

An Industrial Process for Adipic Acid Production by the Liquid-Phase Oxidation of Cyclohexanone with Molecular Oxygen

Atsushi Shimizu,* Katsutoshi Tanaka, Hiroo Ogawa, Yuji Matsuoka, Masami Fujimori, Yukito Nagamori, Hidefumi Hamachi, and Kazuyoshi Kimura

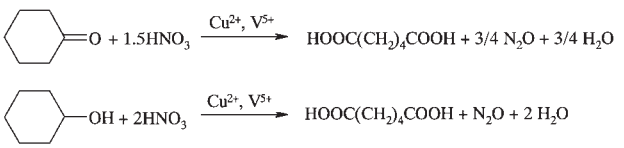
Nylon & Urethane Intermediates Division, Performance Chemicals Company, Asahi Kasei Corporation, Yuraku-cho, 1-1-2, Chiyoda-ku, Tokyo 100-8440

Received April 9, 2003; E-mail: shimizu.ac@om.asahi-kasei.co.jp

Adipic acid is produced industrially by the oxidation of cyclohexanone and cyclohexanol with nitric acid. Dinitrogen oxide (nitrous oxide, N_2O), a non-CO_2 greenhouse gas, is produced as a by-product in this process. We have investigated an industrial process for the production of adipic acid without the generation of N_2O. When acetic acid was used as a solvent and $Mn(OAc)_2/Co(OAc)_2$ were used as catalysts under atmospheric pressure of pure O_2 at 70 °C, the selectivity of adipic acid was 77% and the combined selectivity of carboxylic acids, which consisted of adipic acid, glutaric acid, and succinic acid, was 93% for the 100% conversion of cyclohexanone. We presume that adipic acid is generated via 6-oxohexanoic acid. Glutaric acid was probably generated via 5-oxopentanoic acid in the reaction path that branched at 6-oxohexanoic acid. When air containing less than 10 vol % of oxygen was used at 1.22 MPa in order to avoid explosion hazards, the selectivity of adipic acid was 78% for a 99.3% conversion of cyclohexanone. We conclude that the present reaction can be used as an industrial process for adipic acid production.

Adipic acid is used as an ingredient of nylon 66. It is also used as an ingredient of aliphatic α,ω-dihydroxy polyester (so-called polyesterdiol), a soft segment in polyurethane. The total production of adipic acid was 2300 kt in 1998 at plants all around the world. A major industrial method to produce adipic acid is the oxidation of KA oil (a mixture of cyclohexanol and cyclohexanone) with nitric acid. This reaction gives a mixture of adipic acid, glutaric acid, and succinic acid. The combined yield of the three carboxylic acids is nearly 100%. Furthermore, the reaction is quite useful because the ratio of adipic acid to the total is higher than 95%.[1] Dinitrogen oxide (nitrous oxide, N_2O) is generated in almost stoichiometric quantities in the nitric acid oxidation process (Scheme 1). Dinitrogen oxide, which is used as an anesthetic, is known as a non-CO_2 greenhouse gas.

Thiemence and Trogler pointed out the significance of N_2O generated from adipic acid plants to the atmospheric N_2O budget.[2] The global generation of N_2O, ascribed to both anthropogenic and natural sources, is estimated to be 26000 kt per year.[3] The concentration of N_2O in the air is approximately 300 ppb at present. The rate of N_2O generation now exceeds the global rate of N_2O destruction, such that the concentration of N_2O is growing at the rate of 0.2% per year.[4,5] The amount of N_2O generated during adipic acid production is reported to be 0.25 kg per 1 kg of adipic acid (survey by Miyazaki Prefecture in 1994). Since the rate of adipic acid production was 2300 kt/y in 1998, the total amount of N_2O produced in adipic acid plants in the world is estimated to be ca. 580 kt/y. Because of the need to ensure the conservation of the global environment, major adipic acid manufacturers have introduced N_2O abatement facilities to their adipic acid plants. As a result, 80% of the N_2O generated at adipic acid plants around the world is now being decomposed before it is released to the environment.[6]



Scheme 1. Nitric acid oxidation of cyclohexanone and cyclohexanol.

Considering the above background, we have investigated new processes for the production of adipic acid without N_2O emission to the environment. The O_2 oxidation process is quite useful from the environmental viewpoint because it produces no N_2O. Benzene derivatives such as cyclohexane and cyclohexanone have been used as ingredients in many papers. Originally, Tanaka reported the O_2 oxidation of cyclohexane in acetic acid using $Co(OAc)_2$ as a catalyst for an industrial production process of adipic acid.[7–9] Besides these papers, many scholars have reported the oxidation reaction of cyclohexanone.[10–14] More recently, Ishii et al.,[15–18] Hirai,[19] and Nakano and Ishii[20,21] reported the O_2 oxidation reactions using *N*-hydroxyphthalimide radical (phthalimid-*N*-oxyl) as a catalyst. A review on the cyclohexane oxidation was published by Schuchardt et al.[22] Meanwhile, many papers have dealt with the liquid-phase oxidation of cyclohexanone with O_2. For example, cyclohexanone can be oxidized with O_2 in acetic acid by the use of a manganese salt or a cobalt salt as a catalyst.[23–32] A review concerning the catalytic oxidative carbon–carbon bond cleavage of ketones was published by Brégeault et al.[33] As for other preparation methods for adipic acid, the O_2 oxidation of cyclohexanol,[34] the nitric acid oxida-

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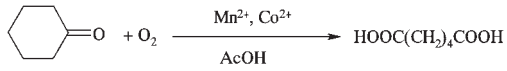


Scheme 2. O_2 oxidation of cyclohexanone.

tion of 1,2-dihydroxycyclohexane without N_2O generation,[35] the H_2O_2 oxidation of cyclohexene,[36] and the hydroformylation of butadiene have also been reported.[37,38]

We have considered cyclohexanone to be a key intermediate in developing a new O_2 oxidation process for adipic acid production. This is because cyclohexanone can be oxidized by O_2 easily, and is also an ingredient in the present nitric acid oxidation process. Moreover, the use of cyclohexanone is desirable since it is consumed in great quantities as an ingredient of ε-caprolactam. The oxidation of cyclohexanone (Scheme 2) is a well-known reaction, but the possibility of any industrial application is still ambiguous.

In this paper, we report the liquid-phase O_2 oxidation (autooxidation) of cyclohexanone by the use of acetic acid as a solvent and Mn and Co salts as catalysts. One hundred percent conversion of cyclohexanone should be a prerequisite condition in the new adipic acid plant, because recycling of cyclohexanone complicates the process. Therefore, we investigated the oxidation reaction for the high conversion of cyclohexanone. We also report the possibility of the industrial applicability of this reaction.

Experimental

Preparation of Adipic Acid under Atmospheric Pressure. Typical reaction conditions (Run 7) are as follows. A 200 mL four-necked flask with a condenser, an agitator, a thermocouple, and a nozzle for O_2 in-feed was placed in a water bath. Into this reactor we placed 9.00 g (0.0918 mol) of cyclohexanone (1st Grade by Wako Pure Chemicals Industries, Ltd.), 1.60 g (6.55 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ (Special Grade, Wako), 1.63 g (6.55 mmol) of $Co(OAc)_2 \cdot 4H_2O$ (Special Grade, Wako), 4.50 g of water, 1.04 g (5.47 mmol) of *p*-toluenesulfonic acid monohydrate, and 72.23 g of acetic acid (Special Grade, Wako). All of the reagents were used without purification. O_2 from a cylinder was introduced at 4 $dm^3\,h^{-1}$ and the temperature was controlled at 70 °C. The oxidation reaction was allowed to proceed for 5 h with 1500 rpm agitation. The color of the reaction solution was dark brown, which was the color of the Mn(III) and Co(III) during the reaction, and the color gradually became light after we stopped feeding with O_2. Gas chromatography and high-performance liquid chromatography under the conditions described below were used to analyze the remaining cyclohexanone and the oxidation products.

Preparation of Adipic Acid under High Pressure. A 0.660 dm^3 autoclave (i.d. = 60 mmϕ) made of Hastelloy-C incorporating an agitator, two baffle plates, a thermocouple, a nozzle for O_2 in-feed, and a condenser was placed in a hot water bath. The flow rates of O_2 from a cylinder and N_2 from a cylinder were controlled automatically to adjust the partial pressure of oxygen at a constant value for the oxidation reaction. Fine bubbles of the mixture gas were injected into the reactor through a fritted metal filter set at the tip of the O_2 feed nozzle. Waste gas was cooled by the condenser fitted to the top of the reactor in order to return the condensate to the reactor and then released to the outside through a backpressure valve. Typical reaction conditions (Run 79) are as follows: 15.0 g (0.153 mol) of cyclohexanone, 2.71 g (11.1 mmol) of $Mn(OAc)_2 \cdot 4H_2O$, 2.55 g (10.2 mmol) of $Co(OAc)_2 \cdot 4H_2O$, 7.40 g of water, 0.85 g (4.47 mmol) of *p*-toluenesulfonic acid (Practical Grade, Wako), and 121.7 g of acetic acid. Oxygen and nitrogen were introduced at 4.9 $N\,dm^3\,h^{-1}$ and 48.1 $N\,dm^3\,h^{-1}$, respectively, and the pressure was controlled at 1.21 MPa (absolute pressure). All of the reagents were used without purification. The temperature was controlled at 70 °C. The oxidation reaction proceeded for 5 h with 1200 rpm of agitation. Gas chromatography and high-performance liquid chromatography under the conditions described below were used to analyze the remaining cyclohexanone and the oxidation products.

HPLC Analysis of the Oxidation Products. Apparatus, Shimadzu LC10A. Column, ODS. Eluent, acetonitrile/H_3PO_4 (volume ratio, 0.15/0.85, H_3PO_4 conc., 0.15 wt %). Flow rate, 0.8 $mL\,min^{-1}$. Temperature, 15 °C. Detector, RI and UV. Standards, adipic acid (Asahi Kasei), glutaric acid (Special Grade, Wako), succinic acid (Special Grade, Wako), 6-oxohexanoic acid prepared using the method in the literature,[39] 5-oxopentanoic acid prepared using the method described below, and 2-hydroxycyclohexanone (Aldrich). Internal standard, pimelic acid (Special Grade, Wako). Retention time for HPLC: succinic acid, 13.4 min; 5-oxopentanoic acid, 14.5 min; glutaric acid, 17.8 min; 2-hydroxycyclohexanone, 20.8 min; 6-oxohexanoic acid, 25.1 min; adipic acid, 30.3 min; pimelic acid, 68.8 min.

GC Analysis for Measuring Cyclohexanone Conversion. Apparatus, Shimadzu GC-14B. Column, DB-1 (0.323 mmϕ × 30 m; film thickness, 0.30 μm). Temperature, 100 °C for 2 min; 100–180 °C for 16 min; 180–300 °C for 12 min; 300 °C for 5 min. Carrier, He (60 kPa). Injection temperature, 300 °C. Detector temperature (FID), 350 °C. Air pressure, 70 kPa. H_2 pressure, 60 kPa. We assumed the oxidation reaction to be a pseudo first-order reaction with respect to cyclohexanone in order to roughly estimate the reaction rates, k (h^{-1}). Reaction rates were estimated from the relationship between cyclohexanone conversion and time.

GC/MS Analysis for Oxidation Products Processed with a Methyl Esterification Reagent. GC apparatus, HP-5890A. Column, CPB10 (0.25 mmϕ × 20 m; film thickness, 0.25 μm). Temperature, 70–250 °C (5 $°C\,min^{-1}$). Carrier, He of 15 $mL\,min^{-1}$. MS apparatus, JEOL AX-500 (EI, CI); methyl pentanoate acid, CI-MS m/z, 117 (M + 1, 100), 59 (5); 2-hydroxycyclohexanone, CI-MS m/z, 115 (M + 1, 100), 99 (10); dimethyl succinate, CI-MS m/z, 147 (M + 1, 100), 115 (20); dimethyl glutarate, CI-MS m/z, 161 (M + 1, 100), 129 (30); methyl 6-oxohexanoate, CI-MS m/z, 145 (M + 1, 100), 113 (20); dimethyl adipate, CI-MS m/z, 175 (M + 1, 100), 143 (25); dimethyl azelate, CI-MS m/z, 217 (M + 1, 100), 185 (10); dimethyl sebacate, CI-MS m/z, 231 (M + 1, 100), 199 (10).

Preparation of 5-Oxopentanoic Acid. 5-Oxopentanoic acid was prepared as an HPLC standard by the following procedure. Using a method reported in the literature,[40] cyclopentanone was oxidized in water by O_2 with $FeCl_3$ and $VOSO_4$ as catalysts. A 200 mL four-necked flask fitted with a condenser, an agitator, a thermometer, and an O_2 bag was placed in a water bath. Into this reactor we added 5.21 g (0.0620 mol) of cyclopentanone, 1.04 g (6.41 mmol) of $FeCl_3$, 1.34 g (8.22 mmol) of $VOSO_4$, and 58.5 g of water. The temperature was controlled at 70 °C. The oxidation reaction proceeded for 5 h with 550 rpm of agitation. GC/MS analysis indicated that the main products were 5-oxopentanoic acid and glutaric acid. The reaction solution was used as an LC standard for 5-oxopentanoic acid. The results of the GC/MS analysis are shown below. GC apparatus, HP-5890A. Column, Dura-

bond DB-1 (0.25 mm $\phi \times 30$ m; film thickness, 0.25 μm). Temperature, 100 °C for 2 min; 100–300 °C (20 °C min^{-1}). Carrier, He 100 dm^3 min^{-1}. MS apparatus, JEOL AX-500 (EI, CI); CI-MS m/z 117 (M + 1, 100), 99 (70).

Results and Discussion

Effect of Metal Salt Catalyst Used with $Mn(OAc)_2$. The selectivity of adipic acid in the liquid-phase oxidation reaction of cyclohexanone with a $Mn(OAc)_2$ catalyst is low. Table 1 summarizes the selectivity of adipic acid quoted in the literature and in Run 1. These results show that the selectivity of adipic acid is 72% or less. It is necessary for the selectivity of adipic acid to be improved to create a viable industrial process. Various attempts have been made to improve the selectivity of adipic acid. Kulrestha and Roch reported a combination of Mn, Cu, and Ba salts,[41] Nishino reported a combination of Mn and Ce salts,[42] and Kusunoki and Ogawa reported a combination of Mn and Pb salts.[43] Shinohara et al. reported the combination of a Co salt and a Mn salt as catalysts in the oxidation of KA oil (a mixture of cyclohexanone and cyclohexanol).[44–46] Figure 1 summarizes the results of screening for different catalysts at over 90% of cyclohexane conversion in our study. The combination of $Mn(OAc)_2$ and $Co(OAc)_2$, for which the selectivity of the adipic acid was 77%, was the most effective in improving the selectivity with respect to adipic acid. Kamiya and Kotake have already reported that a combination of an Mn salt and a Co salt accelerated the rate of oxidation at low catalyst concentration (2×10^{-4} M).[23] However, they did not mention the effectiveness in terms of adipic acid selectivity. The combination of a Mn salt and a Co salt was effective in increasing selectivity with respect to adipic acid under the high concentration (ca. 10^{-1} M) of catalyst employed in this study.

Reaction Mechanism. Scheme 3 illustrates a possible mechanism for the oxidation reaction. When a Mn catalyst is used in the liquid-phase oxidation (auto-oxidation) of cyclohexanone, the first oxidation product, 2-hydroperoxycyclohexanone **6**, is probably generated via the enol tautomer of cyclohexanone **2**.[23] Pritzkow[47] and Ogawa et al.[25] took the intermediates to be 2-hydroperoxycyclohexanone **6** and 6-oxohexanoic acid **12** via compound **11** using a Mn salt catalyst. Druliner and Wasserman concluded that cyclohexane-1,2-dione **5** generated by the disproportionation of compound **4** was the main intermediate from their study of the oscillatory

Table 1. Adipic Acid Selectivity by O_2 Oxidation **1** (Cyclohexanone) with $Mn(OAc)_2$ from the Literatures

	1	$Mn(OAc)_2$	Solvent	Temp	Conv. of **1**	Selectivity of **17**	Time
	M	mM		°C	%	%	h
Kamath and Chandalia, 1973[27]	1.2	7.4	AcOH	80	44.2	61.5	5
Constantini and Krumenacker, 1983[31]	5.4	84	AcOH	65	85	53	5
Kamiya and Kotake, 1973[23]		1	AcOH		82	59	
Ogawa et al., 1967[25]	2.8	12	AcOH	70	>90	72	
Rao and Raghunathan, 1984[30]	1	5	AcOH	105	97.6	70.5	
Ohashi and Mizutani, 1941[28]	5		AcOH	95		33.6	
Run 1	1	73	AcOH	70	99.3	68.1	5

Other conditions of Run 1, H_2O, 5.0 wt %; O_2, 4 dm^3 h^{-1}.

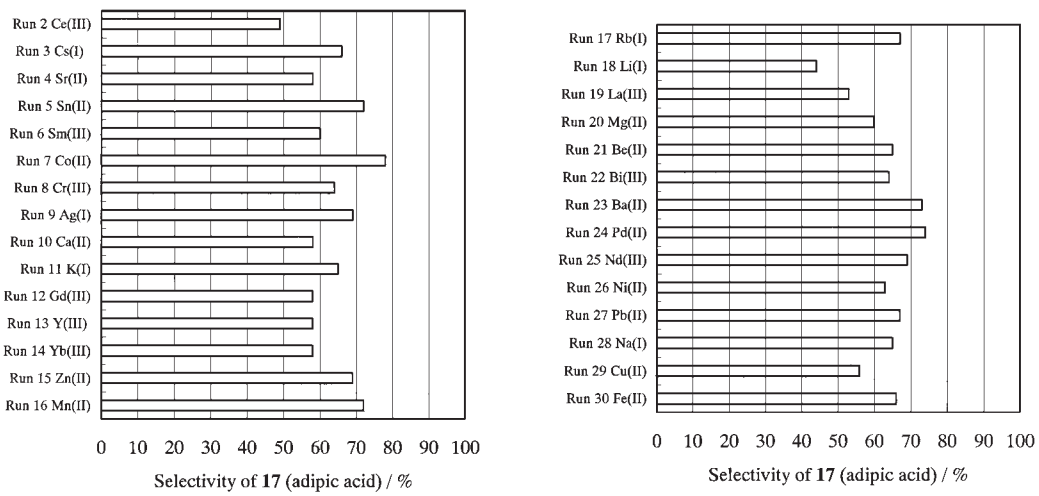
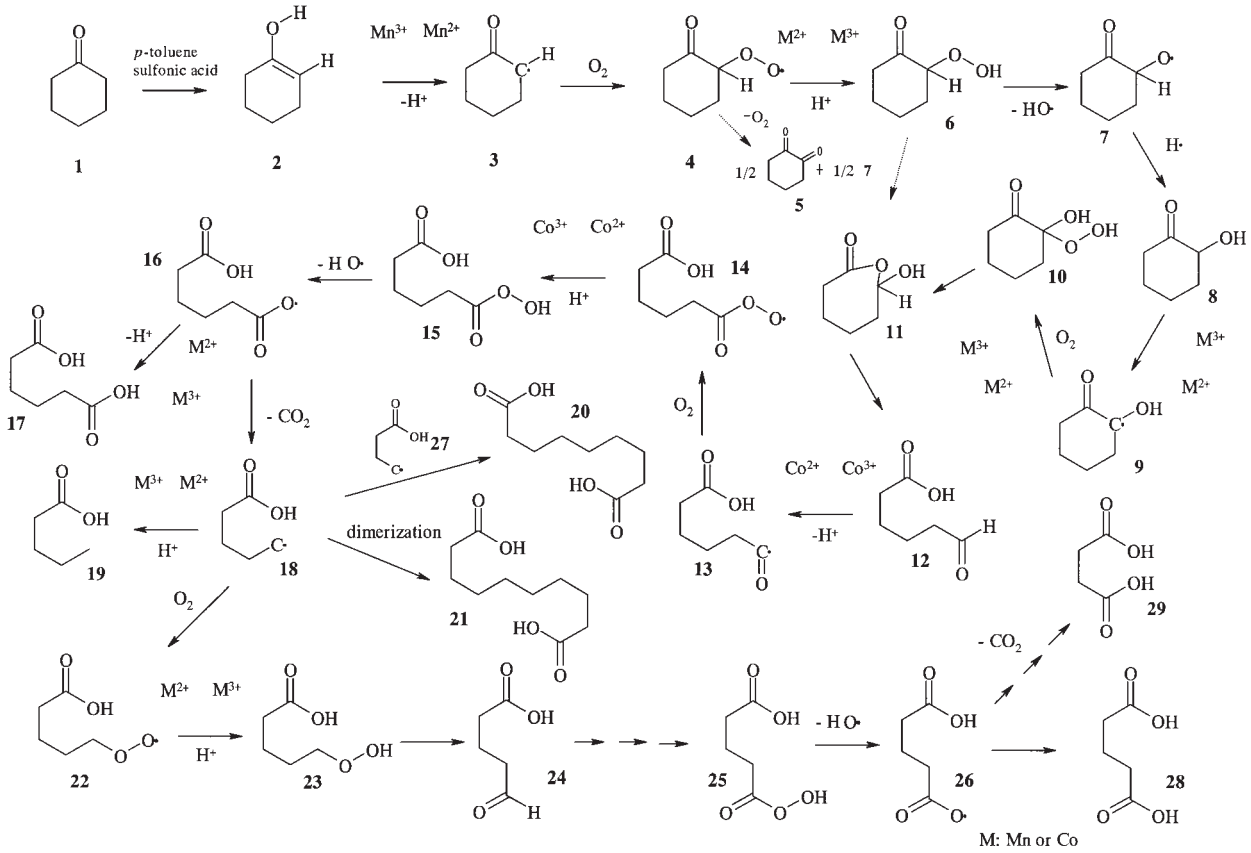


Fig. 1. Effect of metal salt combined with $Mn(OAc)_2$. Reaction conditions: **1** (cyclohexanone), 1.02 M. Mn(II), 72.8 mM. H_2O, 5 wt %. Temp, 70 °C. O_2, 4 dm^3 h^{-1}. Solvent, Acetic acid. All metal salts were metal acetate. Molar ratio of Metal to Mn, Ag/Mn, 0.53; Sn/Mn, 0.25; Cu/Mn, 0.43; Pb/Mn, 0.27; Ni/Mn, 0.49; Nd/Mn, 0.38; Pd/Mn, 0.52; Ba/Mn, 0.40; Bi/Mn, 0.27; Others/Mn, 1.00. Molar ratio of *p*-toluenesulfonic acid (*p*-TS) to Mn, Runs 18, 22, 23, 24, 25, 27, 29, *p*-TS/Mn = 0.84; Others, *p*-TS/Mn = 0.42. Reaction time, Run 24, 2.5 h; Runs 7, 9, 18, 22, 23, 25, 27, 29, 30, 3 h; Runs 16, 20, 4 h; Others, 5 h. Conversion of **1** (cyclohexanone), Run 3, 92.1%; Run 10, 94.9%; Run 11, 92.6%; Run 17, 92.5%; Run 18, 93.9%; Run 19, 96.1%; Run 20, 95.6%; Run 28, 94.2%; Others, >97%.



Scheme 3. Reaction mechanism for the oxidation of cyclohexanone.

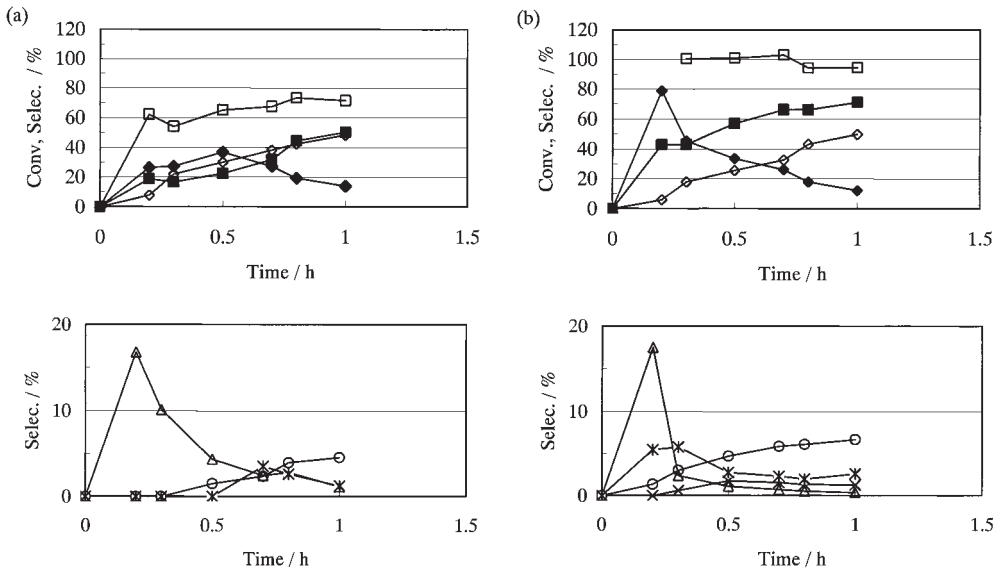


Fig. 2. Changes of intermediates and products with time. ◇, Conv. of **1**; □, Total selectivity; ◆, **12**; ■, **17**; △, **8**; ∗, **24**; ○, **28**; ×, **29**. Reaction conditions: Temp, 70 °C. O_2, 6 dm^3 h^{-1}. (a) Run 31, **1** (cyclohexanone), 9.76 g (1.27 M); AcOH, 50.9 g; H_2O, 15.1 g; $Mn(OAc)_2 \cdot 4H_2O$, 2.9 g (151 mM). (b) Run 32, **1** (cyclohexanone), 18.62 g (1.89 M); AcOH, 74.0 g; H_2O, 4.90 g; $Mn(OAc)_2 \cdot 4H_2O$, 1.60 g (64.7 mM); $Co(OAc)_2 \cdot 4H_2O$, 1.67 g (66.6 mM); *p*-toluenesulfonic acid, 0.56 g (29.1 mM).

oxidation of cyclohexanone with 20 mM of $Co(OAc)_2$.[48] The conversion of cyclohexanone and the selectivity of the oxidation products with time when using the $Mn(OAc)_2$ catalyst and the $Mn(OAc)_2/Co(OAc)_2$ catalyst are shown in Fig. 2. The main products besides adipic acid **17** were 2-hydroxycyclohexanone **8**, 6-oxohexanoic acid **12**, 5-oxopentanoic acid **24**, glutaric acid **28**, and succinic acid **29**. Figure 2 indicates that 2-hydroxycyclohexanone **8** is generated first, followed by 6-oxohexanoic acid **12**. As shown in Table 2, compound **17**, which was accompanied by **28**, **29**, **12**, and **24**, was the main product

Table 2. Oxidation of **12** (6-Oxohexanoic Acid) and **8** (2-Hydroxycyclohexanone)

	Raw material		Cat.			Conv. of	Selectivity/%				
		Conc./M		Conc./mM	Time/h	raw material/%	**17**	**28**	**29**	**12**	**24**
Run 33	**8**	1.08	$Mn(OAc)_2$	138	9	97*	54	2.4	9.4	4.5	7.4
Run 34	**8**	0.438	$Co(acac)_3$	438	4.5	100	24	15	4	3	2
Run 35	**8**	0.438	$Mn(OAc)_3$	438	4.5	100	38	3	10	3	11
Run 36	**12**	0.356	$Mn(OAc)_3$	111	9	94	58	17	2	—	4
Run 37	**12**	0.331	$Co(OAc)_2$	116	3	100	76	12	trace	—	trace

* The color of solution was light brown. Temp, 70 °C. O_2, 6 $dm^3 h^{-1}$. H_2O, Run 33, 18 wt %; Run 34, 0 wt %; Run 35, 2 wt %; Run 36, 7.7 wt %; Run 37, 7.3 wt %. Solv., AcOH.

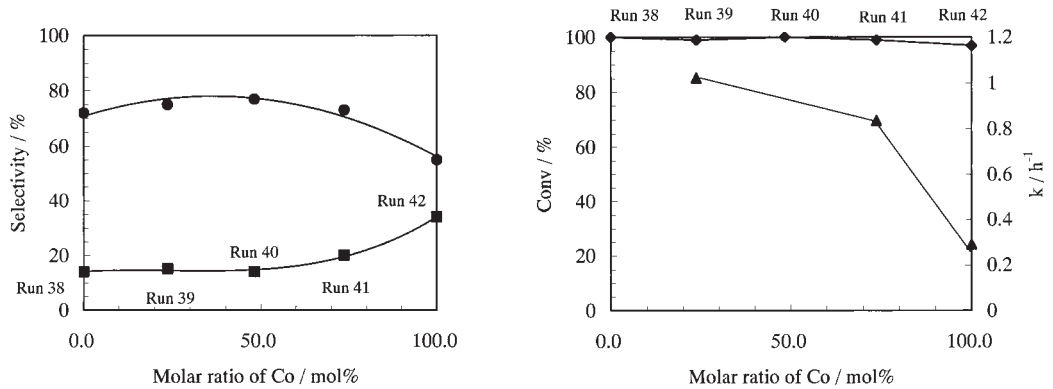


Fig. 3. The influence of the molar ratio of Mn to Co. ●, **17**; ■, **28** + **29**; ◆, Conv. of **1**; ▲, Consumption rate of **1**. Reaction conditions: Total conc. of Metals, Run 38, 136 mM; Run 39, 138 mM; Run 40, 140 mM; Run 41, 143 mM; Run 42, 146 mM. **1** (cyclohexanone), 1.02 M; H_2O, 6 wt %; *p*-TS, 32.0 mM; O_2, 4 $dm^3 h^{-1}$. Solv., AcOH. Temp, 70 °C. Reaction time, Run 38, 4 h; Run 39, 4.5 h; Run 40, 6 h; Run 41, 5.5 h; Run 42, 12 h (containing 2 h of induction period). Conversion of **1**, Run 38, 100%; Run 39, 99%; Run 40, 100%; Run 41, 99%; Run 42, 97%.

generated in the oxidation reaction of 2-hydroxycyclohexanone under a Mn catalyst and a Co catalyst (Runs 33–35). This result probably indicates that 2-hydroxycyclohexanone **8** is one of intermediates. Compound **12**, 6-oxohexanoic acid, which was prepared using the method in the literature,[39] was also converted to compounds **17**, **28**, **29**, **12**, **24** under a Mn catalyst and a Co catalyst (Runs 36, 37). These fact shows that 6-oxohexanoic acid **12** is also one of the intermediates. The oxidation of 6-oxohexanoic acid **12** under a Co(II) catalyst proceeded with a respectable selectivity of 76% in Run 37. This result shows that the Co(II) ion is probably the main catalyst in the oxidation of 6-oxohexanoic acid **12**. In general, an aldehyde compound such as acetaldehyde can be easily converted to carboxylic compounds via peroxyacid.[48,49] Therefore, 6-oxohexanoic acid **12** is probably converted to adipic acid **17** via monoperoxyadipic acid **15**. Measurement of the reaction mixture (processed with a methyl esterification agent) using GC/MS indicated that valeric acid **19**, azelaic acid **20**, and sebacic acid **21** were generated. Valeric acid **19** is generated in the reaction between the pentanoic acid radical (4-carboxybutyl radical) **18**, which is generated from the decarboxylation reaction of monoperoxyadipic acid **15**, and the hydrogen radical. Azelaic acid **20** is probably generated in the reaction between radical **18** and the butanoic acid radical (3-carboxypropyl radical) **27** generated from the decarboxylation reaction of monoperoxyglutaric acid **25**. A possible mechanism for the generation of sebacic acid **21** is the dimerization of radical **18**. The reaction between O_2 and radical **18** would give 5-oxopentanoic acid **24**, which would then be converted to glutaric acid **28** via monoperoxyglutaric acid **25**. Succinic acid **29** is probably generated from radical **27** branched at the radical compound **26**.

Influence of the Ratio of Mn to Co and Metal Concentration. Figure 3 shows the relationship between the molar ratio of Mn to Co and the selectivity of dibasic acids at 136–146 mM of Mn and Co catalysts. The peak of the adipic acid selectivity, which was shown to be 77%, occurred at around 1/1 of Mn/Co (molar ratio). The selectivity of glutaric acid and succinic acid increased with increasing Co. The reaction-rate for cyclohexanone decreased with increasing Co concentration. From the viewpoint of adipic acid selectivity, a suitable molar ratio of Mn to Co is 1/1. The metal ion concentration dependence of the adipic acid selectivity and reaction-rates is indicated in Fig. 4. The acceleration effect on the reaction-rate caused by Co was observed at a low concentration of the catalyst (ca. 10^{-3} M), as reported by Kamiya and Kotake.[23] The selectivity and the reaction-rates increased with metal ion concentration and become constant at a metal ion concentration of more than 150 mM. From the viewpoint of productivity of adipic acid, the concentration of metal ion should be settled at ca. 150 mM.

Optimum Reaction Temperature. Figure 5 shows the temperature dependence of the reaction. The selectivity decreased with temperature above 70 °C. Unknown peaks on an LC chart increased and the selectivity of glutaric acid and succinic acid remained almost constant at the elevated temperatures (Run 57, glutaric acid, 5%, succinic acid, trace; Run 58,

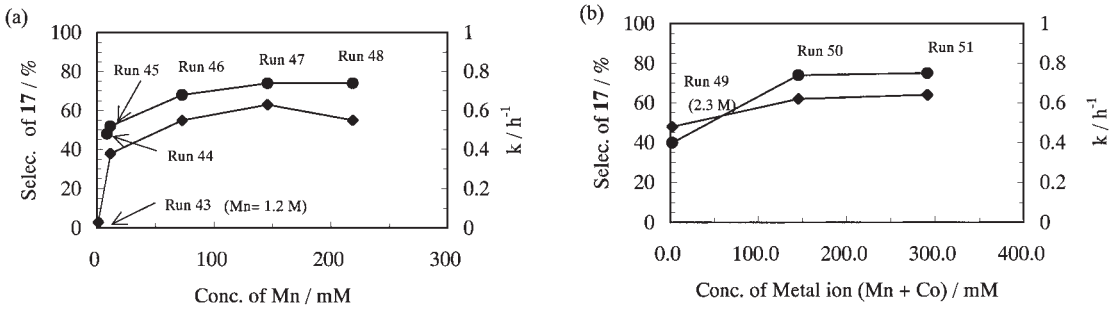


Fig. 4. Selectivity of adipic acid vs concentration of metal ions. ●, Selectivity of **17**; ◆, Consumption rate constant of **1** k (h^{-1}). Reaction conditions: **1** (cyclohexanone), 1.02 M. Temp, 70 °C. O_2, 6 $dm^3\,h^{-1}$. Reaction time, Run 43, 5 h; Run 44, 9 h; Run 45, 5 h; Run 46, 9 h; Run 47, 11 h, Run 48, 9 h; Run, 49, 5 h; Run 50, 5 h; Run 51, 7 h. H_2O, Runs 43–45, 0 wt %; Runs 46–48, 6 wt %; Run 49, 0 wt %; Run 50, 11 wt %; Run 51, 7 wt %. Molar ratio of Mn/Co (Runs 49–51), 1/1. Solv., AcOH. Conv. of **1**, Run 43, 14%; Run 44, 99.4%; Run 45, 85%; Run 46, 99.3%; Run 47, 99.9%; Run 48, 99.3%; Run 49, 91%; Run 50, 95.4%; Run 51, 98.9%.

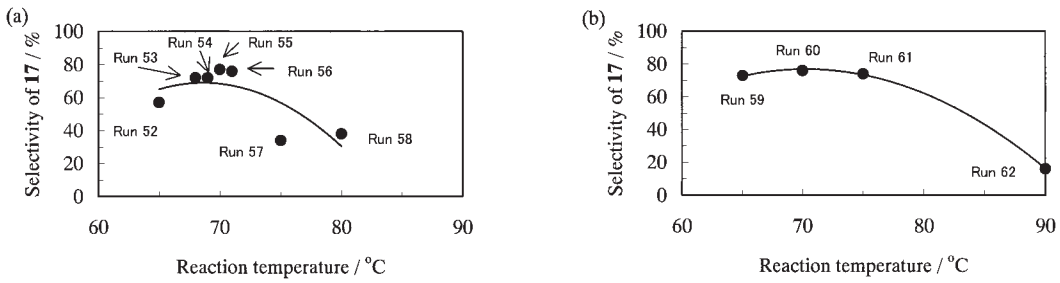


Fig. 5. Temperature dependence of adipic acid selectivity. Reaction conditions: **1** (cyclohexanone), 1.02 M. Mn, 146 mM. H_2O, 3.3 M (6 wt %). O_2, 4 $dm^3\,h^{-1}$. *p*-Toluenesulfonic acid, Runs 53–56, 9.9 mM; Others, 0 mM. Solv., AcOH. Reaction time, Run 52, 5 h; Run 53, 3 h; Run 54, 3 h; Run 55, 3 h; Run 56, 3 h; Run 57, 5 h; Run 58, 5 h. Conversion of **1**, Run 52, 86.0%; Run 53, 93.5%; Run 54, 93.6%; Run 55, 94.7%; Run 56, 96.1%; Run 57, 100%; Run 58, 100%. (a) **1** (cyclohexanone), 1.02 M. Mn, 73 mM. Co, 68 mM. H_2O, 3.3 M (6 wt %). O_2, 4 $dm^3\,h^{-1}$. *p*-Toluenesulfonic acid, 33.7 mM. Solv., AcOH. Reaction time, Run 59, 7 h; Run 60, 5 h; Run 61, 3 h; Run 62, 3 h. Conversion of **1**, Run 59, 99.4%; Run 60, 99.5%; Run 61, 99.4%; Run 62, 99.4%.

glutaric acid, 7%, succinic acid, trace; Run 62, glutaric acid, 7%, succinic acid, 17%). This phenomenon probably indicates the existence of side reactions having large activation energies. From this result, the optimum temperature for the reaction is 70 °C. Ogawa et al. reported that the peak selectivity occurred around 70 °C at low concentrations of Mn (2.8 mM).[25] Kamath and Chandalia also reported peak selectivity around 80 °C at low concentrations of Co (7 mM).[27]

The Effect of the Addition of Acid and Water. Costantini and Krumenacker reported that acids accelerated the oxidation reaction using a Mn salt in acetic acid.[31] Figure 6 shows the relationship between the reaction-rate and the concentration of *p*-toluenesulfonic acid. The addition of acid accelerated the oxidation reaction, both in the reactions with a Mn/Co catalyst as well as a Mn catalyst. The acceleration effect of acid on the oxidation reaction using the Mn catalyst was larger than the effect of acid on the reaction using the Mn/Co catalyst. The acceleration effect can be explained as the catalytic effect of acid on the tautomerism between cyclohexanone **1** and compound **2**. From the viewpoint of productivity, the addition of acid is desirable for an industrial process.

Figure 7 shows the relationship between the concentration of water and the selectivity of adipic acid and the relationship between the concentration of water and the reaction-rate at 52/48 (mol%/mol%) of Mn/Co. Although the effect of water on the selectivity of adipic acid is not prominent below 20 wt %,

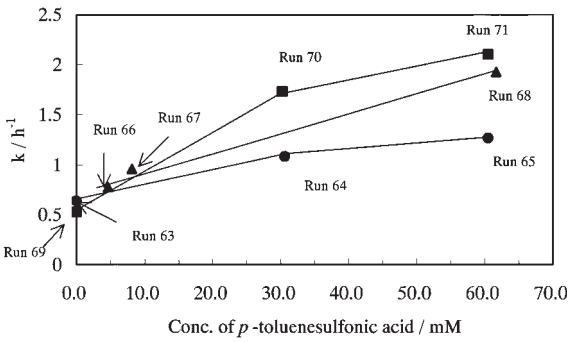


Fig. 6. The effect of *p*-toluenesulfonic acid. ●, Mn (72.9 mM) + Co (73.0 mM); ■, Mn (72.9 mM); ▲, Mn (146 mM). Reaction conditions: **1** (cyclohexanone), 1.02 M; H_2O, 6 wt %; Temp, 70 °C; O_2, 4 $dm^3\,h^{-1}$. Solv., AcOH. Water, 6 wt %. Reaction time, 3–4 h.

it has a small peak at around 10% of water. The reaction-rate decreased slightly with increasing water content. Ogawa reported that the selectivity of adipic acid in the oxidation reaction of a cyclohexanone/cyclohexanol mixture increased with the amount of water, and it was stable at more than 1% water under 8 mM of $Mn(OAc)_2$.[26] Kamiya reported that the reaction-rate had a peak at around 1% water at 20 mM of $Co(OAc)_2$.[24] From the result of this study, the effect of wa-

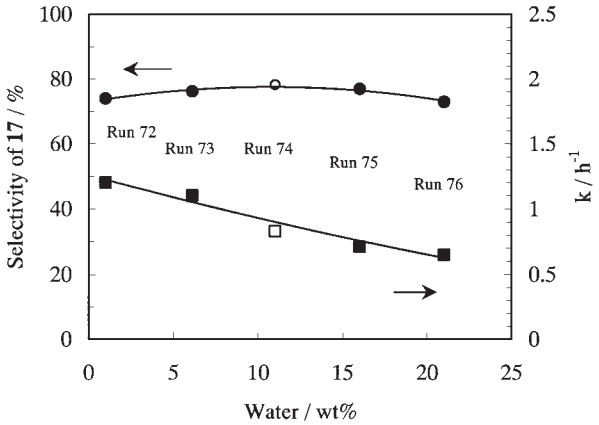


Fig. 7. The effect of water. ●, Selectivity of **17**; ■, Reaction rate. Reference data, ○, Selectivity of **17** in Run 74; □, Reaction rate of **17** in Run 74. Reaction conditions: **1** (cyclohexanone), 1.02 M. $Mn(OAc)_2$, 72.9 mM. $Co(OAc)_2$, 67.9 mM. Temp, 70 °C. O_2, 4 $dm^3\,h^{-1}$. *p*-Toluenesulfonic acid, Run 72, 28.5 mM; Run 73, 30.8 mM; Run 74, 24.4 mM; Runs 75, 76, 29.1 mM. Solv., AcOH. Reaction time, 3–6 h. Conversion, Run 72, 99.7%; Run 73, 99.6%; Run 74, 99.6%; Run 75, 99.6%; Run 76, 99.8%.

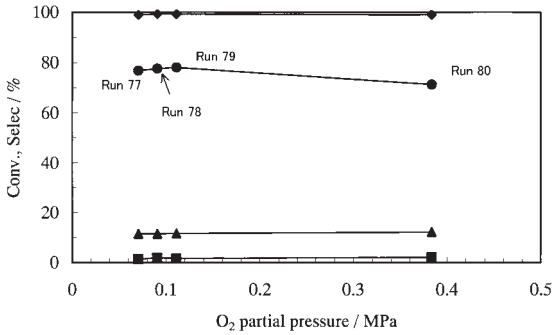


Fig. 8. Conversion and selectivity vs O_2 partial pressure. ◆: Conversion of **1**, ●: Selectivity of **17**, ▲: Selectivity of **28**, ■: Selectivity of **29**. Reaction conditions: **1** (cyclohexanone), 1.02 M. $Mn(OAc)_2$, 72.9 mM. $Co(OAc)_2$, 67.9 mM. Temp, 70 °C. Press. (absolute), Run 77, 0.81 MPa; Run 78, 1.01 MPa; Run 79, 1.21 MPa; Run 80, 4.65 MPa. O_2 partial press., Run 77, 0.071 MPa; Run 78, 0.091 MPa; Run 79, 0.111 MPa; Run 80, 0.384 MPa. Flow rate of N_2 and O_2, Runs 77–79, 53 $Ndm^3\,h^{-1}$; Run 80, 70 $Ndm^3\,h^{-1}$. Solv., AcOH. *p*-Toluenesulfonic acid, 29.7 mM. Water, 6 wt %. Reaction time, Run 77, 5 h; Run 78, 5 h; Run 79, 5 h; Run 80, 3.7 h.

ter in the presence of a high concentration of catalyst is small. When water wasn't used in the reaction, adipic acid precipitated easily. This would cause trouble in an actual industrial plant. Therefore, the existence of water is necessary for the operation of a practical process.

The Effect of O_2 Pressure. Pure oxygen is hard to handle in an organic chemical reaction in an industrial process because of explosion hazards. The concentration of oxygen in the gas emitted during terephthalic acid production, which is commercialized in an acetic acid solvent with a $Co(OAc)_2$ catalyst, is limited to 2–5 vol % to avoid explosion.[50] Figure 8 shows the result of the liquid-phase oxidation reaction under high pressure and low O_2 concentration in the autoclave described in the experimental section. The selectivity of adipic acid has a peak (78%) at around 0.101 MPa of O_2 (partial pressure). We found that the oxidation reaction proceeded under high pressure, even if the O_2 concentration was less than 10 vol %. We think that the industrial process should employ a high-pressure reactor with a low O_2 concentration. From this result, 0.101 MPa of O_2 (partial pressure) should be used in an industrial process.

Industrial Process for Oxidation of Cyclohexanone. Table 3 shows the results of the liquid-phase oxidation using $Mn(OAc)_2/Co(OAc)_2$ under preferable reaction conditions for an industrial process. When the concentration of cyclohexanone was 2 M (Run 82), the selectivity was the same as in the case of 1 M cyclohexanone (Run 7). Therefore, the concentration of cyclohexanone should be 2 M in a practical plant. When the reaction is roughly assumed to be a pseudo first-order reaction with respect to cyclohexane concentration, the rate-constant k (h^{-1}) of the reaction using $Mn(OAc)_2/Co(OAc)_2$ with *p*-toluenesulfonic acid was calculated to be 1.04 h^{-1} (Fig. 9). Figure 10 shows the relationship between the adipic acid yield and the cyclohexanone conversion. The relationship was almost linear and the slope of the line was 0.745. Therefore, the rate of adipic acid generation can be represented by $0.745 \times 1.04\ (h^{-1}) \times$ cyclohexanone conc. ($mol\,dm^{-3}$). Figure 11 explains the block diagram for manufacturing adipic acid from cyclohexanone. The plant consists of 3 high-pressure CSTRs combined in series with each other. The O_2 concentration of the gas phase of those reactors should be controlled at around 5% to avoid explosion as well as terephthalic acid production. The first reactor and the second reactor are operated at 70 °C and the third reactor is operated at over 70 °C. The concentration of cyclohexanone in the first reactor decides the productive capacity of adipic acid. When the concentration of cyclohexanone at the exit of the first reactor is 2 M, adipic acid productivity is 150 $kg\,m^{-3}\,h^{-1}$. This produc-

Table 3. Results of the Oxidation Reaction under Preferable Reaction Conditions for an Industrial Process

	1	$Mn(OAc)_2$	$Co(OAc)_2$	H_2O	*p*-Toluenesulfonic acid	O_2	N_2	Press.	Temp.	Time	Conv. of **1**	Selectivity/%						
	M	mM	mM	wt %	mM	dm^3/h	dm^3/h	MPa	°C	h	%	**17**	**28**	**29**	**8**	**12**	**24**	Total
Run 7	1.02	72.6	72.8	5.0	60.6	4.0	—	0.10	70.0	3.0	97.5	77	12	2	0	1	1	93
Run 40	1.02	72.5	67.5	6.0	32.0	4.0	—	0.10	70.0	6.0	100.0	77	12	2	0	1	1	93
Run 82	2.00	73.2	72.9	5.0	30.4	4.0	—	0.10	70.0	4.0	99.9	77	11	2	1	0	2	92
Run 79	1.02	73.4	67.9	6.0	29.7	4.9*	48.1*	1.21	70.0	5.0	99.3	78	12	2	0	0	0	92
Nitric acid oxidation (SRI, 1996)[1]											100.0	95	3	2				100

∗ $Ndm^3\,h^{-1}$. Solvent in Runs 7, 82, 79, AcOH.

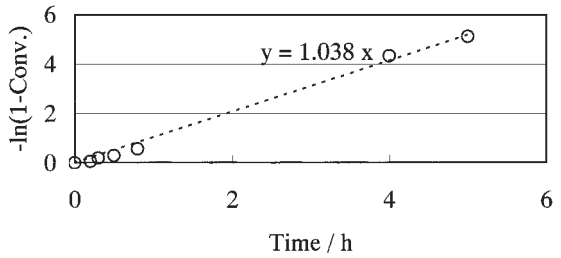


Fig. 9. Time vs $-\ln(1-\text{Conv.})$. Conv., conversion of **1** (cyclohexanone).

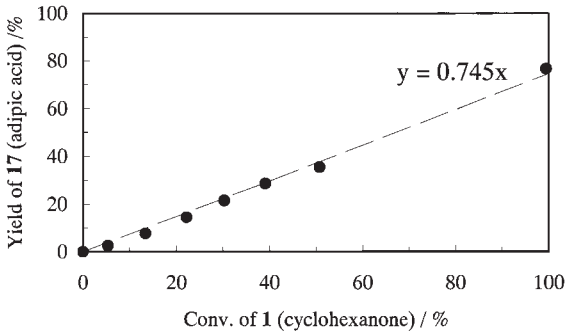


Fig. 10. Yield of adipic acid vs conversion of cyclohexanone in Run 32.

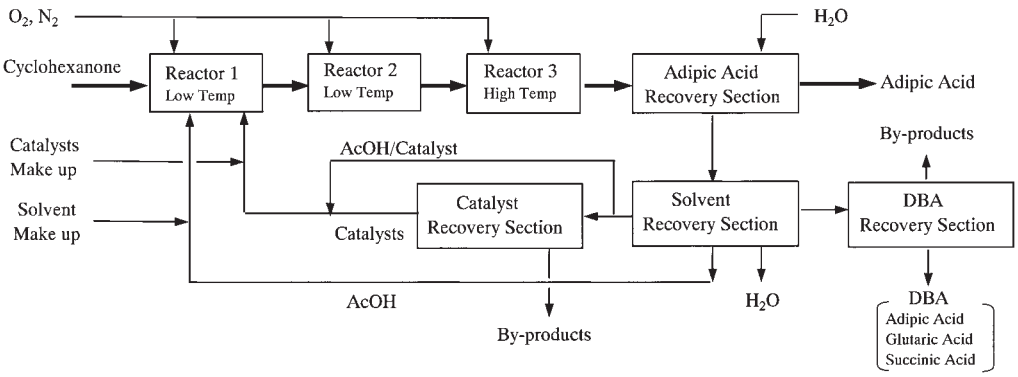


Fig. 11. Block diagram for manufacturing adipic acid from cyclohexanone.

tivity means that a ca. 42 m^3 reactor is necessary for 50000 t/y (50000 t per 8000 h) of adipic acid production. More than 90% of the cyclohexanone is consumed in the second reactor. The remaining cyclohexanone and the intermediates are consumed completely in the third reactor at elevated temperature. The reaction solution is fed into the adipic acid recovery section, where adipic acid is purified by re-crystallization. Three-stage re-crystallization may be necessary, because the selectivity of adipic acid is low when compared to the present adipic acid production process that uses 2-stage re-crystallization.[1] The product, (the adipic acid), is obtained from the adipic acid recovery section. The solution, after removing the adipic acid, is moved to the solvent recovery section where AcOH is recovered by distillation. Water is added in the adipic acid recovery section to wash the adipic acid crystals and to dissolve the adipic acid crystals for re-crystallization. This water is removed in the solvent recovery section. Part of the concentrated solution in the solvent recovery section is moved to the DBA (dibasic acid) recovery section, where DBA is purified. The by-products are removed in the DBA recovery section. The other portion of the concentrated solution in the solvent recovery section is moved to the catalyst recovery section. By-products are removed in the catalyst recovery section as well as in the DBA recovery section. Acetic acid recovered in the solvent recovery section and the catalysts recovered in the catalyst recovery section are recycled to the first reactor. The liquid-phase oxidation process with acetic acid and metal acetate has been commercialized as a production process of terephthalic acid.[50] We think that technologies used in terephthalic acid production, such as solvent recovery, catalyst recovery, and explosion avoidance[50] are applicable to the liquid-phase oxidation of cyclohexanone. The selectivity of adipic acid and the total selectivity of dicarboxylic acids are low in the oxidation reaction of this study when compared to the present adipic acid process (Table 3). The difference in the combined selectivity of dicarboxylic acids between both processes is 7%. Compared to the nitric acid cost in the conventional process, this value is small. (See Appendix.) Furthermore, the fact that N_2O isn't generated and that the HNO_3 plant isn't necessary are significant merits for the liquid-phase oxidation of cyclohexanone.

Conclusion

We summarize the results as follows: (1) The combination of a $Mn(OAc)_2$ catalyst and a $Co(OAc)_2$ catalyst is effective for improving adipic acid selectivity in the liquid-phase oxidation of cyclohexanone with O_2. (2) Adipic acid is probably generated via 2-hydroxycyclohexanone and 6-oxohexanoic acid, and glutaric acid is probably generated via 5-oxopentanoic acid. (3) The optimum molar ratio of Mn to Co is 1/1 from the viewpoint of adipic acid selectivity. (4) The concentration of the metal salt should be set at ca. 150 mM from the viewpoint of productivity. (5) The selectivity of adipic acid shows a maximum at 70 °C. (6) Water concentration, which is less than 20 wt %, doesn't have a significant effect on the reaction. (7) Use of an acid, such as *p*-toluenesulfonic acid, accelerates the oxidation reaction. (8) The oxidation reaction proceeds under high pressure, even if the O_2 concentration is less than 10 vol %. An O_2 partial pressure of 0.101 MPa should be used in the industrial process.

The feasibility of technology required for an industrial adipic acid process depends on not only technical aspects but also capital investment due to the equipment and conditions at the location. Although we should continue further evaluations of the technology from various viewpoints, we think that the O_2 oxidation of cyclohexanone is one of possibility for an industrial adipic acid process.

Appendix

The valuable cost of KA oil and the valuable cost of nitric acid are explained as follows:

KA oil valuable cost/Nitric acid valuable cost = approx. 3/2.

The proportion of nitric acid cost in the total production cost of adipic acid is relatively large. Therefore, the selectivity of carboxylic acids in the present process doesn't have a large influence on the production cost of the carboxylic acids compared with the nitric acid cost in the conventional process.

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