

Innovative Coating Method of MgAl_2O_4 or ZnAl_2O_4 on $\alpha\text{-Al}_2\text{O}_3$ Spheric Nuclei

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Structured materials composed of $\alpha\text{-Al}_2\text{O}_3$ spheres covered with a porous and thin layer of MgAl_2O_4 or ZnAl_2O_4 were obtained. The innovative coating method developed consists in the formation of a precursor gel of MgAl_2O_4 or ZnAl_2O_4 by citrate-nitrate combustion method. The alumina spheres are submerged in this gel and then submitted to a drying process in vacuum and to calcinations with N_2 and N_2/O_2 . SEM results showed that a very rough and porous layer uniformly covers the spheres. The thickness of the layer reaches the maximum value of 16 μm in the sample coated with two layers of ZnAl_2O_4 . XRD results confirmed the MgAl_2O_4 or ZnAl_2O_4 spinel formation in the layered material. The structured materials were used as Pt catalysts supports, showing a good catalytic activity in the n-butane dehydrogenation reaction.

Keywords: thin films, chemical synthesis, electron microscopy, X-ray diffraction, catalytic properties

1. Introduction

The development of new materials for petrochemical processes applications is an interesting area. The use of structured materials as catalysts supports has acquired importance in the last years due to their advantages in mass and heat transfer in fast reactions carried out at high temperatures^{1,2}, like catalytic dehydrogenations, partial hydrogenations, and others. The n-alkane dehydrogenation reactions used for the monoolefins production are very important in the petrochemical industry, since these olefins are used for the synthesis of alcohols, polymers, detergents, naphtha additives, etc. The use of supports with high surface area, low acidity and good interaction with metals is very important for n-alkanes dehydrogenation (endothermic reaction carried out at high temperatures) in order to avoid undesirable reactions like alkanes cracking and alkenes polymerization. Hence, an interesting alternative is the use of zinc and magnesium spinels as catalysts supports for dehydrogenation, which have very low acidity and good capacity to disperse and stabilize the supported metals³⁻⁵. Although there is much information about coating of labs, tubes, honeycombs, etc. with metallic oxides^{6,7}, there is practically no bibliography related with coatings of these materials on spheres^{8,9} and nothing about using MgAl_2O_4 and ZnAl_2O_4 spinels for this purpose. In this work, the method chosen for the synthesis of MgAl_2O_4 and ZnAl_2O_4 spinels was the citrate-nitrate combustion^{7,10,11}, since the precursor gel obtained by this technique presents suitable properties to achieve a good adherence to the $\alpha\text{-Al}_2\text{O}_3$ spheres.

The objective of this work is related with the production of a uniform thin layer of MgAl_2O_4 or ZnAl_2O_4 on an inert

nucleus with an adequate thickness, high specific surface area, and the proper resistance and durability under the operating conditions.

2. Experimental

For the preparation of the materials by coating, the starting material were spheres ($f = 2 \text{ mm}$) of $\alpha\text{-Al}_2\text{O}_3$ ($S_g = 4.7 \text{ m}^2\text{g}^{-1}$) provided by SASOL, $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ (Sigma-Aldrich 99%), $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ (Sigma-Aldrich 99%), $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$ (Sigma-Aldrich 99%) and citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) (Sigma-Aldrich 99%).

2.1. Pretreatment of $\alpha\text{-Al}_2\text{O}_3$ spheres

Spheres were treated at room temperature with 1 M solution of HCl for 24 h (ratio of 1.4 mL HCl g^{-1} $\alpha\text{-Al}_2\text{O}_3$) in order to develop roughness in the external surface and to improve the adherence of the coating material. Then the spheres were rinsed with distilled water until neutral pH followed by a drying step at 120 °C for 24 h.

2.2. Coating of $\alpha\text{-Al}_2\text{O}_3$ spheres with one layer of spinels by the citrate-nitrate method

The spheres (modified with HCl) were submitted to a coating process using both spinels by the following method:

a) Preparation of the spinel precursor solution: **MgAl_2O_4** : A solution of aluminium nitrate nonahydrate, magnesium nitrate hexahydrate and citric acid monohydrate (with Al/Mg molar ratio = 2, and citric acid/nitrate ions molar ratio equal to 0.5) was prepared. The final concentrations of the solutions were 0.42 M ($\text{Al}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$), 0.21 M ($\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$) and 0.84 M ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$). The ratio between the volume

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of the spinel precursor solution and the support weight was 60 mL/g, this being enough to cover the spheres placed in the baker. The spheres were submerged (with soft stirring) in the prepared solution, which was heated and maintained under boiling during 30 minutes forming the gel. ZnAl_2O_4 : The previous process was repeated using zinc nitrate hexahydrate instead of magnesium nitrate hexahydrate.

b) The obtained gel (with the submerged spheres) was dried for 1 h at 75 °C in vacuum furnace and then, the temperature was risen to 100 °C and maintained during 24 h.

c) The dried gel with spheres was calcined in three steps: i) Nitrogen: heating in N_2 flow (100 mLmin⁻¹) up to 300 °C with a heating rate of 2 °C min⁻¹, then the heating was continued up to 500 °C with a heating rate of 5 °Cmin⁻¹, and keeping at 500 °C during 2 h. ii) Mixture of nitrogen and oxygen (5 v/v % $\text{O}_2\text{-N}_2$): heating from 500 °C up to 700 °C (heating rate of 5 °Cmin⁻¹) in gas mixture flow (100 mLmin⁻¹) and keeping at 700 °C during 2 h, iii) Air: two different conditions were used: 1) at 700 °C in air flow (100 mLmin⁻¹) during 2 h, or 2) heating from 700 °C up to 800 °C in air flow (100 mLmin⁻¹) and keeping at 800 °C during 3 h.

Figure 1 shows the scheme of synthesis of the structured materials.

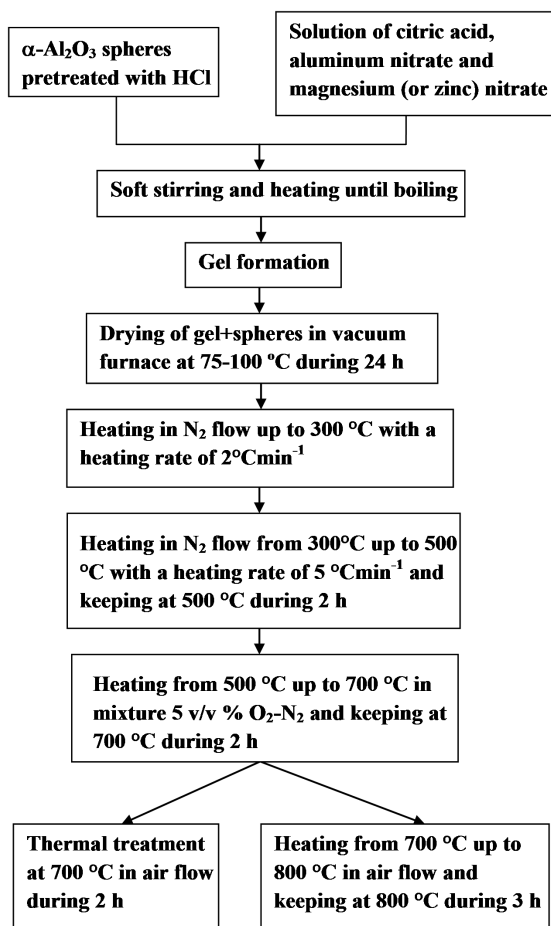


Figure 1. Scheme of synthesis of the structured materials.

2.3. Coating of $\alpha\text{-Al}_2\text{O}_3$ spheres with two layers of spinels by the citrate-nitrate method

The process described in the previous item was repeated two times for coating spheres with two layers of MgAl_2O_4 (or ZnAl_2O_4).

2.4. Characterization of structured materials

In order to determine the thickness and uniformity of the layer deposited on spheres by the coating processes, scanning electronic microscope (SEM) (with a JSM-35C, JEOL model, equipped with SemAfore digital image acquisition system) was used. The observations were carried out under the way of images of secondary electrons using an acceleration voltage of 20 kV. The samples were adhered with silver paint on metallic slides and coated by sputtering with a thin layer of gold to give them the required conductivity before the observation.

The composition of the layer materials was analyzed by X-ray diffraction experiments performed at room temperature in a Shimadzu model XD3A instrument using $\text{CuK}\alpha$ radiation ($\lambda=1,542\text{\AA}$), generated at 30 kV and a current of 30 mA.

The layer adherence of the coated spheres was tested. To obtain this parameter, the coated spheres were immersed in distilled water and a further treatment in ultrasonic equipment (Ultrasonic cleaner Cleanson 200 w) during 20 minutes was carried out. Then the spheres were dried in furnace during 24 h and its weight was determined in order to establish the weight loss. The Formula 1 for the calculus of the weight loss was:

$$\% \text{ Loss weight} = \frac{\text{spheres weight} - \text{spheres weight (after ultrasonic test)}}{\text{spheres weight}} \times 100 \quad (1)$$

2.5. Preparation of Pt catalysts and characterization

The coated spheres were used as catalytic supports. The catalysts were prepared by an excess-solution impregnation method. They were impregnated with a solution of chloroplatinic acid during 6 h at room temperature in order to obtain a catalyst with 0.3 wt % Pt. The ratio between the volume of the chloroplatinic acid solution and the support weight was 1.4 mLg⁻¹. The Pt concentration in the impregnating solution was 2.14 g L⁻¹. Then they were dried in a furnace at 100 °C and calcined during 3 h at 500 °C.

The Pt structured catalysts (coated spheres) were tested in the n-butane dehydrogenation reaction, carried out in a quartz continuous flow reactor at 530 °C for 2 h. The reactor (with a catalyst weight of 0.200 g) was fed with 18 mL min⁻¹ of the reactive mixture (n-butane + hydrogen, $\text{H}_2/\text{n-C}_4\text{H}_{10}$ molar ratio = 1.25). Before reaction, the catalysts were reduced "in situ" at 530 °C under flowing H_2 for 3 h. The reactor effluent was analyzed in a GC-FID equipment with a packed column (1/8" × 6 m, 20 wt% BMEA on Chromosorb P-AW 60/80), which was kept at 50 °C during the analysis. With this analytical device, the amounts of methane, ethane, ethylene, propane, propylene, n-butane, 1-butene, cis-2-butene, trans-2-butene and 1,3 butadiene were measured. The n-butane conversion was calculated as the sum of the percentages of the chromatographic areas of all the reaction products (except H_2) corrected by the

corresponding response factor. The selectivity to the different reaction products (i) was defined as the ratio: mol of product i/Σ moles of all products (except H_2).

In order to determine the Pt dispersion of the catalysts, measurements of hydrogen chemisorption were carried out. The experiments were performed in a volumetric equipment. The sample weight used was 300-500 mg. The sample was outgassed at room temperature, heated under flowing H_2 (60 mL min^{-1}) from room temperature up to $500\text{ }^\circ\text{C}$, and then kept at this temperature for 2 h. Then, the sample was outgassed under vacuum (10^{-4} Torr) for 2 h. After the sample was cooled down to room temperature ($25\text{ }^\circ\text{C}$), hydrogen dosage was performed in the range of 25-100 Torr. The isotherms were linear in the range of used pressures. The chemisorbed hydrogen was calculated by extrapolation of the isotherm to pressure zero. From the data of chemisorbed H_2 , the metallic dispersion in monometallic catalysts was calculated by using the Formula 2:

$$D = \frac{n_H \cdot X \cdot MM_{Pt}}{W_{cat} \cdot C_{Pt}} \quad (2)$$

n_H = moles of chemisorbed H_2

X = stoichiometry of chemisorbed H_2 on Pt

MM_{Pt} = Molar mass of Pt

W_{cat} = catalyst weight

C_{Pt} = Pt content (wt %)

3. Results and Discussion

Table 1 shows results about the increase of weight and thickness of the layers deposited on coated spheres. It is observed that the coating process produced an increase of weight up to 16%. The highest increase of weight values was presented by coating with two layers of $ZnAl_2O_4$. The increase of weight correlates well with the layer thickness (measured by SEM). The $MgAl_2O_4$ or $ZnAl_2O_4$ layers deposited on spheres by coating process described are shown in Figures 2 to 6. Figure 2 displays SEM microphotographs of one sphere coated with one layer of $MgAl_2O_4$, and a coated sphere of uniform aspect can be observed. As the magnification increases (Figures 2b, 2c and 2d), a highly rough and slightly fragmented layer adhered to the sphere surface can be appreciated. The observed fragments have 2 to $5\text{ }\mu\text{m}$ (Figure 2d). In conclusion, with this coating method, a very rough and porous layer covering uniformly the sphere is obtained.

Table 1. Increase of weight and thickness of layers in structured materials prepared by coating with $MgAl_2O_4$ or $ZnAl_2O_4$.

	Increase of weight (%)	Thickness of layer (μm)
$\alpha\text{-Al}_2\text{O}_3$ spheres coated $MgAl_2O_4$ one layer	6.8	2
$\alpha\text{-Al}_2\text{O}_3$ spheres coated $MgAl_2O_4$ two layers	9.4	5
$\alpha\text{-Al}_2\text{O}_3$ spheres coated $ZnAl_2O_4$ one layer	11.1	10
$\alpha\text{-Al}_2\text{O}_3$ spheres coated $ZnAl_2O_4$ two layers	15.9	14

Figure 3a displays a transverse section of the sphere coated with one layer of $MgAl_2O_4$. A magnification of this section is observed in Figure 3b. This microphotograph shows that the layer on the sphere presents a thickness of about $2\text{ }\mu\text{m}$.

Spheres and transverse section of spheres coated with one layer of $ZnAl_2O_4$ are displayed in Figure 4. It is observed that with $ZnAl_2O_4$, a very rough and porous layer is also formed. As Figure 4c shows, the thickness of the layer is about $10\text{ }\mu\text{m}$.

In order to achieve a higher thickness of the spinel layer deposited on the spheres, a modification of the original method was carried out, by adding one more layer of spinel (see experimental section). The SEM microphotographs of spheres with two layers of magnesium spinel are shown in Figure 5, where it is observed that the thickness of the layer increases up to $5\text{ }\mu\text{m}$.

The SEM microphotographs of spheres with two layers of $ZnAl_2O_4$ are shown in Figure 6. In Figure 6c, a layer with a thickness of about $14\text{ }\mu\text{m}$ is observed. In conclusion, for both spinels with the modified method (two layers), an increase of the thickness of the layer deposited on the spheres could be achieved.

In order to determine if the spinel ($MgAl_2O_4$ or $ZnAl_2O_4$) are formed in the deposited layers, X-ray diffraction analysis were carried out by using powders coming from the gel with the spheres calcination step (see experimental section item 2.2), and the results are displayed in Figures 7 and 8. The diffractogram of the powder calcined at $800\text{ }^\circ\text{C}$ (Figure 7b) shows the peaks corresponding to magnesium spinel, but in Figure 7a (calcination step at $700\text{ }^\circ\text{C}$), the peaks corresponding to $MgAl_2O_4$ ($2\theta = 59^\circ$ and 30.6°) are not observed. This fact indicates that it is necessary to calcine the sample at $800\text{ }^\circ\text{C}$ in order to complete the formation of the magnesium spinel.

Figure 8 b shows the diffraction peaks corresponding to zinc spinel, but peaks corresponding to ZnO can also be observed. The diffractogram corresponding to the sample calcined at $700\text{ }^\circ\text{C}$ (Figura 8a) also displays the characteristic peaks of $ZnAl_2O_4$ and ZnO , however ZnO peaks present a higher intensity than the observed for the sample calcined at $800\text{ }^\circ\text{C}$. This residual zinc oxide in the layer could affect the behavior of these materials when using as catalytic support. In conclusion, XRD results indicate that a calcination step up to $800\text{ }^\circ\text{C}$ has to be used.

The layer adherence test carried out with the four samples (Table 1), showed a weight loss lower than 0.5% of the total mass in all cases. These results indicate both a high stability and a good adherence of the layers to the spheres.

The two layers-structured materials (with both spinels) were used as supports of Pt catalysts for n-butane dehydrogenation reaction. The results of catalytic behavior of both samples for different reaction times are shown in Table 2. For the sake of comparison, the results corresponding to a Pt catalyst supported on structured material obtained by washcoating of $\gamma\text{-Al}_2\text{O}_3$ on $\alpha\text{-Al}_2\text{O}_3$ spheres⁸ were included. As Table 2 shows, Pt/ $MgAl_2O_4/\alpha\text{-Al}_2O_3$ catalyst displayed a yield to butenes along the reaction time higher than that of the Pt/ $ZnAl_2O_4/\alpha\text{-Al}_2O_3$ catalyst. Besides, the first catalyst showed similar values of yields to butenes than those of the Pt/ $\gamma\text{-Al}_2O_3\text{-wc}/\alpha\text{-Al}_2O_3$ catalyst. The values of n-butane conversion of Pt/ $MgAl_2O_4/\alpha\text{-Al}_2O_3$ and Pt/ $\gamma\text{-Al}_2O_3\text{-wc}/\alpha\text{-Al}_2O_3$ catalysts

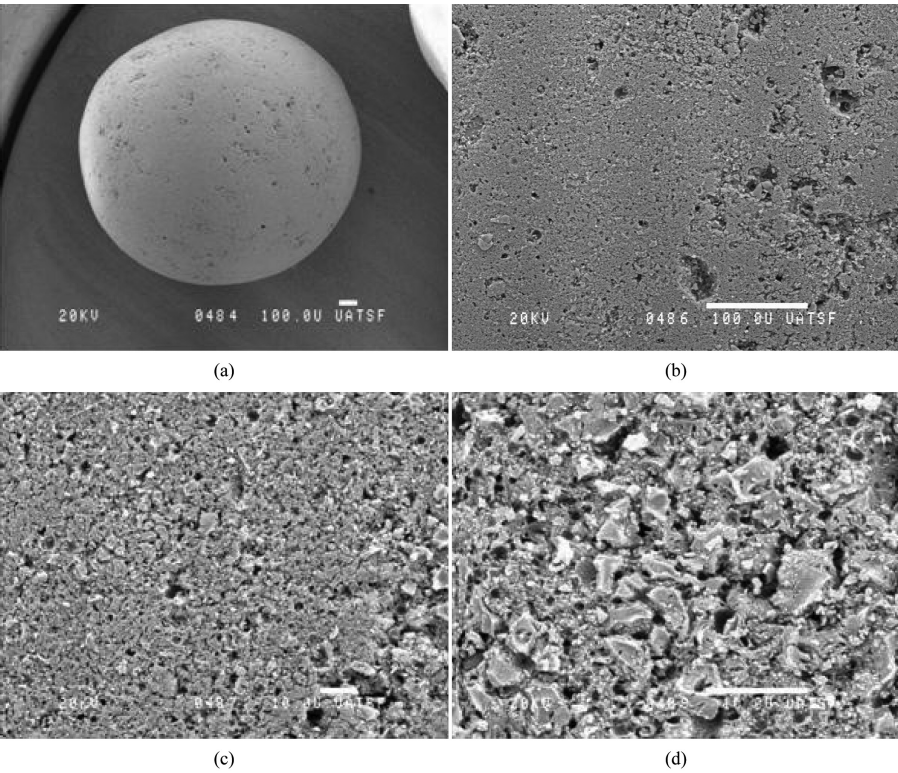


Figure 2. SEM microphotographs of $\alpha\text{-Al}_2\text{O}_3$ sphere coated with one layer of MgAl_2O_4 : a) Nominal magnification x 48, b) Nominal magnification x 300, c) Nominal magnification x 1000, d) Nominal magnification x 3000.

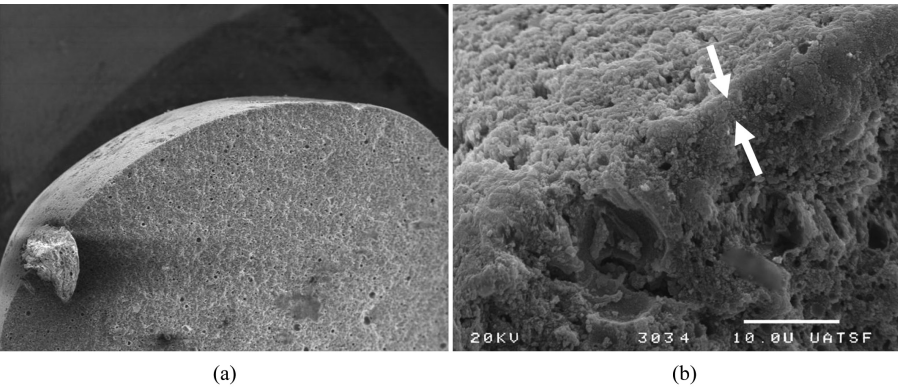


Figure 3. SEM microphotographs of transverse section of the sphere coated with one layer of MgAl_2O_4 : a) Nominal magnification x 100, b) Nominal magnification x 3000.

Table 2. Results of conversion of n-butane (C), selectivity to butenes (S) and yields to butenes (Y) at different reaction times for the Pt catalysts supported on structured materials.

	Y 10 min (%)	Y 60 min (%)	Y 120 min (%)	C 10 min (%)	C 60 min (%)	C 120 min (%)	S 10 min (%)	S 60 min (%)	S 120 min (%)
Pt/ $\text{MgAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$	16.8	15.0	14.4	30.5	24.6	21.4	55.0	62.7	67.4
Pt/ $\text{ZnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$	14.4	11.3	9.9	14.7	11.9	10.0	98.0	95.3	98.3
Pt/ $\gamma\text{-Al}_2\text{O}_3\text{-wc}/\alpha\text{-Al}_2\text{O}_3$ (*)	18.3	--	12.2	31.0	--	19.5	58.7	--	62.4

Yield = (% conversion of n-butane x % selectivity to butenes)/100. *Results extracted from the paper of Ballarini et al.⁸.

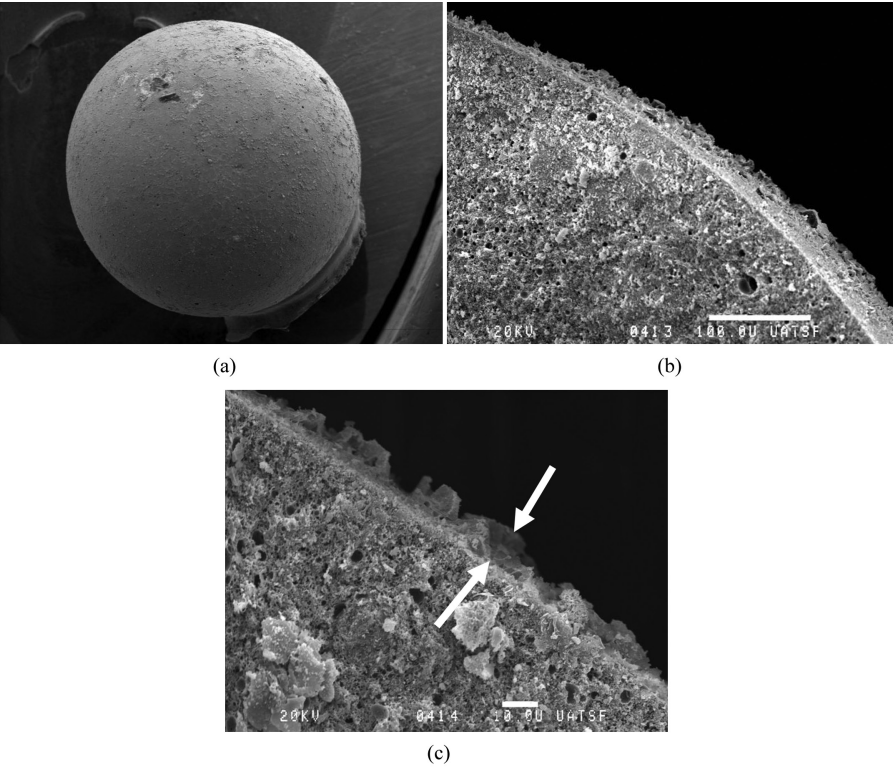


Figure 4. SEM microphotographs of α -Al₂O₃ coated spheres with one layer of ZnAl₂O₄. a) view of one sphere b) transverse section of a sphere with nominal magnification x 300, c) transverse section of a sphere with nominal magnification x 1000.

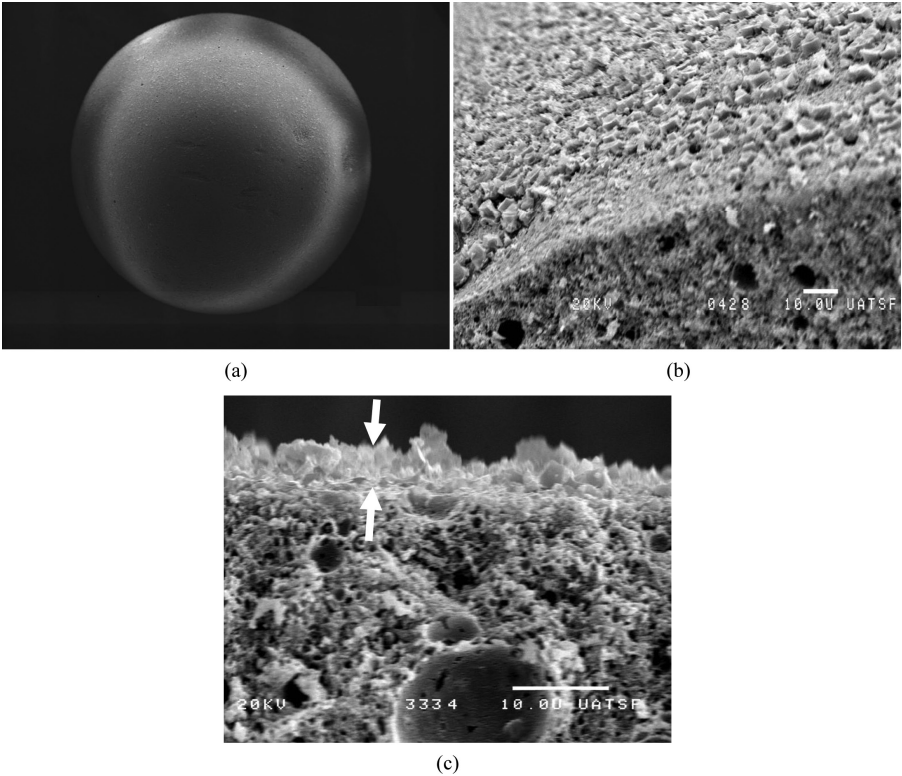


Figure 5. SEM microphotographs of α -Al₂O₃ coated spheres with two layers of MgAl₂O₄. a) view of one sphere b) transverse section of a sphere with nominal magnification x 1000, c) transverse section of a sphere with nominal magnification x 3000.

were similar and high. On the other hand, the conversion values of the $\text{Pt}/\text{ZnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst were low (Table 2). The selectivity values to butenes of $\text{Pt}/\text{ZnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst were higher than those of $\text{Pt}/\text{MgAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ and $\text{Pt}/\gamma\text{-Al}_2\text{O}_3\text{-wc}/\alpha\text{-Al}_2\text{O}_3$ catalysts. The low activity of the $\text{Pt}/\text{ZnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst could be due to ZnO residues in the layer observed by XRD results. Different authors^{12,13} found Pt-Zn alloys in $\text{Pt}/\text{ZnAl}_2\text{O}_4$ catalysts with ZnO impurities, and these alloys could cause a decrease in the catalytic activity. With respect to the high selectivity to butenes of $\text{Pt}/\text{ZnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst, it was found that the Pt particles

supported on ZnAl_2O_4 spinel have a rounded shape with very low density of steps and edges¹⁴. This structure of the metallic particles would inhibit the undesirable reactions, like hydrogenolysis, thus favouring the selectivity to butenes. Note also that the $\text{Pt}/\text{MgAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst showed good catalytic stability, since yield values decreased only 14% along the reaction time, whereas the decrease in the yield was 31% for the $\text{Pt}/\text{ZnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst and 33% for the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ one (Table 2).

Pt dispersion values obtained by hydrogen chemisorption were: 82% for the $\text{Pt}/\text{MgAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst and 46% for

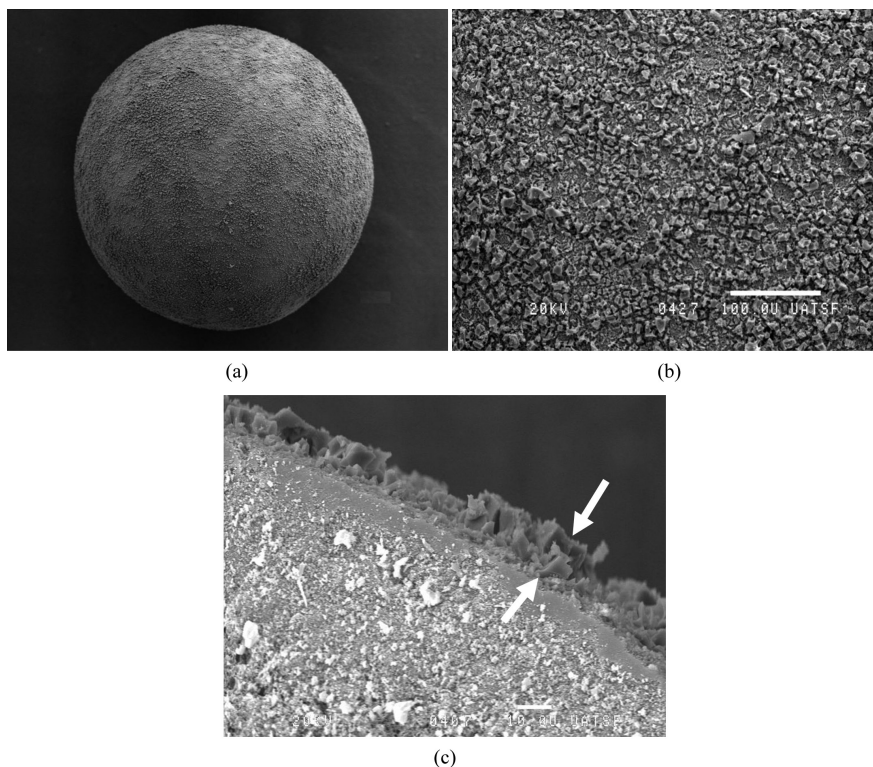


Figure 6. SEM microphotographs of $\alpha\text{-Al}_2\text{O}_3$ coated spheres with two layers of ZnAl_2O_4 : a) view of one sphere b) view of a sector of the sphere with nominal magnification $\times 300$, c) transverse section of a sphere with nominal magnification $\times 1000$.

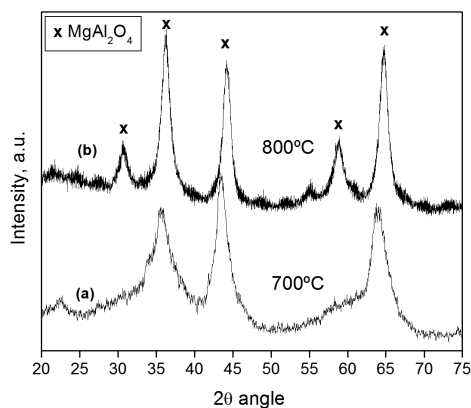


Figure 7. Diffractograms of the powders obtained by the citrate-nitrate method (MgAl_2O_4) calcined at different temperatures: a) 700 °C and b) 800 °C.

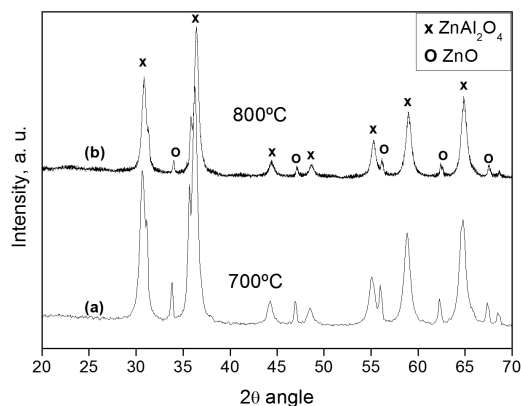


Figure 8. Diffractograms of the powders obtained by the citrate-nitrate method (ZnAl_2O_4) calcined at different temperatures: a) 700 °C and b) 800 °C.

the Pt/ZnAl₂O₄/α-Al₂O₃ one. Considering that the Pt dispersion is a measurement of the surface active sites, these results are in agreement with the higher activity of the first catalyst in the n-butane dehydrogenation reaction.

4. Conclusions

An innovative method based on the deposition of a layer of MgAl₂O₄ or ZnAl₂O₄ on spherical nuclei of α-Al₂O₃, was used for the synthesis of structured materials. A very rough and porous layer of spinel that covers uniformly the spheres was obtained. However, the method need to be

improved in order to eliminate the residual ZnO present in the ZnAl₂O₄ spinel. The deposition of the second layer of MgAl₂O₄ or ZnAl₂O₄ allows to increase the thickness of the layer on the spheres. Pt catalysts prepared using the structured supports with two spinels layers showed a good performance in the reaction of n-butane dehydrogenation, specially the Pt/MgAl₂O₄/α-Al₂O₃ catalyst which displayed both high yields to butenes and high stability along the reaction time. The catalytic results of the Pt/MgAl₂O₄/α-Al₂O₃ catalyst are comparable with those obtained for Pt catalysts deposited on commercial supports. These properties would turn them out to be very promising catalytic materials.

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