



# Selective hydrogenation by novel composite supported Pd egg-shell catalysts



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## ABSTRACT

Two organic–inorganic mixed phase supports were prepared, comprising an alumina filler and polymers of different chemical nature. Four low loaded Pd catalysts were prepared. Good activities and selectivities were obtained during the hydrogenations of styrene, 1-heptyne and 2,3-butanedione. The catalysts were found to have excellent mechanical properties and could be used in applications needing high attrition resistance and crushing strength. In this sense, processes for fine chemicals using slurry reactors or processes for commodities using long packed beds could advantageously use them.

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## 1. Introduction

In reacting systems with severe heat and mass transfer problems one solution is the use of the so-called egg-shell catalysts, in which the active phase is located on a thin layer of the pelletized catalyst. Egg-shell catalysts are widely employed in reactions of selective hydrogenation, because in this case the limitations to mass and/or heat transfer have a pronounced effect on the activity and selectivity. This catalyst design also alleviates problems of formation of gums, undesired complete saturation of reactants and generation of hot spots in the packed bed [1–10].

Manufacture of egg-shell catalysts from standard supports is not a simple process because many preparation variables must be precisely controlled [11]. However they can be easily prepared when the metal is supported over composite supports of mixed inorganic–organic phases. These have a combination of hydrophobic–hydrophilic nature and permit the regulation of the deposition and penetration of the active metal phase during the preparation of the catalysts. Also these supports have better mechanical properties in comparison to the standard supports thus making them attractive for both suspended reactor and packed bed reactor applications.

Despite the good mechanical properties of these novel composite materials there are scarce reports on their catalytic properties, particularly for selective hydrogenation reactions. It seemed therefore important to test them in the partial hydrogenation of molecules with unsaturated bonds of different reactivity and chemical nature, such as vinylic, acetylenic or carboxylic.

In this work the activity of egg-shell Pd/composite catalysts is evaluated for three different reacting systems of both academic and industrial interests: (i) selective hydrogenation of styrene to ethylbenzene; (ii) selective hydrogenation of 2,3-butanedione to 3-hydroxy-2-butanone; and (iii) selective hydrogenation of 1-heptyne to 1-heptene. Pd was chosen as the metal phase due to its good properties of hydrogenation of the chosen reactant molecules [12–15].

## 2. Experimental

### 2.1. Composite support preparation

Two different composite (organic–inorganic) supports were prepared. The inorganic phase is provided by particles of  $\gamma$ -alumina. Two different organic phases were synthesized: a) BTAL, in which the organic phase is composed of the mixture of the monomers bisphenol A glycerolate dimethacrylate (BGMA) and triethylene glycol dimethacrylate (TEG); b) UTAL, a mixture of the monomers diurethane dimethacrylate (UDMA) and TEG. Benzoyl peroxide (BPO) was added in both cases as a radical polymeric initiator. The employed technique for preparing the composite supports began with the intimate mixing of the TEG, BPO

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and UDMA or BGMA monomers in a glass flask for 30 min. Then a proportional amount of  $\gamma$ - $\text{Al}_2\text{O}_3$  powder was added to the flask and the mixture was mixed for another hour. Then the reactants were degassed and the obtained material was extruded into cylinders of 2 mm of diameter. These pellets were placed in a stove at 393 K for 1 h in order to activate the initiator that started the polymerization. Then the rigid pellets were cooled to room temperature in a desiccator and finally cut to a length of 3 mm. More details of the preparation procedure can be found elsewhere [11].

## 2.2. Pd/composite catalyst preparation

The supported metallic catalysts were prepared by means of the incipient wetness technique using an aqueous acidic solution of  $\text{PdCl}_2$  in order to obtain 0.3 and 1.2 wt.% of Pd on the final catalysts. The higher load on BTAl or UTAl was achieved by successive impregnations. The catalysts were then dried in an oven at 393 K for 24 h and put in a desiccator for further use. Before the catalytic tests the catalysts were reduced in a  $\text{H}_2$  flow at 503 K for 1 h. Catalysts were named 0.3PdBTAl, 0.3PdUTAl, 1PdBTAl and 1PdUTAl.

## 2.3. Catalyst characterization

Bulk Pd compositions of the catalysts were obtained by digesting the samples and then analyzing the liquors in a Perkin Elmer Optima 2100DV ICP equipment. CO pulse chemisorption was performed and dispersion values were obtained over reducing the samples. X-ray diffractograms were obtained in a Shimadzu XD-1 equipment, using  $\text{CuK}\alpha$  radiation. Scanning electron microscopy (SEM) measurements were performed in a JEOL JSM-35C equipment equipped with an energy dispersive X-ray analyzer. Optical micrographs (OM) were obtained with a Mitsubishi Microwatcher VS-30H Microscope and a Sony Color Video Printer. Thermogravimetric analyses (TGA) were also realized under an air flow in a TA Instruments 2950 apparatus. X-ray photoelectron spectroscopy (XPS) measurements were recorded with VG-Microtech Multilab equipment. The specific surface area ( $S_{\text{BET}}$ ) values were obtained from nitrogen physical adsorption–desorption isotherms at 77 K using a Quantochrome NOVA-1000 apparatus. Values of the axial and radial mechanical resistance of the pellets were obtained in an Instron Marks Universal Rehearsals equipment, and a compression rate of  $1 \text{ mm min}^{-1}$  was used. Attrition studies were done in accordance to ASTM D 4058 norm.

## 2.4. Activity test

The catalytic performance during hydrogenation reactions was assessed in a batch, stainless steel, stirred tank reactor, using pelletized catalysts (3 mm length and 1.2 mm diameter). The procedure followed was: the reactor was charged with the substrate solution of styrene, 1-heptyne or 2,3-butanedione. The stirring speed was maintained at 1200 rpm. Pressure, temperature, substrate concentration and catalyst mass were particular for each catalytic system. Runs were carried out in triplicates with an experimental error of 3%. Reactants and products were analyzed by gas chromatography with a FID detector and a capillary column.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 contains OM photographs (Fig. 1(a) to (d)) and SEM micrographs (from a primary detector in Fig. 1(e) and (f) and from backscattering in Fig. 1(g) to (l)) of the cross section of the reduced catalysts. In the OM photographs it can be seen that the outer section of the support is darker, indicating the presence of the Pd metal. In the SEM images (Fig. 1(e) to (j)) the topography of the surface can be seen. In images

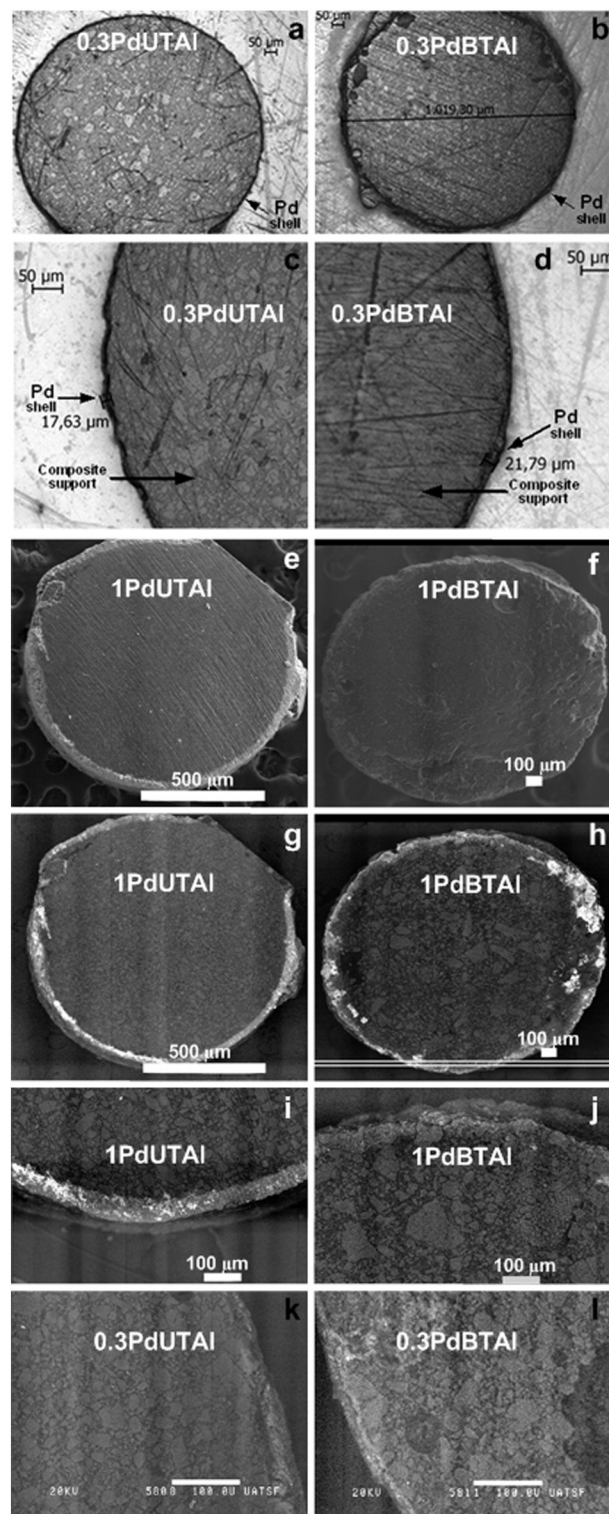


Fig. 1. Catalysts transversal section images. (d) From Ref. [15]; (h) to (j) from Ref. [11].

Fig. 1(g) to (l) the structural composition of the composite catalysts is observed. This is related to the higher electronic density of the inorganic materials, alumina and palladium, with respect to the organic polymer. In these images a lighter region on the outer surface of the support can be seen that would correspond to the region where Pd is deposited. Furthermore in the center of the pellet light color stains appear that are surrounded by structures of gray color. The stains would correspond to the  $\gamma$ -alumina particles while the gray region forms a continuous network and corresponds to the polymeric phase of the composite catalyst.

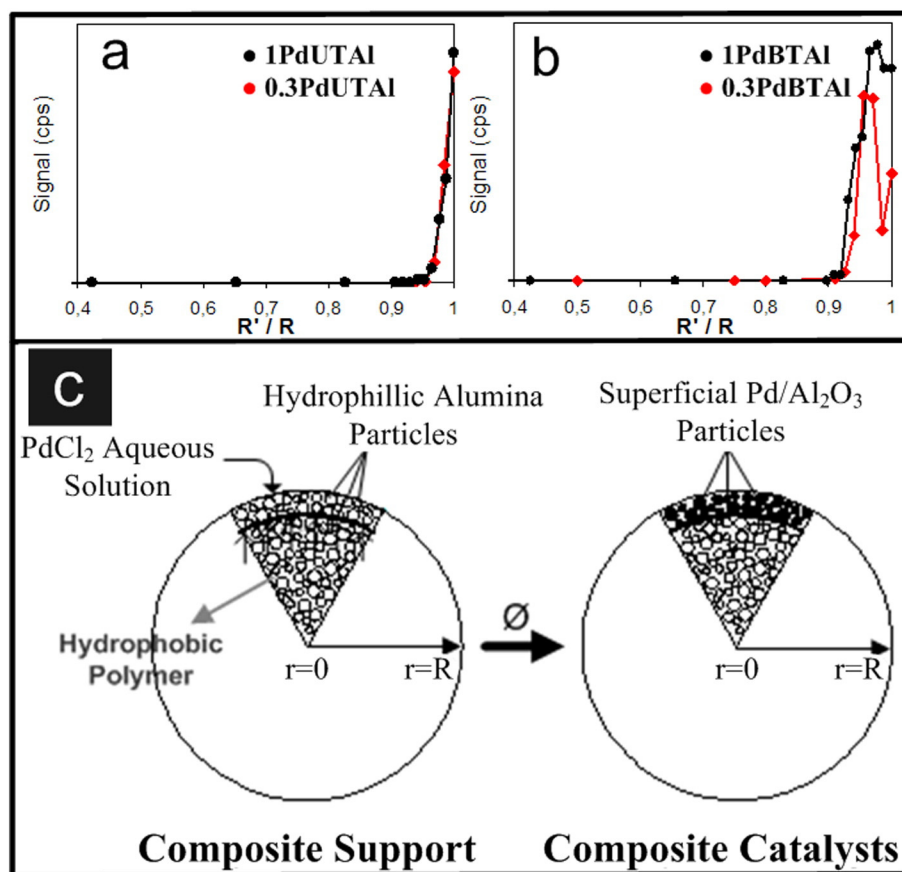


Fig. 2. a) and b) Radial metal penetration profiles. c) Graphical description of composites catalysts synthesis procedure.

This phase is obtained by radical polymerization reactions combining two monomers of functionality 4, in order to obtain a polymeric structure of high degree of crosslinking.

From the inspection of the OM and SEM images it becomes clear that the Pd metal has an egg-shell distribution in the composite catalyst pellets.

The Electron Probe Micro Analyzer (EPMA) technique was used for determining the metal penetration profile (Fig. 2(a) and (b)). Independent of the metal concentration, for the PdUTAl catalysts an egg-shell distribution is clearly seen, with an average maximum penetration of 60  $\mu\text{m}$ . For the PdBTAl catalysts the distribution has an egg-white pattern type, with an average maximum penetration of 90  $\mu\text{m}$ . The small values of thickness of the metal layer on the surface of both supports can be explained by the hydrophilic nature of the inorganic particles of Al<sub>2</sub>O<sub>3</sub>, that have an affinity for the aqueous solution that contains the Pd precursor; and by the hydrophobic nature of the polymeric

phase, that would act as a barrier for the penetration of the solution inside the support. A scheme of the process of preparation of the catalysts is included in Fig. 2(c).

XRD studies were performed using plane slabs of the composite material of  $1.5 \times 1.5$  cm and 1 mm thickness. In these samples the same corresponding amount of Pd was deposited over one of the slab faces in order to emulate the external surface of the pelletized catalysts. These slabs were also reduced in hydrogen at the same temperature of the real catalysts. The results are presented in Fig. 3(a). The obtained X-ray diffractograms of the UTAl and BTAl materials were identical and coincided with that of  $\gamma$ -alumina, not appearing any additional peaks that could be related to the organic phase. This is due to the bulk radical polymerization procedure used, which led to a highly amorphous organic phase. In the case of the Pd containing catalysts not only the peaks related to the  $\gamma$ -alumina phase were present but also a peak at  $2\theta = 39.9^\circ$

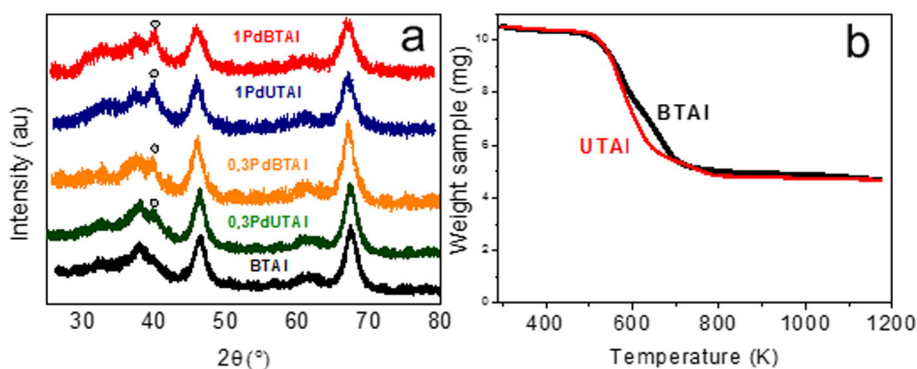


Fig. 3. a) XRD spectra of catalysts and supports. b) Thermogravimetric analysis of the composite supports.



**Table 1**

Pd catalyst loadings, dispersion values, particle size, XPS results and initial hydrogenation reaction rates.

Catalyst	Pd (wt.%)	D% (at <sub>Pd</sub> s/at <sub>Pd</sub> total)	d (nm)	XPS BE (eV) Pd 3d <sub>5/2</sub>	Cl/Pd (at/at)	r <sup>0</sup> <sub>St</sub> (n°/at <sub>Pd</sub> s min)	r <sup>0</sup> <sub>2,3-But</sub> [n°/at <sub>Pd</sub> s min]	r <sup>0</sup> <sub>Heptyne</sub> (n°/at <sub>Pd</sub> s min)
0.3PdUTAI	0.23	5	22.4	335.0 (74%) 337.0 (26%)	0.60	27.80	0.07	2.13
0.3PdBTAl	0.26	3	37.3	335.6 (76%) 336.6 (24%)	0.84	36.40	0.66	3.54
1PdUTAI	1.00	7	16.0	335.0 (89%) 337.0 (11%)	0.20	7.13	0.05	–
1PdBTAl	1.10	4	28.0	335.2 (75%) 336.7 (25%)	0.68	13.80	0.13	–

corresponding to the metal phase Pd(111). The peak is more intense in the catalysts with a higher Pd load.

The TGA results of the composite supports UTAI and BTAl (see Fig. 3(b)) show that at 513 K the decomposition of the organic phase is accelerated and at about 700 K a plateau is reached that coincides with the weight of the inorganic material. These studies indicate that there exist temperature limitations for the use of the composite supports. However many catalytic industrial processes are undertaken at temperatures lower than 513 K, particularly many of selective hydrogenation.

Table 1 contains values of Pd loading as obtained by ICP, dispersion values (D) as obtained by CO chemisorption, particle sizes (d), values of Pd 3d<sub>5/2</sub> binding energies and Cl/Pd superficial atomic ratios as obtained by XPS and initial hydrogenation reaction rates from the catalytic tests.

Particle sizes were calculated from measured dispersion values by assuming a spherical shape. These particle sizes are similar to those obtained by other authors with catalysts with 1% Pd supported on silica, resins or carbonaceous materials and prepared by incipient wetness impregnation [16–18].

On the other hand, very low S<sub>BET</sub> was obtained for the 1PdUTAI y 1PdBTAl catalysts, 0.62 and 1.13 m<sup>2</sup> g<sup>−1</sup>, respectively. Considering the high specific surface area of the alumina filler, 220 m<sup>2</sup> g<sup>−1</sup>, the low resulting final area of the composites points to an encapsulation of most alumina particles by the polymeric phase. This is a consequence of the polymerization technique used for preparing the organic phase.

Fig. 4 shows the XPS spectra of the reduced catalysts. The binding energy (BE) values corresponding to the Pd 3d<sub>5/2</sub> peak are included in Table 1. These values take the Al 2p 74.4 eV as the reference.

In all catalysts two different species were detected. The PdUTAI catalysts had a peak with a BE of 335.0 eV, attributed to Pd<sup>0</sup>, while the PdBTAl catalysts present peaks at BE of 335.6 eV (0.3PdBTAl) and 335.2 eV (1PdBTAl), attributed to Pd<sup>δ+</sup> electrodeficient Pd species [15]. All catalysts had a second signal with BE values between 336.6 and 337.0 eV that would correspond to Pd<sup>n+</sup> species (δ<sup>+</sup> < η<sup>+</sup> < 2), possibly related to the presence of non-reduced Pd oxychloride species. These would be non-reduced Pd atoms stabilized by adjacent Cl atoms not eliminated during the thermal treatments [19].

Table 2 shows the results obtained in the mechanical tests of the UTAI and BTAl supports and other commercial supports [11]. SD and SL are the diametral and longitudinal resistance to compression. It can be seen that the values of SD and SL and the values of attrition resistance are much higher for the composite supports than for the commercial supports. Best values are those obtained with the UTAI composite support.

### 3.2. Activity tests

Fig. 5 shows the results of the catalytic tests of selective hydrogenation of different reactants.

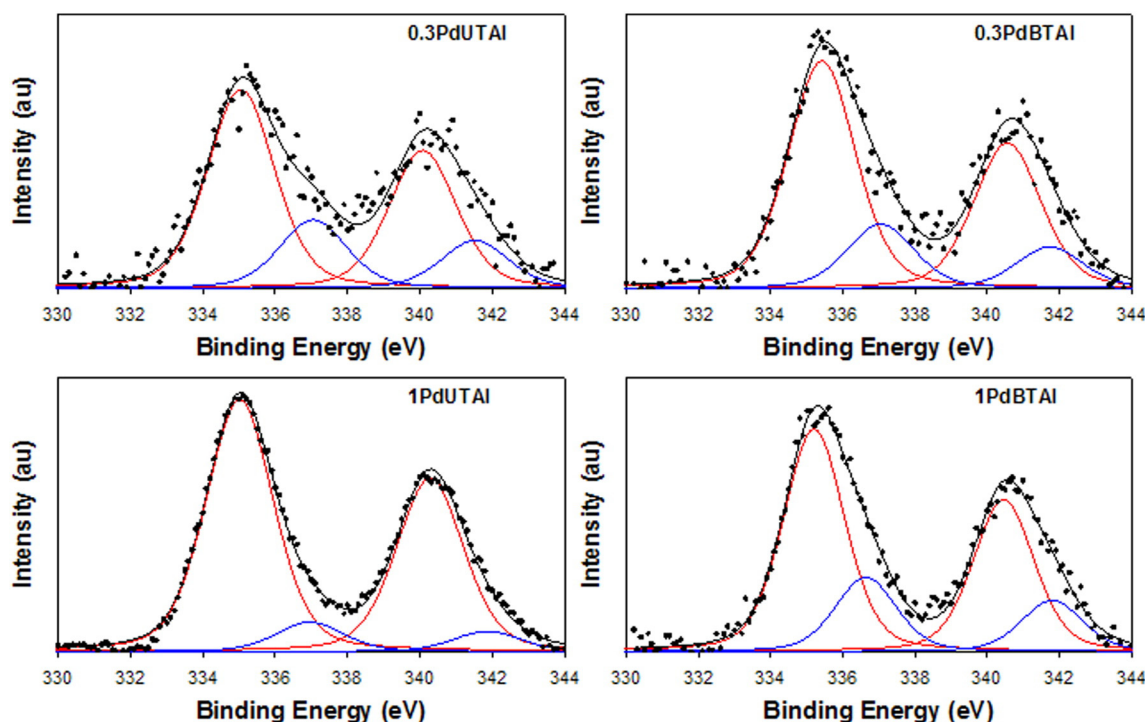


Fig. 4. XPS spectra of the reduced catalysts.

**Table 2**  
Supports mechanical properties.

Support	SD <sup>a</sup> (kg/cm <sup>2</sup> )	SL <sup>a</sup> (kg/cm <sup>2</sup> )	Attrition loss (%) 1800 turns	Attrition loss (%) 1800 turns
Carbon RX3	<100	217 ± 101	1.659	6.859
γ-Al <sub>2</sub> O <sub>3</sub>	<100	703 ± 199	0.167	3.103
α-Al <sub>2</sub> O <sub>3</sub>	282 ± 43	2053 ± 398	1.124	6.002
UTAI	392 ± 57	4708 ± 690	0.028	0.136
BTAI	348 ± 41	3741 ± 900	0.046	0.189

<sup>a</sup> From Badano et al. 2010 [11].

At the reaction conditions used, irrespective of the chemical nature of the organic phase of the composite support, global selectivities to the desired products in excess of 98% were obtained. The desired reactions were the hydrogenation of styrene to ethylbenzene and the hydrogenation of 2,3-butanedione to 3-hydroxy-2-propanone (Fig. 5(a) and (b)). The hydrogenation reaction of styrene to ethylbenzene is used as a reference for the performance of the catalysts for the stabilization of pyrolysis gasoline. Many of them are based on supported Pd due to the good properties of this metal [12]. Pd is also the best noble metal in terms of selectivity for the partial hydrogenation of diketones [13].

Besides the reaction of hydrogenation of 1-heptyne, as seen in Fig. 5(c) and (d), behaved as a consecutive reaction of the type  $A \rightarrow B \rightarrow C$ , where the main product of the first step is 1-heptene. Once the main reactant is depleted, in a second step the hydrogenation of 1-heptene to n-heptane occurs. In both catalysts the selectivity to 1-heptene remained at values of 90–93% until the maximum concentration of the alkene was achieved. The values of initial activity were included in Table 1.

The PdBTAl catalysts have a higher activity than the PdUTAl ones, the effect being more evident in the catalysts with a lower noble metal charge. The difference can be related to the presence of electrodeficient Pd<sup>δ+</sup> species with  $\delta \approx 0$ . In other types of reactions a promoting effect has been attributed to the presence of Pd<sup>n+</sup> species [20].

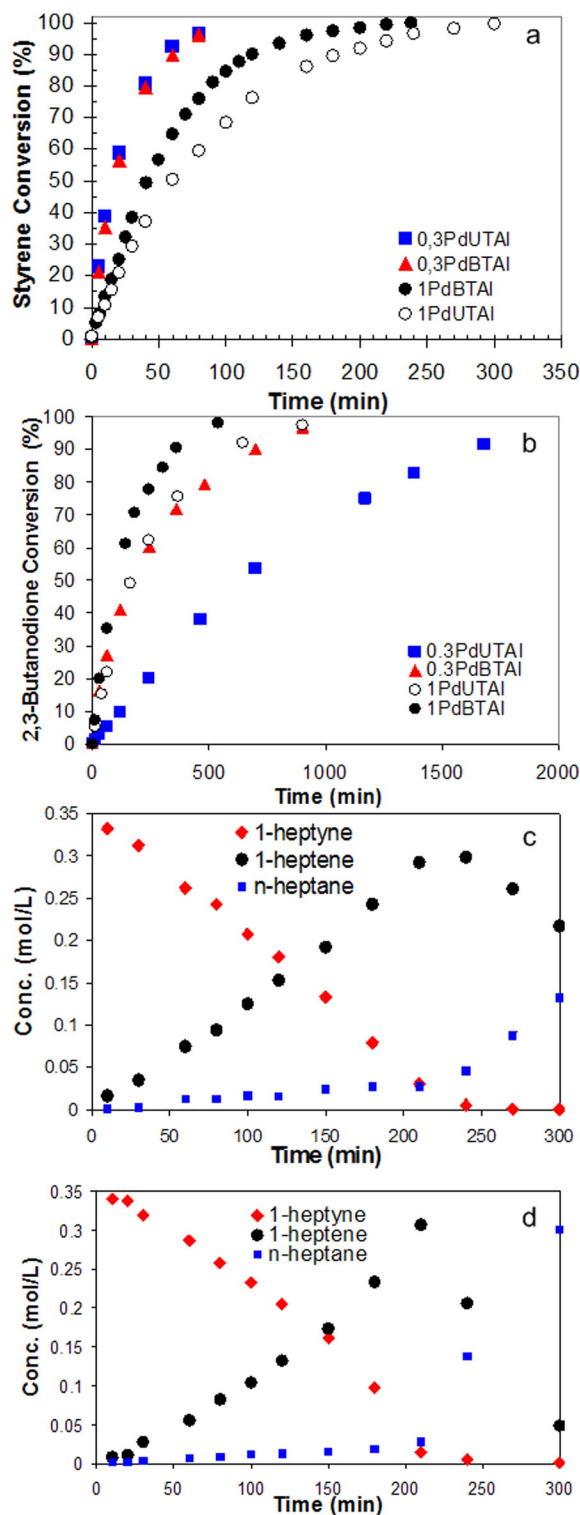
Additional experiments regarding the reusability were made with the 0.3PdBTAl and 0.3PdUTAl catalysts in a series of three consecutive reactions of styrene hydrogenation. The results showed negligible differences in the initial and final conversion, and ICP analysis demonstrated that there was no leaching of the Pd active phase. This points to the high reusability of this kind of novel catalysts.

#### 4. Conclusions

Two composite supports of mixed organic–inorganic nature were synthesized. The inorganic phase is provided by γ-Al<sub>2</sub>O<sub>3</sub> particles and the organic phase by polymers obtained by the combination of two monomers of acrylic base with functionality 4. These new materials proved to have good mechanical properties both to diametral and axial compression as well as attrition resistance, displaying values superior to common commercial supports.

The pelletized egg-shell catalysts were active and highly selective to the desired products in the reactions tested, that were of the  $A \rightarrow B \rightarrow C$  consecutive type. A high concentration to the B intermediate (ethylbenzene, 3-hydroxy-2-butanone or 1-heptene) was obtained in all cases. This pattern was attributed to the low contact time of the reactants and products with the metal phase and to the better heat dissipation from the catalyst surface. The latter would prevent the overheating over the active sites and the formation of undesired by-products. These properties would be related to the small thickness of the metal layer on the outer surface of the catalysts, as indicated by the OM, SEM, EPMA and XPS characterization data.

The highest activity is obtained with the BTAl based catalysts. This could be due to the different electronic state of the metal on these supports. According to the XPS results over BTAl the metal was mainly present as Pd<sup>δ+</sup> while on UTAl it was found as Pd<sup>0</sup>.



**Fig. 5.** Catalytic evaluation results: a) styrene hydrogenation [toluene solvent,  $C^0_{\text{styrene}} = 0.445$  M, 2.0 MPa, 353 K,  $W_{\text{cat}} = 0.3$  g (1 wt.% Pd) or 2 g (0.3 wt.% Pd)]; b) 2,3-butanedione hydrogenation [isopropyl alcohol solvent,  $C^0_{2,3\text{-butanedione}} = 0.057$  M, 4.0 MPa, 368 K,  $W_{\text{cat}} = 2$  g]; and c) 0.3PdBTAl and d) 0.3PdUTAl 1-heptyne hydrogenation [toluene solvent,  $C^0_{1\text{-heptyne}} = 0.350$  M, 0.15 MPa, 303 K,  $W_{\text{cat}} = 0.75$  g].

The results of mechanical resistance and catalytic activity show that these inorganic–organic composites show promise as supports of noble metals for selective hydrogenation reactions. Particularly they enable the synthesis of egg-shell catalysts in a simple way due to the preferential deposition of the metal on the outer layer during impregnation. These catalysts could be advantageously used in slurry reactors and

packed bed reactors for the synthesis of both fine chemicals and commodities.

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