

Catalytic Oxidation with Air of Cyclohexanone to Dicarboxylic Acids on Synthetic Carbons. Effect of Supported Metals and Solvents[†]

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The oxidation with air of cyclohexanone was conducted in the presence of synthetic carbons catalysts. The effect of carbon activation treatment (CO₂ or air burnoff), phosphorus additive, platinum loading, and nature of the solvent (water or water/acetic acid mixture) were studied. Cyclohexanone oxidation at 140 °C yielded a mixture of C₆, C₅, and C₄ dicarboxylic acids. Air activated carbons, including those containing phosphorus or those supporting platinum, resulted in a higher yield of adipic acid. The activity and selectivity was associated with the oxygenated functional groups, essentially carbonyl/quinone groups, created during air activation of the carbon. The incorporation of phosphorus into the carbon increased slightly the selectivity to 34.3%, probably because this additive increased the density of oxygenated functional groups. The deposition of platinum by impregnation and liquid-phase reduction with formaldehyde increased the reaction rate and improved the selectivity to adipic acid, where the highest figure was 38.8%. It was suggested that platinum contributed to molecular oxygen activation. In contrast platinum deposition by cationic exchange followed by reduction under H₂ resulted often in a detrimental effect probably because the density of the oxygenated groups on carbon is decreased upon H₂ reduction in the presence of platinum. When the oxidation of cyclohexanone was carried out in mixtures of water/acetic acid, the selectivity given by the different samples were quite close and generally smaller than those obtained in water which indicates that acetic acid interacts with the oxygenated surface functional groups responsible for the activity and selectivity. Oxidation experiments with methyl-labeled 4-methylcyclohexanone indicated that glutaric acid was produced by oxidative decarbonylation of both the C₁ and C₂ carbon atoms of the molecule.

Introduction

Because of their high specific area and large pore volume, active carbons are useful adsorbing materials from both gas and liquid phases. They also have found many applications as supporting materials for noble metal catalysts employed in fine chemistry because of their stability in various reaction media and of the easiness of metal recovery by burning off. Because of the presence of surface functional groups that may be present originally or introduced by specific chemical modifications, active carbons act also as catalyst per se in gas¹ or liquid phase^{2,3} oxidation reactions with molecular oxygen as oxidizing agent. Dicarboxylic acids such as adipic acid, trimethyladipic acid, and dodecanedioic acid are essential feedstocks for the manufacture of polyamides, polyesters, plasticizers, and lubricating oils. Adipic acid for instance is an important bulk chemical for the production of nylon-6,6. They are currently manufactured in multistep processes by oxidative cleavage of C–C bonds of mixtures containing the corresponding cyclic alcohols and ketones and their derivatives with nitric acid.^{4–6} These processes lead to significant amounts of harmful NO_x effluents. The development of catalytic oxidations with molecular oxygen is desirable from economical and environmental points of view to substitute stoichiometric chemical oxidants.⁷

In a previous study³, it was shown that carbons prepared from phenolic resins were able to catalyze the oxidation with air of

cyclohexanone to C₆–C₄ diacids, namely adipic, glutaric and succinic acids. The activity was mainly dependent upon the surface area and microporosity, whereas the selectivity to adipic acid was related to the presence of oxygen surface groups, particularly lactone/quinone groups. The objective of the present paper was to examine the effects of additives, such as phosphorus or platinum, and nature of the solvent, on the activity and selectivity of synthetic carbons, activated by CO₂ or air, in the catalytic oxidation with air of cyclohexanone. Oxidations of intermediates formed during cyclohexanone oxidation were performed under the same conditions to get information on the mechanism of reaction. Oxidation reactions with air of other cyclic ketones, such as 3,3,5-trimethylcyclohexanone and cyclododecanone, to the corresponding dicarboxylic acids using the same type of catalysts will be described in a separate paper.

Experimental Section

Carbon Materials. The carbon samples used in this study were synthetic carbons (referred as S) supplied by MAST Carbons Ltd.⁸ They were prepared by carbonization at 800 °C of a porous polymeric resin precursor prepared from Novolac resin and hexamethylenetetramine in poly(ethylene glycol) (PEG). PEG acted as solvent and pore former because it decomposed during pyrolysis, generating gaseous substances in the polymer blend spheres. The carbons containing no mineral impurities were under the form of spherical particles with an average diameter of 32 μm. Phosphorus-containing carbon (referred as SP) was prepared by impregnating the polymer with

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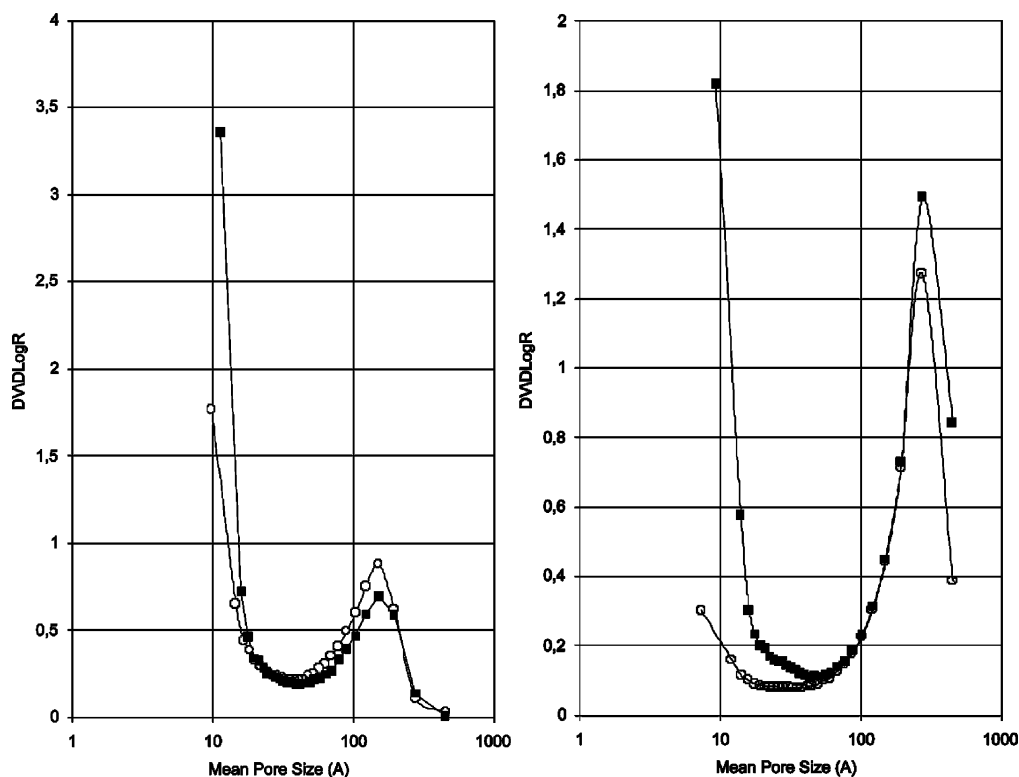


Figure 1. Effect of activation procedure on the porosity of carbons. S carbon series, ■, SC; ○, SA (b) SP carbon series, ■, SPC; ○, SPA.

TABLE 1: Surface Area, Porosity and Elementary Analysis of the Activated Carbons

reference of carbon	burnoff (%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	porous volume ($\text{cm}^3 \text{g}^{-1}$)	mean pore size (nm)	elemental analysis ^a			
					%C	%N	%O	%P
S	0	540	0.60	15	nm	0.51	1.26	
SC	30	929	0.78	15	93.45	0.61	1.22	
SA	40	806	0.79	15	76.70	0.58	18.03	
SPC	34	779	1.22	27	79.14	1.11	11.39	4.3
SPA	40	304	0.76	27	nm	nm	nm	7.4

^a nm: not measured.

phosphoric acid. Upon carbonization of the polymer precursor phosphorus was incorporated into the carbon, and the resulting material exhibited cation-exchange properties similar to those of oxidized carbon.⁹ However, extensive RMN and XPS studies as well as elemental analysis after different treatments would be needed to characterize the state of phosphorus.

Carbons S obtained by carbonization of the resin were mesoporous with a comparatively low pore volume and surface area (Table 1). They were activated by conventional “burnoff” techniques using either CO_2 at 850°C or air at 450°C in order to increase the surface area and develop the microporosity. Thus, carbon S was activated in CO_2 to 30–38% burnoff (SC) or heated in air up to a 40–44% burnoff (SA). Carbon SP was activated in CO_2 and air to 34% and 40% burnoff, respectively (sample code SPC and SPA, respectively). The characterization data of these carbons is given in Table 1. The chemical composition in weight % was determined by elementary analysis of carbon, nitrogen and oxygen. The sum of the percentages adds up to only ca. 95% in all carbons because water adsorbed on carbons was not analyzed. The textural parameters (BET surface area, pore volume and pore distribution using the BJH method) were determined from the measurement of N_2 adsorption isotherms at 77K. Figure 1 gives the pore size distribution of air-activated and CO_2 -activated carbons. The BET area and

carbon microporosity were increased by air, and particularly CO_2 activation treatment, without changing significantly the mesoporosity (Figure 1)

The treatment with air at 450°C introduced a large amount of oxygen in the carbon under the form of oxygenated functional groups. Activation treatments of carbons with gaseous CO_2 or air are known to generate phenolic groups, carboxylic acid groups, quinones, lactones, ethers, and aldehydes.¹⁰ The surface functional groups were characterized by selective acid–base titration in aqueous solutions and by thermal programmed desorption (TPD) of the decomposition products (CO_2 and CO) as described in detail elsewhere³. Air activation resulted in the formation of carbonyl/quinone type functional groups.

Preparation of Platinum Catalysts. Samples of carbon-supported platinum catalysts containing 1–3 wt % metal were prepared, either by ion-exchange using platinum tetramine chloride and reduction under hydrogen gas or by impregnation with chloroplatinic acid followed by liquid-phase formaldehyde reduction. In the cationic exchange, a slurry of carbon was prepared by mixing 5.82 g of carbon with 100 mL of 1 M NH_3 solution under nitrogen at room temperature. After 2 h, a solution of Pt salt was added as $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ in 1 M NH_3 solution dropwise. The mixture was stirred under nitrogen during the night, filtered, and washed with water until neutrality of the filtrate. The reduction was carried out in a double-fritted glass reactor with hydrogen (250 mL min^{-1} , heating rate 1°C min^{-1} up to 300°C , 2 h at 300°C , then cooling under hydrogen). The catalyst was purged with argon for 30 min and passivated with 1% O_2 in N_2 for 30 min. The carbons activated under CO_2 were further oxidized with sodium hypochlorite in order to create carboxylic groups for the platinum exchange (SCox). For the impregnation method, a slurry of carbon was prepared by mixing carbon with water (ca. 10 mL water/g carbon) under nitrogen at room temperature. A solution of the Pt-salt in the form of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ containing the required amount of Pt was added dropwise under stirring. After 5 h of

TABLE 2: Characteristics of Platinum Catalysts Supported on Activated SC and SA Supports

sample code	preparation method	platinum loading (%)	mean particle size by CO chemisorption (nm)	mean particle size by TEM (nm)
Pt3I/SC	impregnation	1.2	1.8	
Pt3E/SC	cationic exchange	0.1		
Pt3E/SCox	cationic exchange	2.95	12.5	9.3
Pt3I/SA	impregnation	1.2	2.5	4.0
Pt3E/SA	cationic exchange	2.5	4.2	5.2
Pt3I/SPC	impregnation	1.9		
Pt3E/SPC	cationic exchange	2.0		
Pt3I/SPA	impregnation	1.2		
Pt3E/SPA	cationic exchange	2.5		

impregnation, the slurry was cooled in an ice bath. The reduction procedure took place as follows: a 37% formaldehyde solution was added dropwise, followed by a 3% KOH solution. The suspension was mixed overnight, filtered and washed with water until neutrality. The catalyst was dried under nitrogen atmosphere at 100 °C for 1 day. Platinum dispersion was determined by volumetric CO chemisorption using a Micromeritics ASAP 2010M apparatus. All samples were heated under a flow of He up to 300 °C, evacuated at 100 °C and heated under hydrogen at 300 °C during 2 h. Hydrogen was then evacuated at 100 °C for 1 h. After cooling in a vacuum, the isotherm was measured at 35 °C. The dispersion was calculated assuming a CO/Pt stoichiometry of 1. Transmission electron microscopy (TEM) studies of the catalysts dispersed ultrasonically in ethanol and spread over a carbon-coated grid were conducted using a JEOL 200EX microscope. The average platinum particle sizes obtained by CO chemisorption and TEM are given in Table 2. It is noteworthy that the particle size obtained by impregnation and formaldehyde reduction were much smaller than those prepared by cationic exchange and H₂ reduction. This is in contrast with former studies of platinum catalysts prepared by cationic exchange on activated carbons obtained from natural sources^{12,13} where Pt particles of ca. 1.5 nm were obtained. May be the preparation of particles on synthetic carbons require an activation process involving a preliminary decomposition of the exchanged ammonium cations before H₂-reduction as required in Pt-exchanged Y-type zeolite to obtain 1 nm large particles.¹⁴

Oxidation Reactions. Unless otherwise stated, the reagents were commercially available in high purity grade. Oxidation reactions of cyclohexanone and corresponding derivatives were carried out in a 250 mL Hastelloy C22 autoclave stirred with a magnetic bar and equipped with baffles. The reactor was loaded with the catalyst and cyclic ketone dissolved in solvent (water or water/acetic acid mixture). The autoclave was outgassed and pressurized with argon to 2 bar, heated to the desired temperature under continuous stirring, and subsequently pressurized with air to 50 bar, which corresponded to time zero. Liquid samples withdrawn from the reaction medium at various time intervals were analyzed using a HPLC equipped with UV detector (in the case of reactions of cyclohexanone in water) or using a GC. A Sarasep Car-H column was used with diluted sulfuric acid (0.005 M) as eluting agent. A HP-5 column was used for GC analysis. Two injections were carried out: the direct injection of the sample allowed the quantitative analysis of the initial substrate using an internal standard (cyclohexanedione for cyclohexanone, cyclohexanone for 2-methylcyclohexanone), whereas the second injection was performed after derivatization of the diacids to methyl esters with trimethylsilyldiazomethane (Aldrich, 2M solution in hexane) with pimelic acid as internal

standard. When the reaction was performed in water, the total organic carbon (TOC) content in solution of some samples was measured with a Shimadzu TOC 5050A analyzer equipped with a nondispersive infrared detector and was compared to the concentration of the various products measured by HPLC or GC. The selectivity was defined as the number of moles of product formed over the number of moles of cyclohexanone converted.

Synthesis of 6-Oxohexanoic Acid. 6-Oxohexanoic acid was synthesized as previously described.¹¹ A total of 6 g of 2-hydroxycyclohexanone were dissolved in 400 mL of THF under argon. It was necessary to heat to get a clear solution. The NaIO₄ solution in water (1.5 mol NaIO₄/mol 2-hydroxycyclohexanone) was added dropwise. After 0.5 h of stirring, the product was extracted with 500 mL of ethyl acetate twice (in the first washing, 1 g of Na₂SO₃ was added to get rid of the iodine). The EtOAc extract was dried with MgSO₄ and the solvent removed in a high-vacuum evaporator. A white crystalline solid was obtained (yield 80%) which was analyzed by ¹H and ¹³C NMR.

Results and Discussion

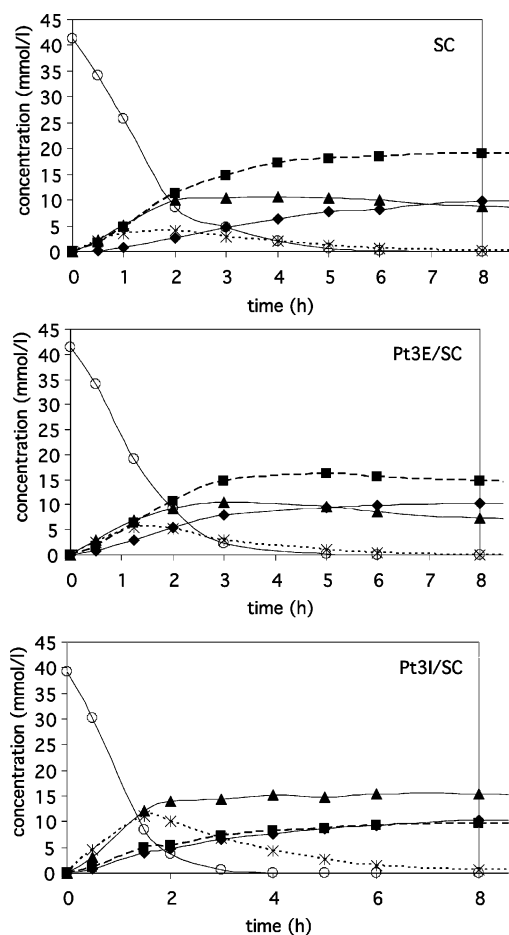
Effect of Platinum Loading on Synthetic Carbons. Oxidation reactions with air of cyclohexanone in water were conducted on various samples of synthetic carbons loaded with platinum and the catalytic performances were compared to those of metal-free synthetic carbons. The experiments were performed under standard conditions: ca. 50 mmol L⁻¹ in water 200 mg of catalyst, temperature 140 °C and 50 bar of air total pressure. In the samples taken at time zero, a deficit of 15–20% in the concentration of cyclohexanone was observed compared to the concentration of the reactant in the feedstock, whatever the carbon and whether platinum was present or not on the carbon. This loss of substrate was attributed to physical adsorption by the high surface area carbon and the vaporization of cyclohexanone during the heating of the autoclave under argon. The carbon mass balance of the reaction medium remained constant subsequently indicating that further loss of products did not occur. The selectivity to the oxidation products are expressed relative to the theoretical concentration introduced into the reactor, and thus are underestimated. Figure 2 shows the distribution of reactant and products as a function of reaction time when the reaction was performed in the presence of SC, Pt3E/SC, and Pt3I/SC. Figure 3 shows the product distribution for the SA carbon series. Table 3 summarizes the catalytic performances.

Platinum catalysts yielded adipic, glutaric, and succinic acids from the beginning of the reaction as previously observed in the presence of metal-free carbons³. 2-Hydroxycyclohexanone was detected as an intermediate product that was further oxidized to C₄–C₆ diacids. The formation of 6-oxohexanoic acid was also detected, as well as acetic and fumaric acids. The other oxidation products formed, amounting to ca. 20 mol %, were not identified and analyzed.

In the presence of carbon SC, cyclohexanone was oxidized with an initial reaction rate of 12.2 mol h⁻¹ g⁻¹. The maximum of 2-hydroxycyclohexanone and of 6-oxohexanoic acid formed were 4.1 and 4.5%, respectively. After the total conversion of cyclohexanone and 2-hydroxycyclohexanone, the selectivity to adipic, glutaric, and succinic acids were 17.3, 37.3, and 19.1%, respectively. Prolonged reaction time up to 24 h caused some oxidation of adipic acid and to a lesser extent of glutaric acid. Platinum loading produced no noticeable difference in activity (12.0 and 13.4 mol h⁻¹ g⁻¹, respectively). In the presence of

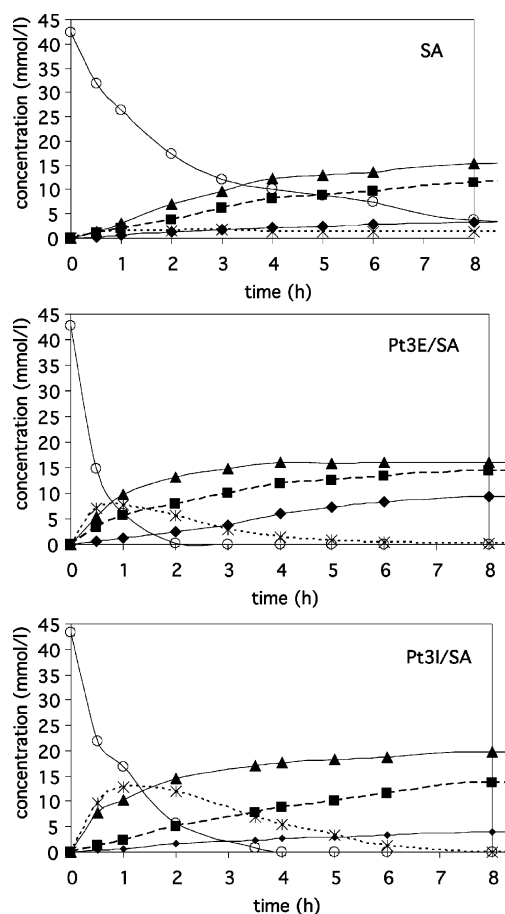
TABLE 3: Oxidation of Cyclohexanone in Water (50 mmol L⁻¹, 150 mL of Solvent, 140 °C, 50 bar Total Air Pressure, 0.2 g of Catalyst)

catalyst	initial reaction rate (mmol h ⁻¹ g ⁻¹)	yield in dicarboxylic acids and intermediates (%) at total conversion					
		adipic acid	glutaric acid	succinic acid	6-oxohexanoic acid	2-hydroxycyclohexanone	fumaric acid
SC	12.2	17.3	37.3	19.1	1.3	0.4	5.3
Pt3E/SC	12.0	16.7	30.7	19.4	5.2	0.9	6.3
Pt3I/SC	13.4	30.2	18.9	20.1	1.2	1.1	11.9
SA ^a	12.1	32.4	24.3	7.2	18.2	2.9	2.0
Pt3E/SA	27.6	31.6	28.3	18.2	2.9	0.5	4.2
Pt3I/SA	16.4	38.8	26.7	7.8	6.6	0	4.3
SPC	21.3	25.6	37.7	10.7	10.1	2.0	5.0
Pt3E/SPC	24.1	25.8	17.6	17.9	9.2	5.8	7.8
Pt3I/SPC	27.7	31.6	22.4	16.6	6.6	0.5	6.6
SPA ^b	8.8	34.3	27.1	9.5	15.4	4.5	2.3
Pt3E/SPA	27.6	26.6	24.0	21.7	2.6	0.8	5.4
Pt3I/SPA	27.6	33.1	26.3	19.9	7.6	1.6	5.7

^a At 92.6% conversion. ^b At 90.7% conversion.**Figure 2.** Oxidation of cyclohexanone in the presence of the SC series in water (50 mmol L⁻¹, 150 mL of water, 140 °C, 50 bar, 0.2 g of catalyst). ○, Cyclohexanone; ▲, adipic acid; ■, glutaric acid; ◆, succinic acid; ×, 2-hydroxycyclohexanone.

Pt3E/SC, the selectivities were little modified due to the very low Pt-loading, but on Pt3I/SC adipic acid became rapidly the major acid formed (Figure 2), and a high amount of 2-hydroxycyclohexanone was transiently observed (25.9% at maximum compared to 5.5%). After the subsequent oxidation of 2-hydroxycyclohexanone into C₄–C₆ diacids, the final selectivity to adipic acid at total conversion on SC carbon-based catalysts remained high (30.2% ADI, 18.9% GLU, and 20.1% SUC).

As already noticed³ for air activated carbon SA, the introduction of oxygenated functionalities improved the selectivity to adipic acid, which increased to 32.4% compared to 17.3% over

**Figure 3.** Oxidation of cyclohexanone in the presence of the SA series in water (50 mmol L⁻¹, 150 mL of water, 140 °C, 50 bar, 0.2 g of catalyst). ○, Cyclohexanone; ▲, adipic acid; ■, glutaric acid; ◆, succinic acid; ×, 2-hydroxycyclohexanone.

SC. Very little 2-hydroxycyclohexanone was formed, but 6-oxohexanoic acid yield attained 18.2%. In the presence of catalyst Pt3E/SA, the initial reaction rate increased to 27.6 mol h⁻¹ g⁻¹ and cyclohexanone was completely oxidized within 2 h. The selectivity to adipic and glutaric acid remained unchanged (31.6% and 28.3% respectively), whereas the selectivity to succinic acid increased to 18.2% and much lower amounts of 6-oxohexanoic acid were formed (2.9%). The selectivities were dependent upon the mode of platinum loading. As in the case of Pt3I/SC, the Pt3I/SA catalyst led to a higher yield in 2-hydroxycyclohexanone (maximum 37.5%) and improved the final selectivity to adipic acid (38.8%). The fact that Pt3E/SA

TABLE 4: Oxidation of Cyclohexanone in 80/20 v/v% Acetic Acid/Water Mixtures (50 mmol L⁻¹, 150 mL of Solvent, 140 °C, 50 bar, 0.2 g of Catalyst)

catalyst	initial rate (mmol h ⁻¹ g ⁻¹)	selectivity to diacids (%) at total conversion of cyclohexanone		
		succinic acid	glutaric acid	adipic acid
SC	21.1	12.6	12.1	27.5
Pt3I/SC	9.0	16.3	14.6	26.9
Pt3E/SCox	8.6	13.0	15.5	29.0
SA	11.4	11.6	11.1	23.7
Pt3I/SA	21.3	16.3	14.6	26.9
Pt3E/SA	14.9	14.9	14.4	27.5
SPC	21.0	12.9	13.7	26.0
Pt3I/SPC	14.3	10.3	16.4	28.8
SPA	3.2	12.3	12.3	24.7
Pt3I/SPA	11.7	15.7	14.2	27.5
Pt3E/SPA	11.5	13.8	13.7	24.7

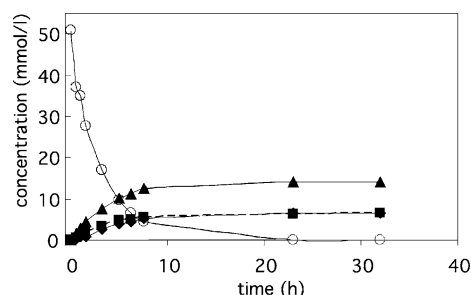
catalyst did not improve the selectivity to adipic acid with respect to SA catalyst whereas Pt3I/SA did may be associated with the elimination of active oxygenated groups occurring upon reduction under hydrogen at 300 °C of Pt3E/SA. Indeed, a loss of oxygenated surface groups has been reported¹⁵ in Pd/C and Pt/C catalysts that was attributed to the metal-catalyzed reduction of these groups by hydrogen. The positive influence of the presence of small particles of platinum on the selectivity to adipic acid might be compensated by the elimination of the oxygenated groups that also contribute to the selectivity to adipic acid.

Effect of Phosphorus Additive. The phosphorus-containing catalysts, either metal-free or loaded with platinum by cationic exchange or anionic adsorption, were tested under the same conditions. The catalytic performances are given in Table 3. Most interestingly, the addition of phosphorus to SC and SA carbons produced an increase of selectivity to adipic acid. In the absence of characterization on the state of phosphorus in the carbon, it is hazardous to interpret this result although one can speculate that the selectivity improvement is due to a higher number of oxygenated functional groups. Addition of platinum on SPC had nearly no effect on the conversion rate, whereas the conversion of cyclohexanone was improved by platinum loading on SPA. The selectivity of Pt/SPC catalysts followed the same trends as Pt/SC, e.g., platinum loaded by impregnation and formaldehyde reduction provided the highest selectivity to adipic acid.

Oxidation of Cyclohexanone in Acetic Acid/Water Mixture. Because the solvent may play a very important role in tuning the performances of carbon catalysts, the oxidation of cyclohexanone was also performed in acetic acid/water mixture in which cyclohexanone is soluble. The reaction temperature, pressure, and substrate concentration were the same as those of reactions in water. The oxidation rates of cyclohexanone in acetic acid were generally close to those measured in water, but platinum loading did not change significantly the selectivity to acetic acid which was in the range 23.7–32.3% on carbon or carbon-supported platinum catalysts (Table 4).

Furthermore, no significant differences could be detected when comparing the results obtained in the presence of catalysts based on SPC or SPA to those based on SC or SA carbons. Interestingly, the dicarboxylic acids formed were very stable as illustrated in Figure 4. The role of acetic acid as selectivity modifier cannot be interpreted presently because the molecular interactions between acetic acid, platinum, carbon and cyclohexanone are not known.

Oxidation of 2-Hydroxycyclohexanone Intermediate. It has been shown that cyclohexanone oxidation can proceed via

**Figure 4.** Oxidation of cyclohexanone in the presence of SC in acetic acid/water 80/20 v/v % (50 mmol L⁻¹, 150 mL of solvent, 140 °C, 50 bar, 150 mL of solvent). ○, Cyclohexanone; ▲, adipic acid; ■, glutaric acid; ◆, succinic acid.

2-hydroxycyclohexanone intermediate. In an attempt to obtain information on the mechanism of reaction leading to glutaric and succinic acids, we carried out a series of oxidation experiments of this substrate in the presence of the SC and SA carbons, in water or in acetic acid, under the same reaction conditions. 2-Hydroxycyclohexanone was cleaved oxidatively to adipic, glutaric and succinic acids. The analysis of the reaction medium showed a progressive deficit of the carbon balance that attained 50% at total conversion of 2-hydroxycyclohexanone indicating that undetected compounds were formed.

Figure 5 shows the oxidation profiles of this intermediate in the presence of SC and SA catalysts, both in water and in acetic acid. The reaction rates of 2-hydroxycyclohexanone were higher in acetic acid than in water (46.7 and 33.4 mmol h⁻¹ g⁻¹ over SC and SA in acetic acid, compared to 16.5 and 6.5 mmol h⁻¹ g⁻¹ in water). It is also apparent from Figure 5 that the selectivity to dicarboxylic acids depended mainly on the solvent. Indeed, at total conversion of substrate in water, glutaric acid was the main diacid on both carbons, albeit to a lesser extent on SA carbon, whereas in acetic acid, adipic acid was by far the major product. In conclusion, 2-hydroxycyclohexanone gave a poor overall yield in dicarboxylic acids. The proportion of adipic acid depended on the solvent, a higher yield of adipic acid was formed in acetic acid.

Oxidation of 6-Oxohexanoic Acid. 6-Oxohexanoic acid was identified as an end-product in the reaction medium in some cyclohexanone oxidation runs. The concentration was the highest in the presence of SA and SPA carbons. This compound was synthesized (see experimental part) and subjected to oxidation in water or in acetic acid/water mixture. The analysis of the reaction products were performed by GC after derivatization of the solution. Figure 6 shows the catalytic results on SC and SA carbons. The carbon balance of products was in large deficit when the reaction was performed in water, whereas it was within 80% of initial carbon in acetic acid. Adipic acid was the major product formed over SC and SA via oxidation of the aldehyde group when the reaction was conducted in acetic acid. In contrast, in water, 6-oxohexanoic acid was mainly oxidized to glutaric and succinic acids in the presence of SC. This may be interpreted by the formation of an enol in water that would oxidize to glutaric acid. Interestingly, the oxidation rate of 6-oxohexanoic acid in water was much lower on SA than on SC, as shown in Figure 6. This accounts for the larger amounts of 6-oxohexanoic acid formed on SA catalysts.

Oxidation of 4-Methylcyclohexanone. Cyclohexanone oxidation yielded always a mixture of diacids by oxidative bond breakages. The presence of lower carbon chain acids was detected from the beginning of the reaction and adipic acid was little degraded to lower acids under the present reaction conditions. This suggests a multiple attack of the cyclic ketone

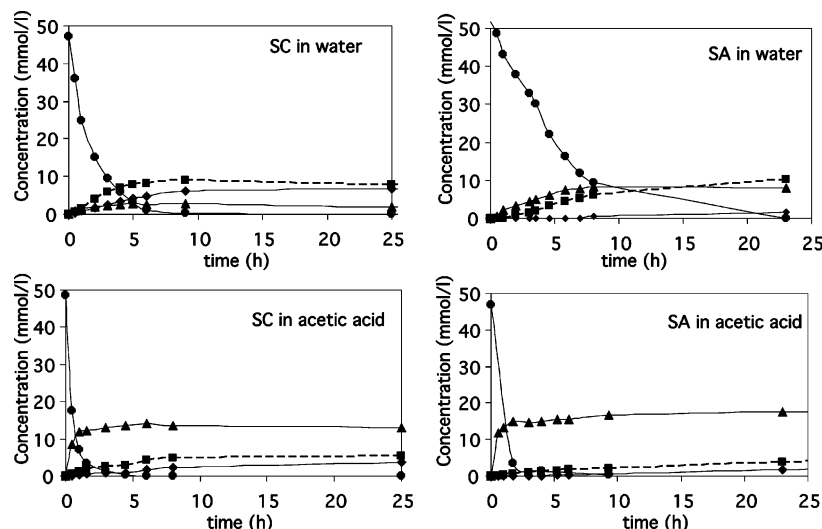


Figure 5. Concentration of reactant and detected reaction products during oxidation of 2-hydroxycyclohexanone in the presence of SC and SA catalysts (50 mmol L⁻¹, 150 mL of solvent, 140 °C, 50 bar, 0.2 g of catalyst). ●, 2-Hydroxycyclohexanone; ▲, adipic acid; ■, glutaric acid; ◆, succinic acid.

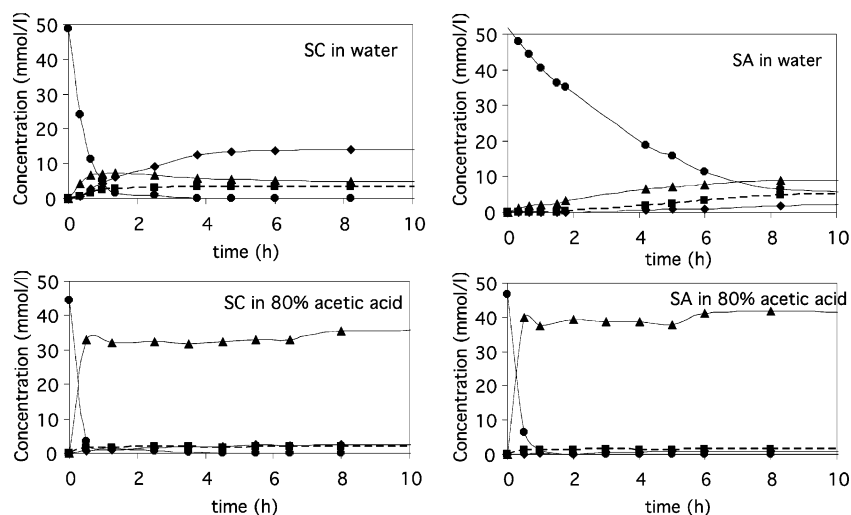


Figure 6. Influence of carbon and solvent during oxidation of 6-oxohexanoic acid (50 mmol L⁻¹, 150 mL of solvent, 140 °C, 50 bar, 0.2 g of catalyst). ●, 6-Oxohexanoic acid; ▲, adipic acid; ■, glutaric acid; ◆, succinic acid.

with C–C bond breakage at different positions of the cycle, but the sequence of oxidative bond breakage is not known. To understand the mechanism of cleavage, the oxidation of 4-methylcyclohexanone, in which the substituting methyl group acts as a label,¹⁶ was performed. Figure 7 gives all of the expected products from oxidative breakage of 4-methylcyclohexanone. The oxidative loss of C1 would give 3-methylglutaric, whereas that of C2 would result in the formation of 2-methylglutaric acid. Similarly, the oxidation with loss of C1 with C2 would provide 2-methylsuccinic acid, whereas the loss of C2 with C3 will yield 4-oxopentanoic (levulinic) acid, which will be further oxidized to succinic acid.

The reaction was performed, either in water or in acetic acid/water 80/20 v/v % at 140 °C and 50 bar at a concentration of 50.9 mmol/L. The carbon balance decreased continuously during oxidation because of the formation of undetected products in the reaction medium (possibly hydroxy or oxo compounds). It was verified with a TOC analyzer that the TOC (total organic carbon) did not decrease significantly. Smaller amounts of unidentified products were observed for the reaction conducted in acetic acid. Table 5 gives the product distribution for these reactions.

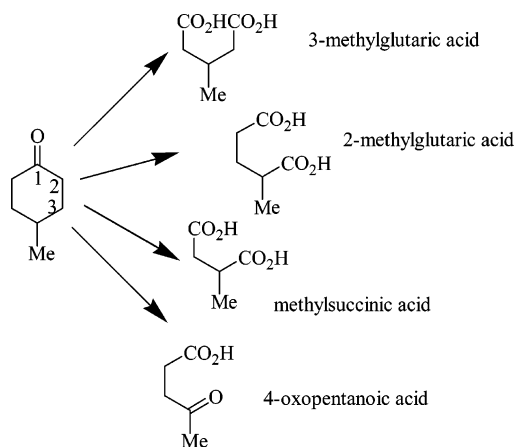


Figure 7. Expected products from oxidative breakage of 4-methylcyclohexanone.

The data given in Table 5 confirm the results obtained for the oxidation of cyclohexanone in water, namely a better selectivity to the corresponding diacids in the presence of SA (19.1% of 3-methylglutaric acid compared to 7.6%) and a negative effect of the Pt– loading by cationic exchange and reduction

TABLE 5: Product Yields from the Catalytic Oxidation of 4-Methylcyclohexanone in Water or in Acetic Acid/Water Solvent (150 mL of a 50.9 mmol/L Solution, 200 mg of Catalyst, $T = 140\text{ }^{\circ}\text{C}$, Total Air Pressure 50 bar)

catalyst	time for total conversion (h)	yield of methyl-dicarboxylic acid (%)				
		3-methyl adipic	3-methyl glutaric	2-methyl glutaric	methyl succinic	3-methylglutaric/ 2-methylglutaric ratio
In Water						
SC	7	7.6	3.7	4.5	1.9	0.82
Pt3E/SC	4.5	8.8	5.7	5	2	1.14
SA	24	19.1	4.9	5.2	1.3	0.94
Pt3E/SA	1.5	11.2	4.6	4.7	0.8	0.98
In Acetic Acid/Water 80/20 v/v %						
SC	24	17.3	3.3	3.6	2.8	0.92
Pt3E/SC	22	13.7	4	3.2	3.1	1.25
SA	33	13.9	2.2	2.1	2.1	1.05
Pt3E/SA	32	15.2	4.2	4.1	3.6	1.02

under H_2 at $300\text{ }^{\circ}\text{C}$ on SA carbon (11.2% instead of 19.2%). Reactions in acetic acid yielded very similar results whatever the catalyst (13.7–17.3%). If one compares the product distribution of 3-methylglutaric acid and 2-methylglutaric acid, a ratio close to 1 was calculated in all cases. This suggests that the most likely pathway to glutaric acid involves the oxidative loss of both C1 and C2 in equal amounts.

Conclusion

The oxidation with air of cyclohexanone in water yields a mixture of C_6 , C_5 , and C_4 dicarboxylic acids, which once formed were stable under the reaction conditions. Interestingly, air activated carbons, including those containing phosphorus, or those supporting platinum, gave higher yields to adipic acid. Although the mechanism by which the cyclic ketones are oxidized to dicarboxylic acids has not been established, it has been suggested that the activity is associated with oxygenated functional groups, essentially carbonyl/quinone groups, created during air activation of the carbon. In the absence of any additives the maximum yield in adipic acid was 32.4% (air activated SA sample). The incorporation of phosphorus onto the carbon increased slightly the selectivity to 34.3% (SPA sample). It is likely that this additive increases the density of oxygenated functional groups able to catalyze the oxidative bond breaking of cyclic ketone. The deposition of platinum by impregnation and liquid-phase reduction with formaldehyde increased the reaction rate, and improved the selectivity to adipic acid, the highest figure was 38.8% obtained with Pt3I/SA catalyst. The mechanism by which platinum enhances the selectivity is not known yet although it can be suggested that platinum contributes to molecular oxygen activation. In contrast platinum deposition by cationic exchange followed by reduction under H_2 resulted often in a detrimental effect probably because the density of the oxygenated groups on carbon decreased upon H_2 -reduction in the presence of the metal. When the oxidation of cyclohexanone was carried out in mixtures of water/acetic, the selectivities given by the different samples were quite close and generally smaller than those obtained in water which indicates that acetic acid interacts with the oxygenated surface functional groups responsible for the activity and selectivity. The nature of these interactions, the very nature of the functional groups and a description of the mechanism of oxidation on

synthetic carbons will require further studies, particularly additional carbon surface characterization, to give a more complete interpretation of the results. Extensive studies are also required to characterize the state of phosphorus in carbon catalysts. In the meantime, the results obtained with the methyl-labeled 4-methylcyclohexanone indicate that glutaric acid can be issued by oxidative decarbonylation of both C_1 and C_2 carbon atoms of the molecule.

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References and Notes

- (1) Pereira, M. F. R.; Orfao, J. J. M.; Figueiredo, J. L. *Appl. Catal.* **1999**, *184*, 153.
- (2) Pinel, C.; Landrion, E.; Lini, H.; Gallezot, P. *J. Catal.* **1999**, *182*, 515.
- (3) Pigamo, A.; Besson, M.; Blanc, B.; Gallezot, P.; Blackburn, A.; Kozynchenko, O.; Tennison, S.; Crezee, E.; Kapteijn, F. *Carbon* **2002**, *40*, 1267.
- (4) Johnson, R. W.; Pollock, C. M.; Cantrell, R. R. Dicarboxylic acids. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Krodchowitz, J., Ed.; J. Wiley & Sons: New York, 1993; Vol. 8.
- (5) Sureh, A. K.; Sharma, M. M.; Sridhar, T. *Ind. Eng. Chem. Res.* **2000**, *39*, 3958.
- (6) Castellán, A.; Bart, J. C. J.; Cavallaro, S. *Catal. Today* **1991**, *9*, 237, 255, 284.
- (7) Sheldon, R. A.; Arends, I. W. C. E.; Dijkman, A. *Catal. Today* **2000**, *57*, 157.
- (8) MAST Carbon, www.mastcarbon.co.uk.
- (9) Puziy, A. M.; Poddubnava, O. I.; Martinez-Alonso, A.; Suarez-Garcia, F.; Tascon, J. M. D. *Carbon* **2003**, *41*, 1181.
- (10) Radovic, L. R.; Rodriguez-Reinoso, F. *Chem. Phys. Carbon* **1997**, *25*, 243.
- (11) Baer, E. *J. Am. Chem. Soc.* **1942**, *64*, 1416.
- (12) Richard, D.; Gallezot, P. Preparation of Catalysts IV; Delmon, B., Ed.; In *Studies in Surface Science and Catalysis* (31); Elsevier: Amsterdam, 1987; p 74.
- (13) Gamez, A.; Richard, D.; Gallezot, P.; Gloaguen, F.; Faure, R.; Durand, R. *Electrochim. Acta*, **1996**, *41*, 307.
- (14) Gallezot, P. In *Molecular Sieves*; Weitkamp, J., Ed.; Springer-Verlag: Berlin, 2002; Vol. 2, pp 258–305.
- (15) Okhlopova, L. B.; Lititsyn, A. S.; Likholobov, V. A.; Gurrath, M.; Boehm, H. P. *Appl. Catal. A* **2000**, *204*, 229.
- (16) Smith, J. R. L.; Richards, D. I.; Thomas, C. B.; Whittaker, M. *J. Chem. Soc., Perkin Trans.* **1992**, *2*, 605.