MULTIFUNCTIONAL SKELETAL CATALYTIC SUPPORT
1. ALUMINA-BASED COMPOSITION FOR POROUS ADSORBING LAYER

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Ceramic and metallic honeycombs present a great importance as catalytic substrates in processes that aim at the ecosystem protection. For an increased functionality of the substrate, the honeycomb surface has to be coated with a highly absorbing layer. The paper presents some of our results referring to the preparation and characterisation of alumina based composition that is to be used as porous adsorbing layer for coatings on metallic substrates. Sample of alumina based compositions were prepared from homogeneous mixtures consisting of γ-Al_2O_3 (adsorbing material), boehmite (binding agent), nitric acid (peptising agent) and water (dispersing medium). Special attention was paid to alumina hydrate preparation and characterisation. The main characteristics of the boehmite type are summarised i.e. crystalline structure, thermal behaviour, FT-IR spectra and surface area.

1. Introduction

Ceramic and metallic honeycombs are of great importance as catalytic substrates in processes that aims at the ecosystem protection. For an increased functionality of the substrate, the honeycomb surface has to be coated with highly porous adsorbing layer [1,2]. Alumina-based compositions are successfully used as coatings on ceramic or metallic substrates for the manufacture of honeycomb type-catalysts.

Our general purpose is to manufacture a special designed catalytic support formed by coating the metallic honeycomb with a porous, highly adsorbing layer. The as obtained multifunctional skeletal catalytic support presents a great importance as substrate in processes that aim at the medium protection i.e. ozone decomposition, control of the waste gases from the intern combustion engines, destruction of residual oils, etc.

In order to manufacture a catalytic support with metallic skeleton (CSMS), a study was initiated referring to the formation of alumina coatings on metallic substrate (ACOMS). ACOMS could be prepared from suspensions containing adsorbing material (alumina type), binding material (alumina hydrate such as boehmite-type), nitric acid (peptising agent) and water (dispersing medium). The suspensions under discussion are based on alumina hydrates whose crystalline structure, particle morphology and size or hydratation degrees could influence the ACOMS quality i.e. adherence, surface area, porosity etc.

The paper presents some of our results referring to the preparation of some alumina-based compositions that are to be deposited onto the metallic substrate in order to manufacture the catalytic support with metallic skeleton.

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2. Experimental part

The sample of porous adsorbing material (code **A₁**) was prepared by firing the technical alumina at 600°C, 4 hours. Alumina hydrate samples **B₂** and **B₃** were prepared by adding diluted nitric acid to sodium aluminate solutions obtained by the reaction of either aluminium powder or aluminium nitrate with sodium hydroxide solution. The nitric acid solution was slowly added, under continuous stirring, until the pH was 9.

The separated gel was centrifuged, washed and dried at 110 °C for 24 hours. The as maturated gel samples were washed with ammonia aqueous solution, dried and then dispersed into isopropanol.

Alumina based compositions were prepared from suspensions consisting of adsorbing material sample, binding agent (alumina hydrate) and very diluted nitric acid. The suspension grinding was performed with a Poulverisette-type mill. In order to check the adherence of the prepared ACOMS, small pieces of AluchromY sheet were immersed into the suspension, taken out, dried at 150ºC and then fired.

The starting materials and the alumina based compositions were investigated by thermal analysis (Paulik-Erdely OD-102 Derivatograff; heating rate = 6 °C/min), X-ray diffraction (DRON 3M Diffractometer; CuK$_\alpha$ radiation), FT-IR spectroscopy (JASCO-610 Spectrophotometer; KBr disks) as well as by BET analysis and particle size measurements (IOR MC 5A Microscope).

3. Results and discussion

The alumina coatings onto metallic substrate (ACOMS) could be prepared from suspensions containing highly porous adsorbing material, binder, peptising agent and water as dispersing medium [3]. The recommended adsorbing material for ACOMS is gamma-alumina, whose surface area and mechanical strength are usually used to ameliorate the catalyst qualities. For our experiments, alumina hydrate of boehmite type [AlO(OH)] as binding material and nitric acid [HNO$_3$] as peptising agent were selected. Special attention was paid to the synthesis of the alumina hydrate whose quality is extremely sensitive to the synthesis conditions [4-8].

Synthesis of alumina hydrate samples

Alumina hydrate samples [Al$_2$O$_3$·xH$_2$O] were prepared by treating sodium aluminate solutions with very diluted nitric acid. Sodium aluminate could be prepared from either aluminium powder or aluminium nitrate [10]. In our experiments, both the synthesis routes were used in order to prepare the alumina hydrate for the manufacture of ACOMS:

- Sample code **B₂**: $\qquad$ Al(NO$_3$)$_3$·9H$_2$O → Na[Al(OH)$_4$] → Al$_2$O$_3$·xH$_2$O
- Sample code **B₃**: $\qquad$ Al → Na[Al(OH)$_4$] → Al$_2$O$_3$·xH$_2$O
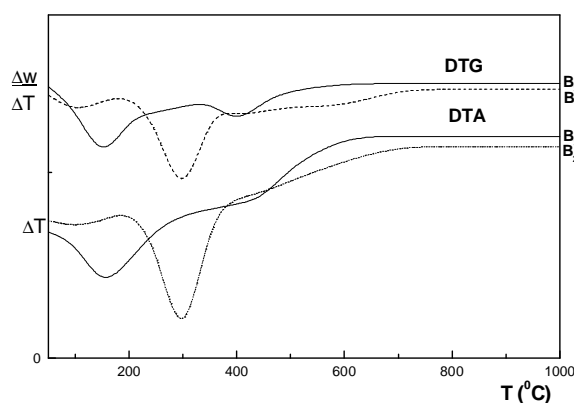
Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal (DTA) analysis, infrared absorption (FT-IR) spectroscopy, and X-ray diffraction (XRD) put in evidence that, in our experimental condition, two different type of alumina hydrate were obtained.

The thermal behaviour of the two-alumina hydrate samples is very different, as shown by the thermal analysis. The experimental thermal weight losses of the two samples, 33.5% for **B₂** and 31.2% for **B₃** are quite equal and almost twice the theoretical value (15%) of the anhydrous boehmite AlO(OH) (Table 1). Every sample is characterised by a very strong endothermic effect (associated with the water removal process) whose position is very different (Fig. 1). The dehydration process is very intense at about 300ºC for sample **B₂** and about 160ºC for sample **B₃**.

One can presume that **B₂** corresponds to aluminium hydroxide (considered alumina trihydrate Al$_2$O$_3$·3H$_2$O) whereas **B₃** is boehmite (considered alumina monoydrate Al$_2$O$_3$·H$_2$O). Large amounts of adsorbed water are present in both samples so that the weight loss is not a criterion to select the appropriate quality of alumina hydrate.

Table 1. Thermal analysis data of sample B_2 and B_3 of alumina hydrate [$Al_2O_3 \cdot xH_2O$].

Code	Weight losses				Main thermal effects		Observations	
	Temperature	T_{max}	Δ_W	$\Sigma_{\Delta w}$	T_{max}	Effect		
B₂	20 – 160 °C	110 °C	5.25%		130 °C	Weak endo-effect	▪	2.85 mole H_2O/mole
	160 – 350 °C	300 °C	19.75%	33.50%	305 °C	Strong endo-effect	▪	> 50% water lost at
	350 – 900 °C	450 °C	8.50%					160 ÷ 350 ºC
B₃	20 – 250 °C	150 °C	16.40%		160 °C	Strong endo-effect	▪	2.57 mole H_2O/mole
	250 – 350 °C	260 °C	5.20%	31.20%			▪	> 50% water lost at
	350 – 520 °C	440 °C	8.00%		440 °C	Weak endo-effect		20 ÷250 ºC
	520 – 900 °C	570 °C	1.60%					

Fig. 1. The differential thermogravimetric (DTG) and differential thermal analysis (DTA)
curves of the two type of alumina hydrate namely **B₂** and **B₃** samples.

The vibrational spectra of alumina hydrate samples put in evidence the difference between the crystalline structures of the two-alumina hydrate samples (Fig. 2). **B₂** sample seems to be better crystallised than **B₃** sample. The structure of the spectrum in the high frequencies domain suggests the simultaneous presence of adsorbed water, crystallisation water and free OH groups. For the **B₂** series, the pair of bands at 980 and 1020 cm^{-1} could be associated with the characteristic vibrations of the Al-OH bonding. The wide absorption band with maximum at ~3470 cm^{-1} is due to the vibration of H_2O molecules, which take part in hydrogen bonding with Al_2O_3 surface [10]. In the case of the **B₃**, an intense broad band at ~3426 cm^{-1} was observed. This suggests a high content of unstable H_2O [3]. Al-O-H bending mode is observed in the region 900-1100 cm^{-1} [11].
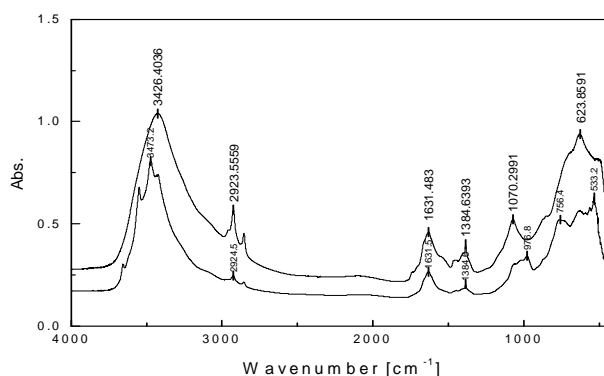
Fig. 2. FT-IR spectra of the two type of alumina hydrate namely **B₂** (down) and
B₃ (up) samples.

The FT-IR analysis suggests the existence of two types of alumina hydrates, i.e. $Al_2O_3 \cdot 3H_2O$ structure for B_2 sample and AlO(OH) (boehmite) for B_3 sample.

This supposition was confirmed by the XRD patterns (Fig. 3). Sample B_2 possesses high cristallinity degree and the spectrum corresponds mostly to aluminium hydroxide with monoclinic structure of bayerite type. In spite of the fact that B_3 show very low cristallinity, the bands of aluminium oxy-hydroxide with orthorhombic structure (boehmite type) could be noticed. In fact, the reflection lines at 13.6 degree (6.5 Å) and 14.5 degree (6.1 Å) suggest that the material is a mixture of boehmite and pseudoboehmite [12]. The latter one is a water-rich variety of boehmite that can be recognised by means of XRD from the shift of the (020) reflection from 6.1 Å towards higher values [13].
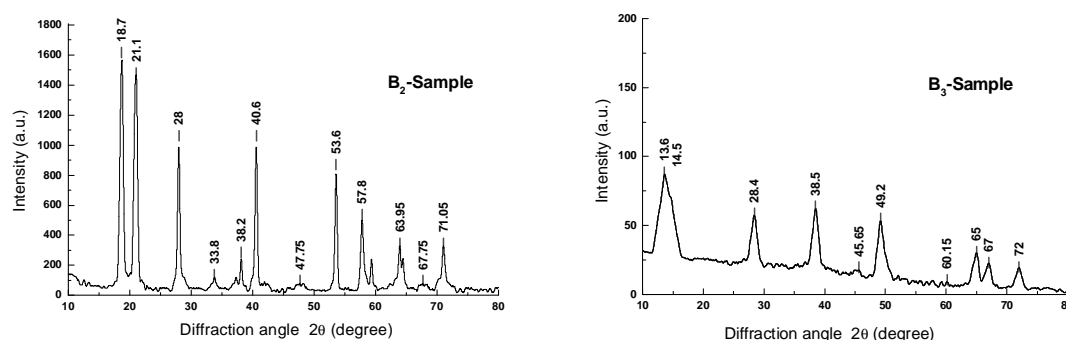

Fig. 3. XRD spectra of the two type of alumina hydrate, namely B_2 (left) and B_3 (right) samples.

Gas absorption measurements illustrates the different porosity and surface area of the two-alumina hydrate powders. The specific surface area (S_σ) and the overall volume of pores (V_p) are $S_\sigma = 88.4 \ m^2/g$ and $V_p = 0.064 cm^3/g$ for sample B_2 and $S_\sigma = 294.0 \ m^2/g$ and $V_p = 0.301 \ cm^3/g$ for sample B_3. The values are in good agreement with the suggested differences between the cristallinity of the samples. Moreover, the high surface area and porosity of alumina hydrate prepared by the route $Al \rightarrow [Al (OH)_4]^- \rightarrow Al_2O_3 \cdot xH_2O$ are in the favour of the utilisation of B_3 sample as binding agent for ACOMS formation.

Selection of the adsorbing material

Two sorts of adsorbing materials based on alumina were characterised in order to be used for ACOMS formation.

- Sample A_1:   prepared from technical alumina (600ºC; 4 hrs); proved to be gamma phase
- Sample A_3:   commercialised as gamma type by an ancient firm from Germany; proved to be alpha form

X-ray diffraction, FT-IR spectroscopy, gas adsorption measurements and optical microscopy were used to evaluate the quality of the two samples of adsorbing material, namely samples A_1 and A_3 (Table 2). In spite of the apparent large particle dimensions, sample A_1 possesses high porosity and good adsorptive characteristics as shown by the very high surface area.

Table 2. General characteristics of the two alumina namely A_1 and A_3 samples.

Alumina type Properties	α - Al_2O_3 Sample A_3	γ - Al_2O_3 Sample A_1
Crystalline structure	Hexagonal $\Leftrightarrow$ alpha phase	Cubic $\Leftrightarrow$ gamma phase
Surface area	$S_\sigma = 13.1 \ m^2/g$	$S_\sigma = 161 \ m^2/g$
Particle size distribution	$d_{50\%} = 3.7 \ \mu m$	$d_{50\%} = 13.1 \ \mu m$

Preparation of some alumina based composition utilisable as ACOMS

By analysing the above mentioned sample characteristics, one can conclude that a porous, uniform layer, adherent to the metallic substrate, could be manufactured from a suspension containing γ-alumina (sample **A₁**) as adsorbing material and mono-hydrated alumina (sample **B₃**) as binder.

One ACOMS sample was prepared from suspension containing γ-alumina (porous material), boehmite (binder), nitric acid (peptising agent) and water (dispersing medium); the adsorbent/ binder ratio was about 1:3.

Small pieces of steel sheet were immersed into the homogeneous suspension, dried and fired at different temperatures. The as obtained samples were characterised by X-ray diffraction, FT-IR spectroscopy and surface area measurements. The surface area values of the ACOMS sample before [sample **A₁B₃₍ᵤ₎**] and after the thermal treatment [**A₁B₃.₁©**; **A₁B₃.₂©**; **A₁B₃.₃©**] are presented in Table 3.

Table 3. The specific surface area of the thermally treated ACOMS sample.

Sample code	Thermal treatment	Specific surface area
$A_1B_{3(u)}$	-	191 m^2/g
$A_1B_{3.1\text{©}}$	450 °C	190 m^2/g
$A_1B_{3.2\text{©}}$	550 °C	173 m^2/g
$A_1B_{3.3\text{©}}$	650 °C	146 m^2/g

Good porosity and high surface area are obtained at 450-550 °C. The demand for a good, consolidated crystalline structure of gamma-alumina phase suggests that the thermal treatment has to be performed at 550 °C.

The crystalline purity is illustrated by the FT-IR spectra of the ACOMS sample before [sample **A₁B₃₍ᵤ₎**] and after the thermal treatment (Fig. 4). The thermal treatment is responsible for the removal of NO_3 groups (specific band at 1384 cm^{-1}) introduced into the alumina composition by the peptising agent. The narrowing of the 747 and 615 cm^{-1} bands, specific to Al-O vibration from gamma-alumina phase, indicate a "structural" purification of the material.
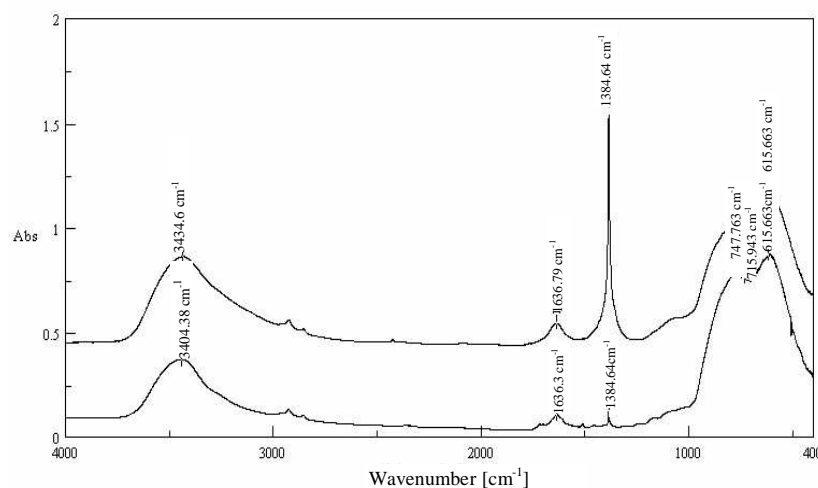

Fig. 4. FT-IR spectra of the ACOMS sample before (A₁B₃₍ᵤ₎ (up)) and after the thermal treatment (A₁B₃.₂© (down)).

The structure of gamma-alumina is well defined by the XRD pattern presented in Fig. 5. The cubic structure of gamma alumina (γ-Al_2O_3) is present in all alumina-based compositions.

General characteristics of the as prepared ACOMS sample are:
- Crystalline structure ⇔ gamma alumina- type
- High homogeneity ⇔ very fine powder ($d_{50\%}$=1.28μm) and uniform particle size distribution
- High surface area ⇔ S_σ = 173 m²/g
- High porosity ⇔ overall volume of pores V_p = 0.283 cm^3/g
- Good adherence to the metallic substrate ⇔ as it is shown by the peeling test.
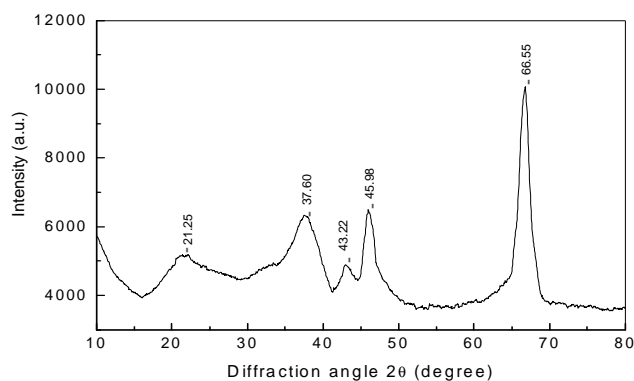
Fig. 5. XRD spectra of the alumina based composition thermally treated al 550 ºC, namely **A₁B₃©**.

4. Conclusions

Alumina based composition that can be coated onto metallic substrate (ACOMS) could be prepared from suspensions containing alumina (porous material), alumina hydrate (binder), nitric acid (peptising agent) and water (dispersing medium).

Porous material prepared by firing the technical alumina $[Al(OH)_3 \cdot xH_2O]$ shows good physical characteristics such as crystalline structure of gamma–alumina, high surface area and uniform particle size distribution.

Good binding properties were shown by the alumina hydrate with boehmite structure obtained via aluminium→sodium aluminate→ alumina hydrate. Very definite physical characteristics could be used to evaluate the material quality i.e. dehydration effect at about 160 ºC, boehmite-type crystalline structure, high surface area and porosity.

Alumina based composition that can be coated onto metallic substrate, i.e. *A*COMS sample is characterised by some partucular qualities such as: gamma-alumina type crystalline structure; high homogeneity due to the uniform particle size distribution in the fine particle domain; high surface area and high porosity and finally, good adherence to the metallic substrate.

Acknowledgements

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