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Intensive pyrolysis of unsaturated organic precursors over acidified oxide surfaces

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Abstract

Carbon-like composite materials fabricated by non-catalytic heterogeneous pyrolysis (NCHP) of organic precursors over porous oxide supports are used in a variety of fields. The intensification of NCHP procedures for fabrication on a commercial scale is technically problematic. Direct intensification of operation parameters cannot be considered as the most effective method. For instance, an increase in support bed temperature often takes the pyrolysis process into the homogeneous reaction field, and greater gas space velocities and initial organic precursor concentrations lead to a rise in operating costs because of considerable losses of raw materials and increased power requirements.

This paper describes an attempt to intensify non-catalytic heterogeneous pyrolysis procedures by optimizing the acid–base properties of the reaction agents (supports, precursors).

A procedure of controlled acidification of the alumina support followed by thermal degradation of surface base salt was applied in order to cover the support surfaces with additional Lewis acid sites functioning as efficient host centres for precursor molecules. Unsaturated organic compounds, powerful Lewis bases, were used as the precursor agents.

A probable elementary mechanism for non-catalytic heterogeneous pyrolysis of unsaturated organic precursors over an oxide surface reinforced by Lewis acids is proposed. The main characteristics of the composite hydrophobic materials produced by the NCHP technique using pre-acidified alumina samples—their chemical compositions, surface affinities to water, thermal stabilities in air, dynamic VOC adsorption and desorption capacities are presented and discussed. The elaborated composites are non-flammable in air until 600 °C, whereas the thermal stability limit of activated carbons is situated in the 250–300 °C range. As compared to activated carbons, these materials manifest really stable surface activities in VOC adsorption–desorption cycles.

Keywords: Alumina; Non-catalytic heterogeneous pyrolysis; Acid–base surface properties; Adsorption; Desorption; Thermal stability

1. Introduction

Products of the non-catalytic heterogeneous pyrolysis (NCHP) of organic precursors over the surfaces of porous oxide supports are used as composite adsorbents [1], tyre fillers [2], catalyst carriers [3] and in some another technical fields. The particular features of the application of this technique to the modification of hydrophobic mineral supports are widely discussed in the literature [4–11].

Intensifying the NCHP procedures is a major technical problem. In order to increase the efficiency of the process, it seems logical to explore, first of all, the avenue of intensifying the operation parameters. Among the main operation parameters of NCHP, the following can be identified as important: the temperature of the mineral support bed, the gas flow rate and the initial concentration of the organic precursor.

However, this type of modification is rather limited in its potential efficiency. Concerning the thermal factor, increasing the bed temperature often takes the pyrolysis process into the homogeneous reaction field [12]. Due to the kinetics of the procedure, exceeding certain limits with regard to the

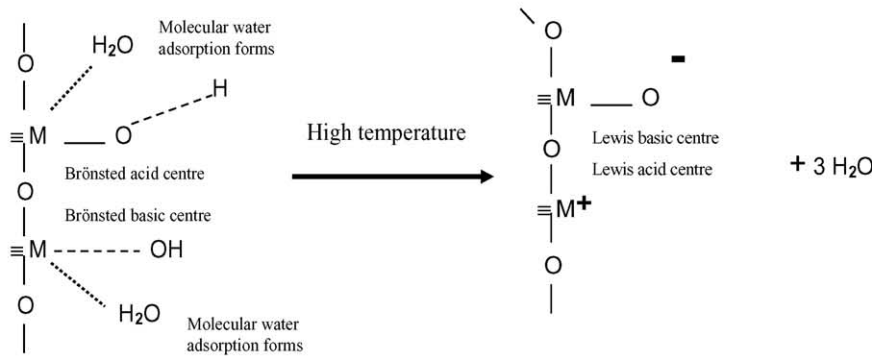
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gas flow rate and initial concentration of organic precursor leads to a less efficient precursor utilization and losses of inert gas carrier, thus causing a general increase in operating costs.

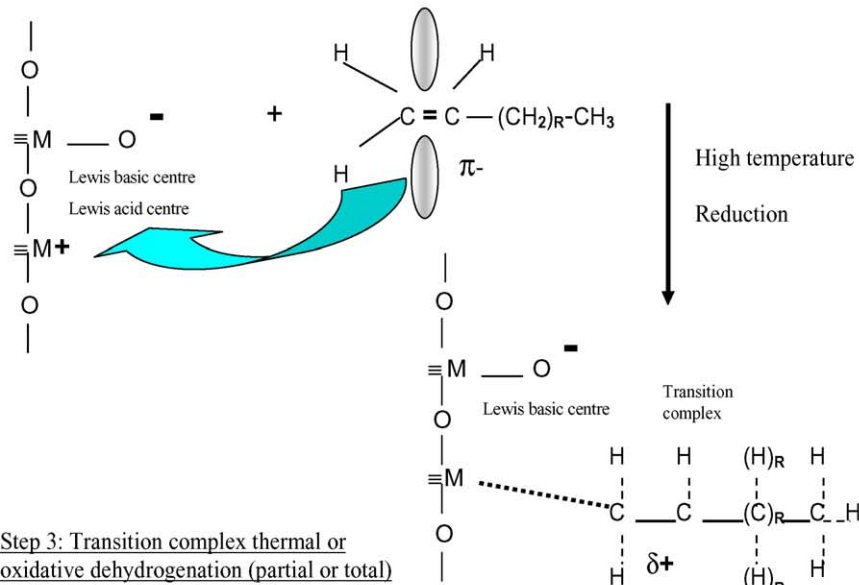
An alternative technical solution for intensifying the NCHP procedure probably consists in optimizing the chemical properties of the reaction medium. The evolution

of an oxide matrix during any common NCHP procedure can be presented as three elementary steps, shown in Fig. 1. After the restoration of its initial state by means of dehydration reactions, the oxide surface acquires electrically charged sites named active Lewis centres. Positively charged sites, Lewis acid (LA) sites, are able to act as reception centres for organic molecules, which generally manifest

Step 1: Support conditioning (conversion of the oxide surface in its initial state)



Step 2: Lewis acid-base interaction of the oxide surface with an organic precursor



Step 3: Transition complex thermal or oxidative dehydrogenation (partial or total)

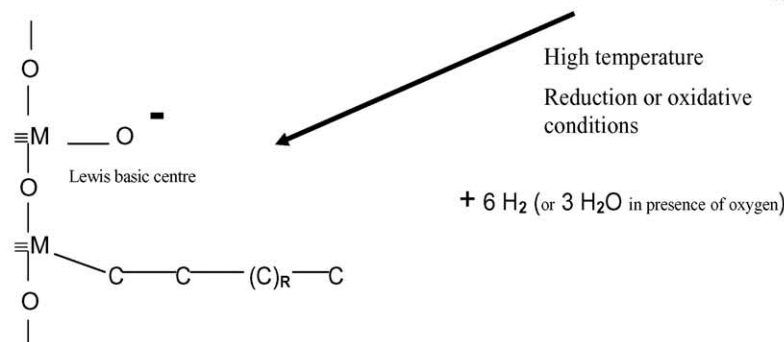


Fig. 1. Probable elementary mechanism of NCHP procedure.

Lewis base (LB) properties because of their well-known reduction capacities. Lewis-type acid–base interactions within a dynamic “organic precursor oxide matrix” system lead to the formation of transition complexes with weakened carbon–hydrogen bonds. This bond weakening is caused by the redistribution of electron densities between the precursor organic molecules and the Lewis acid sites involved. Further, thermal destruction and/or partial oxidation of the transition complexes transforms them into carbonized structures chemically bonded to the support surface. As a rule, because of incomplete dehydrogenation of transition complexes, the chemical compositions of the carbonized surface structures correspond to the general formula C_nH_m , where $n \gg m$. NCHP products with maximal n/m ratios for their carbonized surface layers are considered to be composite materials of the best quality (high thermal stability, considerable hydrophobic surface capacities, etc.).

So, reinforcement of the Lewis-type acid–base interactions within the reaction medium seems to be a promising alternative solution for intensifying the NCHP procedure. This measure is expected to be efficient both for promoting transition complex formation and for further degrading these intermediate structures to carbonized surface products owing to stronger interactions between organic precursor molecules and LA surface centres followed by complementary weakening of carbon–hydrogen bonds.

Unsaturated organic precursors (alkenes, alkynes) can be successfully used as extremely powerful Lewis bases. With regard to oxide matrices, in particular activated alumina supports, their Lewis acidity may be considerably reinforced by means of controlled treatment in inorganic acid solutions followed by thermolysis of the salt layers formed on the surface. This procedure apparently results in a number of new Lewis acid sites over the acidified oxide surface ($AlAn_x, Al(OH)_yAn_z \rightarrow Al^{n+}$).

2. Experimental

2.1. Modification of the surface properties of the activated alumina

The Lewis acidity of activated aluminas was increased by impregnation in a hydrochloric acid solution followed by thermolysis of the salt layers formed on the surface [11]. Activated alumina (50 g) was placed in HCl solution (0.1 mol L^{-1}) for 1.5 h. After this treatment, the new support was washed four times and then dried in ambient atmosphere for 24 h.

2.2. Conditioning of original oxide supports

The mineral support (15 g) was placed in a 25-mm diameter tubular stainless steel reactor (experimental device shown in Fig. 2). It was heated in a furnace over a temperature range between 500 and 900 °C, with an air flow (1.2 L min^{-1}). The gas space velocity was equal to 9300 h^{-1} [11]. The evolution of the humidity content was monitored using a Dostmann P600 electronic probe.

The original adsorbents were activated aluminas. Their pore structure parameters, as well as the surface affinities to water vapour are given in Table 1. The pore size distributions for initial supports are shown in Fig. 2.

2.3. Preparation of hydrophobic adsorbents

Synthesis of carbon–mineral adsorbents was carried out using the chemical vapour deposition (CVD) method according to the NCHP procedure. Firstly, mineral supports (10 g) were heated over the temperature range 500–900 °C, in air flow (1.2 L min^{-1}) for 3 h (internal diameter of reactor 25 mm). Secondly, the support was exposed at the same temperature to a 70 mL min^{-1} flow of inert gas charged with

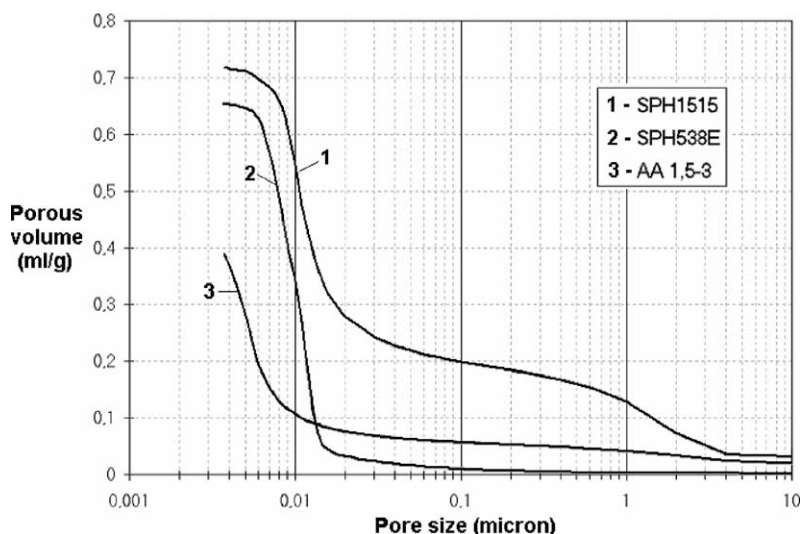


Fig. 2. Pore size distribution in initial activated aluminas.

Table 1
Characteristics of initial activated aluminas as potential supports for carbon deposition

Aluminas	Specific surface, S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Total pore volume, V_{P} (mL g^{-1})	Static water adsorption capacity, $E_{0.6}^{20^\circ\text{C}}$ (mass%)
AA 1.5-3	303	0.393	19.4
SPH 1515	169	0.718	8.4
SPH 538 E	250	0.684	13.3

an olefin-type organic precursor. The precursor concentration was 190 g m^{-3} . The device shown in Fig. 3 was used for this operation.

2.4. Material characterization

2.4.1. Acid–base properties

The acid–base properties of the alumina supports, both initial and after treatment with acid solutions, were characterized according to the analytical method proposed by Tanabe [13] and illustrated in Fig. 4. This method enables the transformation of Lewis active sites to Broensted active sites over different mineral surfaces to be checked by means of the heterolytic water dissociation reactions:

- (I) Lewis base to Broensted acid transformation: $\text{M-O}^- + \text{H}_2\text{O} \rightleftharpoons \text{M-OH} + \text{OH}^-$;
 (II) Lewis acid to Broensted base transformation: $\text{M}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{M-OH} + \text{H}_3\text{O}^+$.

The method consists in putting a powdered oxide sample in contact with distilled water. The heterolytic dissociation of water molecules caused by their interaction with surface Lewis active sites, according to the reactions mentioned above, results in the appearance of additional hydroxyl and hydroxonium ions in the reaction medium. Basification of the medium thus corresponds to a predominance of Lewis base sites over the solid surface: the hydroxyl ion concentration is greater than that of hydroxonium ions. Conversely, acidification of the medium indicates a predominance of Lewis acid sites.

Curves I and II in Fig. 4 correspond to the reactions mentioned above.

2.4.2. Pore properties

Pore volume measurements were based on mercury pore distribution and carried out using a Micromeritics Autop-

ores III. The specific surface was determined using a Micromeritics ASAP 2400.

2.4.3. Hydrophobic properties

The static water adsorption capacities ($E_{0.6}^{20^\circ\text{C}}$) over the surfaces of the initial supports and hydrophobic composite adsorbents were determined. The support was placed in a 20°C atmosphere, at 60% of relative humidity, and the mass increase determined until a stable value was reached.

2.4.4. Amount of carbon-like product quantities in hydrophobic composite materials

The quantities of carbon-like products deposited over the surfaces of the initial support were determined using a Horiba Emia 820 instrument.

2.4.5. Composite material behaviour under thermal treatment

TG/DTA analysis were carried out using a SETARAM 92 ATD model over a temperature range of $25\text{--}800^\circ\text{C}$ in air atmosphere. The heating rate was fixed at 5°C min^{-1} and the sample mass was $35 \pm 1 \text{ mg}$. The content of carbon for each composite sample was $9 \pm 1\%$, in order to avoid any significant influence of the quantitative composition of the material on the measured values. For the activated carbon sample, the carbon matter content was approximately 98%.

2.4.6. VOC adsorption capacity and material regenerability.

The adsorption capacities over the surfaces of an activated carbon (reference product) and hydrophobic composite materials were evaluated by means of dynamic adsorption tests with acetone as a test compound in dry air. The space velocity was 2000 h^{-1} (measured under standard conditions) and the sample mass was fixed at 10.0 g . The initial acetone vapour concentration was $650 \pm 50 \text{ mg m}^{-3}$. Analyses of the inlet and outlet gas flows were carried out using a COSMA Graphic 730 flame ionisation detector (FID). Desorption tests were carried out with an air flow of 500 mL min^{-1} , while heating the adsorbent layer from ambient temperature to 200°C .

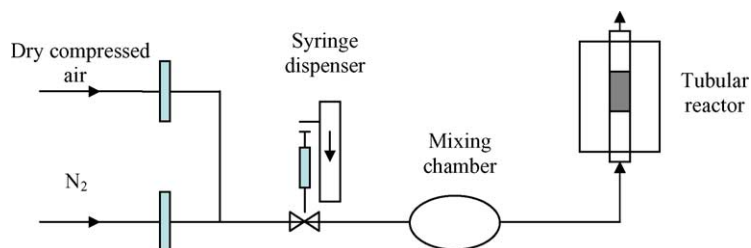


Fig. 3. Experimental device for support conditioning and composite material synthesis.

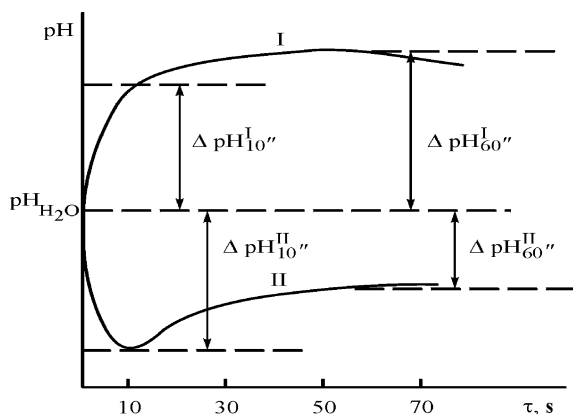


Fig. 4. Characterization principle of sample acid–base properties by pH-metric measurements (according to method described by Tanabe [14]).

3. Results and discussion

3.1. Modification of the acid–base properties of the initial alumina supports

According to the reaction scheme for the elementary mechanism of the NHCP procedure (Fig. 1), acid–base interactions on an initial carrier surface can be intensified in the presence of powerful cationic acceptor centres (LA-centres). An original method was developed to increase the number of such active sites on the surfaces of the alumina samples. The alumina samples were processed in mineral acid solutions to cover their surfaces in a thermally unstable salt layer, which could be easily destroyed by heating, without any significant changes to the initial macroscopic structure of the bulk material. A generalized scheme of this procedure is shown in Table 2.

Among the aluminas tested as potential mineral matrices for hydrophobic composite materials (Table 1), carrier SPH 538E has the lowest Lewis basicity (Fig. 5), so can be considered a priori as the most promising material for altering its surface acid–base properties. This property, together with the well-developed porous structure of this activated alumina (formed especially of meso-pores, which are known to be more suitable than micro-pores for pyrolysis procedures), enabled SPH 538E to be chosen as a model substrate for producing a hydrophobic composite material using pre-acidified oxide supports.

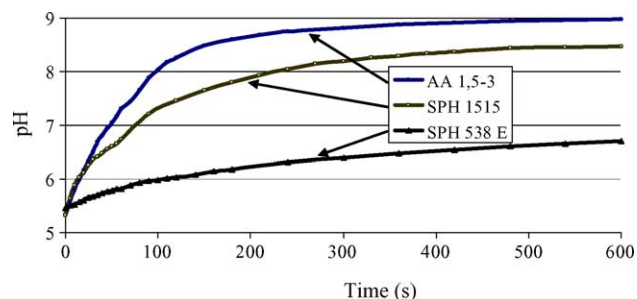


Fig. 5. Acid–base properties of initial support.

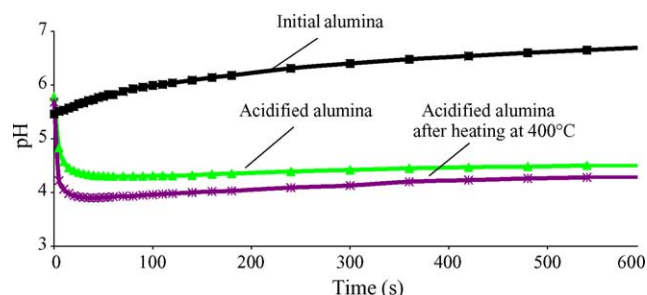


Fig. 6. Comparison of acid–base properties of initial and acidified alumina SPH 538E.

The results, presented in Fig. 6, show that the acid-thermal processing of an activated alumina leads to a complete alteration of its initial acid–base properties by supplying the surface with additional powerful active acceptor centres. Varying the technological parameters of the acid processing (treatment time, mineral acid concentration in solution), it is possible to manage the acid–base surface properties over a wide range of their eventual evolution (Fig. 7).

The acid-thermal processing results, at the same time, in profound changes to the porous structure of the alumina samples, producing a considerable development of their specific surface and increasing their total pore volume. New LA-centres placed over an acidified surface also increase its hydrophilic capacities by means of a strong donor–acceptor linkage of water molecules: $\text{Al}^+ + \text{H-OH} \rightleftharpoons \text{Al-OH} + \text{H}^+$. Data concerning the modification of the structural characteristics and water adsorption capacities of the SPH 538E alumina after acid-thermal processing of the sample for

Table 2
Reactions on activated aluminas during their acidification process

Step	Operation	Reactions	Product
1	–	–	Activated alumina
2	Surface neutralization with mineral acid HAn	$\text{Al}_2\text{O}_3 + 6\text{HAn} \rightleftharpoons 2\text{AlAn}_3 + 3\text{H}_2\text{O}$ $\text{AlAn}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)An}_2 + \text{HAn}$ $\text{Al(OH)An}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2\text{An} + \text{HAn}$	$\text{Al}[(\text{OH})_x\text{An}_y]_3$ with $(x + y) = 1$
3	Extraction, filtration, drying, heating	Thermal destruction of hydroxo-salts $\text{Al}[(\text{OH})_x\text{An}_y]_3$	Al^{n+}

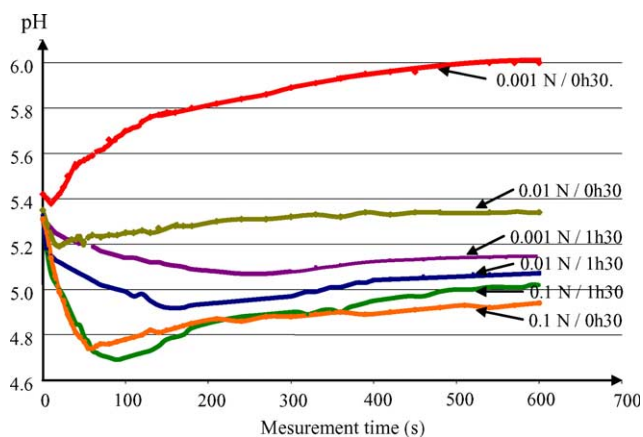


Fig. 7. Influence of impregnation time and acid concentration upon acid–base properties of activated alumina.

1.5 h in 0.1N hydrochloric acid solution are shown in Table 3 (results before pyrolysis process).

3.2. Hydrophobic behaviour of composite material under thermal treatment

The aim of the preliminary acid-thermal support treatment is to intensify the deposition of a carbon-like products over the carrier surface. The data presented in Table 3 confirm that acidified matrices are more active than unconditioned ones (sample 1—initial activated alumina after pyrolysis with an olefin-type precursor, sample 2—activated alumina after acid treatment followed by thermolysis of the surface salt products and pyrolysis with the olefin-type precursor).

Assuming that all the new LA-centres have the same electronic structure (Al^{n+}) and therefore manifest similar acceptor abilities, it is possible to estimate their relative concentration increase for the treated surfaces. For instance, for the SPH 538E alumina sample processed for 1.5 h in 0.1N HCl solution, this increase is around 3.7 times as

Table 3
Characteristics of two alumina samples before and after the hydrophobisation procedure

Material characteristics ^{a,b}	Samples of activated aluminas	
	Sample 1	Sample 2
Type of predominant Lewis centres ^a	LB	LA
Specific surface ^a ($m^2 g^{-1}$)	250	282
Total pore volume ^a ($cm^3 g^{-1}$)	0.684	0.873
Water vapour adsorption capacity (relative humidity: 60%; temperature: 15 °C; static conditions) ^a	13.3	18.6
Level of carbon-like products on the surface ^b (mass%)	7.4	27.5

^a Before pyrolysis process.

^b After pyrolysis process.

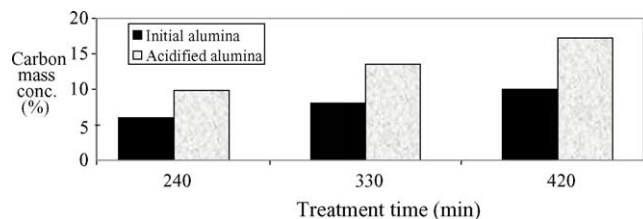


Fig. 8. Evolution of carbon mass concentration over time during NCHP procedure.

compared with the initial alumina sample (Table 3, sample 1). Globally, the activity of acidified alumina samples in their interactions with unsaturated hydrocarbons is about 30–40% greater than for the non-treated templates (Fig. 8). The hydrophilic capacities of the composite materials created over acidified supports are also lower (Fig. 9).

The exceptional thermal stability of the carbon-like products formed over the acidified alumina surface after acid-thermal conditioning should be particularly mentioned. Differential thermo-gravimetric analysis (DTA) data (Fig. 10) show the great difference in behaviour between high-quality activated carbon (trade mark G90, French fabrication, curve 1) and hydrophobic composite materials (created by the NCHP procedure using different oxide supports, curves 2–4).

For the composite species tested during the DTA investigation their thermal oxidation resistances are in the following order:

Activated carbon < 13X composite < initial SPH 538E composite << acidified SPH 538E composite.

The thermal oxidation resistance values are also in good qualitative correlation with the Lewis acidity of the mineral support surfaces.

Indeed, the surface of the well crystallized synthetic molecular sieve 13X is practically free from powerful Lewis active centres, both acid and basic type. An evolution of the pH level in a dynamic “synthetic molecular sieve 13X/water” system appears to be extremely slow. This fact confirms the incapacity of such a material to favour heterolytic water dissociation reactions, due to a low number of aprotic active sites over its surface. In this case, the carbonized surface structures produced by non-catalytic

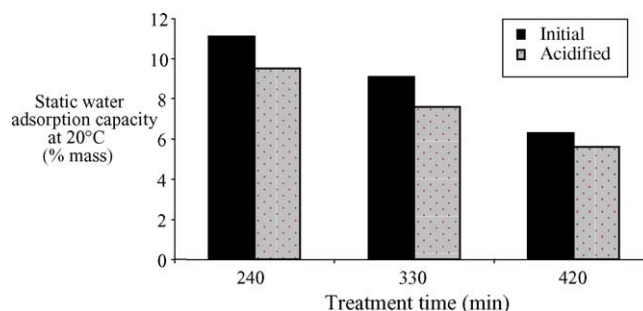


Fig. 9. Evolution of water adsorption capacity.

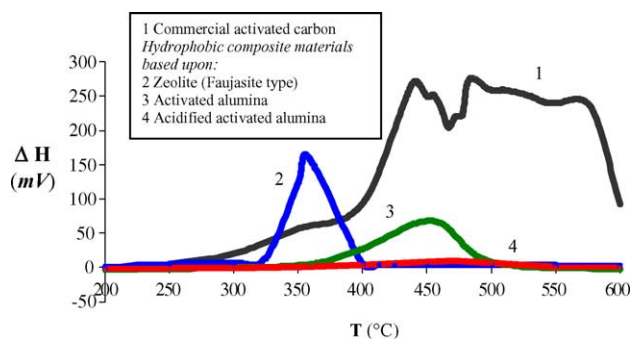


Fig. 10. Comparison of thermal behaviour for different adsorbents.

heterogeneous pyrolysis of hydrocarbon molecules must be relatively rich in hydrogen (see Section 1). Their reduction capacities expressed in terms of resistance to oxidation must therefore be rather high (Fig. 10, curve 2).

Conversely, the structural disorder of amorphous surfaces leads to strong aprotonic site formation. Although the acid–base properties of the initial SHP 538E sample show weak Lewis basicity, it would be reasonable to interpret this fact in terms of the relative dominance of Lewis base sites over acid ones. The hydrophobic composite produced over the surface of the initial SHP 538E is more difficult to oxidize in air (Fig. 10, curve 3). The chemical composition of its surface layer is probably richer in carbon than in the case of hydrophobic composite materials produced over crystalline surfaces.

The better oxidation resistance of the composite created over the acidified alumina surface (Fig. 10, curve 4: no inflammation was observed until 600 °C) apparently corresponds to the chemical composition of its surface layer, which is highly carbon-enriched. The strong acceptor capacities of an acidified alumina surface lead to efficient degradation of transition complexes into carbon-like products (see Section 1).

The extremely high oxidation resistance of this type of hydrophobic composite is a very important element in any successful application of these materials to cyclic adsorption processes carried out according to the technological scheme of in situ “adsorption–thermal regeneration”.

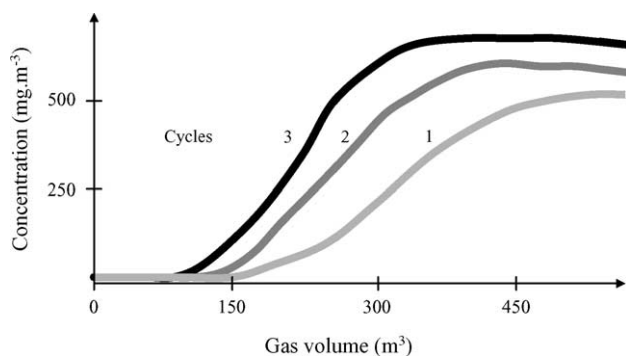


Fig. 11. Evolution of adsorption capacity of activated carbon over three adsorption–regeneration cycles.

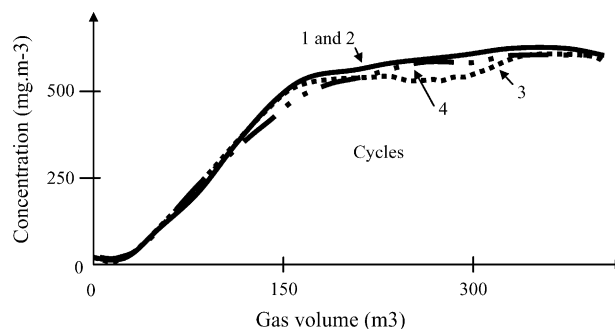


Fig. 12. Adsorption efficiency of hydrophobic composite adsorbent supported on acidified alumina over four adsorption–regeneration cycles.

3.3. Hydrophobic composite material activities in adsorption–desorption cycles

Figs. 11 and 12, together with Table 4, give comparative adsorption–desorption characteristics for a high-quality activated carbon G-90 (from Carbio-12 Ltd., France) and for hydrophobic composite materials over acidified SHP-538E alumina.

Concerning VOC adsorption, the initial capacity of the activated carbon exceeds that of the hydrophobic composite materials (test compound –acetone). At the same time, these materials demonstrate an ability to preserve their adsorption capacities in cyclic use when the adsorption step is followed by “soft” thermal regeneration in situ (Fig. 12), whereas the charcoal is progressively deactivated under the same operational conditions (Fig. 11).

In spite of considerable differences in their specific surface values and porous structures, the adsorption capacities of the two types of adsorbent defined under optimal aerodynamic conditions are rather similar (Table 4). Aerodynamic adsorption conditions for adsorption procedures are considered to be optimal, when the adsorption bed length h is greater than its minimal value h_0 , allowing the adsorption front to be formed inside the bed, without any breakthrough of gas species to be adsorbed ($h > h_0$).

The ratio between the specific surfaces of the activated carbon and hydrophobic composite sample (Table 4) is 5.8 in favour of the first. Moreover, microporous materials, activated carbon included, are considered to be the most suitable adsorbents for VOC treatment procedures [14,15].

Table 4
Comparison of acetone adsorption capacity on activated carbon and hydrophobic alumina

	Activated carbon (coconut charcoal)	Hydrophobic acidified alumina
S_{BET} ($m^2 g^{-1}$)	1400	240
Specific surface ratio	5.8	1
Adsorption capacity for 50% breakthrough ($mg g^{-1}$)	110	28
Ratio of adsorption capacities for 50% breakthrough	3.9	1

However, the adsorption capacity of the mesoporous hydrophobic composite materials supported on acidified aluminas is not less than 25% that of activated carbon. This last fact shows that the adsorption ability of an elementary surface unit of the hydrophobic composites is greater than that of activated carbon.

4. Conclusion

Non-catalytic heterogeneous pyrolysis of unsaturated organic precursors over oxide supports can be considerably intensified by Lewis acidification of the support surfaces.

The Lewis acidification procedure for an activated alumina used as a model oxide support is simple, reliable and well controlled. A mineral support, with a mesoporous structure was chosen after acid–base characterization. After the acidification procedure, a sample of the hydrophobic composite, which contains up to 27% carbon as deposited mass, was produced.

Preliminary Lewis acidification of mineral supports enables the production of hydrophobic composite materials with high adsorption and thermal regeneration capacities and outstanding thermal resistance (no inflammation in air until at least 600 °C).

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References

- [1] USA Patent 52,70,278 (1993).
- [2] Japan Patent 10,30,5709 (1998).
- [3] L.R. Radovic, F. Rodriguez-Reinoso, in: P.A. Thrower (Ed.), *Chemistry and Physics of Carbon*, vol. 25, 1997, pp. 243–358.
- [4] P.M. Barata-Rodrigues, T.J. Mays, G.D. Moggridge, *Carbon* 41 (2003) 2231–2246.
- [5] M.S. Mel'gunov, V.B. Fenelonov, R. Leboda, B. Charmas, *Carbon* 39 (2001) 357–367.
- [6] A.M. Puziy, B. Charmas, O.I. Poddubnaya, M.S. Mel'gunov, R. Leboda, B.J. Trznadel, *Colloid Surf. A* 21 (2003) 45–57.
- [7] V.M. Gun'ko, R. Leboda, V.A. Pokrovskiy, B. Charmas, V.V. Turov, J. Ryzkowski, *J. Anal. Appl. Pyrolysis* 60 (2001) 233–247.
- [8] R. Leboda, E. Mendyk, A. Gierak, V.A. Tertykh, *Colloid Surf. A* 105 (1995) 181–189.
- [9] R. Leboda, E. Mendyk, A. Gierak, V.A. Tertykh, *Colloid Surf. A* 105 (1995) 191–197.
- [10] J. Skubiszewska-Zieba, B. Charmas, R. Leboda, P. Staszczuk, P. Kowalczyk, P. Oleszczuk, *Mater. Chem. Phys.* 78 (2002) 486–494.
- [11] L. Majoli, A. Evstratov, J.M. Guillot, J.F. Chapat, J.L. Le Loarer, *Zéolithes et aluminés Hydrophobés: Adsorbants Alternatifs de Composés Volatils*, 20ème Réunion du Groupe Français des Zéolithes, 17–19 March 2004, Dijon, France, Proceedings, Poster Summaries, p. A1.
- [12] N.A. Bogomolov, S.K. Gordeev, E.P. Smirnov, *Reports of USSR Academy of Sciences*, 4 (1985) pp. 876–880 (in Russian).
- [13] K. Tanabe, *Solid Acids and Bases*, Academic Press, New York, 1970, 175 p.
- [14] P. Le Cloirec, *Les Composés Organiques Volatils Dans L'Environnement*, Tec&Doc Lavoisier, Paris, 1998, ISBN: 2-7430-0232-8.
- [15] S.W. Blocki, *Environ. Prog.* 12 (1993) 226–230.