Kinetic of Gas-Liquid Homogeneous Catalytic Oxidation of Cyclohexane

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Adipic acid is an important industrial chemical product, principally used in nylon 66 production, synthetic resins and lubricants. Mostly, adipic acid is produced by a two step oxidation process of cyclohexane with air and nitric acid as oxidants (Reis, 1965; Danly and Campbell, 1978). Cyclohexane is initially oxidized with air at 150°-160°C to cyclohexanol and cyclohexanone. The latter two products are then converted to adipic acid by a further oxidation performed with nitric acid. The use of nitric acid is characterized by its high consumption and to serious corrosion problems. For these reasons, several studies were performed to extend the use of air as oxidizing agents also in the second step of the process (Reis, 1971; Tanaka, 1974; Rao and Raghunathan, 1984, 1986). In these processes the adipic acid synthesis is then performed in a single step, using acetic acid as solvent and cobalt, manganese or copper salts as catalyst. To reduce the induction time, particularly relevant in the considered reaction, and to obtain higher yields to adipic acid, the addition of a promoter is necessary. Most used promoters are aldehydes, cyclohexanol and cyclohexanone. The main reaction products are the dibasic acids as the adipic, the glutaric and the succinic acids. Recently, the reaction was studied also on a heterogenous catalysts, in particular on a cobalt catalyst supported on ion exchange resins (CoAPO-5) still operating with the main reactant diluted in acetic acid (Shen and Weng, 1988; Lin and Weng, 1993, 1994). The heterogeneous process above is promising but some problems still remain, mainly due to the cobalt elution out of the resins by the water formed as by-product of the reaction. Thus, a strong catalyst deactivation is observed shifting the process from heterogeneous to homogeneous. To contrast these phenomena, the addition of acetic anhydride is necessary, leading to a less attractive process from the economical point of view.

Here, the single step oxidation of cyclohexane to adipic acid using homogeneous catalyst will be examined. The reaction was studied at lab scale in a well stirred semi-batch reactor using cobalt and zirconium salt as catalysts and acetaldehyde as promotor. By the acquisition of enough experimental data inherent the time evolution of the different reaction products, a reasonable reaction path will be proposed. Furthermore, the rates of the different reactions involved in the proposed scheme will be evaluated. The considered kinetic scheme will be finally used for the interpretation of the role of the reactants, of the catalyst and of the operative conditions on the process yield and selectivity.

1. Experimental

1.1 Apparatus and Chemicals

A 1000 cm^3 well stirred glass reactor, suitable to operate up to 20 bar and to 350°C, equipped with a stirring system was used to perform the considered reaction. The reactor was operated as semi batch for liquid reactants and as continuous for gas reactants. The gas was injected in the liquid through suitable holes manufactured inside the impellers of the stirring apparatus to obtain the greatest as possible gas dispersion within the liquid phase. The maximum available stirring speed was 2500 rpm but with a rotation speed greater than 900 rpm the system was found to operate in kinetically controlled regime. The reactor was operated in isothermal conditions assured by a thermostatic bath using oil as thermostatic fluid. The observed fluctuation of the temperature of the reacting mixture around the mean value resulted of the order of around 2°C. The reactor was equipped also with a sampling system for the liquid phase and with a top condenser that refluxes back the stripped components. The liquid feed (acetaldehyde) was performed through an external micrometric pump operating in the range 0.2-3.0 cm^3/min. The gas feed was controlled by a mass flow meter in between the range 2-100 Nl/h. A sketch of the described reactor is illustrated in Figure 1.

The following reactants were used for the here considered study: cyclohexane (CHX), acetic acid 100%, cobalt (II) acetate, zirconium (II) acetate, acetaldehyde, cyclohexanol (COH), cyclohexanone (ONE), glutaric acid (GLA), adipic acid (ADA) and succinic acid (SUA).

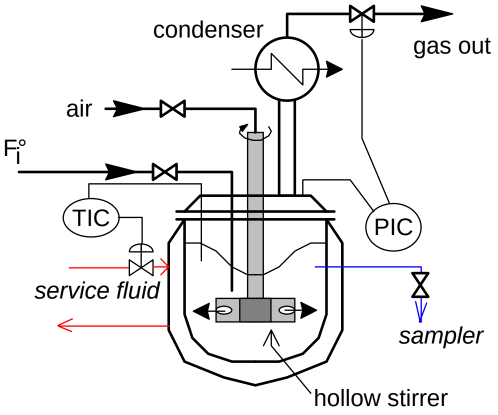

Figure 1. Schematic of the adopted reactor for the kinetic analysis

1.2 Analitical Methods

Cyclohexane, cyclohexanol, cyclohexanone, adipic acid, glutaric acid and succinic acid were determined by gas chromatographic analysis. In particular, a wide-bore Supelcovax 10 column (poly-ethylenglycol as stationary phase, length = 30 m, diameter = 0.53 mm, film thickness = 1 µm) was used in a Fisons 8100 chromatograph operating in the following conditions: Carrier He 5 cm^3/min, FID detector, detector temperature = 250°C, 0.1 µl injected sample, temperature programmed cycle (80°C x 3 min, 5°C/min, 200°C x 10 min). Internal standard method (chlorobenzene for cyclic compounds, pimelic acid for acid compounds) as described by Lin and Weng. The acid compounds need to be derivatized by BF_3/CH_3OH before to proceed the gas chromatographic analysis. In this case, pimelic acid was used as internal standard.

Also the exhaust gases (O_2, CO, CO_2) were determined by gas chromatographic analysis. A Dani 3800 chromatograph, equipped with a Carboxen 1000 column (length 4.5 m, diameter 1/8”), carrier He 25 cm^3/min, detector HWD, detector temperature 250°C, wire temperature 300°C, injector temperature 80°C, temperature programmed cycle (35°C x 8 min, 20°C/min, 250°C x 10 min) was adopted. Besides the analysis above, oxygen in the exhaust was continuously monitored by PMA 200 HORYBA. The water content in the liquid mixture was determined using the Karl-Fisher titration at the end of the reaction.

1.3 Experimental Procedure

The above described reactor was loaded with 35 g of cyclohexane and 150 g of acetic acid as solvent. The loaded catalyst in the reference run was 1.2 g of cobalt acetate and 0.03 g of zirconium acetate. When the role of catalyst was investigated those latter quantities were suitably varied as it will be discussed later. As reaction promoter, also 2 g of acetaldehyde were loaded. The reactor was then filled with nitrogen up to reach a pressure of about 10-12 atm, depending of the considered run. Finally, the reacting mixture is heated under stirring up to the desired temperature (e.g., 70°-95°C). When the liquid mixture reaches the desired temperature, the gas and the liquid feed were started. The gas mixture fed to the reactor had a variable oxygen/nitrogen molar ratio in between 20/80 and 40/60, while the liquid mixture contained 15% in weight of acetaldehyde in acetic acid. The temperature remained constant and no oxygen consumption was observed for all the induction time, then a sharp temperature increase of about 10°C was observed, meaning the start-up of the oxidation reaction. The reached temperature as described above was then kept constant by the thermostatic apparatus. The pressure control was achieved by a controller operating on the gas outlet. Finally, liquid samples were taken regularly during all the reaction time.

1.4 Experimental Results

The influence of temperature, oxygen partial pressure, stirring rate and catalyst concentration were explored. The main features of the performed experimental runs are summarized in Table 1. For each run, samples of the liquid mixture were taken at different times and then analyzed as previously described.

Only the compounds summarized in this Table will be considered for the kinetic analysis, being the amount of cyclohexylacetate negligible in all the performed runs. The behavior of such components vs time is illustrated in Figure 2, while the role of reaction temperature and of oxygen inlet mole fraction on cyclohexane conversion and adipic acid yield is reported in Figure 3 a-b. The influence of catalyst loading on the cyclohexane conversion and the selectivity towards the most important oxidation products has been also examined and the obtained results are given Figure 4a-b. Also the evolution of the oxidation state of cobalt has been analyzed. The obtained results, showed in Figure 5, reveal that except for the initial range of time a stationary concentration of Co^{III} is present in the reacting mixture.

Table 1. Main features of the performed experimental runs.

run	Temperature (°C)	Pressure (atm)	Initial Co acetate concentr. (weight %)	Stirring rate (rpm)	O_2 inlet (%mol)	gas flow rate (Nl/h)	initial CHX concentrat. (weight %)	liquid flow rate (ml/min)
1	71	12	0.637	900	20	20	18.6	0.25
2	86	12	0.637	900	20	20	18.6	0.25
3	96	12	0.637	900	20	20	18.6	0.25
4	86	12	0.637	500	30	20	18.6	0.25
5	86	12	0.637	500	40	20	18.6	0.25
6	85	10	0.683	900	20	20	14.2	0.25
7	85	10	0.67	500	20	20	14.2	0.25
8	85	10	0.68	1400	20	20	14.1	0.25
9	88	10	0.686	900	20	20	8.9	0.25
10	88	10	0.727	900	30	20	9.0	0.25
11	87	10	0.72	300	30	20	9.4	0.25
12	88	10	0.75	500	30	20	9.1	0.25
13	88	10	0.72	100	30	20	9.2	0.25
14	88	10	0.395	900	20	20	9.1	0.25
15	88	10	0.148	900	20	20	9.1	0.25
16	88	10	0.072	900	20	20	9.0	0.37
17	76	10	0.875	900	20	20	11.0	0.34
18	76	10	0.871	900	15	20	10.8	0.37
19	76	10	0.861	900	30	20	10.7	0.40
20	76	10	0.155	900	20	20	9.1	0.42
21	76	10	0.073	900	20	20	9.0	0.37

Solvent: acetic acid. Zr acetate 0.03 g, liquid feed: acetic acid, acetaldhyde (85:15)

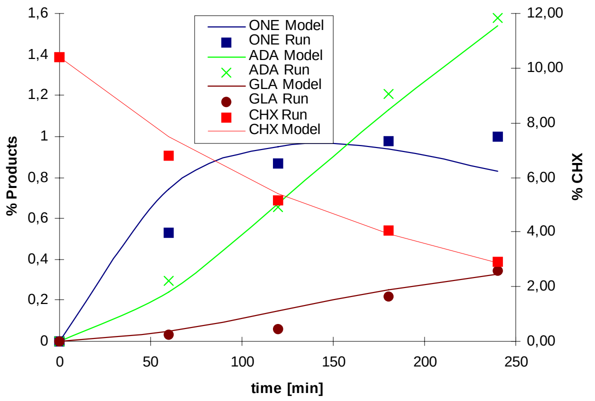

Fig.2 Behavior of different components vs time

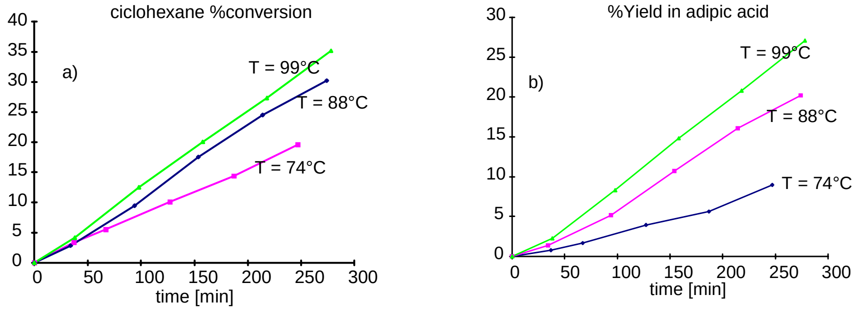

Figure 3a. Role of reaction temperature on: conversion of cyclohexane (left), yield to adipic acid (right). Time normalized setting is to zero at induction time.

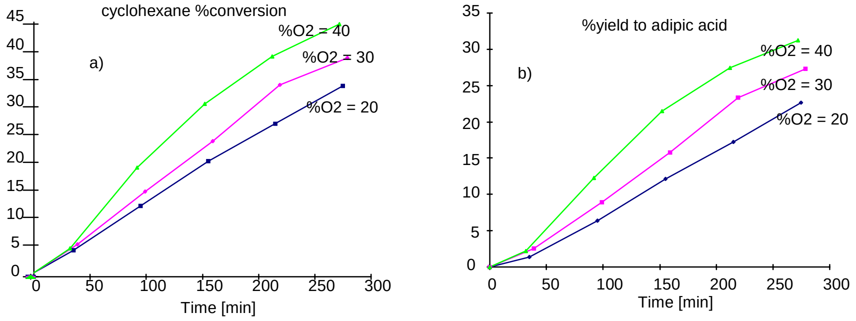

Figure 3b. Role of oxigen inlet mole fraction on: conversion of cyclohexane (left), yield to adipic acid (right). Time normalized setting is to zero at induction time.

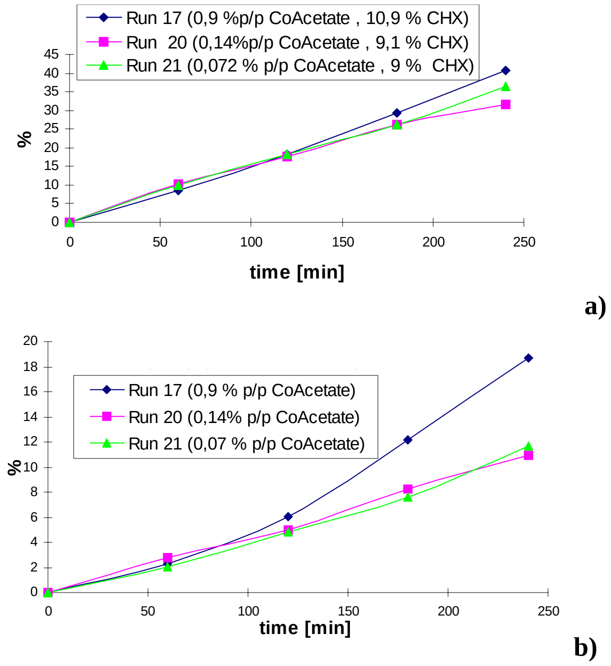

Figure 4. a) influence of catalyst loading on the cyclohexane conversion; b) yield to adipic acid.

2. Role of the Catalyst

The catalyst here adopted was a bimetallic catalyst of cobalt and zirconium acetate in the presence of acetaldehyde as promoter. The direct correlation between the Co(III) concentration and the cyclohexane oxidation rate was demonstrated by Tanaka (1974). In such a paper the presence of a considerable induction time required for the oxidation of the cobalt from bivalent to trivalent has been also evidenced (Figure 5). Also Scott and Chester (1972) confirmed that the reaction rate increases by increasing the Co(II) concentration during the study of toluene oxidation with cobalt acetate in acetic acid. The acetaldehyde in solution promotes the formation of hydro peroxides, as peracetic acid. Furthermore, a synergic effect was observed by the addition of small quantities of zirconium to cobalt, acting as co catalysts. This action is probably due to the tendency of zirconium to coordinate Co(III), stabilizing such an oxidation state. Acetaldehyde contributes to decrease the induction time. During the oxidation of cyclohexane on cobalt, Tanaka, by operating at a concentration of 0.017 M, found an induction time, of the order of 7 h. The addition of acetaldehyde reduces such a time by a factor of about four (Tanaka). This effect is enhanced by the presence of cobalt, zirconium and acetaldehyde, as it was evidenced by our experimental runs summarized in Table 2, where both runs were performed with 20% of oxygen in the gaseous stream.

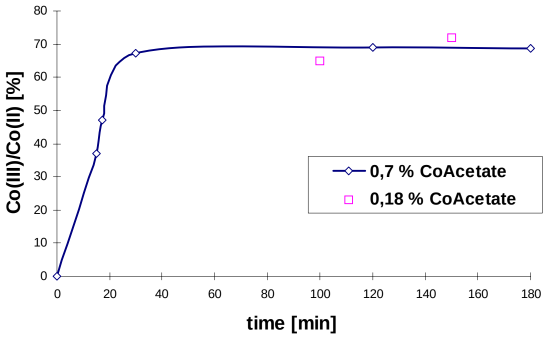

Figure 5. Evolution of Co(III) concentration in the runs

Table 2. Induction time as function of acethaldeyde, Cobalt and Zirconium.

Catalyst & operative conditions	induction time (min)	cyclohexane conversion
Cyclohexane 2.31 M, Co 0.064 M, Zr 0.00304 M, acetaldehyde 15 g.	13-15	42.2
Cyclohexane 2.31 M, Co 0.021 M, acetaldehyde 15 g.	20	35.2

3. References

Danly, D.E.; Campbell, C.R. “Adipic Acid” In Kirk Othmer Encyclopedia of Chemical Technology, 3rd ed.; Wiley: New York, 1978; Vol. 1 pp 510-531.

Lin, S.S, Weng,H.S., Appl. Catal. A: General; 1993, 105, 289-308

Lin, S.S, Weng,H.S., Appl. Catal. A: General; 1994, 118, 21-31.

Rao, D.G.; Raghunathan, T.S.”Oxidation of cyclohexanone to adipic acid with a cobalt acetate / oxygen / acetic acid system J. Chem. Technol. Biotechnol. 1984, 34A, 381-386.

Rao, D.G.; Raghunathan, T.S. “Liquid phase oxidation of cyclohexane to adipic acid in a single stage” Ind. Eng. Chem. Process Des. Dev. 1986, 25, 299-304

Reis, H.C. “Adipic acid” Report 3, 1965; SRI International, Menlo Park, C.A.

Reis, H.C. “Adipic acid” Report 3A, 1971; SRI International, Menlio Park, CA.

Shen, H.C., Weng, H.S. “Liquid phase oxidation of cyclohexanone to dibasic acids wiyh immobilized cobalt catalyst” Ind. Eng. Chem. Res. 1988, 27, 2246-2254

Scott, E.J.Y., Chester, A.W. “Kinetics of the Cobalt-Catalyzed Autoxidation of Toluene in Acetic Acid”, J. Physic. Chem., 1972, 78 (11), 1520-1524

Tanaka, K. “adipic acid in one step”. CHEMTECH 1974, 555-559