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Synthesis and characterization of high surface area aluminium and alumina microtubes from carbonaceous materials

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An original synthesis route to obtain high surface area metallic aluminium and alumina microtubes was developed. Samples were prepared by adsorption of an aluminium hydride solution in diethyl ether on fibrous carbonaceous substrates, followed by calcination at temperatures ranging from 250 °C to 1600 °C. The surface area (BET) of samples obtained after substrate elimination is about 45 $m^2\ g^{-1}$. The crystallinity of samples was determined by X-ray diffraction and their morphology was observed by scanning electron microscopy.

Introduction

Metallic oxides are widely used as catalysts because of their high surface area, which can reach several hundred meters squared per gram. Usually, metallic powders present very low surface areas, never exceeding a few meters squared per gram. This is one of the reasons why many catalysts are composed of metals supported on high surface area oxides.[1] The most common method of synthesis to obtain high surface area materials is the sol–gel technique.[2,3] This method is relatively easy to perform although it sometimes requires drastic conditions (pH, gel aging…). Recently, laser ablation was used to obtain high surface area nanometer particles. Iron oxide or iron nanoparticles were for example generated by laser ablation.[4] However, this technique is expensive and only allows the synthesis of very small amounts of materials. No chemical method to synthesize mesoporous metals has been reported in the literature yet.

Recently, Sieber *et al.* synthesized ceramic composites by adsorption of reactants containing silicon and aluminium on cardboard.[5] High stiffness and high temperature stability materials were obtained. Carbonaceous materials such as activated charcoal, activated carbon fibers or cellulose fibers present a high mesoporosity and high surface areas[6] and could also be used as substrates for adsorption.

In this paper, we describe the synthesis of high surface area aluminium microtubes by adsorption of an aluminium hydride solution on high surface area carbonaceous substrates, followed by thermolysis and oxidation of the substrate. Subsequent calcinations at high temperatures lead to the formation of high surface area alumina. Thermolysis of an hydride or an alkyl metal at low temperature is frequently used in the CVD technique to deposit metals.[7] Due to the high reactivity of hydrides, it is necessary to work under rigorous anhydrous conditions: our syntheses were thus performed in dried diethyl ether under an argon atmosphere.

Using specific synthesis conditions, we obtained high surface area aluminium and alumina microtubes, the texture and porosity of which are a fine replica of the initial substrate.

Experimental

Synthesis

All sample preparations were performed in a glove box under an anhydrous argon atmosphere. Three different types of carbonaceous substrate were used for the syntheses:

(1) a rough felt (Mitsubishi, $S \sim 8\ m^2\ g^{-1}$),
(2) an activated felt (FPA1000, Carbone Industrie, $S = 930\ m^2\ g^{-1}$),
(3) cellulose fibers (cotton wool, $S \sim 8\ m^2\ g^{-1}$).

Substrates were first dried in an oven at 200 °C before being immersed in a 0.3 mol L^{-1} aluminium hydride solution. The preparation of the solution was as follows: aluminium trichloride ($AlCl_3$, >98.5%, Acros Organics) and lithium aluminium hydride ($LiAlH_4$, >97%, Prolabo) were weighed in stoichiometric proportions, according to the Schlesinger reaction:[8]

$$AlCl_3 + 3\ LiAlH_4 \rightleftarrows 4\ AlH_3 + 3\ LiCl$$

Reactants were dissolved separately in dried diethyl ether ($C_4H_{10}O$, >99%, Acros Organics). The obtained solutions were carefully mixed and the solvent volume was adjusted to obtain a 0.3 mol L^{-1} AlH_3 solution. This concentration corresponds roughly to the experimental limit of solubility of aluminium hydride in diethyl ether. About 1 g of carbonaceous substrate (previously dried at 200 °C) was then immersed in 100 mL of the AlH_3 solution for five minutes. The evaporation of the impregnated diethyl ether was almost spontaneous when the sample was taken out of the glove box, due to the low boiling point of the solvent. The substrate was then heated at 250 °C for 25 minutes under an argon flow (450 mL min^{-1}), in order to thermolyse the hydride according to the following reaction:[9]

$$AlH_{3(s)} \rightleftarrows Al_{(s)} + 3/2\ H_{2(g)}$$

Subsequent calcination at 500–600 °C led to the substrate decomposition and/or oxidation. Aluminium samples were then oxidized at 1000–1600 °C to obtain α-alumina.

Physicochemical characterization

The X-ray diffraction (XRD) patterns were recorded on an INEL XRG 3000 diffractometer using $CuK_{\alpha1}$ radiation ($\lambda = 154$ pm). The morphology of the crystalline solids was characterized by scanning electron microscopy, using a Cambridge 440 SEM coupled to an EDS analyzer. Thermogravimetric analyses were performed in a Pyrox furnace coupled to a Mettler balance. Surface area (BET) of the samples was measured using a Pyrex apparatus conceived in our laboratory,

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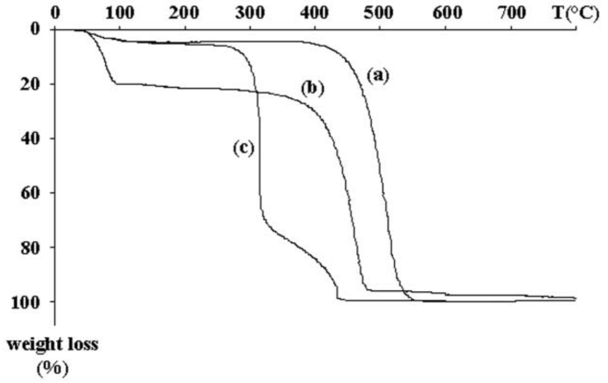

Fig. 1 Thermogravimetric curves of the rough felt (a), the activated felt (b) and the cellulose fibers (c) under air flow.

after degassing the samples at 250 °C for 2 hours. Samples were placed in a glass cell of known volume. Surfaces were calculated using the BET equation after successive nitrogen expansion–adsorption cycles.

Results and discussion

Thermogravimetric analyses of used substrates were performed under air (150 mL $\min^{-1}$) with a slow heating rate (0.7 °C $\min^{-1}$). All substrate surfaces adsorb significant amounts of water, *i.e.* 5 to 20 weight percent (Fig. 1). The elimination of this adsorbed water is necessary to avoid its reaction with the aluminium hydride during the substrate immersion according to the following reaction:

$$AlH_3 + 3\ H_2O \rightleftarrows Al(OH)_3 + 3\ H_2$$

Aluminium hydroxide would be formed in the presence of water; its calcination would first lead to boehmite (AlO(OH)) and α-alumina at higher temperatures. Prior to their immersion in the hydride solution, substrates were thus dried at 200 °C for 12 hours: at this temperature, the substrate oxidation has not started. Indeed, the carbon oxidation begins at about 410 °C for the activated felt and 460 °C for the rough felt (Fig. 1a and b). The oxidation of cellulose fibers begins at a lower temperature and occurs in two steps (Fig. 1c):

- a rapid combustion starting at 310 °C attributed to the heteroatoms (O, H) loss:

$$(C_6H_{10}O_5)_n \rightleftarrows 6n\ C + 5n\ H_2O$$

- a slow oxidation of the residual carbon between about 320 °C and 440 °C.

According to these data, an oxidation temperature of 500 °C was chosen. Indeed, at this temperature, the carbon oxidation kinetics are rapid, aluminium does not flow (mp = 667 °C) and the formation of aluminium carbide (Al_4C_3) is avoided (at 500 °C under oxygen, the reduction kinetics of aluminium by carbon is very slow. The formation of Al_4C_3 only starts at 800 °C to a measurable extent in the presence of oxygen).[10]

Table 1 Evolution of the surface area of activated felt–aluminium composites during substrate oxidation at 500 °C

Sample number:	1	2	3	4	5	6
Calcination temperature, T_c/°C	500	500	500	500	500	600
Dwell time at T_c/min	0	15	30	45	60	1200
Surface area/$m^2\ g^{-1}$	610	575	444	183	44	42

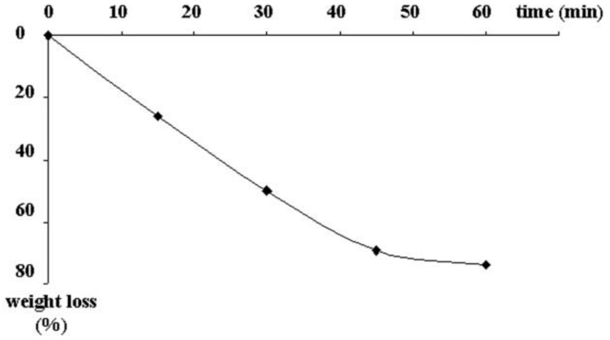

Fig. 2 Oxidation of the activated felt during calcination at 500 °C under air.

The substrate oxidation kinetics were determined for an activated felt–aluminium composite. Dried samples were oxidized at 500 °C under an air flow (150 mL $\min^{-1}$) for increasing times and the surface area of residual materials was measured (Table 1). Fig. 2 presents the weight loss during calcination which corresponds to the carbon oxidation in carbon dioxide. After one hour at 500 °C the substrate is fully oxidized and metallic aluminium microtubes covered by a superficial alumina layer are obtained. During the oxidation process, the surface area of samples decreases from 610 down to 44 $m^2\ g^{-1}$ (Table 1). After 20 hours of heating at 600 °C, the surface area has not changed (sample 6, Table 1), which demonstrates the thermal stability of the aluminium fibers with time.

Under similar conditions (600 °C, 20 hours), the surface area of samples prepared with cellulose fibers or the rough felt as substrates is equal to 90 $m^2\ g^{-1}$. This result seems surprising as the surface area of these substrates is very low (8 $m^2\ g^{-1}$), whereas the activated felt has a surface area of 930 $m^2\ g^{-1}$. In fact, in the case of sorption on a cellulose substrate, aluminium hydride acts as an activating agent developing the specific area of the fibers, as mentioned by Bansal *et al.*[11] Moreover, after a heating treatment at 600 °C for several hours, the rough felt is also activated. Actually, the activation of both substrates favors interactions between the aluminium hydride and the fibers, leading to a surface area increase.

The porous structure of carbon fibers strongly depends on the activation process. However, the pores can be divided into four size groups as shown in Table 2. A theoretical macroporous solid can be modeled as a compact stack of pores of same sizes assimilated to half spheres. In such conditions, the specific surface area can be calculated by the following formula:

$$A = \frac{9 \times 10^3 \varphi}{\rho \varnothing}$$

with A being the surface area ($m^2\ g^{-1}$); ρ the density of the material (g cm^{-3}, $\rho_{Al} = 2.7$ g cm^{-3}); $\varnothing$ the pore diameter (nm) and φ the occupation rate of space by the pores ($\varphi \leqslant 0.74$, which is the highest value obtained for a face centered cubic lattice). The theoretical surface area of each type of pore can thus be calculated (Table 2).

The mesopore adsorbents are characterized by a capillary

Table 2 Different pore types and estimated surface areas for metallic aluminium

Pore type	Macropore	Mesopore	Supermicropore	Micropore
Pore diameter, $\varnothing$/ nm	$\varnothing > 100$–200	$1.6 < \varnothing < 100$–200	$0.6 < \varnothing < 1.6$	$\varnothing < 0.6$
Surface area, A/$m^2\ g^{-1}$	$A < 12$–25	12–25 $< A < 1541$	$1541 < A < 4111$	$A > 4111$

condensation of organic compounds in their pores, while it is the polymolecular sorption of organic compounds that takes place in macroporous adsorbents.[7] Thus, a compound such as $AlH_3 \cdot Et_2O$ is adsorbed from the organic solution into the meso/macroporosity of carbonaceous materials. This explains the obtained surface area for sample 5, *i.e.* 44 $m^2\ g^{-1}$ (Table 1).

Alumina preparation

The aluminium oxidation begins at about 820 °C under air as shown by Fig. 3. At 1000 °C, the oxidation is not yet finished. Traces of gray metallic aluminium are observed on samples calcined at this temperature. The surface area of the obtained material is 36 $m^2\ g^{-1}$. Calcination at 1600 °C for 6 hours leads to the complete oxidation of aluminium and a surface area of 38 $m^2\ g^{-1}$ for the final product. Surface areas of obtained aluminas are very similar to those obtained for the metallic aluminium, *i.e.* 44 $m^2\ g^{-1}$, which suggests that the formed microstructures do not collapse and can be explained by the formation of a superficial alumina layer on the liquid aluminium surface. This rigid layer prevents the microstructures' collapse.

X-Ray diffraction and morphology

X-Ray diffraction patterns of samples obtained with the activated felt FPA 1000 and calcined at several temperatures are presented in Fig. 4. No crystallization occurs after the hydride thermolysis at 250 °C for 1 hour. The diffraction pattern of sample 1 is characteristic of amorphous material (Fig. 4a) and similar to the pattern of FPA1000 (not shown). The structure disorganization of the activated felt can be explained by the fact that this substrate was not graphitized during its preparation process. After calcination at 600 °C for 20 hours, well crystallized aluminium is obtained (Fig. 4b). Traces of γ-alumina are observed on the pattern, probably due to the superficial oxidation of aluminium during the substrate elimination. No crystallization of aluminium carbide was observed, the absence of residual carbon was confirmed by EDS analyses. A calcination at 850 °C for 10 hours led to the formation of well crystallized γ-alumina (Fig. 4c). However, after calcination at 1000 °C for the same time, the obtained material is less crystallized, probably due to a disorganization prior to its transformation from γ to α-alumina (Fig. 4d). After calcination at 1600 °C for 10 hours, well crystallized α-alumina is finally obtained (Fig. 4e).

Sample morphologies are presented in Fig. 5. FPA1000 felt is composed of 3–8 μm large fibers (Fig. 5a). After thermolysis of the hydride aluminium at 250 °C, the surfaces of the fibers are covered by an aluminium layer surmounted by micrometer metallic aluminium particles (Fig. 5b). The substrate calcination at 600 °C leads to the formation of hollowed and almost transparent fibers. The texture of these fibers is very similar to the texture of the initial substrate (Fig. 5c). However, the internal microporosity of the carbon fibers is not replicated. Indeed, the surface area of the substrate is equal to 930 $m^2\ g^{-1}$, whereas the surface area of the aluminium fibers is only 44 $m^2\ g^{-1}$. The surface of alumina fibers (Fig. 5d) is very irregular. During the calcination process to 1600 °C, no significant changes in fiber sizes are observed, which confirms the validity of this synthesis method to obtain metal and oxide replicas of a carbonaceous substrate.

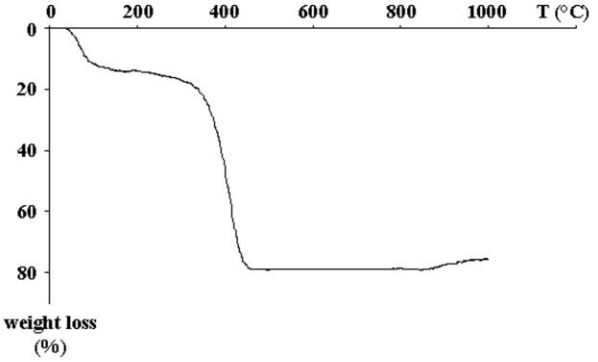

Fig. 3 Weight loss during the aluminium–activated felt composite calcination.

Conclusion

A new synthesis method was developed to obtain high surface area metallic aluminium. Materials were obtained by adsorption of an aluminium hydride solution on different fibrous substrates, followed by calcination at 500–600 °C, leading to the substrate elimination. Metallic aluminium samples with a 44 $m^2\ g^{-1}$ surface area were obtained using low surface area substrates. Calcination at higher temperatures led to the formation of alumina. The morphology of the synthesized materials is very similar to the morphology of the substrate: after its calcination, microtubes of aluminium or alumina, the sizes of which are very similar to the initial fibers, are obtained. These materials probably present interesting mechanical properties as their structure does not collapse during the heating treatment.

This novel synthesis route leads to the formation of materials with a texture which is a fine replica of the texture of the used substrate. The generalization of this method to other metallic hydrides could allow the synthesis of a large variety of high

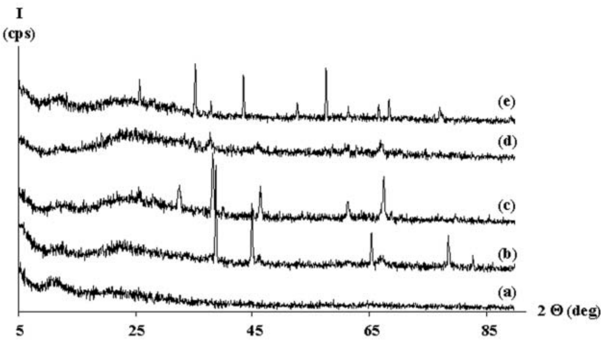

Fig. 4 X-Ray diffraction patterns of samples prepared with the activated felt and calcined at 250 °C (a), 600 °C (b), 850 °C (c), 1000 °C (d) and 1600 °C (e).

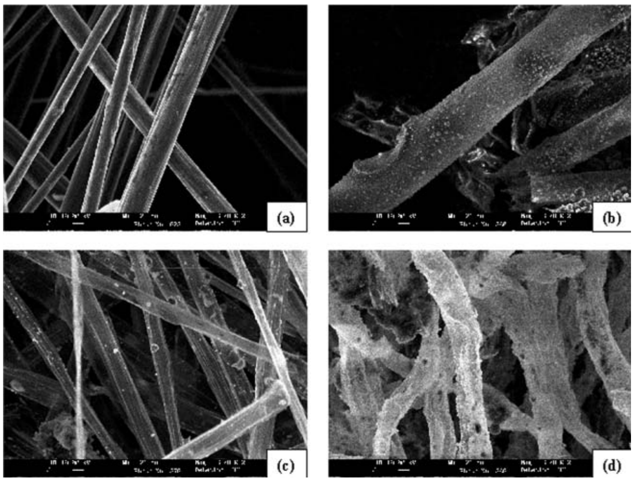

Fig. 5 Scanning electron micrographs (× 5000) of the activated felt (a) and samples calcined at 250 °C (b), 600 °C (c) and 1600 °C (d).

surface area metal and oxide microtubes. Moreover, the surface functionalization of the obtained microtubes could give them specific catalytic applications.

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