LIQUID-PHASE OXIDATION OF CYCLOHEXANE USING Co-P-MCM-41 CATALYST

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Abstract – Co-P-MCM-41 catalyst was prepared by introduction of cobalt nitrate and phosphoric acid during gel-preparation for the synthesis of MCM-41. The catalyst, which was found to have very high surface area (995 m^2/g), was tested for the one step liquid oxidation of cyclohexane to adipic acid using a semi-batch autoclave reactor (without addition of any promoter and solvent) at 115 °C and in a flow of 5 bar of oxygen. The effect of the amount of catalyst on the induction time, catalytic conversion of cyclohexane, and selectivity to adipic acid was investigated. Depending on the amount of catalysts used in the reaction (from 0.1 to 3.0 g), an induction period from about 100 min to less than 10 min, cyclohexane conversion from 30 to 99 %, and a selectivity to adipic acid from 15 to 40 %, could be achieved using Co-P-MCM-41 as the catalyst.

Key words : Liquid Phase Oxidation, MCM-41, Adipic Acid, Cyclohexane

INTRODUCTION

Adipic acid can be considered to be the most important of all aliphatic dicarboxylic acids. Its primary use is in the manufacture of nylon-6,6, the polyamide formed by its reaction with 1,6-hexamethylenediamine. The commercial method of adipic acid production is a two-step cyclohexane oxidation process with air and nitric acid as the oxidants. In the first step, cyclohexane is air oxidized at 160 °C and 15 bar in the presence of cobalt naphthenate or cobalt octate as the homogeneous catalyst. Only 3-4 % conversion of cyclohexane is obtained with 80 % selectivity to cyclohexanone and cyclohexanol. The recycling of the large amount of cyclohexane unreacted and separation of cyclohexanol and cyclohexanone from cyclohexane and catalyst presents a major problem. In the second stage, cyclohexanone and cyclohexanol are oxidized into adipic acid by nitric acid in the presence of a homogeneous catalyst, vanadium or copper compounds. The major problems associated with this step are the high concentration and large consumption of nitric acid as well as the separation of adipic acid from the effluent of nitric acid. The highly corrosive nature of nitric acid and the production of dinitrogen oxide gas create serious environmental problems.

Some research effort has thus been concentrated in the past few years to search for the suitable alternative heterogeneous acid catalysts in order to ease separation of catalyst from reaction products and to minimize the use of corrosive nitric acid. For example, Shen and Weng [1988] investigated liquid-phase oxidation of cyclohexane to dibasic acids using immobilized cobalt resin as the catalyst, cyclohexanone as the promoter, and glacial acetic acid as the solvent. They found that, depend-

ing on the reaction conditions, the fractional yield of dibasic acids (such as adipic, glutaric, and succinic acids) ranged from 0.75 to 0.85. The fractional yield of adipic acid was about 0.58-0.70. The oxidation of cyclohexane to dibasic acids was proposed to occur through cyclohexanone as the intermediate.

Shen and Weng [1990] also studied liquid-phase oxidation of cyclohexanone over cerium oxide catalyst with glacial acid as the solvent. The products obtained at 5-15 bar and 98-118 °C were mainly adipic, glutaric, and succinic acids, as well as caprolactone, and carbon oxide.

Lin and Weng [1993] studied liquid-phase oxidation of cyclohexane using CoAPO-5 as the catalyst and glacial acetic acid as the solvent (without any promoter). The reaction was carried out in a semi-batch autoclave reactor at 5-15 bar and 115-135 °C for a period of 8 hours. The overall conversion of cyclohexane was reported as high as 50 % with cyclohexanone, cyclohexanol, dibasic acids and caprolactone as the major products. The selectivity to adipic acid was as high as 45 % under certain conditions. It was also found that increasing the surface area of the catalyst increased the conversion of cyclohexane. The surface areas of the catalysts employed ranged from 200 to 240 m^2/g. The structure of the catalyst was, however, gradually destroyed during the reaction.

Beziat et al. [1996] reported that carbon-supported platinum catalyst was also effective to catalyze the oxidation of cyclohexanol. The selectivity to adipic acid was found to be about 50 %, with glutaric and succinic acids as the main by-products.

Although the heterogeneous catalytic systems mentioned above were found to be able to catalyze the oxidation of cyclohexane, most of the above systems used glacial acetic acids as solvents in order to remove the water produced during the oxidation reaction (water was found to destroy the catalysts during the reaction). Acetic acid tends to be corrosive at the reaction temperature (around 100 °C) and to cause the separa-

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tion of reaction products to be quite difficult. An active solid catalyst that is relatively hydrophobic and acidic in nature seems to be suggested to overcome this problem.

A family of M41S mesoporous materials recently prepared by Mobil researchers have been widely studied for various adsorptive and catalytic applications, and the application of MCM-41 materials for liquid-phase catalytic oxidation has started to gain intense interest. It is believed that MCM-41 material can have great potential for liquid phase oxidation of cyclohexane due to its high surface area (>1,000 m²/g), uniform mesopores (diameter adjustable from 15 to 100 Å), easy incorporation of transition metals, and relative hydrophobicity [Branton et al., 1995]. The uniform and large mesopores of MCM-41 would provide less mass diffusion resistance for reactants and reaction products through the pores.

In this paper, we report our preliminary results of the oxidation of cyclohexane using Co-P-MCM-41 as the catalyst and oxygen as the oxidant. Neither a promoter nor glacial acetic acid was added in the catalytic system. The incorporation of phosphorous atom into MCM-41 makes the Co-P-MCM-41 catalyst more acidic [Lee and Chon, 1997]. The active cobalt species and the very high surface area of MCM-41 improve the activity of the catalyst for the oxidation of cyclohexane.

EXPERIMENTAL

1. Catalyst Preparation

A cetyltrimethylammonium hydroxide (CTMAOH) aqueous solution was prepared by ion exchanging the CTMABr solution with Amberlite® IRA-400(OH) ion-exchange resin. The CTMAOH solution was concentrated to 29 wt%.

Co-P-MCM-41 was prepared as follows. The 29 wt% CTMAOH and TMAOH (Merck) solutions were added to a solution containing sodium aluminate (NaAlO₂, Merck) and Co(NO₃)₂·6H₂O (Merck). After the mixture was stirred for 30 mins, Ludox (40 wt% SiO₂ solution, Aldrich) and H₃PO₄ solutions were added to the mixture under stirring. The composition of the resulting gel was: $0.2 \text{ CoO} : 1 \text{ P}_2\text{O}_5 : 1 \text{ Na}_2\text{O} : 27.8 \text{ SiO}_2 : 5.1$ (CTMA)₂O : 3.6 (TMA₂)O : 650 H₂O. The resulting gel was placed in a Teflon-lined autoclave and heated in an oven at 105 °C for 48 hours. After hydrothermal treatment, the solid sample was recovered by filtration, thoroughly washed with deionized water, dried at 50 °C overnight, and then calcined at 600 °C for 12 hours in air (with a ramping rate of 1 °C/min). The calcined sample was then ground and sieved to have particles of mesh number 40-60.

2. Characterization

Nitrogen adsorption/desorption isotherms, BET surface areas, and BJH (Barrett, Joyner and Halenda) pore size distributions of the calcined catalysts were determined at 77 K on a NOVA-1000 Gas Sorption Analyzer (Quantachrome Corporation) using a continuous adsorption procedure.

X-ray diffraction patterns of the catalysts were determined on a Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation (λ=1.5418) and a scan speed of 2 degrees/min at 40 kV and 30 mA.

In order to find whether Co ion is leached out from Co-P-MCM-41 into the solution mixture during the course of the

reaction, a sample of the reaction mixture at the end of the reaction was analyzed with a Shimadzu Atomic Absorption Spectrophotometer.

3. Experimental Set-Up and Reaction Procedures

The catalytic oxidation of cyclohexane was carried out in a semi-batch reactor (schematically shown in Fig. 1). The reactor was a 1,000-ml stainless-steel autoclave equipped with a four-bladed stirrer. Then 400 ml of cyclohexane and a required amount of catalyst were charged into the reactor. Before reaction, nitrogen gas was continuously introduced into the reactor to purge the oxygen from the reactor. When the temperature reached 115 °C, 5 bar of oxygen (at a flow rate of 500 ml/min) was then introduced into the reactor and the mechanical stirrer was switched on; this was counted as the beginning of the reaction.

Samples of the reaction medium were taken periodically during the course of the reaction and the products were analyzed with an HP 6890 GC-MS. Cyclohexane, cyclohexanone, cyclohexanol, and esters were separated with an HP-5 (cross-linked polyethylene glycol-TPA) capillary column. The analysis of dibasic acids (i.e. adipic, glutaric and succinic acids) was done through the esterification of these acids with methanol and subsequent injection into the HP-FFAP capillary column. The temperature of the column was maintained initially at 45 °C for 5 min, then heated to 275 °C at a heating rate of 15 °C/min, and held at 275 °C for 3 minutes. Helium was used as the carrier gas with a flow rate of 0.8 ml/min.

RESULTS

1. Catalyst Characterization

Fig. 2 shows the XRD spectrum of Co-P-MCM-41, showing a sharp and intense peak at about 2.3° (2 θ) accompanied by a smaller peak at around 4.5° (2 θ). This result indicates
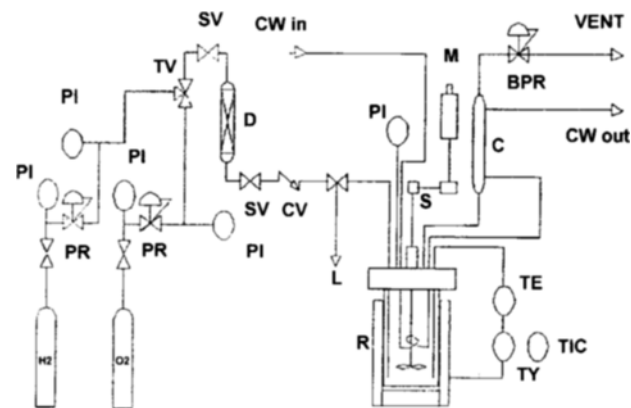

Fig. 1. Schematic diagram of the experimental set-up.
BRK=Back-pressure regulator

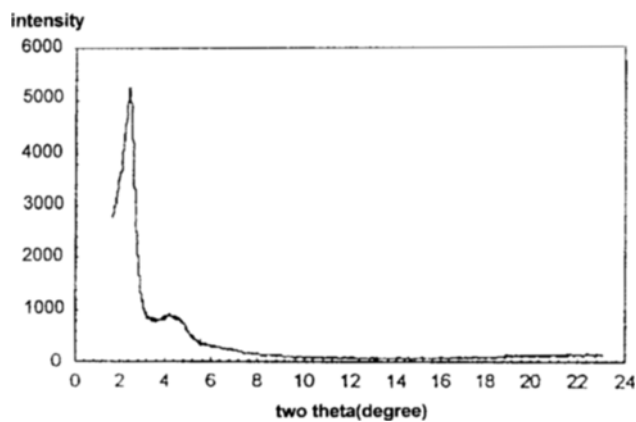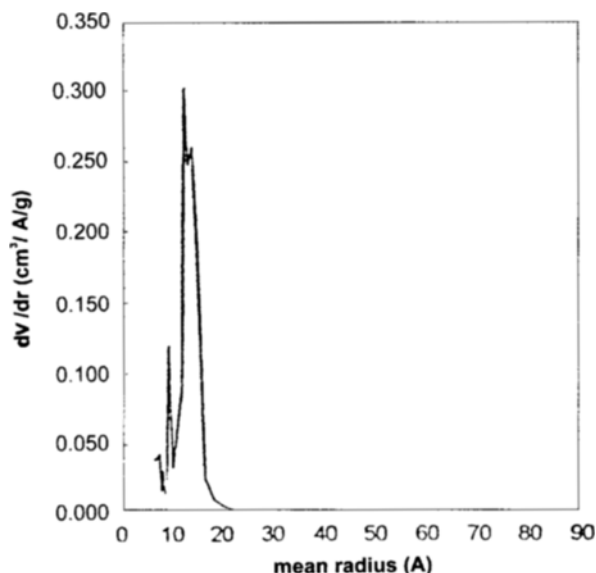|	
D : Dryer	L : Liquid sampling
M : Variable-speed motor	CW : Cooling water
TV : Two-way valve	CV : Flow-check valve
PI : Pressure indicator	C : Condenser
PR : Pressure regulator	TIC : Temperature indicator
r : Reactor	and controller
S : Stirrer	TY : Thermoheater
SV : Shut-off valve	TE : Thermocouple

Fig. 2. XRD pattern of Co-P-MCM-41 catalyst.

Fig. 3. Pore size distribution pattern of Co-P-MCM-41 catalyst.

that Co-P-MCM-41 contains mesoporous structures. The XRD lines presented indicate that the Co-P-MCM-41 sample is very disordered, which should be attributed to the disruption of micelles caused by the addition of the Co and P sources. Channel branching due to the disordering effect would increase the diffusion rate dramatically.

Fig. 3 shows the pore size distribution of Co-P-MCM-41. It can be seen that the mesopores of Co-P-MCM-41 are quite uniform, with a mesopore diameter at around 35 Å, which is typical of those reported for MCM-41 materials [Beck et al., 1992; Kresge et al., 1992]. Based on the N_2 adsorption measurement, the BET surface area, pore volume, and mean pore diameter of Co-P-MCM-41 were calculated to be 995 m^2/g, 0.91 ml/g, and 35 Å, respectively.

2. Catalytic Activity

Three experimental runs were carried out to study the effect of the amount of Co-P-MCM-41 catalyst on the cyclohexane conversion and reaction product distribution as well as the stability of the catalyst. The starting amount of cyclohexane was 400 ml, and the reaction was run at 115°C under 5 bar of oxygen in a semi-batch mode.
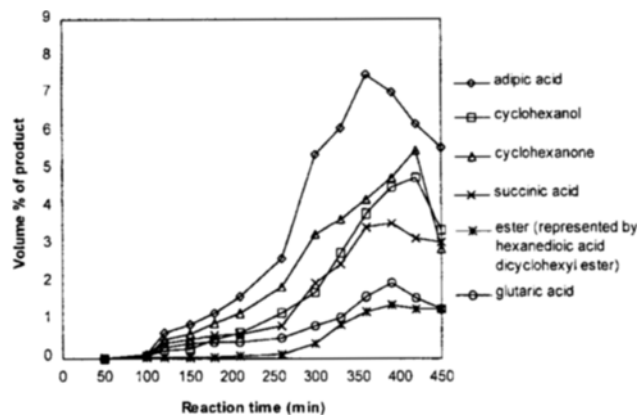
Fig. 4. Product distribution for the oxidation of 400 ml of cyclohexane as a function of time at 115 °C and under 5 bar of oxygen (catalyst loading: 0.10 g Co-P-MCM-41).

Run 1: 0.1 g of Co-P-MCM-41 catalyst

Fig. 4 shows the product distribution of the reaction as a function of time for 0.1 g of Co-P-MCM-41 catalyst. The reaction started after a 100 min induction period; the induction time is suggested to be due to the nature of radical reactions to produce radicals to initialize the reaction.

The products of the reaction were mainly cyclohexanone, cyclohexanol, dibasic acids, dibasic acid dicyclohexyl esters and some cracking products. The large fraction of dibasic acids produced consisted of adipic and succinic acids. The common undesirable products included 1-hexene, methyl-cyclohexane, heptene, 5-hexanal, and toluene. The reaction intermediates, such as cyclohexanone and cyclohexanol, were also produced in large quantities during the course of the reaction. After 6 hours of reaction, the conversion of cyclohexane reached up to 30 % and the selectivity for adipic acid was 25 %.

As can be seen from Fig. 4, during the last stage of the reaction, the concentration of each organic product decreased. This might be due to the deep oxidation of reaction products to carbon oxide and water.

Run 2: 0.25 g of Co-P-MCM-41 catalyst

Fig. 5 shows the reaction product distribution as a function of time for 0.25 g of Co-P-MCM-41 catalyst. It can be seen that the induction time required to initialize the reaction using 0.25 g of Co-P-MCM-41 was about 50 min, which is shorter than the 100 min required using 0.10 g of Co-P-MCM-41. The rate of formation of major reaction products was much faster than that in run 1, indicating that increased amount of catalyst enhanced the reaction rate.

As the reaction rate was relatively fast, the reaction produced a greater amount of undesirable products. It is noticed that the reaction intermediates, such as cyclohexanone and cyclohexanol, had a larger amount in proportion than adipic acid during the reaction; this reaction behavior differs from that observed in run 1. After 9 hours of reaction, the conversion of cyclohexane reached about 50 % and the selectivity of the reaction product to adipic acid was 40 %.

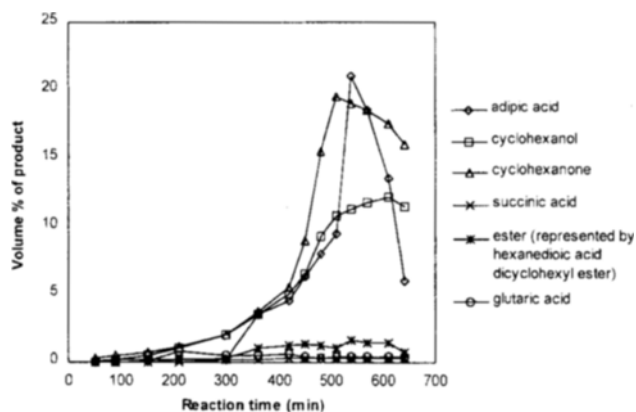Fig. 5 also shows that the concentrations of succinic and

Fig. 5. Product distribution for the oxidation of 400 ml of cyclohexane as a function of time at 115 °C and under 5 bar of oxygen (catalyst loading: 0.25 g Co-P-MCM-41).

glutaric acids are very low compared to adipic acid. It was reported that the main dibasic acids produced were adipic and succinic acids using CoAPO-5 as the catalyst [Lin and Weng, 1993]. These results seem to suggest that, as the Co-P-MCM-41 catalyst has much bigger pores (about 35 Å) than CoAPO-5 zeolite (about 8 Å), Co-P-MCM-41 catalyst offers less resistance to the diffusion of the reaction products from the pores. Hence, for Co-P-MCM-41 catalyst, there is less chance for the resultant reaction product (i.e., adipic acid) to undergo oxidative decarboxylation to form either succinic or glutaric acids as the adipic acid could quickly diffuse out from the pores into the bulk solution. This could account for the higher selectivity of the reaction products to adipic acid.

Run 3: 3.0 g of Co-P-MCM-41 catalyst

It was observed in this run that, within the first 20 min after the introduction of oxygen into the system, the reactor temperature increased very quickly from 115 °C to 135 °C (giving a temperature jump of 20 °C), indicating that the oxidation of cyclohexane occurred very quickly. Sample analysis using GC-MS indicated that, within the first 10 min, a series of reactions had taken place. More than 90 % of the cyclohexane had been converted. The major products were adipic acid, 1,2-benzenedicarboxylic acid diisoctyl ester, and water. The 1,2-benzenedicarboxylic acid diisoctyl ester is suggested to be due to the esterification of 1,2-benzenedicarboxylic acid and isoctyl alcohol produced during the reaction.

The composition of the three major components during the

first 10 min of the reaction was 30 % adipic acid, 40 % 1,2-benzendicarboxylic acid diisoctyl ester, and 10 % water. After 10 min of reaction, the concentration of each resulting organic compound continuously decreased, while the amount of water in the reaction mixture increased rapidly, indicating that deep oxidation of the organic compounds to CO_2 and water might have occurred. After 100 min of reaction, all the cyclohexane had been converted. The final concentration of adipic acid in the liquid mixture was 15 % (volume).

The results of the above three experimental runs are summarized in Table 1. It shows that the induction time required to start the reaction, the cyclohexane conversion, and the selectivity to adipic acid depend on the amount of Co-P-MCM-41 catalyst used in the reaction.

It should be noted that, for all the 3 experimental runs, no cobalt ions from the Co-P-MCM-41 catalyst were found in the liquid phase reaction mixture after the oxidation reaction. This result suggests that the Co ions did not elute or leach from the Co-P-MCM-41 catalyst, making the catalyst stable during the oxidative reaction.

DISCUSSION

1. Effect of the Surface Area of Catalyst

With CoAPO-5 used as the catalyst, it was reported that the higher the surface area of the catalyst, the better the catalytic activity of the catalyst for the oxidation of cyclohexane; however, the highest surface area of the CoAPO-5 catalyst used by Lin et al. for the oxidation of cyclohexane was less than 250 m^2/g [Lin and Weng, 1993]. In contrast, the Co-P-MCM-41 catalyst used in this study has a surface area of 995 m^2/g, which is about 4 times as high as that of CoAPO-5. As Co-P-MCM-41 catalyst has very high surface area, this catalyst is shown (using 0.25 g of Co-P-MCM-41) to be able to oxidize 50 % of cyclohexane, with a selectivity to adipic acid close to 40 %, which is comparable to that of CoAPO-5.

Although the conversions of CoAPO-5 and Co-P-MCM-41 catalysts are comparable, the high-surface-area Co-P-MCM-41 catalyst should be much more active than the CoAPO-5 catalyst. This can be seen clearly by comparing the reaction conditions performed using Co-P-MCM-41 and CoAPO-5 [Lin and Weng, 1993] as the catalysts. For example, the Co-P-MCM-41 catalyst was run in this work at lower temperature (i.e. 115 °C vs. 125 °C), lower oxygen pressure (i.e. 5 bar vs. 10 bar), catalyst amount (i.e. 0.25 g vs. 2.5 g), and larger amount of cyclohexane (i.e. 400 ml vs. 125 ml). The results clearly

Table 1. Effect of the amount of Co-P-MCM-41 catalyst on induction time, conversion of cyclohexane, and selectivity to adipic acid

Catalyst amount used	Induction time (min)	Conversion of cyclohexane	Main products	Selectivity to adipic acid
0.1 g	-100	-30 %	Adipic acid, cyclohexanone Cyclohexanol succinic acid	25 %
0.25 g	-50	-50 %	Adipic acid Cyclohexanone Cyclohexanol	40 %
3.0 g	<10	>99 %	Adipic acid 1,2-benzenedicarboxylic acid diisoctyl ester	15 %

show that an increase in the surface area of the catalyst increases the activity of the catalyst for the liquid-phase oxidation of cyclohexane.

2. Effect of Water Produced in the Reaction

With immobilized cobalt catalyst or CoAPO-5 catalyst, it was reported that acetic anhydride had been used as the solvent for the oxidation of cyclohexane [Shen and Weng, 1988; Lin and Weng, 1993]. One important function of this acetic anhydride is to act as a medium to absorb and remove the water produced during the reaction. The amount of acetic anhydride charged into the reactor is usually small as a large amount of acetic anhydride in the reaction mixture would dilute the concentration of cyclohexane and, as the oxidation rate of cyclohexane is dependent on the amount of cyclohexane, this would then cause the oxidation rate of cyclohexane to decrease.

When the limited amount of acetic anhydride is completely consumed with water, excess water would be produced in the reaction mixture. It has been suggested that this excess water would have detrimental effects on the oxidation of cyclohexane to adipic acid. For example, the excess water has been suggested to cause the elution of cobalt ion [Co^{2+}] from the catalyst into the reaction medium. This Co^{2+} ion in the solution may then act as an inhibitor to the oxidation of cyclohexane [Shen and Weng, 1988]; hence the reaction rate would be slowed down. In addition, water itself has a retarding effect on the reaction rate and product distribution of the oxidation of cyclohexane [Shen and Weng, 1988]. Furthermore, elution of the cobalt ions from the catalyst may deactivate the catalyst. When the acetic anhydride is absorbed with water, it produces acetic acid, which may then react with cyclohexanol to give undesired by-products (such as ester, cyclohexyl acetate).

Using Co-P-MCM-41 catalyst, it is shown in this study that no glacial acetic anhydride was necessary to be present in the reaction mixture, avoiding such by-reaction products, and to make the reactor system easier to handle (such as easier separation of the catalyst from reaction products, and non-corrosiveness of the reaction mixture to the reactor and to the environment). Due to the hydrophobicity of the Co-P-MCM-41 catalyst [Branton et al., 1995], the water formed during the course of the reaction had very little chance to contact with the catalyst or little effect on the catalyst performance, making the catalyst stable during the reaction.

Another function of the added acetic acid is to increase the acidity of the reaction system. In our case, the presence of phosphorous elements in the Co-P-MCM-41 catalyst made the catalyst more acidic [Lee and Chon, 1997], and subsequently increased the catalytic activity of the catalyst with oxygen.

3. Effect of Catalyst Concentration

The amount of Co-P-MCM-41 catalyst used in the oxidation of the 400-ml of cyclohexane (without the use of a promoter or an acidic medium) is shown in this work to have some effect on induction time, conversion of cyclohexane, and selectivity to adipic acid.

As shown in Table 1, the induction time required to initialize the oxidation of cyclohexane decreases from 100 min to <10 min as the amount of Co-P-MCM-41 catalyst increases

from 0.10 g to 3.0 g. The results suggest that, as the oxidation of cyclohexane is a radical reaction, the rate of production of radicals in the reaction mixture increases as the amount of catalyst increases, hence decreasing the induction time required to produce sufficient radicals to start the oxidation reaction.

Increasing the Co-P-MCM-41 catalyst amount in the reaction has also been shown (Table 1) to lead to an increase in the conversion of cyclohexane from 30 to 99 %. This is not surprising as an increase in the amount of catalyst would provide more catalyst to react with the given amount of cyclohexane. The result shows that the selectivity to adipic acid increases as the catalyst amount increases, and then decreases as the catalyst amount gets much larger. The highest selectivity to adipic acid was about 40 %, which was achieved when 0.25 g of Co-P-MCM-41 catalyst was used. It is not so clear with this preliminary result why the selectivity to adipic acid behaves in this way. It may be postulated as follows: As the Co-P-MCM-41 catalyst amount was increased, the reaction rate became so fast that the adipic acid produced during the reaction might then have been converted to form some by-products or be oxidized to CO_2, resulting in lower selectivity to adipic acid. The results suggest that there should be an optimal amount of catalyst required for the oxidation of cyclohexane to produce an optimal yield of adipic acid.

CONCLUSION

Co-P-MCM-41 synthesized in this work is shown to be a selective and active catalyst for the one-step liquid phase oxidation of cyclohexane to adipic acid, even without the use of glacial acetic acid as the solvent. The catalyst amount was shown to affect the induction time, conversion of cyclohexane, and selectivity to adipic acid. The catalyst was quite stable as Co ions did not elute from the catalyst. Conversion and selectivity of the present system could be further improved by optimizing the Co contents of the Co-P-MCM-41 catalyst.

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