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**Synthesis of Spherical Structured Catalysts by Dip-Coating. Application to N-Butane Dehydrogenation<sup>†</sup>**

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<sup>†</sup>This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: [10.1002/cjce.23000]

**Received 15 March 2017; Revised 17 May 2017; Accepted 7 July 2017**  
**The Canadian Journal of Chemical Engineering**  
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**DOI 10.1002/cjce.23000**

## Abstract

This work analyzes the deposition conditions of thin layers of  $\gamma$ - $\text{Al}_2\text{O}_3$  by dip-coating on a spherical substrate of  $\alpha$ - $\text{Al}_2\text{O}_3$  spheres. Results showed that under controlled deposition conditions, a structured support of  $\alpha$ - $\text{Al}_2\text{O}_3$  spheres coated by a uniform  $\gamma$ - $\text{Al}_2\text{O}_3$  layer (thickness  $\approx 15 \mu\text{m}$ ) of good adherence, can be attained. Optimal preparation conditions for the coating, that involved pretreatment of the substrate, gel formation, deposition conditions and thermal treatments, were obtained.

Pt catalysts supported on this structured material can be used as promising dehydrogenation systems. In this sense, a monometallic structured catalyst showed both good metallic dispersion and catalytic performance in n-butane dehydrogenation reaction compared to another conventional catalytic system. This article is protected by copyright. All rights reserved

Keywords: structured catalyst, dip-coating, dehydrogenation catalyst.

## Introduction

The importance of structured catalysts<sup>[1]</sup> is based on the advantages in the mass and heat transfer in fast reactions carried out at high temperatures,<sup>[2]</sup> which increase the energy efficiency and the heat recovery.<sup>[3]</sup>

Different methods can be used to deposit a thin layer of a given material (e.g.  $\gamma$ - $\text{Al}_2\text{O}_3$ ) on the surface of an inert and non-porous substrate. The different preparation methods take into account the properties of the substrate and the characteristics that the material to be deposited should have, e.g. the thickness of the layer.

According to the literature, there are different procedures for coating that includes wash-coating and dip-coating,<sup>[4-13]</sup> plasma spraying,<sup>[9,14]</sup> granulation,<sup>[15]</sup> deposition without electrodes,<sup>[16]</sup> coating based on polymers,<sup>[17]</sup> chemical vapour deposited layer (CVD) and physical vapour deposited (PVD) layers,<sup>[7]</sup> coating via sol gel-route.<sup>[7,13,15,18,19]</sup> In all cases the objective is related with the production of a uniform and stable thin layer, with both high thermal resistance and specific surface area.

The above mentioned preparation methods can include a previous treatment of the substrate that modifies the textural properties of the external surface so as to obtain layers with a very good adherence and therefore high stability along the reaction time. Several pre-treatments such as anodic oxidation, thermal oxidation and chemical treatment with inorganic and organic acids have been reported.<sup>[4,6,7,8,20]</sup>

In the dip-coating method, the substrate is immersed in a vessel containing the precursor of the material to be deposited. Then the material is dried and calcined in order to obtain a stable layer. This method is widely used for the deposition of thin layers on substrates of different geometry. According to Valentini et al.,<sup>[8]</sup> the thickness of the deposited layer depends on the rate of both the immersion and the extraction of the substrate solution and the viscosity of the precursor solution. The dip coating technique has several applications such as for the deposition of  $\gamma$ - $\text{Al}_2\text{O}_3$  on different substrates (slabs of aluminium and FeCr, foils of FeCrAl foils, and tubes of  $\alpha$ - $\text{Al}_2\text{O}_3$ ).<sup>[8,10]</sup> However, a deep study of the deposition conditions of thin layers of bohemite on a substrate with spherical geometry has not been reported yet. Besides, few papers investigate the catalytic performance of bimetallic catalysts supported on  $\gamma$ - $\text{Al}_2\text{O}_3$  deposited on  $\alpha$ - $\text{Al}_2\text{O}_3$  spheres.<sup>[21-</sup>

24]

Hence, in this paper a technique to deposit thin layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on an inert substrate of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres with very low porosity is developed. In this case, bohemite was used as precursor of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, which has high surface area, low acidity and good interaction with metals. The objective of this paper is to obtain adequate structured supports for the deposition of noble metals to be used in paraffin dehydrogenation processes.

## Experimental

### a) Preparation of the structured supports

Spheres of a commercial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> CERALOX (provided by SASOL company) of very low surface area were used as substrate. The textural properties of the substrate were: bulk density = 0.83 mL g<sup>-1</sup>, mean sphere diameter= 2 mm, specific surface area, S<sub>BET</sub>= 4.70 m<sup>2</sup> g<sup>-1</sup>, mean pore size= 14.4 Å.

The deposition of a thin layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on the substrate involves the following steps: i) pre-treatment of the support, ii) preparation of the bohemite gel, iii) deposition of bohemite on the substrate and iv) thermal treatments of the samples.

The pre-treatment of the support involves a thermal treatment at 500° C in air for 3 h to stabilize the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase followed by a chemical treatment with different inorganic acids (HCl, HNO<sub>3</sub> or HF) to achieve the surface roughness necessary to improve the adherence of the deposited  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers.<sup>[8]</sup> Table 1 shows the different acid treatments of the substrate (acid type, concentration and exposure time) carried out at 25 °C. The acid concentration in the aqueous solutions and the contact time were also studied. In this sense, the concentrations of HCl and HNO<sub>3</sub> solutions were 0.5, 1.0 and 2.0 mol/L, whereas HF ones were 0.10, 0.20 and 0.40 g/g. Two contact times were studied: 12 and 24 h, and the volume of acid solution / mass of substrate  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ratio was 1.4 mL/g for all the experiments. After the pre-treatment, the substrate was washed with distilled water, then submitted to a drying step at 120° C for 12 h and finally calcined at 500° C for 3 h.

The bohemite gel consists of the formation of aggregates of charged colloid particles to produce a uniform network.<sup>[11]</sup> In a first step, a technique to obtain the gel with adequate rheological characteristics was optimized. For this purpose, bohemite gels (in nitric acid media) were prepared by using different concentrations of a commercial

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bohemite (Disperal P2) and different HNO<sub>3</sub> concentrations. The concentration of bohemite is important since it directly affects the amount of precursor deposited on the substrate. The addition of HNO<sub>3</sub> is used to modify the gel formation and its stability. Besides, the HNO<sub>3</sub> addition modifies the rheological characteristics of the gel. Two bohemite concentrations (0.10 and 0.20 g/g) and three HNO<sub>3</sub> concentrations (0.1, 0.2 and 0.4 mol/L) were used.

For the deposition of bohemite on the substrate, the dip-coating method was used in all the cases. In this sense, the spheres of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate were introduced in a rotating (80 rpm) cylindrical basket with walls of steel mesh for 1 h. This step can be repeated several times in order to increase the thickness of the deposited layer. After the deposition of the bohemite layer, the basket was removed from the gel at 0.02 cm min<sup>-1</sup>. Then the basket was kept rotating until the gel stops dripping. The spheres were dried with air flow. It must be indicated that the drying velocity is an important parameter since it could affect the integrity of the deposited layers. In this sense, two experiments were made, one at a slow drying (5 m s<sup>-1</sup> for 0.5 h) and low temperature (30° C) and the other one at a fast drying (10 m s<sup>-1</sup> for 0.5 h) and high temperature (50 °C).

The thermal treatments of the samples were carried out in order to transform the deposited bohemite into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The substrate covered by a bohemite layer was dried at 120° C for 12 h and then calcined at 500 ( $\gamma$ -A-wc-500) or 650 °C ( $\gamma$ -A-wc-650) for 3 h.

#### **b) Preparation of Pt catalysts**

The monometallic Pt catalysts were prepared by impregnation of the coated spheres with a solution of chloroplatinic acid. In all cases, the concentration of the aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> was such as to obtain the desired Pt loading (0.003 g/g). The ratio between the impregnation solution volume and the support weight was 1.4 mL/g. The spheres were kept in contact with the liquid for 6 h at room temperature. Then they were dried at 120 °C for 12 h and finally calcined at 500 °C.

#### **c) Characterization of the structured supports and catalysts**

The structured support was characterized by its textural properties, adherence test, X-ray diffraction, SEM, TPD of pyridine and 2-propanol dehydration. The metallic dispersion and the carbon formation of the catalysts were also determined.

The specific surface area (S<sub>BET</sub>) and the mean pore size were determined by using an Accusorb 2100 E-Micromeritics equipment. The samples were first outgassed at 200° C

for 2 h at  $10^{-4}$  mm Hg. The dead volume of the equipment was determined with He (AGA 99.999%) at the temperature of liquid N<sub>2</sub>. The isotherms were obtained at 77 K using N<sub>2</sub> as adsorbate in the range of pressure between 35 and 150 mm Hg, and the S<sub>BET</sub> was obtained by linearizing the BET equation and extrapolating at zero pressure.

The layer adherence of the coated spheres was tested by immersing them in distilled water (a) or organic solvent (b), followed by a treatment in an ultrasonic equipment (Ultrasonic cleaner Cleanson 200 w) during 30 minutes.<sup>[6]</sup> Then the spheres were dried in a furnace during 12 h and weighted to determine the weight loss.

The samples were analyzed in an X-ray Shimadzu diffractometer using a Cu K $\alpha$  radiation ( $\lambda=1,542\text{\AA}$ ), generated at 30 kV and a current of 30 mA. The XRD pattern was taken between 10 and 80°. The diffraction lines were compared with standard JCPDS in order to identify the detected species.

SEM measurements were carried out in a Scanning Electronic Microscopy JEOL, JSM-35 operated at 2 kV equipped by system digital imaging SemAfore. The samples were coated with a gold film deposited by sputtering using a brand Veeco evaporator, VE-300 operated by Ar atmosphere. This microscopy is connected to a microprobe EDAX 9100 where the samples were coated by graphite film using the same evaporator.

For the experiments of Temperature Programmed Desorption (TPD) of pyridine, 200 mg of sample were previously impregnated with an excess of pyridine (Merck 99.9 %) for 4 h. The excess of pyridine was eliminated under vacuum at room temperature to obtain a dried powder. Then the samples were put into a quartz reactor and a flow of 40 mL min<sup>-1</sup> was passed through the bed. The pyridine weakly adsorbed was eliminated at 110 °C for 2 h. Then the sample was heated from 110° C up to 500° C at a heating rate of 10 °C min<sup>-1</sup>. The amount of pyridine desorbed during the TPD experiments was measured with a FID detector in the exhaust of the reactor.

The 2-propanol dehydration reaction was carried out in continuous flow reactor at atmospheric pressure in order to determine the acidic properties of the deposited layers. 2-propanol was vaporized in a H<sub>2</sub> stream (H<sub>2</sub>/2-propanol molar ratio = 19) and it was fed with a space velocity of 0.52 mol alcohol h<sup>-1</sup> g cat<sup>-1</sup>. Prior to the reaction, the samples were treated in situ with H<sub>2</sub> at 500° C for 3 h. The mass of sample was 0.1 g, the reaction temperature 210° C and the flow of the feed was 600 mL min<sup>-1</sup>. The reaction products were

analyzed by GC using a column Carbowax 20 (20 % Chromosorb WAW, length 2 m and 1/8" diameter).

Pt dispersion was measured by H<sub>2</sub> chemisorption in a volumetric equipment. The sample (0.3 g) was outgassed at room temperature, heated under flowing H<sub>2</sub> (60 mL min<sup>-1</sup>) from room temperature up to 500 °C, and then kept at this temperature for 2 h. At the same temperature, the sample was outgassed under vacuum (10<sup>-5</sup> kPa) for 2 h and then cooled down to room temperature (25 °C). The hydrogen dosage was performed in the range of 3-13 kPa. The isotherms were linear in the range of the used pressures. The chemisorbed hydrogen was calculated by extrapolation of the isotherm to pressure zero. From the data of chemisorbed H<sub>2</sub>, the metallic dispersion was calculated, assuming an adsorption stoichiometry of 2 mol Pt/mol H<sub>2</sub>.

The carbonaceous deposits were quantified by temperature-programmed oxidation (TPO) of the catalysts before and after the dehydrogenation reaction by a thermogravimetric analysis (TGA) technique. The experiments were carried out on the SDTA Mettler STARE. Fresh (used as a reference) and used catalysts were stabilized under nitrogen flow at 250 °C for 1 h before TPO experiments. The samples (0.010 g) were heated at 5 °C·min<sup>-1</sup> from 250 to 500 °C under air flow.

#### **d) Evaluation of the catalysts**

The catalytic behaviour of the Pt monometallic catalyst was tested in the n-butane dehydrogenation reaction carried out at 530 °C and atmospheric pressure, with a H<sub>2</sub>/C<sub>4</sub>H<sub>10</sub> molar ratio of 1.25. The catalyst (0.2 g) was previously reduced in H<sub>2</sub> at 530 °C for 3 h. The reactive mixture was prepared in situ by using mass flow controllers. All gases, n-butane, N<sub>2</sub> (used for purge), and H<sub>2</sub> (used for the previous reduction of catalysts and for the reaction) were high purity ones (>99.99 %). The reactor effluent (that consisted of methane, ethane, ethylene, propane, propylene, n-butane, 1-butene, cis-2-butene, trans-2-butene and 1,3-butadiene) was analysed in a GC-FID equipment with a packed chromatographic column (1/8", 6 m, 20 % BMEA on Chromosorb P-AW 60/80) which was kept at 50 °C during the analysis. The n-butane conversion was calculated as the sum of the percentages of the chromatographic areas of all the reaction products (except H<sub>2</sub>) corrected by the corresponding response factor. The selectivity to the different reaction products (i) was defined as the ratio: mol of the product i/∑mole of all products (except H<sub>2</sub>). Taking into

account the high temperatures used for the reaction (for thermodynamic reasons), it was necessary to determine the contribution of the homogeneous reaction. For this purpose, a blank experiment was performed by using a quartz bed and the results showed a negligible n-butane conversion (<1 %).

## Results and Discussion

XRD was used to characterize the substrate. Figure 1a shows the XRD pattern of a  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase, reported in the bibliography,<sup>[25]</sup> which is coincident with the diffractogram of the substrate ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres), shown in Figure 1b.

The treatments of the substrate with different acids (see Table 1) were used to develop roughness in the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, thus favouring the further deposition, adherence and stability of the deposited layer. Figure 2 shows SEM microphotographies of the surface of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres without treatment (Figure 2a) or treated with different acid concentrations and exposure times (from Figure 2b to Figure 2k). It can be observed that the treatment with HCl 0.5 mol/L for 12 h (see Figure 2 b) produces a small effect on the roughness of the substrate surface. On the other hand, the use of HCl 1 mol/L and 2 mol/L highly increases the surface roughness with the formation of surface cavities (see Figures 2c and 2d). It must be noted that the effect of HCl 2 mol/L is very similar to that produced by HCl 1 mol/L. In the case of the treatment with HNO<sub>3</sub> for 12 h, it was not observed the formation of surface rugosity at low concentration (0.5 mol/L) (see Figure 2e), whereas for HNO<sub>3</sub> 1 and 2 mol/L (Figures 2f and 2g) it was developed roughness on the surface although the effect was lower than that produced by HCl. When  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres were treated with HF 0.10 g/g for 12 h (Figure 2 h) or 0.20 g/g for 12 h (Figure 2i), it was observed the formation of small cavities but little roughness. The use of HF 0.40 g/g for 12 h (Figure 2 j) produces a lot of large cavities. Finally, the treatment of the surface with HF 0.20 g/g for 24 h leads to a good rugosity but with large cavities (see Figure 2 k). In conclusion, the better acid surface treatments appear to be those with HCl 1 mol/L or 2 mol/L. On the basis of these observations, the treatment with HCl 1 mol/L was selected.

With respect to the optimal concentrations of both bohemite and HNO<sub>3</sub> to obtain a gel with the adequate rheological characteristics, two bohemite concentrations (0.10 and 0.20 g/g) and three HNO<sub>3</sub> concentrations (0.001, 0.002, and 0.004 g/g) were used. The



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optimal consistency of the gel was determined by a simple experiment by dipping a glass rod in the gel. When a continuous filament is formed in rising up the rod, an adequate viscosity is attained. By using a concentration of 0.10 g/g bohemite (with the three different HNO<sub>3</sub> concentrations), a gel with low viscosity was always obtained. However, a gel with an adequate viscosity could be formed from a solution of 0.20 g/g bohemite. In order to determine the optimal concentration of HNO<sub>3</sub>, three experiments were carried out:

- i) Addition of 0.001 g/g of HNO<sub>3</sub>: the gel was formed, but after 24 h ripening, a gel with very high viscosity was obtained.
- ii) Addition of 0.004 g/g of HNO<sub>3</sub>: the gel was formed but after a short time, a very viscous or “hard” gel was produced, which would make the deposition difficult.
- iii) Addition of 0.002 g/g of HNO<sub>3</sub>: the gel showed a moderate and stable viscosity, this being the better HNO<sub>3</sub> concentration.

With respect to the HNO<sub>3</sub> addition, the best results were obtained by adding two successive and equal fractions of the acid, the second one 24 h after the first one. Figure 3 shows SEM microphotography of the transversal section of the coated sphere obtained with HNO<sub>3</sub> 0.002 g/g in the bohemite dispersion (0.20 g/g). It can be observed a thin and uniform layer deposited on the substrate.

Taking into account the above mentioned results, the technique adopted for the preparation of a bohemite gel was the following: 50 g of bohemite were added to 200 mL of distilled water. This dispersion was stirred at 450 rpm for 1 h. Then, the dispersion was kept for 1h until a consistent gel was formed. After this, HNO<sub>3</sub> was dropped under stirring until a concentration of 0.001 g/g was achieved. Then the gel was aged for 24 h and finally another portion of HNO<sub>3</sub> solution was added in order to reach 0.002 g/g. The second addition of HNO<sub>3</sub> produces certain denaturalization of the gel, thus giving a stable gel with the adequate viscosity to carry out the coating. The thus obtained gel was stable during one week, the final pH being 4.5. At higher times, the viscosity increases.

In order to increase the thickness of the coating material on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres, the bohemite deposition on the substrate (described in the experimental section) was repeated twice. The deposited layer on the substrate was about 15  $\mu$ m and the loading was close to

8.5 mg cm<sup>-2</sup> (obtained by a gravimetric method). It must be indicated that the first layer acts as an anchorage surface for the second one.

The conditions used during the drying step (airflow rate and temperature) would be relevant for the integrity of the layers. In Figure 4a, a transversal edge of a coated sphere (with one deposition) dried at both high air rate (10 m s<sup>-1</sup>) and temperature (50 °C, 30 min) can be observed. It can be seen that some portions of the layer are absent, this meaning that the coated sphere suffered cracking and peeling. On the other hand, when lower air rate (5 m s<sup>-1</sup>) and temperature (30 °C, 30 min) are used, a continuous and uniform layer is observed (see Figure 4b). In consequence, the drying of the gel should be carried out at low air flow (5 m s<sup>-1</sup>) and temperature (30 °C, 30 min). In this step, a very important loss of water was observed.

After the above mentioned treatment, the coated spheres were dried at 120 °C for 12 h and finally calcined at 500 °C ( $\gamma$ -A-wc-500) or 650 °C ( $\gamma$ -A-wc-650) in air (100 mL min<sup>-1</sup>) in order to transform the bohemite phase into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>[26]</sup> This calcination process involves the loss of water and the simultaneous surface dehydroxylation (whose extension depends on the temperature of the treatment). The specific surface area of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer was 282 m<sup>2</sup> g<sup>-1</sup> after calcination at 500° C and 235 m<sup>2</sup> g<sup>-1</sup> after calcination at 650° C, close to that of the commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

In order to verify the formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the layer, XRD measurements on samples calcined at 500 or 650 °C were made according to the conditions indicated in the experimental section. Figure 5 shows the diffractograms of the bohemite gel (a), bohemite deposited on the substrate after drying at 120 °C (b) and the deposited layer after calcination in air at 500 °C (c). The samples were obtained as a residual powder coming from the drying or the calcination steps of the coated spheres. The XRD pattern obtained after calcination at 650°C was similar to that obtained after calcination at 500°C. It can be observed in Figure 5 b (after drying at 120 °C) the main typical peaks of bohemite ( $2\theta = 13.9, 27.8, 38.3$  and  $49.3^\circ$ , File N° 211307), while Figure 5 c shows the characteristic peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $2\theta = 38, 45$  and  $67^\circ$ , File N° 10-0425). In this way the thermal treatment (calcination in air at 500 or 650 °C) leads to the complete transformation of bohemite into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

It should be noted that using the above mentioned preparation method, the weight of the structured support (after the deposition of the layer) was about 10 % higher than the substrate spheres.

Adherence test results of  $\gamma$ -A-wc-500 sample show a weight loss of the layer of 0.7% when the experiment was carried out in water (a) and 0.5% for the experiment in organic solvent (b), this showing the very good adherence and mechanical resistance of the deposited layers. Similar results were obtained for  $\gamma$ -A-wc-650 sample.

In order to determine the acidity of the structured supports, tests of 2-propanol reaction and TPD of pyridine were carried out on samples calcined at 500 °C ( $\gamma$ -A-wc-500) and 650 °C ( $\gamma$ -A-wc-650). It is known that the 2-propanol reaction is very useful to characterize the acidic properties of solids.<sup>[27]</sup> Figure 6 shows that the 2-propanol conversion for the coated sample calcined at 500 °C is lower than the conversion of the coated sample calcined at 650 °C. Moreover, Figure 7 shows pyridine desorption as a function of the temperature for the same supports. From TPD of pyridine, the samples calcined at two different temperatures ( $\gamma$ -A-wc-500 and  $\gamma$ -A-wc-650) display sites with different acid strength distribution: weak acidity (desorption between 200 °C and 300 °C), moderate acidity (desorption between 300 and 400 °C), and strong acidity (desorption between 400 °C and 550 °C). It can be observed in Figure 7 that the low temperature sample ( $\gamma$ -A-wc-500) has lower weak acidity and lower strong acidity than the high temperature sample ( $\gamma$ -A-wc-650), while the moderate acidity is similar for both samples. Hence the total acidity (defined as the sum of the three types of acid sites) of the low temperature sample is lower than that corresponding to the high temperature sample. In conclusion the lower dehydration activity of the coated sample calcined at 500 °C with respect to that calcined at 650 °C correlates well with the lower total acidity of the first sample. In this sense the amount of acid sites and the surface acid distribution depends on the calcination temperature, such as it was reported by Ashour.<sup>[28]</sup> In conclusion, a calcination temperature of 500 °C for the coated substrate was chosen since a support with low acidity is necessary to avoid undesirable reactions, like cracking and isomerization, in dehydrogenation catalysts.

SEM microphotographies were taken for the sample prepared under the best conditions: the substrate ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres) was previously treated with HCl 1 mol/L, then

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bohemite solution (0.20 g/g and HNO<sub>3</sub> 0.002 g/g -added in two steps-) was deposited and it was dried in air flow at 5 m s<sup>-1</sup> and 30 °C for 30 min, and finally it was calcined in air at 500 °C. Results are shown in Figure 8. Figure 8 (a) depicts complete views of a sphere with a homogeneously deposited  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. Moreover, Figure 8b displays the transverse section of a coated sphere by using the same conditions as in Figure 8a. This Figure shows a uniform thickness of the layer of about 15  $\mu$ m.

After that, the coated spheres calcined at 500°C were used as a structured support for the preparation of the Pt monometallic catalyst: Pt/ $\gamma$ -A-wc-500/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This catalyst and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CK300 one (taken as a reference) were tested in n-butane dehydrogenation reaction. The metallic dispersion of both catalysts, obtained by H<sub>2</sub> chemisorption measurements, were 60 % for the structured catalyst and 54 % for the reference one, which indicates that the Pt/ $\gamma$ -A-wc-500/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst has slightly lower particle sizes than Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CK300. Results of n-butane conversion and selectivity to all butenes are shown in Figures 9a and 9b, respectively. The initial and final n-butane conversions (Figure 9a) of the structured catalyst were 30 % and 20 %, respectively, the deactivation parameter (DP=[initial conversion-final conversion].100 / initial conversion) being 33 %. The catalytic stability of this structured catalyst was much better than that obtained for the reference catalyst (Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CK300), which shows a high initial conversion (44 %), but it quickly deactivates to a very low final n-butane conversion (10 %), this having a high deactivation parameter of 77 %. This important decrease of the activity showed by the reference catalyst is mainly due to the coke deposition along the reaction. In fact, the carbon content (obtained by TPO measurements) of the Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CK300 catalyst after the reaction was 1.3 wt%, higher than that obtained for the more stable structured catalyst (0.5 wt% C).

With respect to the selectivity to all butenes (Figure 9b), the Pt/ $\gamma$ -A-wc-500/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst has an initial value of 76 % and a final selectivity of 80 %. These values are higher than those obtained with the reference catalyst, whose selectivity to butenes is 70 % along the reaction time. In consequence, the structured catalyst displays a lower selectivity to hydrogenolysis products (undesirable reaction) than the reference catalyst. These behaviours could be related to a different structure of the metallic phase. It is known that the hydrogenolytic capacity is related to the concentration of big ensembles of metallic atoms, probably placed in corners or edges of the crystallites.<sup>[29]</sup> Hence, Pt catalyst

supported on the structured support, which shows a very good catalytic performance for n-butane dehydrogenation, would have a metallic phase with well dispersed metallic particles, this favoring the dehydrogenation reactions and inhibiting hydrogenolytic ones.

## CONCLUSIONS

- Advancements in the development of a structured support with spherical geometry prepared by the "dip coating" technique were achieved.
- From the optimal preparation conditions, that involved pretreatment of the substrate, gel formation, deposition conditions and thermal treatments, a support of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres coated with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained. This structured support showed uniform thickness of the deposited layer (15  $\mu$ m), good adherence of the coating material and low acidity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer.
- The Pt catalyst with the structured support displays high metallic dispersion and good catalytic performance in the n-butane dehydrogenation reaction compared with another conventional catalytic system, thus showing both high n-butane conversion and selectivity to butenes, and a good stability with low carbon formation.

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### Caption to Figures

**Figure 1.** XRD pattern of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (a) compared with the diffractogram corresponding to the substrate (b).

**Figure 2.** SEM photographs of the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> without treatment (a), treated with HCl 0.5 mol/L for 12 h (b), HCl 1 mol/L for 12 h (c), HCl 2 mol/L for 12 h (d), HNO<sub>3</sub> 0.5 mol/L for 12 h (e), HNO<sub>3</sub> 1 mol/L for 12 h (f), HNO<sub>3</sub> 2 mol/L for 12 h (g), HF 0.10 g/g for 12 h (h), HF 0.20 g/g for 12 h (i), HF 0.40 g/g for 12 h (j) and HF 0.20 g/g for 24 h (k) at 25° C.

**Figure 3.** SEM microphotography of the tranverse section of the sample obtained by using HNO<sub>3</sub> concentration (0.002 g/g). Contact time: 2h. Bohemite concentration: 0.20 g/g.

**Figure 4.** (a) Transverse section of a sample with one layer deposited dried at high air flow (10m.s<sup>-1</sup>) and temperature (50 °C, 30 min) and (b) dried at low air flow (5m.s<sup>-1</sup>) and temperature (30 °C, 30 min).

**Figure 5.** XRD of deposited bohemite (a), deposited bohemite after drying at 120° C (b) and after calcination at 500°C in air (c).

**Figure 6.** 2-propanol conversion versus time of the coated supports after calcination of bohemite at 500 °C, 3h ( $\gamma$ -A-wc-500) and 650 °C, 5h ( $\gamma$ -A-wc-650).

**Figure 7.** TPD of pyridine curves of the coated supports after calcination of bohemite at 500 °C, 3h ( $\gamma$ -A-wc-500) and 650 °C, 5h ( $\gamma$ -A-wc-650).

**Figure 8. (a):** complete views of a sphere of substrate with the deposited  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer, previous treatment of the substrate with HCl 1 mol/L, deposition of bohemite (0.20 g/g), HNO<sub>3</sub> 0.002 g/g (in two steps)), dried in an air flow at 5 m s<sup>-1</sup> and 30 °C for 30 min. Samples were finally calcined at 500°C. **(b):** Transverse sections of a sphere corresponding to the sample indicated in Figure 8a.

**Figure 9.** n-butane conversion (a) and selectivity to all butenes (b) along the reaction time for Pt catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> deposited on the substrate calcined at 500 °C, 3h (Pt/ $\gamma$ -A-wc- 500) and Pt/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CK 300 (Pt/ $\gamma$ -A) as a reference.



**Table 1.** Acidic treatment of the substrate. Temperature: 25 °C

Substrate	Acid	Concentration	Time (h)
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	HCl	0,5 mol/L	12
	HCl	1 mol/L	12
	HCl	2 mol/L	12
	HNO <sub>3</sub>	0,5 mol/L	12
	HNO <sub>3</sub>	1 mol/L	12
	HNO <sub>3</sub>	2 mol/L	12
	HF	0.10 g/g	12
	HF	0.20 g/g	12
	HF	0.40 g/g	12
	HF	0.20 g/g	24

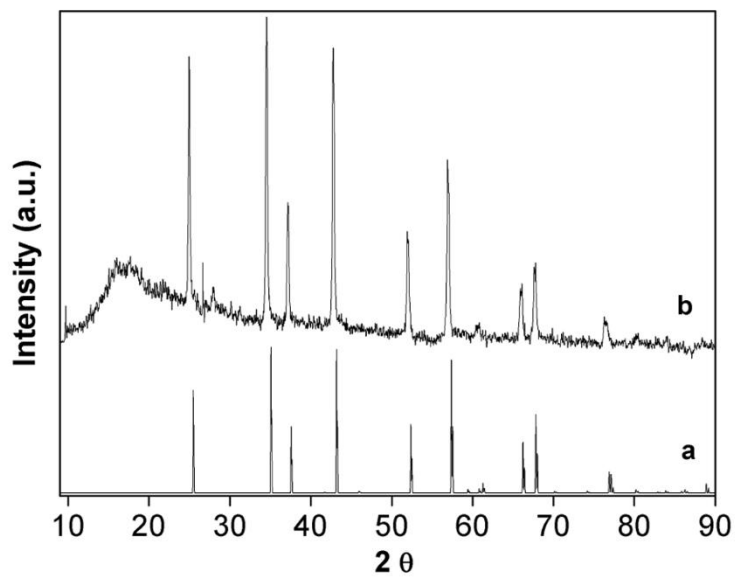


Figure 1

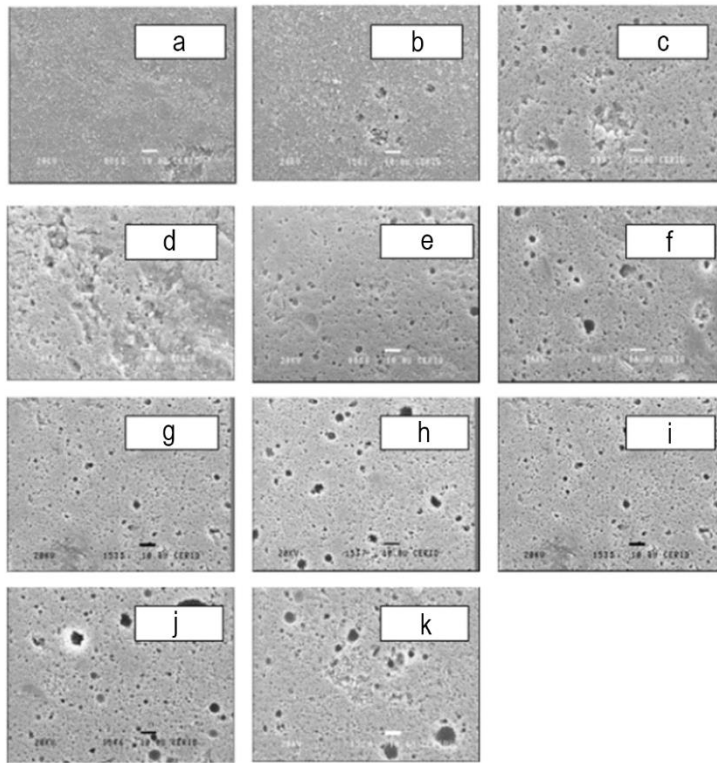
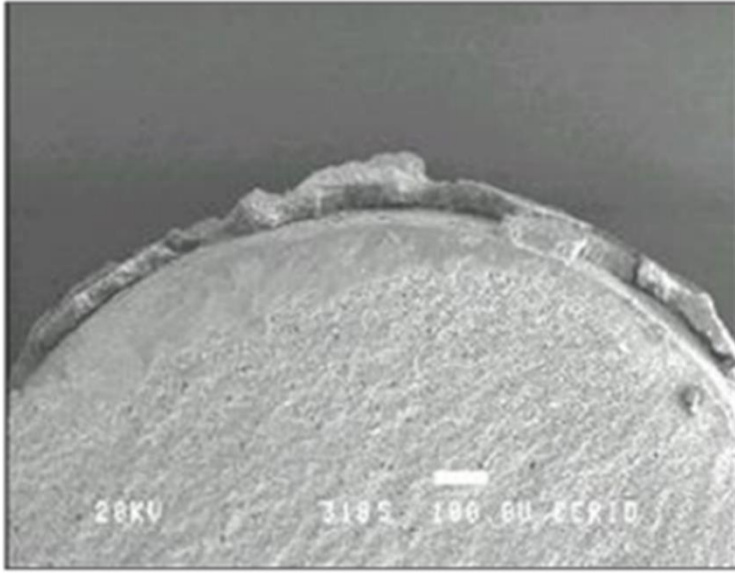


Figure 2



*Figure 3*

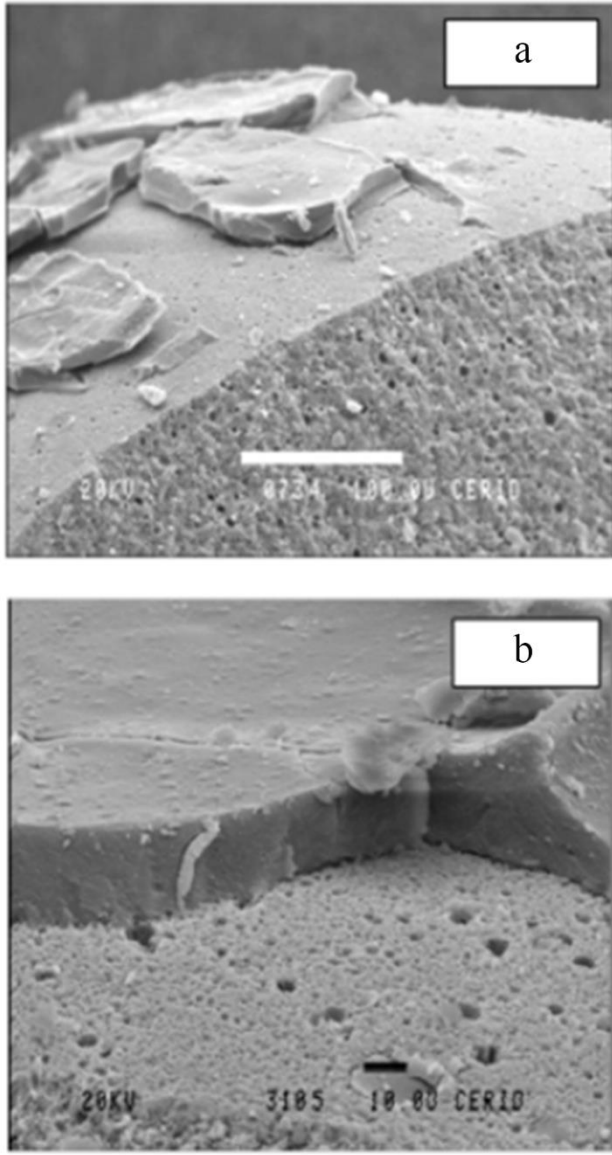


Figure 4

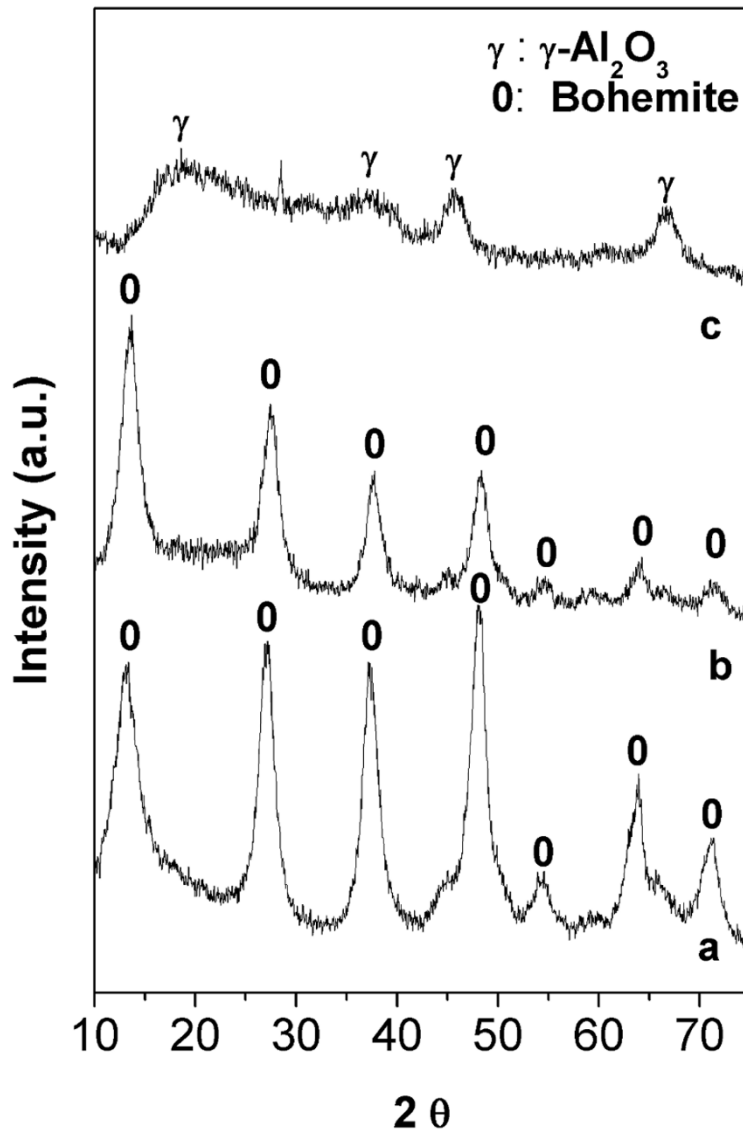


Figure 5

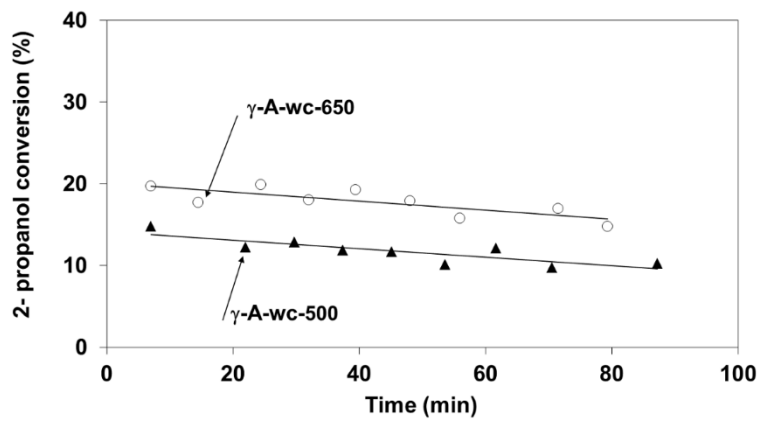


Figure 6

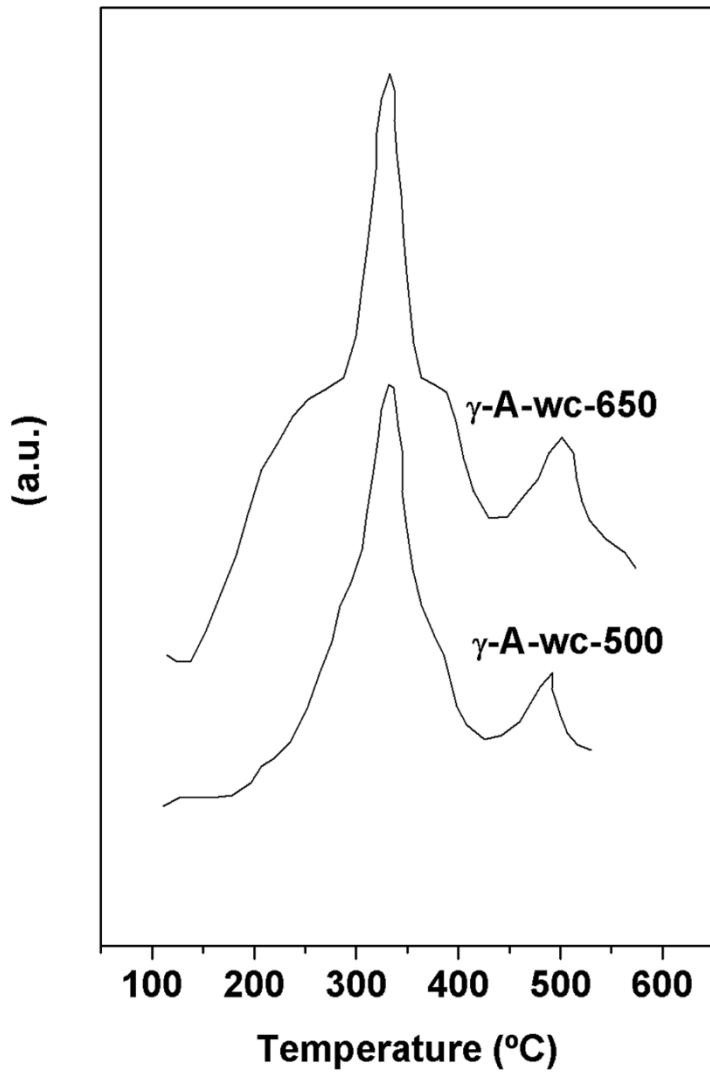
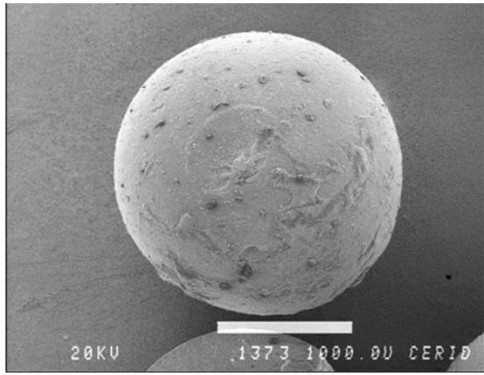
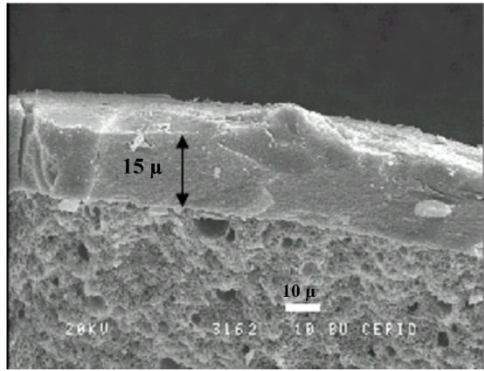


Figure 7





(a)



(b)

Figure 8

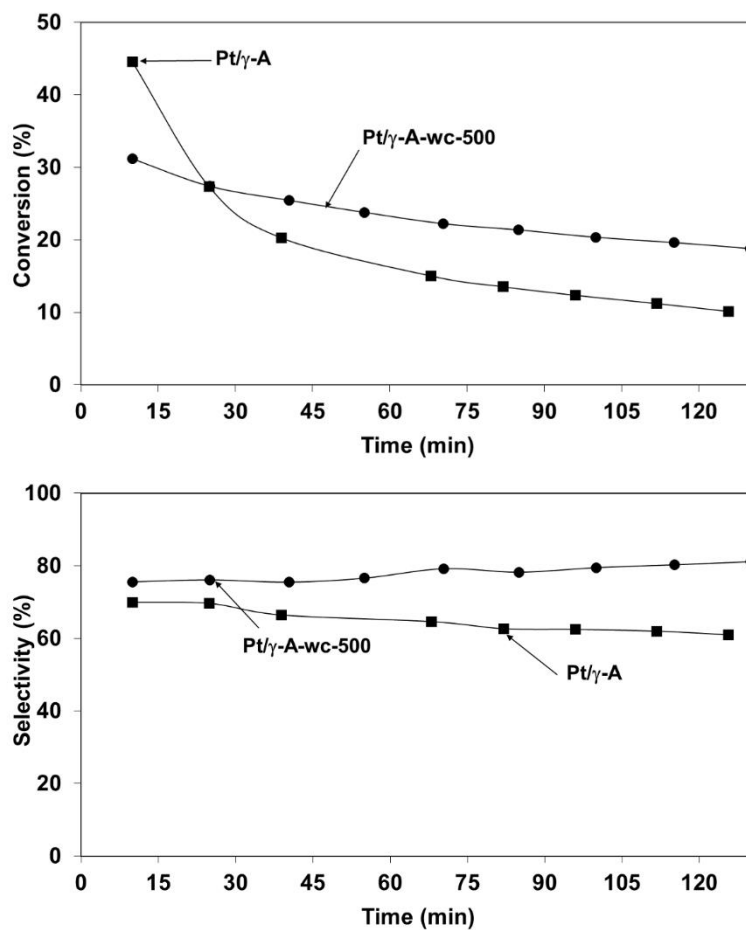


Figure 9