	11.7	2.5	1.0	21.8	6.1	8.0	6.0	18.9	19.9
	260	34.9	2.5	1.4	0.2	3.1	2.8	15.24	1.2	8.3	11.9
V–P	270	51.6	3.1	1.6	0.4	6.5	0.0	26.4	3.0	10.7	9.8
(1-1.06)	280	77.3	4.6	1.7	0.5	10.5	0.0	43.0	4.3	12.5	9.0
	290	92.4	5.3	1.4	0.6	14.5	0.0	60.4	7.3	2.4	7.9
	260	47.0	14.2	1.7	0.9	7.2	2.2	3.4	2.6	6.7	35.7
Fe-P-Mo	270	54.3	18.0	2.5	1.3	10.8	2.3	4.6	3.2	11.7	40.0
(1-1-0.01)	280	64.0	21.0	2.3	1.5	17.1	0.0	6.4	3.8	11.9	38.9
	290	78.2	22.8	1.9	1.8	24.0	0.0	8.5	5.4	13.8	33.8

Amount of Catalyst used: 5.0 g; Feed rates: ethylene glycol, oxygen, water, nitrogen = 14.5, 25.0, 954, 500 mmol/h. EG = ethylene glycol, GX = glyoxal, GALD = glycolaldehyde, GXAD = glyoxylic acid, AcH = acetaldehyde. $S_{G \text{ total}}$: selectivity to the sum of GX, GALD, and GXAD.

up and sieved to a 7–20 mesh size. Finally, the precursor was calcined in a stream of air at 400 °C for 8 h. The product consisted of tridymite-type FePO₄.²² The presence of quartz-type FePO₄²³ was not detected in the XRD patterns. The BET surface area was 8.9 m²/g and the bulk density was 0.66 g/mL.

Iron(III) phosphate samples doped with molybdenum(VI) were prepared according to the following procedures. A required of molybdenum(VI) compounds, such amount as (NH₄)₆Mo₇O₂₄·4H₂O or H₃PMo₁₂O₄₀, was dissolved in water. Unless indicated othwerwise, (NH₄)₆Mo₇O₂₄·4H₂O was used as the source of molybdenum. The solution was added into the abovementioned fine powder of iron(III) phosphate precursor. 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 other procedures were the same as those of the original iron phosphate.

2. Reaction Procedures. The reaction was carried out 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 sample (1 to 20 g) was placed near 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 sample. The reaction temperature was in the range of 230 to 340 °C. A mixture of nitrogen and oxygen was fed in from the top of the reactor; the feed rate of nitrogen was fixed at 200 mL/min. An aqueous solution containing 100 g (1.60 mol) of ethylene glycol per liter was introduced into the preheating section of the reactor with a feed rate of either 9.04 or 18.08 mL/h by a syringe pump and a fine stainless steel tube. Unlss indicated otherwise, the feed rates of ethylene glycol, oxygen, water, and nitrogen were 14.5, 15.0, 452, and 500 mmol/h, respectively. The effluent gas from the bottom of the reactor was led successively into four chilled scrubbers to recover the watersoluble compounds. The reaction products and the unreacted ethylene glycol were analyzed by both GC and LC.

The conversion of ethylene glycol was defined as: $100 \times [1 - (\text{moles of unreacted ethylene glycol})/(\text{moles of ethylene glycol} fed)]. The yields of C₂ products were defined as: <math>100 \times (\text{moles of product})/(\text{moles of ethylene glycol fed})$. The yields of C₁ products were defined as; $50 \times (\text{moles of product})/(\text{moles of ethylene glycol fed})$. The selectivity was defined as: $100 \times (\text{yield})/(\text{conversion})$. The selectivity to the sum of glyoxal, glycolaldehyde, and glyoxylic acid (abbreviated as $S_{G \text{ total}})$ was defined as: $100 \times (\text{sum of yields of glyoxal, glycolaldehyde, and glyoxylic acid})/(\text{conversion})$.

The contact time (s) was defined as: (volume of catalyst used)/ (volume of reactant gas mixture per second).

Results

1. Comparison of the Performances of Various Catalysts. The performances of the following four catalysts in the oxidation of ethylene glycol were compared: (1) iron(III) molybdeate with a Fe/Mo atomic ratio of 3/7; (2) H₃PMo₁₂O₄₀ supported (10 wt%) on natural pumice; (3) vanadium(V) phosphate with a P/V atomic ratio of 1.06, consisting of (VO)₂P₂O₇; (4) iron(III) phosphate doped with molybdenum(VI), with a Mo/Fe atomic ratio of 0.01 (abbreviated as Fe–P–Mo = 1–1–0.01). The amount of catalyst used was kept constant at 5.0 g.

The main products were glyoxal, glycolaldehyde (CH₂OH– CHO), glyoxylic acid (HOOC–CHO), acetaldehyde, formaldehyde, and carbon oxides. Glycolic acid (CH₂OH–COOH) was not detected in the products. Formic acid was found in some cases. In the case of the Fe–P–Mo = 1–1–0.01 catalyst, a small amount (yield of less than 3 mol%) of formic acid was found, only when the extent of reaction was low. The discrepancy between the amount of consumed ethylene glycol and the sum of the assigned products corresponds to the amount of unidentified compounds; it was listed as "others". The selectivity to the sum of glyoxal, glycolaldehyde, and glyoxylic acid (abbreviated as $S_{G \text{ total}}$) is important, because these three compounds are not the degradation products. The results are listed in Table 1.

The results may be summarized as follows:

(1) The Fe–P–Mo (1-1-0.01) catalyst shows clearly a yield of glyoxal higher than those obtained from the other three catalysts. The yield reaches 22.8 mol% and the selectivity to the sum of glyoxal, glycolaldehyde, and glyoxylic acid reaches 40 mol% at a conversion of 54%.

(2) The main by-products over the Fe–P–Mo catalyst are formaldehyde and unidentified compounds.

(3) Oxidation activity of the Fe–P–Mo catalyst is of the same order of magnitude as that of the other three catalysts.

(4) The main product over the V–P oxide catalyst is acetaldehyde.

(5) The main products over the Fe–Mo oxide and $H_3PMo_{12}O_{40}$ catalysts are formaldehyde and unidentified compounds.

2. Effects of the Molybdenum Content on the Oxidation

Conv

%

20.3

29.4

47.7

56.8

70.5

82.3

48.7

66.3

74.2

47.0

64.0

83.8

44.7

65.4

81.4

50.0

75.0

Table 2. Effects of the Molybdenum Content on the Catalytic Propertirs

GX

1.7

2.5

3.5

15.3

17.9

19.8

18.0

22.2

24.0

14.2

21.0

22.9

12.0

19.0

22.6

13.3

18.0

GALD

1.0

1.3

1.1

2.2

2.2

2.1

2.3

2.0

1.8

1.7

2.3

1.6

2.6

2.0

1.6

1.1

2.1

GXAD

0.4

0.5

0.6

2.5

2.9

3.3

0.0

0.0

0.0

0.9

1.5

1.7

0.0

0.0

0.0

0.8

1.5

Activity. Effects of the content of molybdenum(VI) doped into iron(III) phosphate on the oxidation activity were studied. The reaction was performed using 5 g-portions of catalysts with different Mo/Fe atomic ratios (contact time of about 1.2 s). The catalysts with a Mo/Fe atomic ratio of more than 0.2 were prepared using $H_3PMo_{12}O_{40}$ as the source of molybdenum(VI). Some representative results obtained from each catalyst are listed in Table 2.

The conversions of ethylene glycol at a fixed temperature of 260 °C are plotted as a function of the content of molybdenum(VI) (Mo/Fe atomic ratio) in Fig. 1 (open circles). The catalytic activity increases markedly by the doping of a very small amount of molybdenum(VI) (Mo/Fe atomic ratio of 0.001). Therefore, the conversions obtained from the samples with a Mo/Fe atomic ratio lower than 0.04 were also studied in more detail. The results are shown in Fig. 2 (open circles).

The results can be summarized as follows. The oxidation activity increases sharply as the content of molybdenum(VI) increases up to a Mo/Fe atomic ratio of around 0.01, it increas-

 $\overline{CO_x}$

5.8

8.3

11.8

4.9

6.4

9.4

3.8

5.8

7.0

2.6

3.8

6.9

3.6

6.5

7.3

3.9

6.2

AcH

4.4

10.6

21.5

9.7

11.2

16.6

5.6

8.7

11.4

3.4

6.4

10.7

3.7

6.7

10.0

7.3

6.6

others

4.8

2.0

3.0

9.7

15.4

10.5

7.9

10.0

7.9

6.7

11.9

10.1

12.8

13.9

14.8

12.5

18.7

 $S_{\rm G\ total}$

mol%

14.9

14.3

11.0

36.5

32.5

30.6

41.7

36.5

34.8

35.7

38.9

31.2

32.6

32.5

29.6

30.2

28.8

Conv

 $\overline{O_2}\%$

10.5

15.2

24.2

31.5

45.2

55.6

32.3

41.1

46.8

26.4

36.0

50.4

23.4

39.5

49.6

25.0

41.9

51.6

52.0

53.6 68.0

26.4 37.6 47.2

(5 g)	300	83.8	24.3	1.4	0.0	28.3	0.0	11.1	6.7	12.0	30.7
Fe-P-Mo	260	59.2	11.9	2.3	0.8	11.6	3.0	4.7	2.0	22.8	25.4
1-1-0.075	270	66.4	13.5	1.9	1.0	15.9	0.0	5.8	2.4	26.0	24.7
(5 g)	280	78.6	17.0	2.0	0.0	23.1	0.0	7.9	3.2	25.3	24.3
Fe-P-Mo	240	75.0	9.8	1.8	1.7	21.3	0.0	4.1	6.0	30.4	17.7
1-1-0.5	245	79.4	10.7	1.8	1.8	30.1	0.0	4.2	7.4	23.4	18.0
(5 g)	255	89.2	11.8	2.0	2.0	44.0	0.0	4.7	9.7	15.0	17.7
Fe-P-Mo	240	55.1	6.1	1.7	0.7	12.9	0.0	3.2	2.5	28.0	15.5
1-1-1	250	73.8	8.0	1.6	1.0	26.8	0.0	3.9	4.4	28.1	14.4
(5 g)	260	84.6	9.6	1.7	1.3	39.1	0.0	3.3	6.4	22.2	14.9
Abbreviatio	ons are the	e same as	those in T	able 1 C	$onv O_{2} = c$	onversion of	forvæn				

Yield/mol%

HCOOH

1.0

1.9

2.1

0.0

0.0

0.0

0.0

0.0

0.0

2.2

0.0

0.0

3.3

0.0

0.0

3.2

0.0

HCHO

1.4

2.4

4.2

11.7

14.6

20.6

11.0

17.6

22.4

7.2

17.1

29.9

6.8

17.3

25.2

8.7

21.8

Abbreviations are the same as those in Table 1. Conv $O_2 = \text{conversion of oxygen}$.

Catalyst

Fe-P-Mo

1-1-0.000

(10 g)

Fe-P-Mo

1-1-0.0012

(10 g)

Fe-P-Mo

1 - 1 - 0.005

(5 g)

Fe-P-Mo

1 - 1 - 0.01

(5 g)

Fe-P-Mo

1-1-0.02

(5 g)

Fe-P-Mo

1-1-0.04

Т

°C

260

280

300

280

290

300

280

290

300

260

280

300

260

280

300

260

280



Fig. 1. Effects of the content of molybdenum(VI) on the conversion and selectivity (Part 1). (○): Conversion of ethylene glycol at 260 °C. Selectivity at a conversion of 60%;
(●): glyoxal, (■): formaldehyde, (▲): sum of glyoxal, glycolaldehyde, and glyoxylic acid.



Fig. 2. Effects of the content of molybdenum(VI) on the conversion and selectivity (Part 2). The symbols are the same as those in Fig. 1.

es more dully in a Mo/Fe atomic ratio ranging from 0.01 to 0.3, and then it levels off with a further increase in the molyb-denum(VI) content.

3. Relation between the Conversion and the Selectivity. The relations between the conversion and the selectivity were studied. Since the oxidative dehydrogenation of ethylene glycol consists of several consecutive reactions, it is reasonable that the selectivity changes depending on the variation in the extent of reaction. The reaction was performed over a 5 g-portion of the Fe–P–Mo = 1-1-0.01 catalyst. The conversion was changed by changing the temperature from 260 to 310 °C, while fixing the rate of feed. The values of selectivity to each product are plotted as a function of the conversion in Fig. 3.

As the conversion increases, the selectivity to glyoxal and that to the sum of glycolaldehyde and glyoxylic acid decrease a little, while that to formaldehyde clearly increases. The selectivity to acetaldehyde, that to carbon oxides, and that to uni-



Fig. 3. Relation between the selectivity and conversion. (○): glyoxal, (■): formaldehyde, (▲): acetaldehyde, (●): carbon oxides, (♦): unidentified compounds, (◊): sum of glycolaldehyde and glyoxylic acid, (□) sum of glyoxal, glycolaldehyde, and glyoxylic acid.

dentified compounds are relatively low. The selectivity to carbon oxides increases with the conversion, but the relation between the conversion and the selectivity to acetaldehyde and that to unidentified compounds are not clear.

4. Effects of the Molybdenum Content on the Selectivity. Since the selectivity varies depending on the extent of reaction, the values of selectivity obtained from the catalysts with different molybdenum(VI) contents were compared at a fixed level of conversion. The selectivity to glyoxal, that to formaldehyde, and that to the sum of glyoxal, glycolaldehyde, and glyoxylic acid at a conversion of 60% are shown in Figs. 1 and 2 (closed symbols).

As the content of molybdenum(VI) increases, the selectivity to glyoxal increases sharply, shows a broad maximum at a Mo/ Fe atomic ratio of 0.01, and then falls gradually. The selectivity to the sum of glyoxal, glycolaldehyde, and glyoxylic acid also shows a broad maximum at a Mo/Fe atomic ratio of 0.005. It is likely that the catalysts with a Mo/Fe atomic ratio of lower than 0.05 are beneficial to the formation of glycolaldehyde and glyoxylic acid. On the other hand, the selectivity to formaldehyde increases by the doping of a very small amount of molybdenum(VI) (Mo/Fe atomic ratio of 0.001), but it levels off with a further increase in the molybdenum(VI) content. That is, it is kept constant at around 25 mol% over the whole range of Fe/ Mo atomic ratio.

5. Effects of the Reaction Temperature on the Selectivity. Several series of reaction runs were performed with the Fe–P– Mo = 1-1-0.01 catalyst by changing both the amount of catalyst used from 1.25 to 20.7 g and the reaction temperature from 230 to 340 °C. The feed rates of ethylene glycol, oxygen, water, and nitrogen were 14.5, 25.0, 954, and 500 mmol/h, respectively. The values of selectivity to each product at an ethylene glycol conversion of 60% are plotted as a function of the reaction temperature in Fig. 4.

The selectivity to glyoxal shows a broad maximum at 290 to 310 °C, while the selectivity to the sum of glycolaldehyde and glyoxylic acid decreases steadily as the temperature is raised. Accordingly, a maximum value of the selectivity to the sum of



Fig. 4. Effects of the temperature on the selectivity at a conversion of 60%. The symbols are the same as those in Fig. 3.

glyoxal, glycolaldehyde, and glyoxylic acid is achieved at a lower temperature ranging from 260 to 280 °C. The selectivity to formaldehyde falls markedly as the temperature is raised, while that to unidentified compounds (others) and that to acetaldehyde increase. The selectivity to carbon oxides increases slightly with the temperature.

6. Effects of Oxygen Concentration. Five series of reaction runs were performed using a 5 g portion of the Fe–P–Mo = 1-1-0.01 catalyst and by changing both the feed rate of oxygen from 5 to 25 mmol/h and the reaction temperature from 260 to 320 °C, while fixing the feed rate of ethylene glycol as 14.5 mmol/h.

The conversions of ethylene glycol at 260 °C are plotted as a function of the feed rate of oxygen in Fig. 5 (open circles). The conversion increases almost proportionally to the feed rate of oxygen.

Table 3. Effect of the Water Concentration on the Performances



Fig. 5. Effects of the feed rate of oxygen on the conversion and selectivity. (○): Conversion of ethylene glycol at 260 °C. Selectivity at a conversion of 80%; (●): glyoxal, (♦): sum of glycolaldehyde and glyoxylic acid, (▲): sum of glyoxal, glycolaldehyde, and glyoxylic acid.

The selectivity to glyoxal, that to the sum of glycolaldehyde and glyoxylic acid, and that to the sum of glyoxal, glycolaldehyde, and glyoxylic acid obtained at a fixed ethylene glycol conversion of 80% are also plotted in Fig. 5 (closed symbols). The values of selectivity increase only slightly as the oxygen feed rate is increased.

7. Effects of the Concentration of Water on the Selectivity. Three series of reaction runs were performed over a 5 g portion of the Fe–P–Mo = 1-1-0.01 catalyst by changing the feed rate of water. The feed rate of oxygen was fixed as 20 mmol/h. The results are listed in Table 3. The selectivity to each product and that to the sum of glyoxal, glyxolaldehyde, and glyoxylic acid obtained at a fixed ethylene glycol conversion of 60% are plotted as a function of the feed rate of water

Water feed	Т	Conv	Yield/mol%								$S_{\rm G\ total}$
(mmol/h)	°C	%	GX	GALD	GXAD	HCHO	HCOOH	AcH	CO_x	others	mol%
	260	63.9	16.3	3.4	0.0	8.9	0.0	5.4	2.9	27.1	30.7
200	270	75.0	17.6	2.8	0.0	13.7	0.0	6.8	4.1	30.1	27.1
	280	83.4	21.1	2.4	0.0	19.5	0.0	9.0	6.0	25.4	28.2
ct = 1.55 s	285	88.2	21.7	2.2	0.0	22.5	0.0	9.9	6.6	25.3	27.1
	290	89.8	22.0	2.2	0.0	27.5	0.0	10.8	83	19.2	26.8
	270	59.0	18.5	2.3	1.3	10.7	0.0	4.4	3.1	18.7	37.5
452	280	72.0	22.2	2.8	2.1	16.5	0.0	7.0	4.2	19.4	34.7
	285	76.7	23.2	2.6	0.0	18.4	0.0	8.3	5.2	19.0	33.6
ct = 1.15 s	290	79.3	24.6	1.9	0.0	24.5	0.0	8.4	6.5	11.3	36.0
	295	84.6	25.8	2.2	2.3	25.1	0.0	11.3	6.8	11.1	35.8
	270	45.9	17.8	3.3	1.4	11.2	0.0	5.9	2.0	4.3	48.9
954	280	54.7	20.7	2.6	1.6	13.2	0.0	4.5	2.9	9.2	45.6
	290	64.4	23.5	2.3	1.9	19.0	0.0	6.3	3.8	7.7	42.8
ct = 0.763 s	300	76.0	25.9	2.0	2.3	25.6	0.0	.6	5.1	6.6	39.7
	305	83.0	26.3	1.7	2.3	29.7	0.0	10.5	6.1	6.4	36.6
	310	86.4	26.5	1.6	2.4	33.2	0.0	11.7	7.9	3.1	35.3

Catalyst: Fe–P–Mo (1-1-0.01), 5.0 g. Feed rates of ethylene glycol, oxygen, nitrogen = 14.5, 20, 500 mmol/h. Abbreviations are the same as those in Table 1.



Fig. 6. Effects of the feed rate of water on the selectivity. Selectivity at a conversion of 60%. The symbols are the same as those in Fig. 3.

in Fig. 6.

It is clear that the selectivity to glyoxal and that to formaldehyde increase as the concentration of water is increased, while that to unidentified compounds falls.

Discussion

As seen in Table 1, the iron(III) molybdate, which is known as a typical catalyst for oxidative dehydrogenation of methanol to formaldehyde, is very active, but it is not suitable for the oxidative dehydrogenation of ethylene glycol to glyoxal, because it promotes mainly an oxidative C–C bond fission to form two moles of formaldehyde.

$HOCH_2$ - $CH_2OH + 0.5 O_2 \rightarrow 2HCHO + H_2O$

The supported $H_3PMo_{12}O_{40}$, which is a typical acidic oxidation-catalyst, shows a sufficient oxidation activity, but the selectivity to the sum of glyoxal, glycolaldehyde, and glyoxylic acid is less than 20 mol%. The main products are formaldehyde and unidentified compounds. It is interesting to note that the catalyst produces uniquely a relatively large amount of formic acid. This finding suggests that the catalyst is inactive for decomposition of formic acid. Possibly, the catalyst is poor in the basic properties which would activate acidic compounds.²⁴

The vanadium(V) phosphate is not effective for the formation of glyoxal. Interestingly, it promotes mainly the formation of acetaldehyde. It is likely that ethylene glycol is dehydrated to form ethylene oxide (C_2H_4O) and the obtained ethylene oxide is then transformed into acetaldehyde by isomerization. These two steps are acid-catalyzed steps, but not oxidation steps. The dehydration of ethylene glycol may be the ratedetermining step. It is still hard to understand why the vanadium(V) phosphate promotes the dehydration more strongly than the $H_3PMo_{12}O_{40}$ catalyst does.

$$HOCH_2$$
- $CH_2OH \rightarrow C_2H_4O + H_2O \rightarrow CH_3CHO + H_2O$

The pure iron(III) phosphate is very low both in the oxidation activity and in the selectivity to glyoxal (Table 2). The main products are acetaldehyde and carbon oxides. The pure iron(III) phosphate is not suitable as a catalyst for the formation of glyoxal.

However, both the oxidation activity and the selectivity to glyoxal are improved dramatically by doping of a very small amount of molybdenum, as in the case of oxidative dehydrogenation of lactic acid to pyruvic acid.¹⁹ The oxidation activity of the catalyst with Mo/Fe atomic ratio of 0.001 is of the same order of magnitude as those of iron(III) molybdete, $H_3PMo_{12}O_{40}$, and vanadium(V) phosphate.

As seen in Figs. 1 and 2, the oxidative C–C bond fission to form formaldehyde always takes place in parallel to the oxidative dehydrogenation to form glyoxal. On the other hand, as the extent of reaction increases, the selectivity to glyoxal falls, while that to formaldehyde increases (Fig. 3). This finding suggests that a part of glyoxal is transformed consecutively to formaldehyde. Since the formation of CO was much smaller than that of CO_2 , the decomposition reaction is assumed to be oxidative, as follows:

 $OCH\text{--}CHO\,+\,0.5~O_2\rightarrow HCHO\,+\,CO_2$

The selectivity to glyoxal may be governed by two factors: (1) side-reactions parallel to glyoxal formation, (2) consecutive degradations of glyoxal. Therefore, it is reasonable that one ascribes the enhancement of selectivity by the molybde-num(VI) doping to the enhancement of the rate of glyoxal formation relative to the rate of C–C bond fission which takes place in parallel to the glyoxal formation and to the rate of consecutive degradation of glyoxal. To understand the role of molybdenum(VI) in more detail, further information seems to be necessary.

The rate of consumption of ethylene glycol increases almost in proportion to the feed rate of oxygen (Fig. 5). Similar results were observed in the cases of oxidation of other compounds over iron phosphate catalysts.^{2,7,14–16} On the other hand, the selectivity to glyoxal is not much affected by the feed rate of oxygen (Fig. 5). The finding suggests that the oxygen dependency of side-reactions is the same as that of glyoxal formation reaction.

The selectivity increases markedly as the concentration of water increases (Table 3 and Fig. 6). Similar results were usually observed in the oxidative dehydrogenation reactions performed over iron phosphate catalysts.^{2,9,12–17} It has been proposed that the crystalline water of iron phosphate takes part in promoting the oxidative dehydrogenation,^{13,25} and that the redox cycles in iron(III) phosphate are performed in a manner different from that in oxides or phosphates of molybdenum(VI) and vanadium(V), since iron(III) phosphate has no metal-oxygen double bond species, unlike oxides or phosphates of molybdenum and vanadium.¹⁷

It is interesting to note that the selectivity to formaldehyde and that to unidentified compounds vary in opposite directions. As the temperature is raised, the selectivity to formaldehyde falls, while that to unidentified compounds increases (Fig. 4). On the other hand, as the feed rate of water is increased, the selectivity to formaldehyde increases, while that to unidentified compounds falls (Fig. 6). Lower temperatures and higher water concentrations are beneficial to the formaldehyde formation, while higher temperatures and lower water concentrations are beneficial to the formation of unidentified compounds. At present it is hard to explain fully the results.

The selectivity to acetaldehyde increases as the temperature is raised (Fig. 4). It is likely that a higher temperature is beneficial to the dehydration of ethylene glycol to ethylene oxide.

Iron(III) phosphate is considered to be inactive for promoting oxygen insertion reactions. However, ethylene glycol is very susceptible to C–C bond fission by oxygen insertion, accordingly the formation of glyoxal from ethylene glycol seems to be one of very difficult reactions. At present it is still hard to suppress completely the C–C bond fission of ethylene glycol even with the promoted iron(III) phosphate catalysts, though clearly improved performances are achieved.

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