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Active carbons as catalysts for liquid phase reactions

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Abstract

This paper gives three examples of applications of activated carbons, including synthetic carbons obtained from polymers, in selective liquid phase organic reactions. It is shown that ruthenium supported on activated carbon cloths (ACC) obtained by carbonisation of woven rayon fabric are very selective in the hydrogenation of glucose to sorbitol. This is attributed to an easy mass transfer from the micropores to the liquid phase which favours the fast desorption of sorbitol avoiding epimerisation to mannitol. Synthetic carbons obtained by carbonisation of cross-linked phenolic resins are active in the oxidation with air of cyclic ketones (cyclohexanone, cyclododecanone, 3,3,5-trimethylcyclohexanone) to the corresponding dicarboxylic acids. The activity and selectivity depend upon treatments favouring the presence of surface functional groups, particularly quinone/carbonyl groups. This paper also shows that activated carbons obtained from natural sources can be modified by thermal treatments favouring the presence of basic sites which improve the rate of the oxidative decarboxylation of *N*-phosphonomethyl iminodiacetic acid to glyphosate. The nitrogen-containing basic functions generated by high temperatures thermal treatment of the activated carbon in NH_3 are particularly active.

Keywords: Activated carbon; Liquid phase organic reactions; Carbon cloths; Hydrogenation

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1. Introduction

Carbon materials offer a wide range of applications in adsorption, catalytic processing and structural reinforcement of polymers. In heterogeneous catalysis, they are often used as support because they present all the required characteristics such as large surface area, chemical stability and well-developed porosity [1]. Many commercial catalysts for fine chemicals applications consist of carbon-supported metal catalysts, because carbon is chemically inert towards functionalised organic molecules in comparison to conventional supports such as alumina or silica [2]. Activated carbons are usually available in powder or granular form, but new forms such as activated carbon cloths (ACC) are promising supports because of their flexibility of use in different reactor types and easier recyclability than powder or granules [3–6]. So far, there are scarce literature data on liquid phase reactions conducted with ACC-supported catalysts, in the present paper, it will shown be that ruthenium/ACC catalysts are active and very selective to sorbitol in the hydrogenation of aqueous solutions of glucose.

However, the application of carbons in catalysis is not restricted to supporting materials. Surface functional groups-containing heteroatoms (oxygen, nitrogen) introduced by suitable thermal or chemical treatments of a carbon are potential active sites making the carbon a catalyst by itself for selective oxidation, chlorination and dechlorination reactions [7]. This paper reports two successful examples of liquid phase oxidation reactions with air catalysed by surface functional groups namely, the oxidative decarboxylation of *N*-phosphonomethyl iminodiacetic acid catalysed by nitrogen-containing basic sites and the oxidation of cyclic ketones to the corresponding dicarboxylic acids catalysed by oxygenated functionalities.

2. Efficient Ru/ACC catalysts for carbohydrate hydrogenation

An activated carbon cloth, supplied by Carbon Industry (subsidiary of Messier-Bugatti Co.) was obtained from a

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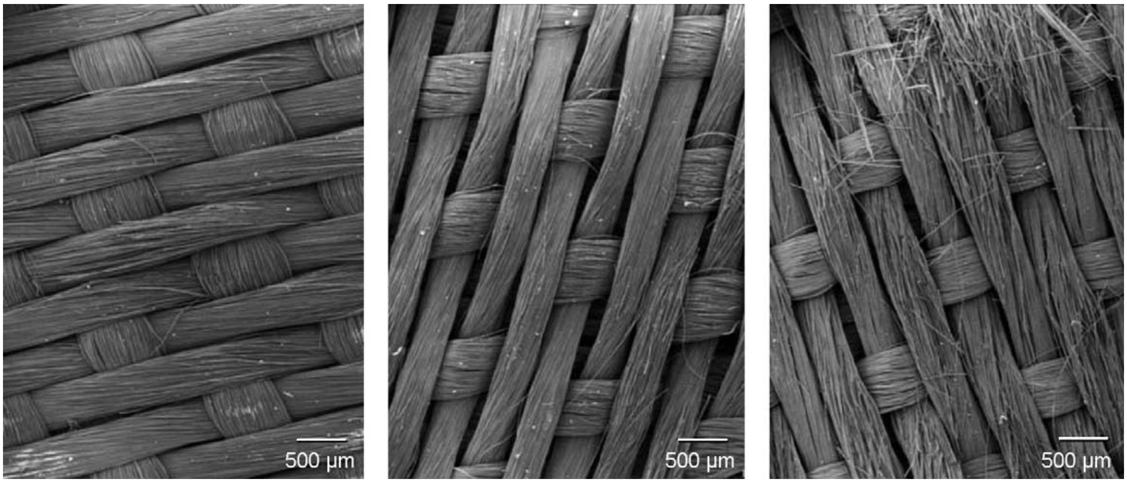


Fig. 1. SEM view of ACC as received, ACC_{Ox} and 10%Pt/ACC_{Ox} (from left to right).

woven rayon cloth, which was dry cleaned, precarbonised by pyrolysis at 400 °C, and carbonised at 1200 °C under a nitrogen flow. The final ash content was 0.1 wt.%. The carbon cloth was then activated at 900 °C under a CO_2 flow to get a 50 wt.% burn-off.

Ru and/or Pt-based metal catalysts supported on ACC were prepared with different metal contents in the range 1–2 wt.% up to 10 wt.% by two classical methods [8]: cationic exchange with $Ru(NH_3)_6Cl_3$ and $Pt(NH_3)_4Cl_2$ in 1 M ammonia solution after oxidation of ACC with 3% active chlorine NaClO aqueous solution, and then reduction under flowing hydrogen and passivation with 1%O_2/N_2 (samples noted metal/ACC_{Ox}) or anionic adsorption from $RuCl_3$ and H_2PtCl_6 in 0.1N aqueous hydrochloric medium and alkaline liquid phase reduction with formaldehyde (samples noted metal/ACC). During the oxidation and metal loading steps, the cloth was fixed on a cylindrical glass grid fixed around the inner wall of the treatment vessel equipped with a stirrer. This design allowed the best possible contact between the solutions and the cloth, leading to reproducible preparations.

Fig. 1 shows scanning electron microscopy (SEM) images at 25-fold magnification showing the texture of the woven ACC as received, of ACC after oxidation with NaOCl (ACC_{Ox}) and of 10%Pt/ACC_{Ox}. It can be observed that the cloth is more stretched after NaClO oxidation and that some threads are damaged after Pt deposit. An examination at higher magnification showed that the threads are made up of lobed fibres of 8 μm diameter that did not decrease noticeably in the course of the different treatments. The transmission electron microscopy (TEM) view taken through an ultramicrotome section of 50–80 nm thickness across a carbon fibre of a 10%Pt/ACC_{Ox} catalyst (Fig. 2) shows the uniform distribution of Pt particles inside the fibres. Particle sizes were in the range 2–8 nm with a distribution displaced towards small particles.

The nitrogen physisorption isotherms at 77 K, measured after heating the samples at 130 °C overnight under nitrogen are of type I, typical of microporous solids. The BET surfaces S_{BET} of ACC, ACC_{Ox} and 10% Pt/ACC_{Ox} were 1300, 680 and 580 $m^2\,g^{-1}$, respectively, with microporous volumes V_p of 0.54, 0.30 and 0.25 $cm^3\,g^{-1}$, respectively. The order of magnitude of the mean size d_P given by 2 V_P/S_{BET} of pores assumed slit-shaped is always close to 1 nm whatever the treatment undergone by the samples. It was observed that outgassing the ACC_{Ox} under argon up to 550 °C increased the surface and pore volume up to 960 $m^2\,g^{-1}$ and 0.42 $cm^3\,g^{-1}$. This suggests that the micropore access was restricted in ACC_{Ox} because of a partial pore blockage by oxygen functional groups. These catalysts were used for the hydrogenation of 40% aqueous solutions of glucose at 100 °C under 80 bar H_2 pressure, either in a 300 ml batch reactor or in a micropilot trickle-bed reactor. The stirred autoclave was equipped with a fixed

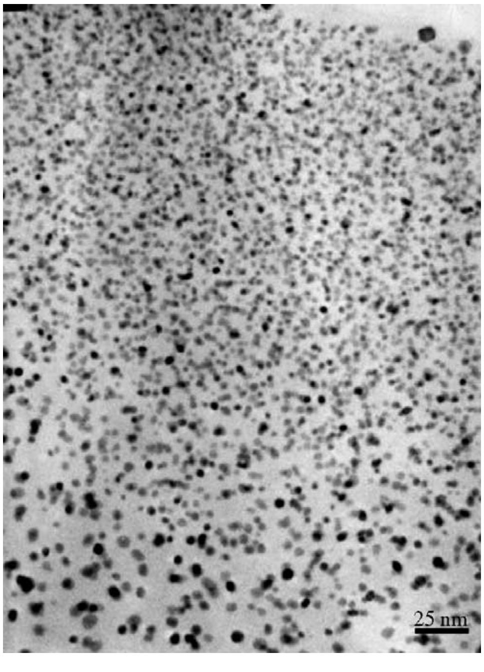


Fig. 2. TEM view of 10%Pt/ACC_{Ox}.

Table 1
Initial specific activity and selectivity to sorbitol of Ru catalysts in glucose hydrogenation (160 g of a 40% glucose aqueous solution, 100 °C, 80 bar hydrogen pressure and 3 g catalyst)

aa	1.9%Ru/ACC$_{Ox}$	0.9%Ru/ACC	5%Ru/C
Activity (mol h^{-1} g^{-1})	1.8	2.4	2.5
Selectivity (%)	99.8 (98% conversion)	99.5 (99.7% conversion)	2.599.0 (99% conversion)

cylindrical grid basket, fitting around the inner wall. Rectangular pieces of cloth were cut to dimension and fixed around the grid. In the trickle-bed reactor, the cloth was rolled up along the axis of reactor between the inner stainless steel tube and the central immersed thermocouple shaft.

Table 1 gives the specific activity and selectivity to sorbitol measured in batch experiments of two ruthenium catalysts prepared on ACC compared to the performances of a commercial 5%Ru/C catalyst in powder form [9]. The selectivity at nearly total conversion of glucose was higher than 99.5% on 1.9%Ru/ACC$_{Ox}$ and 0.9%Ru/ACC compared to 99.0% on 5%Ru/C. The first decimal is significant, i.e. the accuracy on such sorbitol selectivities at high glucose conversion is 1‰ as determined by HPLC and by GC after derivatization by silylation. The high selectivity can be explained by a lower probability of sorbitol epimerization to mannitol in ACC than in a conventional support. This is based on a suggestion [10] that the micropores of ACC open directly to the outer surface so that one can expect a faster desorption of sorbitol than on conventional activated carbons.

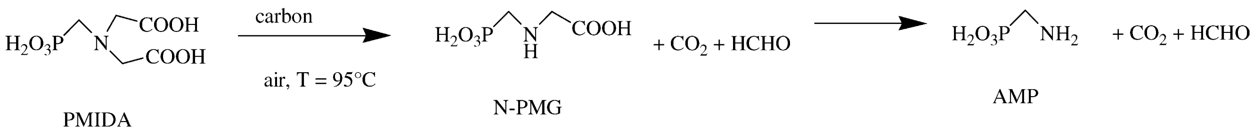
Two bimetallic catalysts were also compared in reactions carried out in trickle-bed reactor. Catalyst 0.8%Ru–1.2%Pt/C$_{ox}$ (Ru/Pt atomic ratio = 0.8) was prepared by cationic co-exchange of Norit rox 0.8 active carbon extrudates. The metal particles were very homogeneously distributed on the support with particle sizes of 1 nm or less. Catalyst 3.4%Ru–6.6%Pt/ACC$_{Ox}$ (Ru/Pt atomic ratio = 1) was prepared by cationic co-exchange of ACC$_{Ox}$. In the same experimental conditions, the two bimetallic catalysts yielded a 98% selectivity to sorbitol at 15% conversion, i.e. less than that measured on Ru/ACC or Ru/C catalysts.

3. Modified active carbons as oxidation catalysts for glyphosate synthesis

Glyphosate or *N*-(phosphonomethyl)glycine (PMG) is a very efficient herbicide sold under the name of Roundup®. Monsanto developed the synthesis of PMG from PMIDA (*N*-phosphonomethyl iminodiacetic acid) by an oxidative decarboxylation reaction in the presence of a Pt/C catalyst or of activated carbons using oxygen as oxidizing agent [11] (Scheme 1).

Activated carbon catalysts of different origins and characteristics were tested to determine the influence of their chemical and physical properties on the rate of PMIDA oxidative decarboxylation [12]. The reaction was carried out in a 500 ml thermostated reactor equipped with mechanical stirring, condenser and inlet/outlet gas tubings. Whatever the catalyst, until almost complete conversion of PMIDA, 100% selectivity to PMG and to decarboxylation co-products (CO_2 and HCHO) was obtained. At total PMIDA conversion, the selectivity to glyphosate decreased because of a subsequent decarboxylation yielding aminomethylphosphonic acid (AMP).

Several commercial carbons prepared from pinewood with a large range of porosity, carbon blacks and graphite were tested without any pretreatment (Table 2). The specific activity (A_S (mmol h^{-1} g^{-1})) and areal activity (A_A (mol h^{-1} m^{-2})) were calculated from the slope of the linear curve giving the glyphosate yield as a function of time.



Scheme 1.

Table 2
Influence of the nature of the carbon on the rate of the oxidative decarboxylation of PMIDA (12 g PMIDA, 3 g catalyst, 300 ml water, 95 °C and air flow 20 l h^{-1})

Catalyst	Origin	S_{BET} (m^2 g^{-1})	A_S (mmol h^{-1} g^{-1})	A_A (mol h^{-1} m^{-2})
4S	Pinewood, physical activation	1164	2.8	2.4
ENO	Pinewood, chemical activation	1631	2.1	1.3
CBP	Pinewood, no activation	146	0.3	2.1
NoritSX1G	Peat, physical activation	1055	4	3.8
SNK	N-containing polymer	1121	4	3.6
HSAG 300	Graphite	364	0.1	0.3
Vulcan XC72R	Carbon black	297	0.5	1.8

Table 3
Influence of treatment of active carbon 4S on the reaction rate

Treatment	Acidic groups (mmol g^{-1})	A_S (mmol h^{-1} g^{-1})
None	0.2	2.8
NaOCl/RT	1.3	1.5
HNO_3	2.9	1.1
H_2	n.d.	1.8
NH_2–NH_2	n.d.	2.1
N_2/450 °C	0.04	2.9
N_2/700 °C	n.d.	2.9
N_2/900 °C	0	4

Carbons with small surface area (CBP active carbon, HSAG graphite or Vulcan carbon black) had low specific activities (0.1–0.5 mmol h^{-1} g^{-1}). However, the comparison of areal rates (0.3–2.1 mol h^{-1} m^{-2}) indicated that there was no direct correlation between the activity and the surface area of catalysts.

The nature and amount of oxygenated functional groups present at the surface of activated carbons may play a significant role in their activity. Thus, 4S activated carbon was submitted to oxidizing treatments with NaOCl or HNO_3 to increase the number of oxygen-containing groups, or, on the contrary, to thermal treatment under N_2, H_2 and NH_2–NH_2 intended to reduce their number. The amount of acidic groups was titrated with sodium hydroxide. As shown in Table 3, the presence of acidic groups on the surface had a negative effect on the activity of the catalyst. On the other hand, reductive treatment that removed acidic groups yielded active carbons with high activity. Thermal treatment of the active carbons reduced the amount of acidic groups present on the surface of the catalyst. However, treatment at temperature less than 700 °C did not affect the activity of the catalysts, whereas the specific rate measured on the active carbon treated at 900 °C was 40% higher than that of untreated sample. Such thermal treatment is known to create basic groups such as pyrone type, which could be responsible for the improvement of the catalytic activity [13].

The two most active untreated carbon catalysts (Table 2) were SNK prepared from polyvinylpyrolidine polymer (2.1 wt.% N) and Norit from peat (0.34 wt.% N) while almost nitrogen-free carbon 4S exhibited much lower activity. This suggested that the activity of carbon catalysts could be improved by increasing the amount of basic nitrogen sites. It was shown previously that carbon–nitrogen surface groups can be introduced by high temperature treatment of carbons, therefore, active carbon 4S was heated at 900 °C under flowing ammoniac vapour. The treatment resulted in a 20–30% weight loss, a 30% increase of the surface area, a significant introduction of nitrogen in the structure (4.2 wt.% N) and an increase of both specific and areal activities (Table 4). The same treatment applied to CBP, a low surface area carbon, produced a five-fold increase of the areal activity (from 2.1 to 11 mol h^{-1} m^{-2} after ammonia treatment) and a 17-fold increase of the specific activity (from 0.3 to 5.1 mmol h^{-1} g^{-1}). A recycling experiment of carbon 4S/NH_3/900 °C showed that the activity was not modified and that the basic sites were not eliminated.

It can be concluded that the activity of carbon catalysts in the oxidative decarboxylation of PMIDA is enhanced by the presence of surface basic sites, involving either nitrogen functional groups or sites introduced by thermal treatment under inert gas. However, the mechanism of action of these basic sites remains to be established.

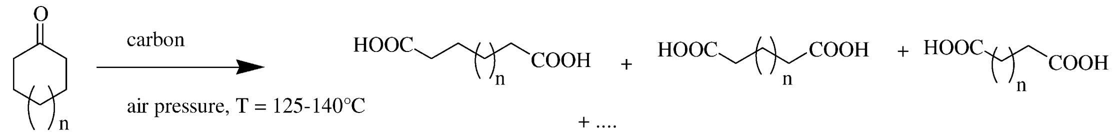
4. Synthetic carbon catalysts for cyclic ketone oxidation to dicarboxylic acids

The development of catalytic oxidations with molecular oxygen is desirable from economical and environmental points of view in place of stoichiometric chemical oxidants. Dicarboxylic acids such as adipic acid, trimethyladipic acid and dodecanedioic acid enter important industrial processes (polyamide and polyester manufacture, plasticizers, lubricating oil, etc.). They are currently manufactured in multistep processes by oxidation with nitric acid of mixtures containing the corresponding alcohol and ketone [14]. In a former study aimed at using carbons as catalysts for liquid phase oxidation reactions, it was shown that metal-free, synthetic carbons were able to catalyse the oxidation of cyclohexanone to adipic, glutaric and succinic acids at 140 °C under air pressure [15,16]. In the framework of a European project [17], this type of investigation was extended to the oxidation of other cyclic ketones to the corresponding dicarboxylic acids. Thus, cyclododecanone and 3,3,5-trimethylcyclohexanone were oxidized with air in an attempt to prepare selectively 1,12-dodecanedioic acid and a mixture of 2,2,4- and 2,4,4-trimethyladipic acids, respectively (Scheme 2).

The oxidation runs were conducted in a 250 ml autoclave equipped with a magnetically driven impeller. Typically, the reactor was loaded with a solution of cyclic ketone and carbon catalyst, heated to the desired temperature under

Table 4
Influence of nitrogen content on the activities of active carbons

Catalysts	N content (%)	S_{BET} (m^2 g^{-1})	A_S (mmol h^{-1} g^{-1})	A_A (mol h^{-1} m^{-2})
4S	0.03	1164	2.8	2.4
4S/NH_3/900 °C	4.2	1501	5.1	3.4
CBP	0.42	146	0.3	2.1
CBP/NH_3/900 °C	2.67	462	5.1	11.0



Scheme 2.

Table 5
Textural properties and elementary analysis of the synthetic carbons

Reference of carbon	Burn-off (%)	S_{BET} (mV)	Porous volume (cm g^{-1})	Mean pore size (nm)	Elementary analysis (%)		
					C	H	O
$MAST_{CO_2}$	30–38	929–1223	0.78–1.1	15–18	93.45	0.61	1.22
$MAST_{air}$	40–47	750–806	0.79–0.81	15–18	76.70	0.58	18.03

argon, and then pressurized with air. The zero reaction time corresponded to the start of reactor stirring. Samples of the reaction medium were withdrawn from the reactor at definite time intervals.

Synthetic carbon samples used in this study were activated carbons with controlled pore size derived from phenolic resin supplied by MAST (Table 5) [18,19]. The nonactivated materials were prepared by carbonisation at 800 °C of a porous polymeric resin precursor prepared from Novolac resin and hexamethylenetetramine in polyethylene glycol. The carbon particles thus produced were in the form of spherical particles (diameter ca. 50 μm, specific surface area 540 m^2 g^{-1}, pore volume 0.60 cm^3 g^{-1}). Then, they were activated by conventional ‘‘burn-off’’ techniques using either CO_2 at 850 °C, or air at 450 °C in order to increase the surface area and pore volume and to modify the surface properties. The BET surface area and micropore volume increased upon CO_2 activation. It was also observed by elemental analysis and X-ray photoelectron spectroscopy that oxygen functional groups were generated at the carbon surface upon oxidation treatment. A variety of techniques were used to characterize the functional groups among them temperature-programmed desorption (TPD), which in a previous investigation of air activated carbons revealed high temperature CO peaks, assigned to carbonyl/quinone groups [15,16].

Upon oxidation of cyclohexanone in water adipic acid was formed, but also glutaric and succinic acids. They all appeared from the beginning of the reaction suggesting that the C_5 and C_4 diacids were not secondary products formed from adipic acid. Similarly, the oxidation of cyclododecanone in acetic acid/water resulted in the formation of cyclododecanedioic acid as well as diacids with smaller carbon chains (C_4–C_{11}) formed by oxidative bond breakages.

Figs. 3 and 4 give the product selectivity at nearly total conversion of the cyclic ketone in two different oxidation reactions. The conversion and selectivity to diacids depended drastically on the treatment of active carbon. $MAST_{air}$ obtained by activation under air at 450 °C was less active but afforded higher selectivity to the desired dicarboxylic acid than $MAST_{CO_2}$ obtained by activation in CO_2 at 850 °C. Indeed, the selectivity to adipic acid was 32.4 and 17.3%, respectively, and the selectivity to cyclododecanedioic acid was 28 and 14%, respectively. The selectivity to the desired dicarboxylic acid is thus controlled by the presence of oxygen surface groups, in particular carbonyl/quinone groups introduced by activation of the carbon under air. In the oxidation of 3,3,5-trimethylcyclohexanone in acetic acid, the influence of the activation was smaller with a selectivity to trimethyladipic acids of 26.5 and 23.4%, respectively, possibly due to a steric effect of the methyl groups.

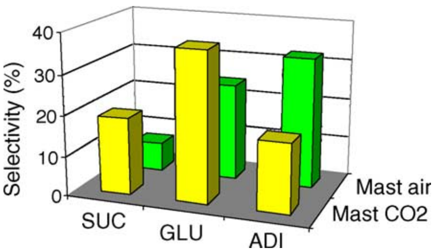


Fig. 3. Product selectivity for cyclohexanone oxidation as a function of the activation treatment of the carbon (150 ml of cyclohexanone in water, 50 mmol l^{-1}, 0.2 g catalyst, 140 °C and 50 bar total air pressure). SUC: succinic acid, GLU: glutaric acid and ADI: adipic acid.

The stability of $MAST_{air}$ carbon was studied in recycling experiments in oxidation of cyclohexanone. The perfor-

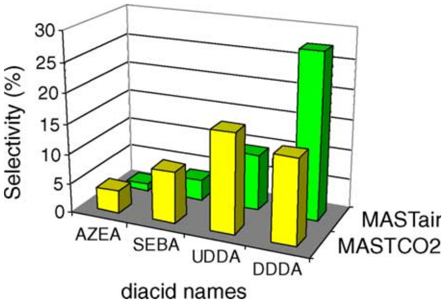


Fig. 4. Product selectivity for cyclododecanone oxidation as a function of the activation treatment of the carbon (150 ml of cyclododecanone in water, 165 mmol l^{-1}, 1 g catalyst, 125 °C and 40 bar total air pressure). AZEA: azelaic acid (C9), SEBA: sebacic acid (C10), UDDA: undecanedioic acid (C11) and DDDA: dodecanedioic acid (C12).

mances of the catalyst were not significantly modified [15], suggesting that the oxygen active sites were not eliminated during the reaction. Furthermore, the carbon materials (500 μm spheres) have been tested in a continuous reactor over a period of 1 month (60 ml h^{-1} of a 5 g l^{-1} aqueous solution of cyclohexanone over 500 mg catalyst). The oxygen groups of the carbon if consumed are regenerated under the reaction conditions. The mechanism of action of the functional groups in cyclic ketone oxidation is presently under investigation.

5. Conclusion

Three examples of liquid phase reactions involving the conversion of highly functionalized molecules were studied in batch reactors using activated carbons used either as support for noble metals or as catalysts per se. These studies illustrate the importance of the porous structure and of the functionalities on the carbon surface to control the rate and selectivity of liquid phase reaction. Two of these studies show the interest of using synthetic activated carbons that can be prepared reproductively and free from the metal impurities found in activated carbons obtained from natural sources.

It was shown that the particular texture of ACC allows an easy mass transfer from the micropores to the liquid phase improving the selectivity to sorbitol of Ru/ACC catalysts because of an easier desorption of sorbitol compared to conventional carbon-supported catalysts.

It was demonstrated that the presence of basic functional groups, particularly nitrogen-containing groups, present initially in the carbon or introduced by ammonia treatment at high temperature, increased the rate of oxidative decarboxylation reaction of *N*-phosphonomethyl iminodiacetic acid.

It was also shown that quinone/carbonyl groups generated by air activation of synthetic carbons are able to catalyse the liquid phase oxidation of cyclic ketones under air pressure in the absence of metal. The selectivity to the corresponding dicarboxylic acids is limited by multiple decarboxylation reactions giving dicarboxylic acid with smaller carbon chains; however, these co-products may also find applications.

Acknowledgements

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References

[1] L.R. Radovic, F. Rodriguez-Reinoso, in: P.A. Thrower (Ed.), Chemistry and Physics of Carbon, vol. 25, Dekker, New York, 1997, p. 243.
[2] E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl. Catal. A 173 (1998) 259.
[3] M.C. Macias Perez, C. Salinas Martinez de Lecea, A. Linares Solano, Appl. Catal. A 151 (1997) 461.
[4] Y. Schindler, Y. Matatov-Meytal, M. Scheintuch, Ind. Eng. Chem. Res. 40 (2001) 3301.
[5] E. Joannet, C. Horny, L. Kiwi-Minsker, A. Renken, Chem. Eng. Soc. 57 (2002) 3453.
[6] Y. Matatov-Meytal, Y. Shindler, M. Sheintuch, Appl. Catal. B 45 (2003) 127.
[7] R. Schlögl, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997.
[8] P. Gallezot, A. Giroir-Fendler, D. Richard, in: W.E. Pascoe (Ed.), Catalysis of Organic Reactions, vol. 47, Marcel Dekker, New York, 1992, p. 1.
[9] A. Perrard, P. Gallezot, Catalysis of Organic Reactions, in press.
[10] I. Mochida, Y. Korai, M. Shirahama, S. Kawano, T. Hada, Y. Seo, M. Yoshikawa, A. Yasutake, Carbon 38 (2000) 227.
[11] German Patent 2,519,388 Monsanto, 1974.
[12] C. Pinel, E. Landrivon, H. Lini, P. Gallezot, J. Catal. 182 (1999) 515.
[13] B. Stöhr, H.P. Boehm, R. Schlögl, Carbon 29 (1991) 707.
[14] R.W. Johnson, C.M. Pollock, R.R. Cantrell, fourth ed. in: J. Krodchwitz (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 8, John Wiley & Sons, New York, 1993.
[15] M. Besson, A. Blackburn, P. Gallezot, O. Kozynchenko, A. Pigamo, S. Tennison, Top. Catal. 13 (2000) 253.
[16] A. Pigamo, M. Besson, B. Blanc, P. Gallezot, A. Blackburn, O. Kozynchenko, S. Tennison, E. Creeze, F. Kapteijn, Carbon 40 (2002) 1267.
[17] Contract GRD1-2001-40331.
[18] S.R. Tennison, Appl. Catal. A 173 (1998) 289.
[19] MAST Carbon, www.mastcarbon.co.uk.