ELSEVIER

Catalysis Today 69 (2001) 283–290

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Carbon coated monolithic catalysts in the selective oxidation of cyclohexanone

Edwin Crezee*, Arjan Barendregt, Freek Kapteijn, Jacob A. Moulijn

Industrial Catalysis, Delft University of Technology, DelftChemTech, Julianalaan 136, 2628 BL Delft, The Netherlands

Abstract

The application of carbon coated monolithic catalysts in selective oxidation is compared with slurry phase operation. As a model reaction, the liquid phase air oxidation of cyclohexanone into adipic acid was chosen. The reaction was performed in water at moderate temperature (413 K) and pressure (5.0 MPa). Total conversion of cyclohexanone was achieved over metal-free carbon supports yielding several dicarboxylic acids. Increasing the pore access of these carbon supports is beneficial for the activity. The application of highly dispersed platinum yields similar activities, but enhances the selectivity to adipic acid from 9.2 to 20.6%. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Cyclohexanone; Adipic acid; Monolithic catalyst; Pt/C

1. Introduction

One of the major chemical processes utilizing liquid phase hydrocarbon oxidation is the oxidation of cyclohexane to adipic acid. The global adipic acid production is estimated to be 2.2×10^6 tpa [1,2]. A large proportion of this total output is used as an intermediate in the production of nylon-6.6, especially via the condensation of hexamethylenediamine. Although there are variations of the cyclohexane oxidation process, the basis of the industrially applied two-step procedure is still fundamentally the same as originally developed in the early 1940s [3]. In the first step, cyclohexane is oxidized with air to cyclohexanol–cyclohexanone (olone) using cobalt naphtenate or stearate as the catalyst. In order to promote the selectivity (80–85%), low conversion levels (5–8%) are maintained, the unconverted cyclohexane being recycled. After distillation, a 99.5% olone mixture is obtained which is then converted to adipic acid by oxidation with nitric acid employing copper and vanadium as catalysts. In this latter step, about 1 mol of nitrous oxide per mole of product is formed. These nitrogen oxides need to be removed, since N_2O contributes to catalytic stratospheric ozone destruction and is also a greenhouse gas component [4]. To circumvent this problem and to avoid the risk of corrosion, air instead of HNO_3 can be used as an oxidant.

Castellan et al. [5] describe a process in which olone is oxidized by air in an acetic acid solution in the presence of Cu and Mn acetate catalysts (353–358 K, 0.7 MPa), which results in an 80% yield of adipic acid. This process has been tested on a commercial scale by Halcon Int., but seems to have resulted in adipic acid of poor quality. Another possibility is to subject the olone first to dehydrogenation to form cyclohexanone, which is then catalytically oxidized to adipic acid in air. The information on this process is, however, rather limited [5]. Gallezot and coworkers [6,7] showed that platinum supported on active charcoal is an effective catalyst for the oxidation of cyclohexanol

---

* Corresponding author.

E-mail address: e.crezee@tnw.tudelft.nl (E. Crezee).

0920-5861/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.

PII: S0920-5861(01)00401-1

with air to produce diacids such as adipic acid. Although Gallezot performed the process in batch operation, the reaction could very well be performed in continuous mode using fixed-bed catalytic reactors.

This study focuses on the application of carbon (coated) monolithic catalysts for the selective oxidation of cyclohexanone by air while comparing with slurry phase operation. The monolithic reactors provide the advantage of better control of the contact time of reactants and products with the catalyst, which may lead to additional gains in selectivity. Compared to the conventional trickle-bed reactors, monolithic reactors provide the additional advantages of low-pressure drops, large external surface areas and short diffusion lengths [8]. These properties make the monolithic reactors extremely suited for application in consecutive reaction schemes, like selective oxidation.

2. Experimental

2.1. Catalyst preparation

Carbon coated monolithic catalysts have been prepared according to a method developed by Vergunst et al. [9]. Furfuryl alcohol and pyrrole are used as carbon yielding precursors. After blending to a homogeneous fluid, the mixture is polymerized at ambient conditions using nitric acid as a catalyst. The presence of pyrrole decreases the reactivity of the polymerization mixture and thus facilitates handling. Furthermore, the addition of pyrrole results in a stronger polymer leading to less cracks upon carbonization. Ceramic monolithic structures (62 cells cm^{-2}) are dip-coated in the partially polymerized mixture. After complete solidification, the polymer is carbonized at 823 K. The carbon obtained is activated by partial oxidation at 603 K, followed by further functionalization in 1 M HNO_3. Platinum is applied by exchange with $Pt(NH_3)_4Cl_2$ in diluted NH_3 (aq). The catalysts are reduced in hydrogen at 573 K and afterwards passivated by a mixture of 1% O_2 in nitrogen.

For the slurry catalysts, the coating step has been omitted. To the polymerization mixture poly(ethylene glycol)methyl ether $M_n = 5000$ was added as a pore-former. The carbonized polymer is crushed and sieved and a particle size of 53–75 μm has been used for further preparation steps.

The 3% Pt/CP97 catalyst was purchased from a commercial source (Engelhard De Meern, NL) and applied as received.

2.2. Characterization

2.2.1. Supports

All samples were characterized by N_2 adsorption at 77 K by applying the BET equation to the N_2 adsorption isotherm. Using this technique, pore diameters in the region of 1.5–200 nm could be analyzed. Mercury porosimetry data were obtained using CE Instruments PASCAL 140/440, which is capable of measuring pore diameters in the range 4 nm–100 μm. The CO_2 adsorption isotherm at 273 K has been measured with the Quantachrome NOVA 1200. The microporosity from the CO_2 isotherm has been calculated using the Dubinin–Raduskevich (DR) equation.

The surface chemistry of the carbon supports was studied by TPD–MS. TPD measurements were performed in a conventional flow apparatus using a quartz microreactor and He as carrier gas flowing at 50 STP $cm^3\,min^{-1}$. About 200 mg of sample was heated with a rate of 10 K min^{-1} up to 1273 K. The desorption processes of gaseous species from the sample were monitored by a quadruple mass spectrometer (Balzers) connected on-line with the reactor. Mass spectra were recorded in multiple ion detection (MID) mode using a channeltron detector. Evolved CO and CO_2 were calibrated by a method described by Wang and McEnaney [10] using the thermal decompositions of calcium carbonate and calcium oxalate.

2.2.2. Catalysts

The active platinum surface area and dispersion of the catalysts were determined by volumetric CO chemisorption. Analysis was performed on the Quantachrome Autosorb-1C at 303 K after reduction of the passivated samples at 303 K for 0.5 h in hydrogen. The active metal surface area was calculated assuming a Pt:CO stoichiometry of 1:1 and correcting for weakly adsorbed CO.

2.3. Reaction procedure

Oxidation of aqueous solutions of cyclohexanone (5 g dm^{-3}) was performed in a screw impeller stirred reactor (SISR) of 300 cm^3 capacity. This reactor, which is suited for testing monolithic and slurry catalysts, is described in more detail by Van de Riet et al. [11]. The reactor is operated semi-batch with respect to air. After loading of the autoclave with catalyst and feedstock, the reactor was pressurized with air to 0.3 MPa while maintaining the stirrer speed at $3.3\,\mathrm{s}^{-1}$. The reaction mixture was heated to the desired reaction temperature and the total pressure was subsequently increased to 5.0 MPa. The reaction was started by increasing the stirrer rate to the desired speed ($t = 0$). Samples withdrawn from the vessel are analyzed using HPLC equipped with UV and RI detector. Separation of the components was achieved by a Rezex ROA-organic acid column operated at 323 K. Elution was performed at $0.6\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ flowrate of mobile phase (0.005 M H_2SO_4).

3. Results and discussion

3.1. Catalyst characterization

The monolithic platinum catalyst, prepared by cationic-exchange, contained 0.75 wt.% metal and had a carbon load of 13.7 wt.% and an average coating thickness of 5 μm. Per unit carbon mass, the platinum content comes to 5.5 wt.%. The active platinum surface area amounted to $0.80\,\mathrm{m}^2/\mathrm{g}_{\mathrm{sample}}$. This corresponds with an average metal particle size of 2.6 nm and a Pt dispersion of 43%. The high dispersion is attributed to the selective exchange of the precursor cations with the acidic (carboxylic) groups of the support and to the interaction of the particles with the functional groups [12].

For the 3% Pt/CP97 slurry catalyst (Engelhard), the active platinum surface area amounts to $2.87\,\mathrm{m}^2/\mathrm{g}_{\mathrm{sample}}$, corresponding with an average metal particle size of 2.9 nm and a metal dispersion of 39%.

3.2. Oxidation of cyclohexanone

Oxidation of cyclohexanone was carried out in a stainless steel reactor. To assess the extent of the uncatalyzed oxidation of cyclohexanone and the effect of the support, oxidations were performed without catalyst and with metal-free supports at 413 K and 5.0 MPa. The uncatalyzed oxidation did occur up to 14% in 7 h with a selectivity to adipic acid of 16%. According to Lee and Kim [13], at the elevated temperature formation of oxygen radicals occurs, which in turn can react with water to form hydroxyl radicals. These radicals might have oxidized cyclohexanone. The use of noble metal-free carbon support (CP97, Engelhard) enhanced the oxidation appreciably and resulted in total cyclohexanone conversion after 1 h (Fig. 1). At the start of the reaction, a short induction period of ca. 10 min was detected. It is proposed that during this period the support is in situ oxidized [14]. Before reaction, CP97 hardly contains any oxygen surface complexes as can be seen from Table 1. The initial concentration of cyclohexanone ($t = 0$) differs from the amount of reactant present in the feedstock due to adsorption of cyclohexanone onto the carbon (ca. 20% in the case of CP97). The major products detected are acetic/fumaric, succinic, glutaric and adipic acids. Also some unsaturated acids, like maleic and acrylic acids are initially produced, but these are slowly converted to carbon dioxide as shown by Gallezot et al. [12]. 2-Hydroxycyclohexanone is the main intermediate oxidation product before complete conversion of cyclohexanone. To establish the reaction pathway of the cyclohexanone oxidation over the active carbon sites, this intermediate was oxidized under reaction conditions over CP97. From Fig. 2, it can be concluded that 2-hydroxycyclohexanone is no intermediate to adipic acid, but mainly yields acetic/fumaric acid and succinic acid.

For the activated carbon supports based on polyfurfuryl alcohol, the monolithic carbon (MPCA, Fig. 3) shows a higher activity (Table 2) than the slurry carbon (SPCA, Fig. 4). Since the textural properties of both supports are comparable (Table 3) and the difference in density of oxygen surface groups only exerts an effect on the selectivity to adipic acid [14], there must be another explanation for this observation. From calculations of the transport resistances [15], it was seen that the slurry process is internal diffusion limited, while no mass transport limitation occurs for the monolithic operation. The thin carbon layer on the monoliths results in short diffusion lengths. Compared to CP97, the carbons based on polyfurfuryl alcohol are less reactive and selective. If the textural properties of these supports are compared (Table 3), it is obvious that CP97 has a larger specific surface area and a more (meso-)porous character. So apparently,

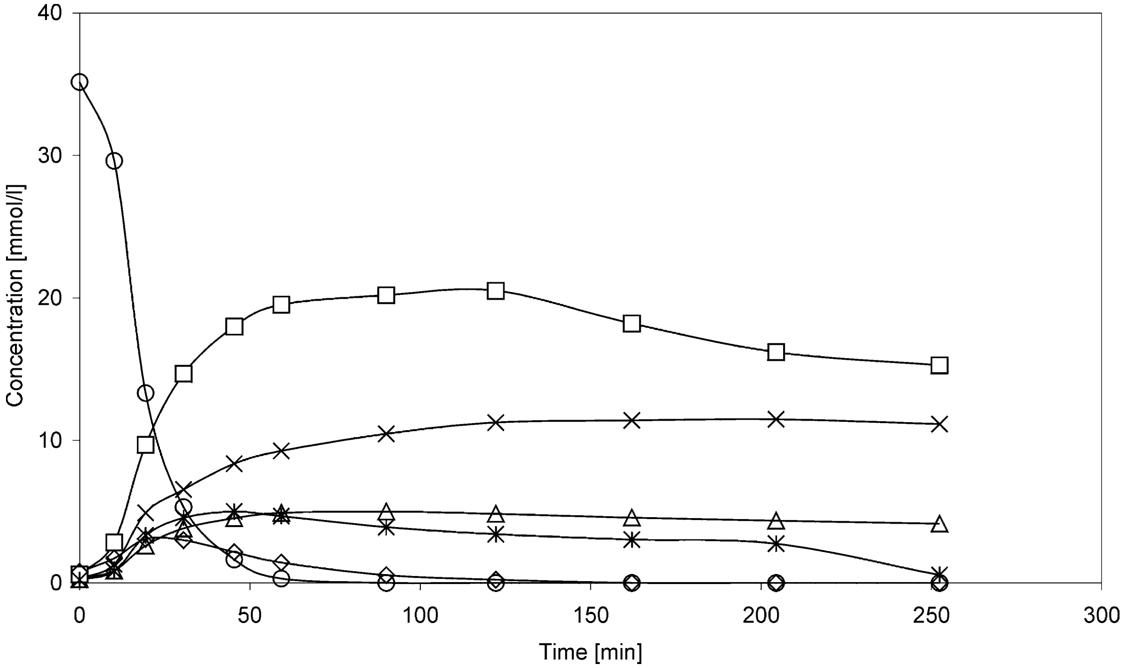

Fig. 1. Oxidation of an aqueous solution of cyclohexanone (200 cm^3, 5 g dm^{-3}) over 0.8 g of CP97 at 413 K, 5.0 MPa and 1500 rpm: (○) cyclohexanone; (◇) 2-hydroxycyclohexanone; (∗) adipic acid; (△) glutaric acid; (×) succinic acid; (□) acetic/fumaric acid.

Table 1
Temperature programmed desorption quantifications of supports

Sample	Amount desorbed (mmol g^{-1}_{carbon})		CO/CO$_2$ ratio (–)	O-content sample (wt.%)
	CO	CO$_2$		
MPCA	5.0	1.6	3.1	13
SPCA	3.7	0.83	4.4	8.5
CP97	0.77	0.41	1.9	2.6
3% Pt/CP97	1.8	1.0	1.8	6.1

Table 2
Comparison of the catalytic behavior of the various supports in the oxidation of cyclohexanone at 5.0 MPa

Sample	T (K)	Initial rate (mmol h^{-1} g^{-1})	t (h)	Conversion (mol%)	Product selectivities (mol%)	
					Adipic	Diacids sum
MPCA	413	10	3.0	45	4.4	11.1
SPCA	413	3	9.6	45	7.8	20.0
CP97[a]	373	13	6.5	100	6.6	33.0
	413	134	1.0	100	9.2	36.6
3% Pt/CP97	373	24	4.5	100	12.6	27.4
	413	103	1.0	100	20.6	46.3

[a] For CP97 the initial rate was determined after the induction period was completed.

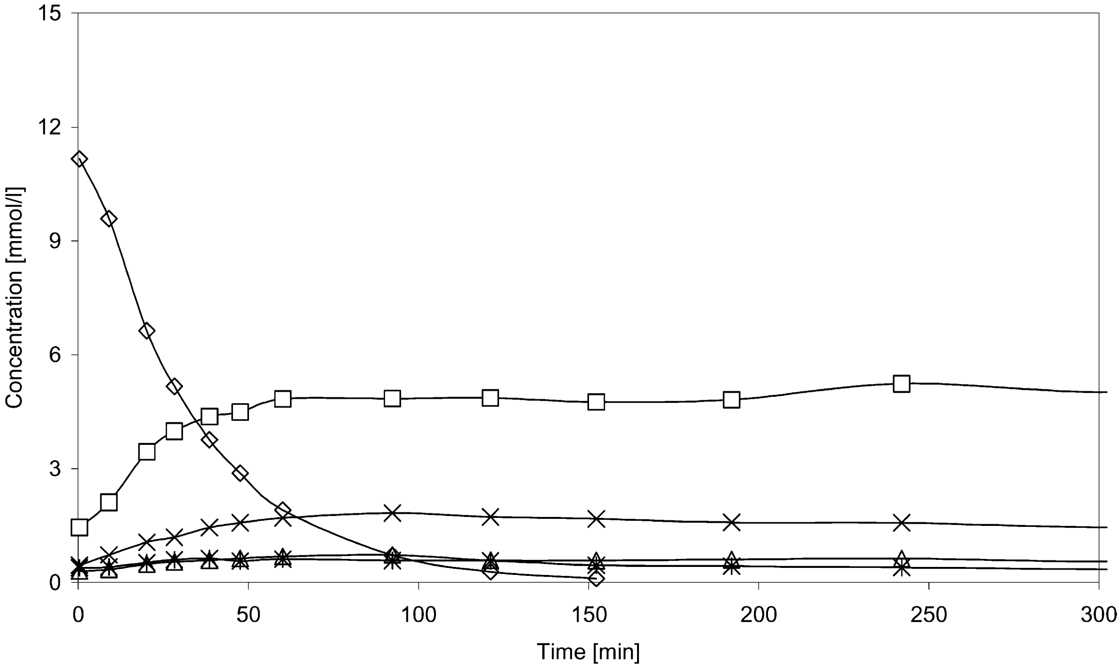

Fig. 2. Oxidation of an aqueous solution of 2-hydroxycyclohexanone (200 cm^3, 2 g dm^{-3}) over 0.8 g CP97 at 413 K, 5.0 MPa and 1500 rpm: (◇) 2-hydroxycyclohexanone; (∗) adipic acid; (△) glutaric acid; (×) succinic acid; (□) acetic/fumaric acid.

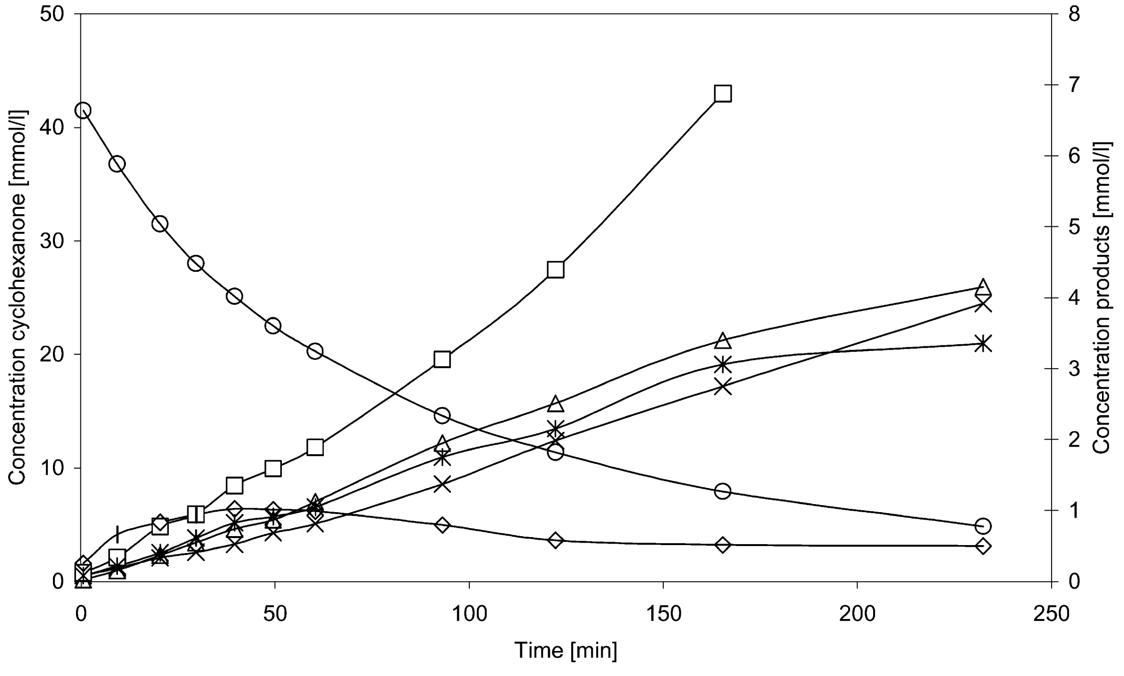

Fig. 3. Oxidation of an aqueous solution of cyclohexanone (140 cm^3, 5 g dm^{-3}) over MPCA (3.1 g carbon mass) at 413 K, 5.0 MPa and 2500 rpm: (○) cyclohexanone; (◇) 2-hydroxycyclohexanone; (∗) adipic acid; (△) glutaric acid; (×) succinic acid; (□) acetic/fumaric acid.

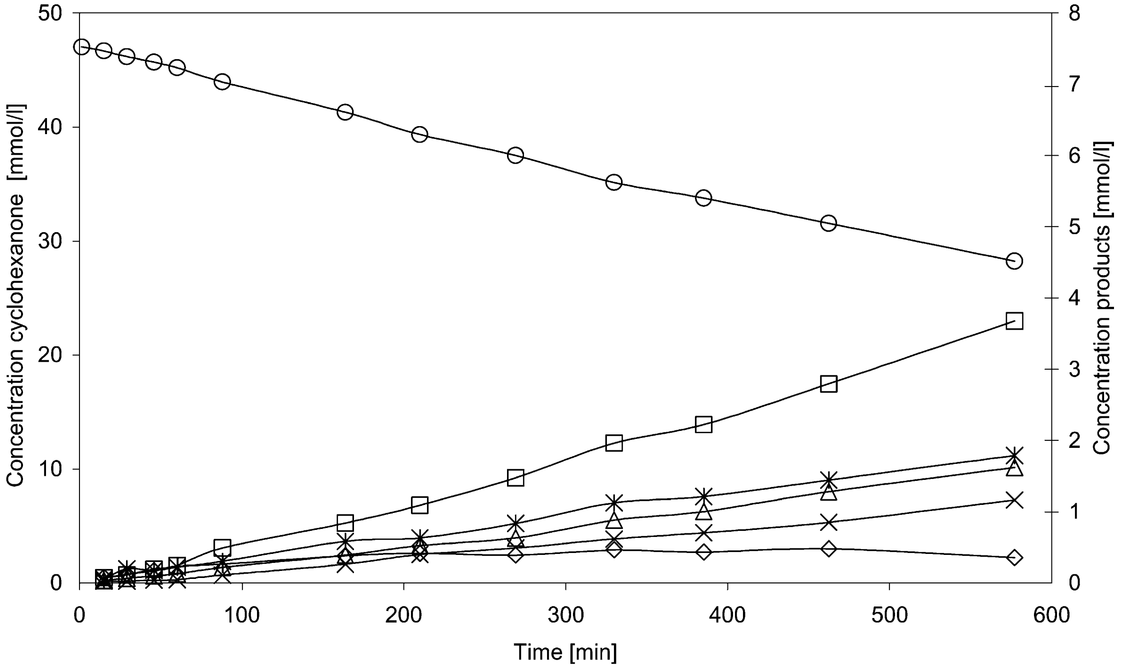

Fig. 4. Oxidation of an aqueous solution of cyclohexanone (200 cm^3, 5 g dm^{-3}) over 0.8 g of SPCA at 413 K, 5.0 MPa and 1500 rpm: (○) cyclohexanone; (◇) 2-hydroxycyclohexanone; (∗) adipic acid; (△) glutaric acid; (×) succinic acid; (□) acetic/fumaric acid.

increasing the pore access is beneficial for the activity. Moreover, CP97 has a large ash content (3.5%) and these inorganic constituents (P, S, metals) may affect the catalytic activity.

Experiments performed at 413 K using 3% Pt/CP97 catalysts (Fig. 5) yield an activity similar to that obtained with the CP97 support. The selectivity to adipic acid, however, at total conversion of cyclohexanone is 20.6% compared to 9.2% for the CP97 support. Furthermore, under reaction conditions the formed carboxylic acids are stable in case of the 3% Pt/CP97 catalyst, while over the carbon material they are slowly converted. The activity/selectivity of 3% Pt/CP97 is therefore influenced by both the active carbon sites and metal sites.

To discriminate between the carbon and platinum sites responsible for the oxidation of cyclohexanone, the reaction temperature was lowered to 373 K. For CP97 the induction period was extended to ca. 30 min, since in situ oxidation of the support is slower at lower temperatures. At 373 K the activity for 3% Pt/CP97 is higher than for CP97, which implies that the reaction pathway catalyzed by the active metal sites has a lower activation energy. For both catalysts lower

Table 3
Textural properties of supports determined by physical adsorption, N_2 at 77 K and CO_2 at 273 K, and mercury porosimetry

Sample	N_2 physisorption		CO_2 physisorption		Hg intrusion V_{pore} (cm^3 g_{sample}^{-1})
	S_{BET} (m^2 g_{carbon}^{-1})	V_{pore} (cm^3 g_{carbon}^{-1})	$S_{DR,micro}$ (m^2 g_{carbon}^{-1})	$V_{DR,micro}$ (cm^3 g_{carbon}^{-1})	
MPCA	390	0.19	471	0.17	0.26
SPCA	340	0.20	400	0.15	0.062
CP97	1140	0.80	860	0.31	0.36

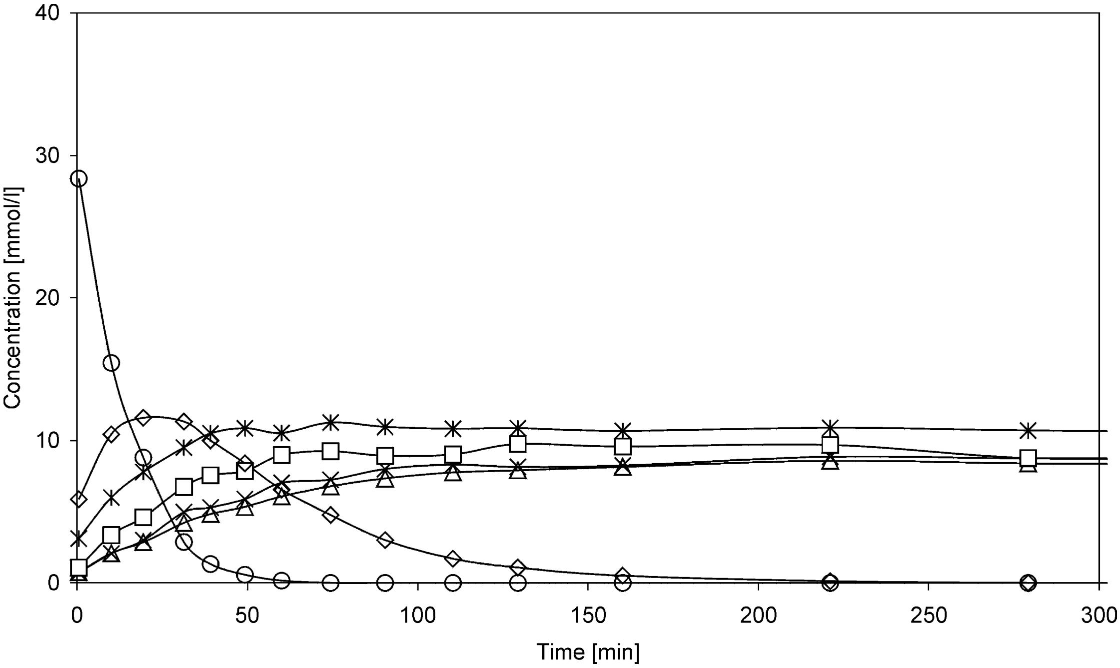

Fig. 5. Oxidation of an aqueous solution of cyclohexanone (200 cm^3, 5 g dm^{-3}) over 0.8 g 3% Pt/CP97 at 413 K, 5.0 MPa and 1500 rpm: (○) cyclohexanone; (◇) 2-hydroxycyclohexanone; ($*$) adipic acid; (△) glutaric acid; (×) succinic acid; (□) acetic/fumaric acid.

selectivities are obtained at 373 K, indicating that C–C bond rupture of the cyclohexanone to form adipic acid is favored at higher temperatures.

Significant amounts of succinic and glutaric acids are always formed together with adipic acid. The purification of adipic acid to obtain polymer-grade product poses considerable problems. For this reason, only applications that do not require adipic acid of high purity can be considered.

4. Conclusion

In this preliminary study, it was shown that carbon materials, even in the absence of platinum, are active in the liquid phase oxidation of cyclohexanone to valuable diacids. It is, therefore, of great importance to understand the nature of the active sites on the carbon surface responsible for the oxidation activity to improve the activity and selectivity of the cyclohexanone oxidation. Increasing the pore access of the carbon supports is beneficial for the activity. The application of highly dispersed platinum enhances the selectivity to adipic acid at 413 K from 9.2 to 20.6%. Significant amounts of succinic and glutaric acids are always formed together with adipic acid.

Work is in progress to determine the optimum pore structure, carbon surface chemistry as well as catalyst stability in successive recycling.

Acknowledgements

This work was supported by the European Union under contract number BRPR-CT97-0561. Corning Inc. (Corning, NY) is acknowledged for the supply of ceramic monolithic substrates. Engelhard De Meern B.V. is acknowledged for the supply of the 3% Pt/CP97 catalyst and the bare support.

References

[1] S. Pittman, S. Richardson, Adipic acid, AEA Technology, http://themes.eea.eu.int/binary/g/group04.pdf, 1995.

[2] S. Blacher, B. Sahouli, B. Heinrichs, P. Lodewyckx, R. Pirard, J.P. Pirard, Langmuir 16 (2000) 6754–6756.

[3] A.K. Suresh, M.M. Sharma, T. Sridhar, Ind. Eng. Chem. Res. 39 (2000) 3958–3997.

[4] M.H. Thiemens, W.C. Trogler, Science 251 (1991) 932–934.

[5] A. Castellan, J.C.J. Bart, S. Cavallaro, Catal. Today 9 (1991) 237–254.

[6] P. Gallezot, Catal. Today 37 (1997) 405–418.

[7] J.C. Béziat, M. Besson, P. Gallezot, Appl. Catal. A 135 (1996) L7–L11.

[8] F. Kapteijn, J.J. Heiszwolf, T.A. Nijhuis, J.A. Moulijn, CATTECH 3 (1999) 24–41.

[9] Th. Vergunst, F. Kapteijn, J.A. Moulijn, Carbon coating of ceramic monolithic substrates, in: Preparation of Catalysts VII, Stud. Surf. Sci. Catal. 118 (1998) 175–183.

[10] J. Wang, B. McEnaney, Thermochim. Acta 190 (1991) 143–153.

[11] A.C.J.M. Van de Riet, F. Kapteijn, J.A. Moulijn, in: Proceedings of the Second International Symposium on Catalysis in Multiphase Reactors, Toulouse, 1998, pp. 153–159.

[12] P. Gallezot, N. Laurain, P. Isnard, Appl. Catal. B 9 (1996) L11–L17.

[13] D.K. Lee, D.S. Kim, Catal. Today 63 (2000) 249–255.

[14] M. Besson, A. Blackburn, S. Claverie, P. Gallezot, O. Kozynchenko, S.R. Tennison, in: Proceedings of the Fifth International Symposium on Heterogeneous Catalysis and Fine Chemicals, Lyon, 1999, p. 46.

[15] F. Kapteijn, G.B. Marin, J.A. Moulijn, in: R.A. Van Santen, P.W.N.M. Van Leeuwen, J.A. Moulijn, B.A. Averill (Eds.), Catalytic Reaction Engineering, 2nd Edition, Elsevier, Amsterdam, 1999, pp. 375–431.