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New Strategies for Obtaining Inorganic-Organic Composite Catalysts for Selective Hydrogenation

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Additional information is available at the end of the chapter

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Abstract

Pd/composites are catalysts in which the catalytically active metal phase is located in a small layer on the support surface. The metal distribution obtained on these supports corresponds to a structure commonly known as “egg-shell”. This distribution is optimal for reactions that have heat or mass transfer resistances. The small thickness of the metal layer is mainly attributed to the use of support pellets of mixed organic–inorganic composition, the special interaction between the hydrophobic–hydrophilic support surface and the metal species (Pd or Pt) present in the impregnating aqueous solution. Pd/composite catalysts are active and selective for the reactions of selective hydrogenation of styrene, 1-heptyne, 3-hexyne and 2,3-butanone, and enantioselective hydrogenation of ethyl pyruvate. These reactions are of interest in both academic and industrial aspects.

Keywords: composite catalyst, inorganic–organic supports, selective hydrogenation, improved mechanical resistance, egg-shell catalysts

1. Introduction

Industrial selective hydrogenation processes mostly make use of solid catalysts and three-phase reactors (slurry or packed bed). Most catalysts are of the supported metal kind, and the metal carriers are either completely inorganic (e.g., alumina, titania, silica) or organic (e.g., resins, activated carbons).

Nowadays, a great variety of materials are being used as support, such as alumina, mordenite, silica, titania, magnesia, zeolites, refractory metal oxides of groups III, IV, V, VI, VIII, activated carbons, and polymers.

The preparation of the support is an important step in the manufacture of commercial catalysts. The size and shape of the supports are determined by the kind of reactor and the set of reaction conditions [1].

Supported metal catalysts for industrial reactors are preferably available in the physical form of cylinders, tablets, spheres, rings, fibers, cloths, etc. The form of the support in the catalyst preparation step is important since it is closely related to the structure of the final catalyst.

At the time of choosing a catalyst, its mechanical properties cannot be disregarded. Catalysts are generally placed inside the packed beds, commonly 10 m or more in height. This arrangement makes the bottom pellets support the weight of the bed above and thus need a high crushing resistance [1]. If the resistance is not high enough, the pellets get broken and smaller particles and dust are generated. As a result the pressure drop in the packed bed gradually increases until the bed is plugged; the unit must then be shut down for maintenance. Thus, the smallest particles of catalyst could be eluted from reactor with solvents and reaction products. This leads to an activity loss and a decrease of catalyst life.

In the preparation of the inorganic carriers employed in the fabrication of supported metal catalysts, the support is first obtained in the form of a powder or tiny particles, which are mixed with water and/or organic compounds. The mixture is then extruded, granulated, or pelletized to give it the final shape [1, 2]. Once the material has the desired shape, it is dried at temperatures between 353 and 673 K for one or more hours. Then, depending on its nature and final use, the support is calcined at higher temperatures to give mechanical resistance [1–9]. This procedure is long and energy consuming. However, the preparation of organic materials is energetically less costly.

Carbons and polymers are commonly used among the organic supports. Carbons are obtained by controlled combustion in oxygen-poor atmosphere and the final product can be surface treated to modify its catalytic properties. When carbon particles of a certain shape and size are needed, the carbon material must be agglomerated. Polymeric supports are mainly obtained by reactions in emulsions and suspensions. Carbons and polymeric supports have the common disadvantage of low mechanical resistance.

Among the supported metal catalysts we prefer the catalysts with metal “profile” that comprise an inert support and a metal phase of specially tailored distribution. Depending on this distribution catalysts are classified as “egg-yolk,” “egg-white,” or “egg-shell”. They are usually available in the form of rings, spheres, tablets, or pellets [10].

Metal-supported catalysts of the egg-shell type are mainly used in heterogeneous catalytic reactions in which the mass or heat transfer limitations have an important effect on the activity and selectivity to the desired products. They also tend to prevent or minimize the deactivation phenomena. Their main advantages are low mass transfer resistance, support-independent pore structure, and high heat transfer rate at the catalyst surface [2].

It is known that a uniform access of reactants to active sites is important for getting high activity and selectivity in chemical processes [11]. For example, consecutive reactions of the form $A \rightarrow B \rightarrow C$ in which product C should be suppressed or minimized are of great industrial interest. Due to the interaction of intraparticle diffusion and reaction, the occurrence of C can be minimized in catalysts where the active sites are preferentially located on a surface layer [11–13].

Egg-shell catalysts are used with great benefits in reactions of selective hydrogenation [14–16], Fischer-Tropsch synthesis [17], methane reforming [18, 19], partial oxidation of methane [20], etc.

It is also known that diffusional restrictions decrease the chemical reaction rate and negatively affect the selectivity to the desired products. These phenomena are mainly enhanced in processes using pelletized catalysts in packed beds, such as Fischer-Tropsch synthesis [17] or selective hydrogenation reactions [14–16]. In these reactions the maximum yields and selectivities are obtained with egg-shell catalysts in which the active phase is located on the external surface of the pellet, where the thickness of the active phase plays an important role [17].

Making egg-shell catalysts with common supports is not a simple process because there are many preparation variables that have to be carefully controlled: pH and viscosity of the impregnating solution, concentration of the metal salts in solution, time of contact of the impregnating solution with the support, temperature during impregnation, drying temperature, and calcination temperature. Other complexities arise from the phenomena involved in the grafting of the active phase, the variable nature of the impregnating solution (aqueous, organic, mixed phases), etc. [12, 13, 17, 20–30].

The field of materials science has grown significantly in the past few decades. This growth has been partly due to the development of complex composite materials that combine different properties of the individual components, sometimes with convenient synergism of physical and chemical features, thus leading to materials with unique properties. Composite-based catalysts can have enhanced mechanical resistance, selective adsorption properties, and unique selectivity for regio, stereo, or enantio hydrogenation reactions, etc.

Composite supports using organic (polymer) and inorganic components are of special interest for modern chemistry and material science because of their potential use in photochemistry, nanoelectronics, optics, and catalysis. This chapter focuses on composite supports for heterogeneous catalysts. In these supports the inorganic phase can be supplied by metal oxide or metal particles or their mixture. The organic phase is supplied by polymers of different chemical nature, with chosen surface functional groups available for acting as active sites for adsorption and catalysis.

Synthesis and use of metal catalysts supported over functional polymers or their mixture with other inorganic materials are the areas of focus. Organometallic or metal complex catalysts are not included in this work, though they can be mentioned for the sake of discussion when reviewing the chemistry of the active sites.

Two main advantages of functional polymers when used as supports of metal particles with catalytic properties are described below:

1. Metal supported particles with controlled size and distribution can be synthesized. Particle size may range from a few nanometers to hundreds of nanometers.
2. Chemical performance advantages of the catalyst can be improved because of an intimate interaction between the metal particle and the different functional groups of the polymer. The used polymers can be either soluble or insoluble in the reaction medium. The focus here is on insoluble polymers, involving a bundle of physically and/or chemically cross-linked polymer chains in which the metal nanoparticles are embedded.

Pd/composite catalysts with egg-shell structure can be easily obtained because the hydrophilic-hydrophobic action of the support regulates the penetration of the metal (active phase). The good mechanical properties of these materials give them an advantage over traditional supports where their use is intended for packed bed or basket reactors.

To evaluate the properties of the metal/composite egg-shell catalysts, the test reactions of selective hydrogenation of styrene to ethylbenzene, 1-heptyne to 1-heptene, 3-hexyne to 3-hexene, 2,3-butanodione to 3-hydroxy-2-butanone and ethyl piruvate to (R)-ethyl lactate are used.

2. Preparation of composite supports and catalysts

2.1. Preparation of composite supports

A brief summary is presented about the preparation and use of different organic-inorganic supports and catalysts. The materials are divided into three classes and each one is studied separately:

- A. Metals supported over functional polymers
- B. Metals supported over inorganic materials
- C. Metals supported over new inorganic-organic composite materials

2.1.1. Metals supported over functional polymers

The different strategies of synthesis of these metal/polymer catalysts are shown in **Figure 1**.

For the preparation of these catalysts, the organic support is commonly prepared from acrylic or vinylic monomers. Polymerization cross-linking is adjusted by the use of additives, with a minimum value for preventing the dissolution in the solvents used in the subsequent reactions. Metals with catalytic properties are placed over these supports. Oxidized metal precursors are reduced to the metal state with the help of reducing chemical agents in solution or by the use of molecular hydrogen. For these kind of supports styrene and divinylbenzene N,N-dimethylacrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid, 4-vinylpyridine, glycidyl methacrylate ethylene glycol dimethacrylate, etc. are the monomers of choice.

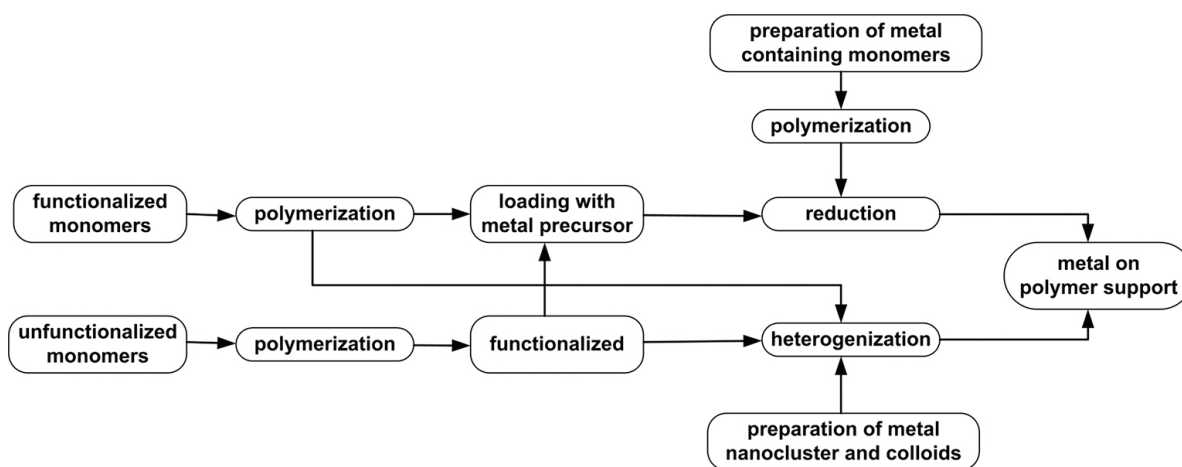


Figure 1. Routes for the preparation of metal catalysts supported on functional polymers.

2.1.2. Metals supported over inorganic materials

Here a functionalized polymer is used. This is generally soluble or slightly soluble in organic or aqueous solvents. Organometallic compounds or metal particles are grafted over the polymer matrix. These compounds act as metal active sites. Once the metal is firmly supported on the polymer surface, particles of this polymer are deposited over inorganic supports.

2.1.3. Metals supported over new inorganic-organic composite materials

Lately our research group developed new composite organic-inorganic supports in which the organic phase is made out of polymers of functionality 4. In these composites the polymeric phase has a high cross-linking degree and the inorganic phase is supplied by particulated metal oxides. The method of preparation of these composite supports is described in **Figure 2**.

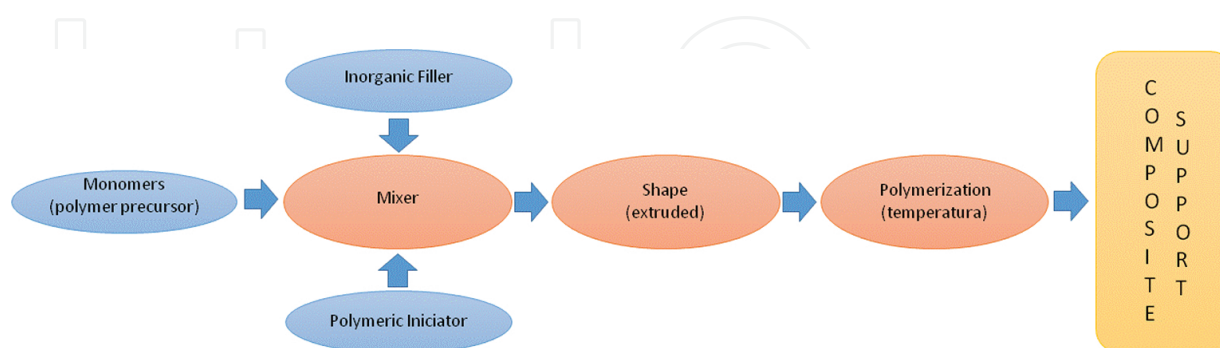


Figure 2. Scheme of preparation of a composite support.

Structured materials in the form of rings, spheres, tablets, or pellets can be prepared with this preparation technique. Metals can be deposited on them, preferentially with an egg-shell structure of small thickness of the active phase. These materials have improved mechanical

resistance in comparison with other existing commercial supports. They also combine dual hydrophilic/hydrophobic, inorganic/organic surface properties; this is the main property behind the preparation of egg-shell catalysts.

The process of preparation of the composite supports is described in **Figure 2**. It comprises the following steps:

1. Weighing of monomers, polymerization starters, and inorganic material.
2. Mixing of the monomers, polymerization starters, and inorganic material.
3. Shaping of the support by means of extrusion, pelletizing, etc.
4. Polymerization of the organic phase by means of the thermal activation of the polymerization starter.
5. Making the support ready for use in the preparation of the metal catalyst.

In the preparation of the composite precursors the following polymeric phase precursors were used: bisphenol A glycerolate dimethacrylate (BGMA), triethylene glycol dimethacrylate (TEGDMA), and diurethane dimethacrylate (UDMA). The thermally activated polymerization starter used was benzoyl peroxide (BPO). **Figure 3** shows the chemical structure of the monomers and the polymerization starter used during the preparation of the UTAl and BTAl supports.

Two different composites, that is, UTAl and BTAl used in this work were made by mixing γ -alumina powder, two monomers, and BPO. The main difference between composites supports was the type of monomers used; UDMA and TEGMA were used for composite called UTAl, and BGMA and triethylene glycol dimethacrylate (TEGMA) were used for composite called BTAl. The alumina used was γ -alumina with a particle size of 0.074 μm .

UTAl and BTAl were prepared as describe by Badano et al. [31], monomers joined BPO were intimately mixed with 45 wt% γ -alumina. Then, mixture was degassed and extruded into a cylinder of 2 mm diameter. Polymerization of the paste was carried on a stove at 393 K for 1 h. The final composite were pellets of 2 mm diameter and 2–3 mm long.

2.2. Catalysts preparation

Gamma alumina (CK-300, Ketjen), activated carbon (NORIT RX3 Extra and CNR), and composite support, BTAl and UTAl were used as supports to prepared metal catalyst. Platinum was loaded with PtCl_2 and $\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$ by incipient wetness technique. After impregnation, catalysts were dried at 393 K in an oven for 24 h and were maintained in desiccator for further use. The catalysts were reduced in a H_2 flow at 503 K for 1 h after catalytic test.

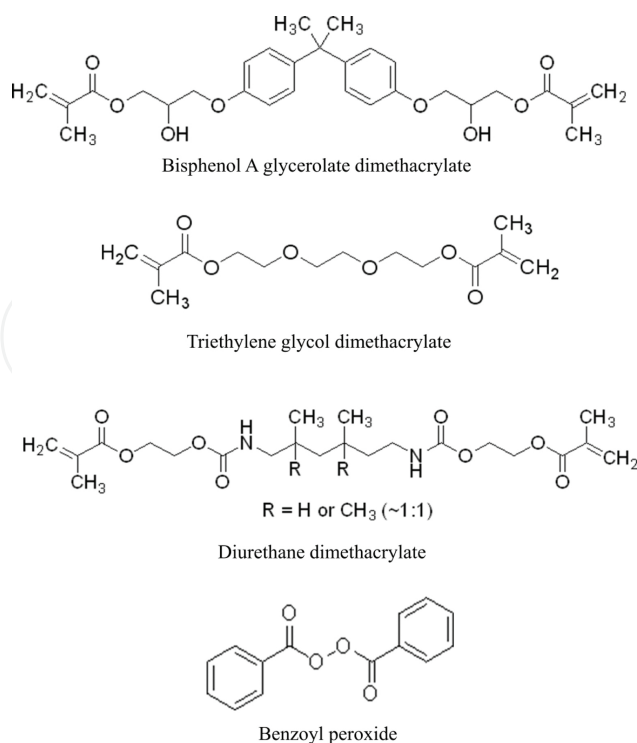


Figure 3. Monomer precursors of the polymeric phase and polymerization starter.

3. Catalyst activity test

The catalytic activity and selectivity during the hydrogenation reactions were measured in a batch, PTFE-coated, stainless steel, stirred tank reactor, using pelletized or powder catalysts. The procedure used for starting the reaction comprised of the following steps. The reactor was charged with a solution of the substrate (styrene, 1-heptyne, 3-hexyne, 2,3-butanodione, ethyl pyruvate). The stirring rate used in each catalytic test was 1200 rpm. Pressure, temperature, and catalyst concentration values were different for each system.

4. Results

4.1. Catalysts characterization

Values of the axial and radial mechanical resistance of the pellets were obtained in an universal rehearsals equipment. A compression rate of 1 mm min^{-1} was used. The attrition resistance was assessed by means of the method depicted in the ASTM D 4058 norm.

The specific surface area (S_{BET}) values were obtained from nitrogen physical adsorption-desorption isotherms at 77 K. In order to get a surface free of water and adsorbed compounds, the samples were degassed overnight at 523 K in vacuum ($<10^{-4} \text{ Pa}$) before adsorption.

The palladium and platinum content of the catalysts was obtained by digesting the sample and then analyzing the liquors in ICP equipment. Hydrogen chemisorption measurements were performed in a pulse apparatus at atmospheric pressure. Before the test the samples were reduced in a gas mixture containing 5% v/v H₂/Ar for 1 h and degassed in an Ar flow at the same temperature of reduction for 3 h. After that, the samples were cooled in an argon flow, and the chemisorption test was done by injecting hydrogen pulses to the flowing stream until the samples became saturated.

X-ray photoelectron spectroscopy (XPS) was done over the reduced catalysts with a VG-MicrotechMultilab equipment.

Samples were analyzed using scanning electron microscopy (SEM) equipped with an energy dispersion system (EDAX) that enablesto analyze elementary chemical with an X-ray microbeam. This technique is known as electron probe microanalyzer (EPMA) and it was allowed to elucidate metal distribution and create elemental mappings. Before measure, catalyst pellets were coated with thin carbon film in order to avoid influence of charge effect during the SEM operation. The scanning speed was 0.02 mm min⁻¹ and the acceleration voltage of electron beam was 20kV.

The thickness of the metal surface shell was also determined optically with the aid of micrographs of the cross section of the catalysts. Micrographs were obtained with a microscope equipped with a color video printer. To analyze the samples, this technique required to be encapsulated with a thermoplastic resin and then polished with sandpaper. Sanding encapsulated samples were done with finer paper (down 500 grit) until exposing the cross section of catalyst particles. The finest paper used was 2500 grit.

The XRD measurements were performed in a diffractometer with CuK α radiation filtered with Ni. Spectra were scanned at a rate of 0.25 min⁻¹ in range between 25 and 80°. Catalyst required different preparation before analyzing. For alumina and carbon samples, material was grinded and reduced in hydrogen flow. In the case of composites, a slab of 1 cm² of area was impregnated with Pt or Pd, then was grinded and reduced as previous samples thermo gravimetric analysis (TGA) traces were also obtained. These traces show the dependence of the thermal weight loss of a sample as a function of the temperature. In the experiments catalyst samples (about 10 mg) were heated in an air flow of 40 mL min⁻¹ from room temperature up to 1173 K at a heating rate of 5 K min⁻¹.

To measure the acidity of the supports, the reaction of dehydration of 1,4-butanediol to tetrahydrofuran (THF) was followed.

5. Results

5.1. Catalyst characterizations

Table 1 shows the results of the tests of mechanical properties, i.e., resistance to diametrical compression (SD), resistance to longitudinal compression (SL), and attrition loss obtained for

the composite supports UTAI, BTAI and for the commercial supports of alumina and carbon. It can be seen that the composite supports have better mechanical properties than the commercial supports. This is especially important when γ -alumina is taken as a reference.

Support	SD ^a (Kgf/cm ²)	SL ^a (Kgf/cm ²)	Attrition loss (%) ^b	
			1800 Turns	18,000 Turns
Carbon RX3	<100	217 ± 101	1.659	6.859
γ -Al ₂ O ₃	<100	703 ± 199	0.167	3.103
α -Al ₂ O ₃	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

^aFrom Ref. [31].

^bFrom Ref. [32].

Table 1. Supports mechanical properties.

Table 2 contains the results of metal concentration, metal dispersion, specific surface area, binding energy of Pd3d_{5/2} and Pt 4d_{5/2} and Cl/metal atomic ratios obtained by XPS, and metal penetration depth, as determined by different techniques.

Catalyst	Metal (wt%)	D % (at _{ad} /at _{total})	S _{BET}	XPS BE (eV) Pd 3d _{5/2} and Pt 4d _{5/2}	Cl/Metal (at/at)	EMPA e (μm)
0.3PdUTAI	0.23	5	nd	335.0 ^(74%) 337.0 ^(26%)	0.60	60
0.3PdBTAI	0.26	3	nd	335.6 ^(76%) 336.6 ^(24%)	0.84	90
0.3PdCNR	0.49	62	nd	335.2 ^(100%)	-	nd
1PdAI	1.1	19	234	335.3 ^(62%) 337.2 ^(38%)	3.76	Up to Pellet center
1PdRX	1.31	4	1073	335.2 ^(100%)	-	600
1PdUTAI	1.00	7	0.62	335.0 ^(89%) 337.0 ^(11%)	0.20	60
1PdBTAI	1.10	4	1.13	335.2 ^(75%) 336.7 ^(25%)	0.68	90
1PtUTAI	1.00	nd	nd	313.5 ^(48%) 315.5 ^(52%)	1,23	nd
1PtBTAI	1.10	nd	nd	313.5 ^(55%) 315.5 ^(45%)	0,87	nd

Table 2. Metal catalyst loadings, dispersion values, XPS results, and metal penetration to EMPA.

Regarding the Pd surface species, except for the 0.3PdCNR and 1PdRX catalysts, only two different species were detected. The PdUTAl catalysts had a peak with a binding energy (BE) of 335.0 eV, attributed to Pd⁰, while the PdBTAl catalysts had peaks at 335.6 (0.3PdBTAl) and 335.2 eV (1PdBTAl), and attributed to Pd δ^+ electrodeficient Pd species [33]. All catalysts had a second signal with BE values between 336.3 and 337.0 eV that would correspond to Pdⁿ⁺ species with $\delta^+ < \eta^+ < 2$. This could possibly be related to the incomplete removal of chlorine ligands of the metal salt during the thermal treatment, leading to the presence of surface nonreduced Pd oxychloride species [34]. The same behavior can be seen for the Pt catalysts. In this case the 4d_{5/2} signals at 313.5 and 315.5 eV would be attributed to Ptⁿ⁺, oxychlorided platinum species [34].

In **Figure 4** optical microscopies of the catalysts 0.3PdBTAl, 0.3PdUTAl, 1PdBTAl, and 1PdUTAl are shown. In this figure it can be observed that the pellets images form before the catalytic tests. In the cross-sectional images of these catalysts it can be observed in the clearer region, the presence of support on the inside of the pellet, and on the outer surface, the darker region, the metal is located. Identical behavior can be seen in **Figure 5** where the microscopies for 1PtUTAl and 1PtBTAl catalysts were obtained.

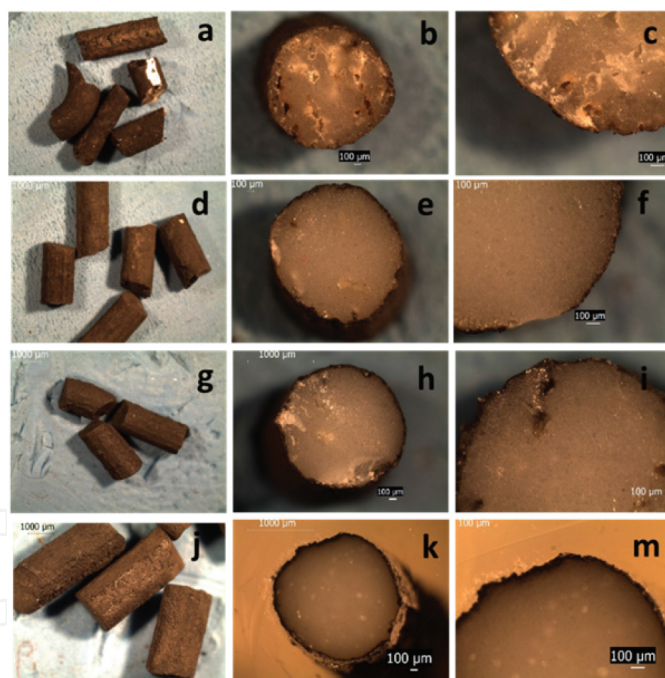


Figure 4. Optical micrographs images for transversal section of catalysts: (a)–(c): 0.3PdBTAl; (d)–(f): 0.3PdUTAl; (g)–(i): 1PdBTAl; (j)–(m): 1PdUTAl.

Figure 6 presents SEM images obtained for the catalysts 0.3PdBTAl, 0.3UTAl, 1PdBTAl, and 1PdUTAl. In the SEM images, **Figure 6(a)** and **(b)**, the topography of the surface catalysts 1PdBTAl and 1PdUTAl can be seen. Images from **Figure 6(c)–(h)** were obtained using the detector in backscattering mode in order to see the structural composition of the composite catalysts. From such images it is possible to see Pd particles as darker region on outer surface

of the support. In the center of the pellet light color spots surrounded by a structure of gray color can be seen, which corresponds to γ -alumina particles gird for a continuous network of polymeric phase of the composite catalyst.

The egg-shell profile of the catalysts was confirmed by EPMA obtained by the penetration of Pd on the support of 60 and 90 μm for UTAl and BTAl supports, respectively.

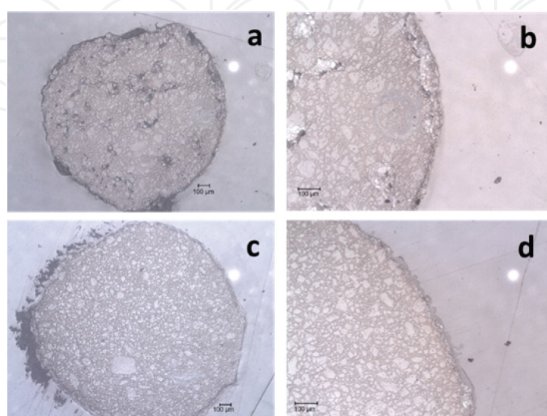


Figure 5. Optical micrograph images of the cross section of the pelletized catalysts: 1PtBTAl (a and b); 1PtUTAl (c and d).

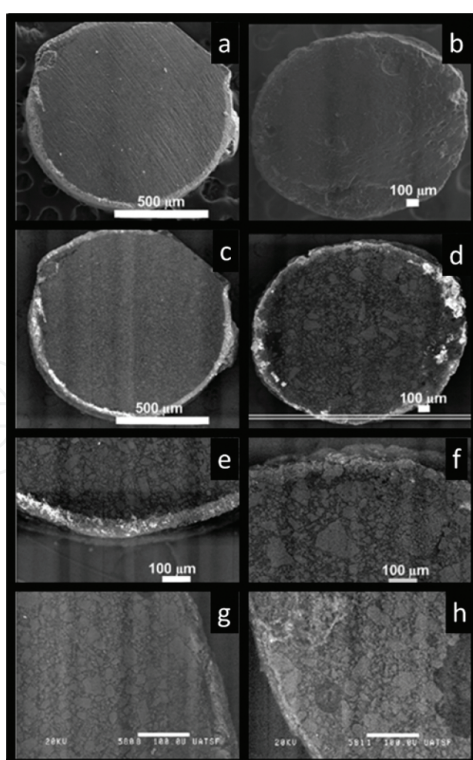


Figure 6. Catalysts transversal section SEM images. (a), (c), and (e) 1PdUTAl; (b), (d), and (f) 1PdBTAl; (g) 0.3PdUTAl, (h) 0.3PdBTAl. From Ref. [32].

Figure 7 shows the X-ray diffractograms of the composite supports, γ -alumina, Pt/composite, and Pd/composite catalysts. Comparing the results of gamma alumina with those of the composite supports, a close similarity can be seen. This is due to the fact that the inorganic phase used for the preparation of the composite supports is also γ -alumina and that the polymeric phase is amorphous. For all catalysts a peak at 20–39.9° would correspond to the reflections of the (111) planes of Pd⁰ and Pt⁰.

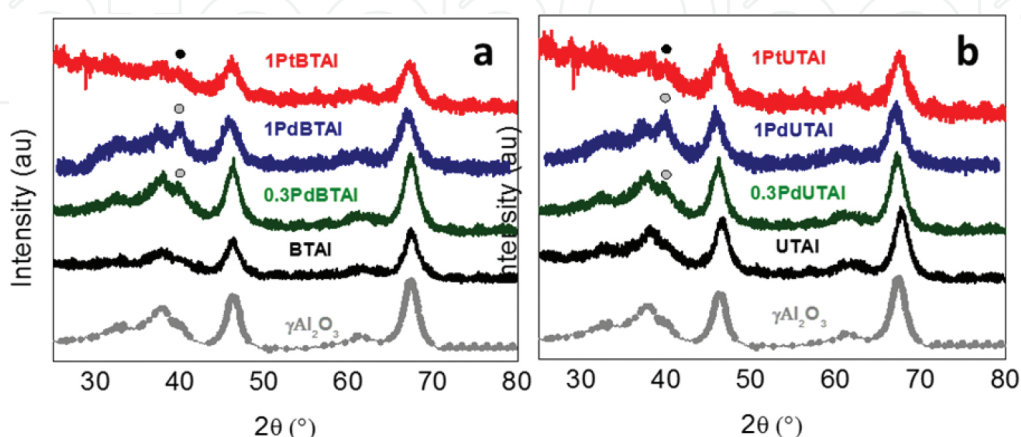


Figure 7. X-ray diffractograms of the composite BTAI (a) and UTAI (b) supports and the corresponding Pd and Pt catalysts.

Figure 8 contains the TGA results of the UTAI and BTAI composites, and 1 wt% Pd and Pt composite catalysts.

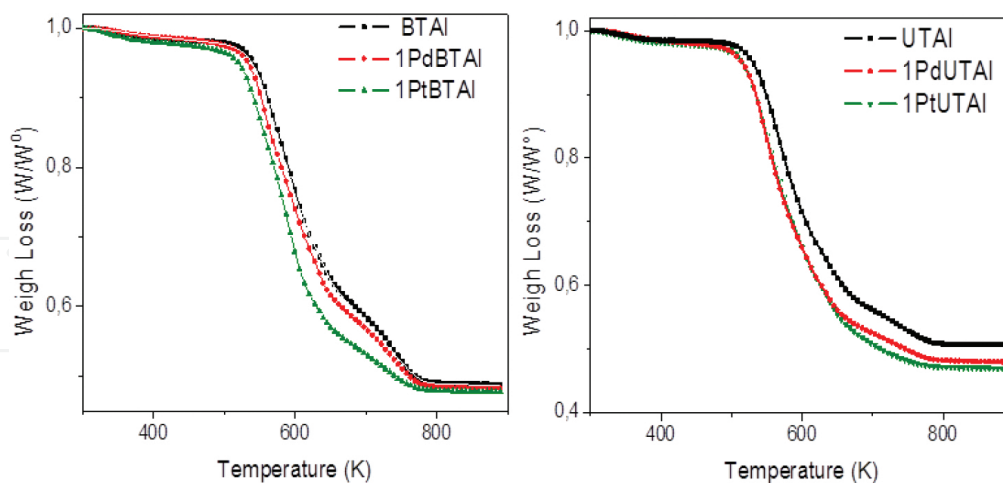


Figure 8. TGA traces of the composite supports and the corresponding Pt and Pd catalysts using air as carrier gas.

Inspection of the TGA traces indicates that for both composites the presence of the metal enhances the rate of decomposition of the organic phase. This effect is more important in the case of Pt. This behavior correlates with the nature of these metals that act as combustion catalysts in the presence of oxygen.

In order to assess the acidity of the support the reaction test of dehydration of 1,4-butanediol to THF was used. The results of the test are shown in **Figure 9**. As expected the catalyst with the highest activity is the Amberlyst 15 resin. $\gamma\text{-Al}_2\text{O}_3$ alumina has a catalytic activity lower than the resin but higher than other supports. The composite and the Norit RX3 carbon supports display alcohol conversion values much lower than those of the resin or the alumina. There are only slight differences in activity between the activated carbon and UTAI composite while BTAl displays the lowest values of conversion as a function of time. From these results it could be inferred that the acid resin Amberlyst 15 has the highest concentration of acid sites and the BTAl composite the lowest.

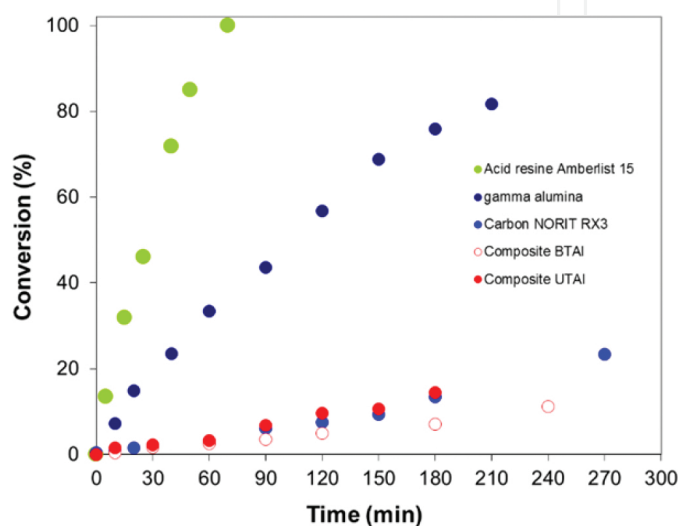


Figure 9. Acidity test. Dehydration of 1,4-butanediol to THF. Reaction conditions: 1,4-dioxane solvent, $C_{1,4\text{-butanediol}}^0 = 1 \text{ M}$, 0.1 MPa , 473 K , $W_{\text{cat}} = 0.2 \text{ g}$.

5.2. Hydrogenation tests

5.2.1. Styrene hydrogenation

Figure 10 shows a scheme of the reaction of selective hydrogenation of styrene to ethylbenzene. In this reaction the hydrogenation of the aromatic nucleus is undesired.

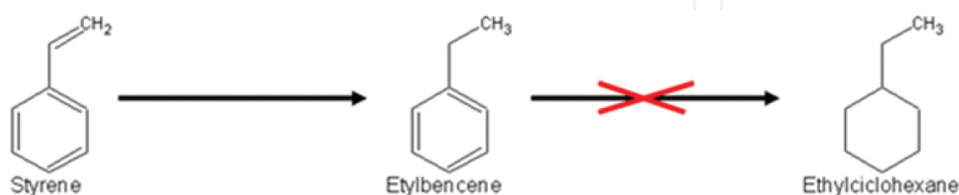


Figure 10. Scheme of the reaction of selective hydrogenation of styrene to ethylbenzene.

The reaction of hydrogenation of styrene to ethyl benzene is used as a reaction test for the process of purification of some refinery hydrocarbon streams. In this reaction the interest is to

hydrogenate the vinylic external C=C bond, while keeping unaltered the bonds of the aromatic ring [34, 35].

In order to determine the mass transfer limitations in the inside of the catalyst particles, the effectiveness factor (η) was used:

$$\eta = \frac{\text{real reaction rate}}{\text{unrestricted reaction rate}} \quad (1)$$

The real reaction rate corresponds to the measured rate of the reaction at the conditions of temperature and concentration of the bulk reaction medium. The unrestricted reaction rate corresponds to the ideal reaction rate of a catalyst particle with no intraparticle or fluidparticle gradients of concentration or temperature that has the temperature and concentration of the bulk fluid phase. The unrestricted reaction rate was measured by grinding the catalyst pellets to a particle size smaller than 100 μm . For this particle size and the reaction conditions used it was estimated that all mass and heat transfer gradients were negligible.

The results of styrene conversion as a function of reaction time for the pelletized and powder catalysts are shown in **Figure 11**. The catalysts prepared with the composite supports UTAl and BTAl have higher activities (higher conversion values) than the catalysts prepared with commercial supports.

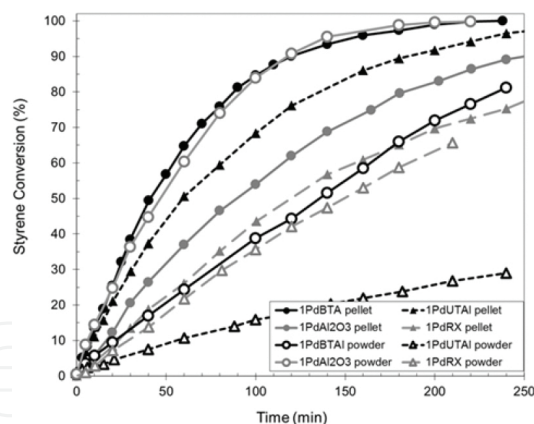


Figure 11. Styrene conversion as a function of reaction time. Catalysts with 1% Pd. Reaction conditions: toluene solvent, $C_{\text{styrene}}^0 = 0.445 \text{ M}$, 2.0 MPa H_2 , 353 K, $W_{\text{cat}} = 0.3 \text{ g}$ (pellet) or 0.01 g (powder).

In all the tests, for all catalysts, at all reaction conditions used, the obtained values of selectivity to ethylbenzene were higher than 99%.

Initial reaction rates were calculated by calculating the conversion rate as a function of time and extrapolating to zero conversion. With the values corresponding to the pellet and powder catalyst the effectiveness factor or could thus be estimated using the following equation:

$$\eta = \frac{\text{Initial reaction rate of pellet catalyst}}{\text{Initial reaction rate of powder catalyst}} = \frac{r_{\text{pellet}}^0}{r_{\text{powder}}^0} \quad (2)$$

Table 3 contains the values of r_{pellet}^0 , r_{powder}^0 and for the different catalysts. It can be seen that the composite supports have high values than PdRX and PdAl catalysts. The higher effectiveness values are directly related to the lower mass transfer limitations when using the composite catalysts.

Catalyst	r_{pellet}^0 (n°/gcat min)	r_{powder}^0 (n°/gcat min)	η
PdRX	0.0014	0.0295	0.048
1PdAl	0.0019	0.1183	0.016
1PdUTAl	0.0029	0.0097	0.299
1PdBTAl	0.0038	0.0300	0.127

Table 3. Styrene hydrogenation initial reaction rate for catalyst pellets (r_{pellet}^0) and catalysts powders (r_{powder}^0). Effectiveness factor (η) [31].

Catalysts with a metal loading lower than 0.5 Pd wt% were also tried with this reaction test. The catalysts are named 0.3PdUTAl and 0.3PdBTAl in the case of the composites (with 0.3% Pd). LD265 is a procatalyse Pd/Al₂O₃ catalyst (0.3% Pd) and Engelhard is a BASF Pd/Al₂O₃ catalyst (0.5% Pd). The results are plotted in **Figure 12**.

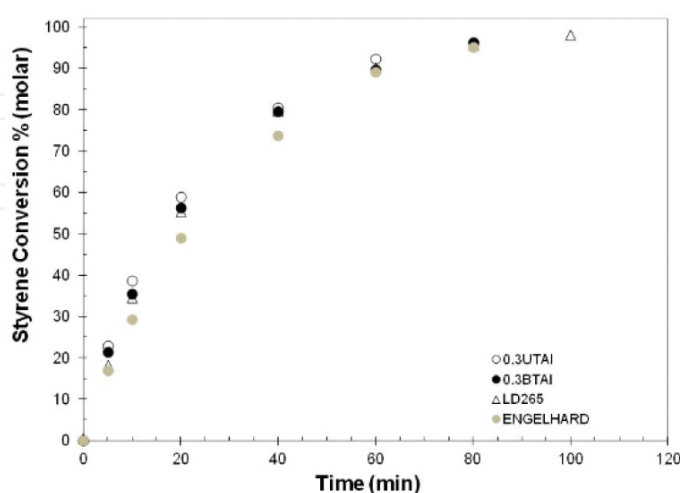


Figure 12. Styrene hydrogenation catalysts with less of 0.5 wt % of Pd. Reaction conditions: toluene solvent, $C_{\text{styrene}}^0 = 0.445$ M, 2.0 MPa H₂, 353 K, $W_{\text{cat}} = 2$ g pellet.

It can be seen that for all catalysts the pattern of conversion as a function of time are quite similar, though the catalytic activity is slightly better for the composite 0.3PdUTAl and 0.3PdBTAl catalysts.

5.2.2. Alkyne hydrogenation

The partial hydrogenation of alkynes to obtain olefinic compounds is a reaction of industrial and academic interest. It is of big importance for the petrochemical, pharmaceutical, and agrochemical industries. Most of the times the alkyne compounds to be hydrogenated are not raw materials for synthesizing new products but impurities to be removed from a certain process feedstock. The conversion of these alkynes, when the feedstock has a high concentration of alkenes, demands specialized catalysts that can react with the triple bond while keeping intact the double bonds of the alkenes. Moreover, the conversion of alkynes to valuable alkenes is usually desired [36–40].

Figure 13 shows the scheme of reaction of the selective hydrogenation of 1-heptyne, a terminal alkyne, to 1-heptene. The objective of this reaction is to hydrogenate 1-heptyne with a maximum selectivity to the intermediate product 1-heptene. The product of deep hydrogenation, n-heptane, should be completely disfavored.

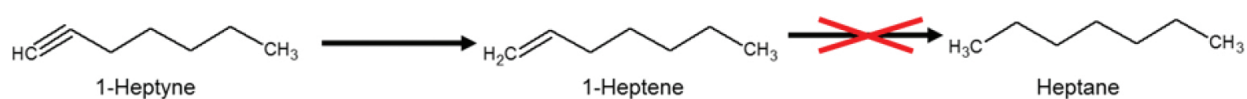


Figure 13. Scheme of the reaction for the selective hydrogenation of 1-heptyne to 1-heptene.

Figure 14 shows the values of conversion of 1-heptyne and selectivities to 1-heptene and n-heptane as a function of time for the catalysts 0.3PdAl, 0.3PdCNR, Lindlar, and 0.3PdUTAl. It can be seen that the egg-shell Pd supported catalyst base on the UTAl support is the most active for hydrogenation. At 3 h, 95% conversion of heptyne is seen while the other tested pellet catalysts did not reach 30%. The Lindlar catalysts (0.75 g) with a Pd content of 5% had at 180 min values of conversion similar to 0.3PdUTAl but with selectivities to heptene close to 85%, lower than the selectivity of 0.3PdUTAl. When compared to 0.3PdUTAl, the Lindlar catalyst is disadvantaged as it is supplied in powder form. Once the reaction is finished it must be filtered from the reaction medium with a process that is lengthy and costly due to the high efficiency required for recovering the high priced, high Pd content (5%) Lindlar catalyst. 0.3PdUTAl has a much lower Pd content (0.22%), and is cheaper and has no filtering problems.

Figure 15 shows the scheme of reaction of selective hydrogenation of 3-hexyne, a nonterminal alkyne, to 3-hexene. In this reaction the desired compound is the product of mild hydrogenation, the intermediate 3-hexene, while the product of deep hydrogenation, n-hexane, is undesired.

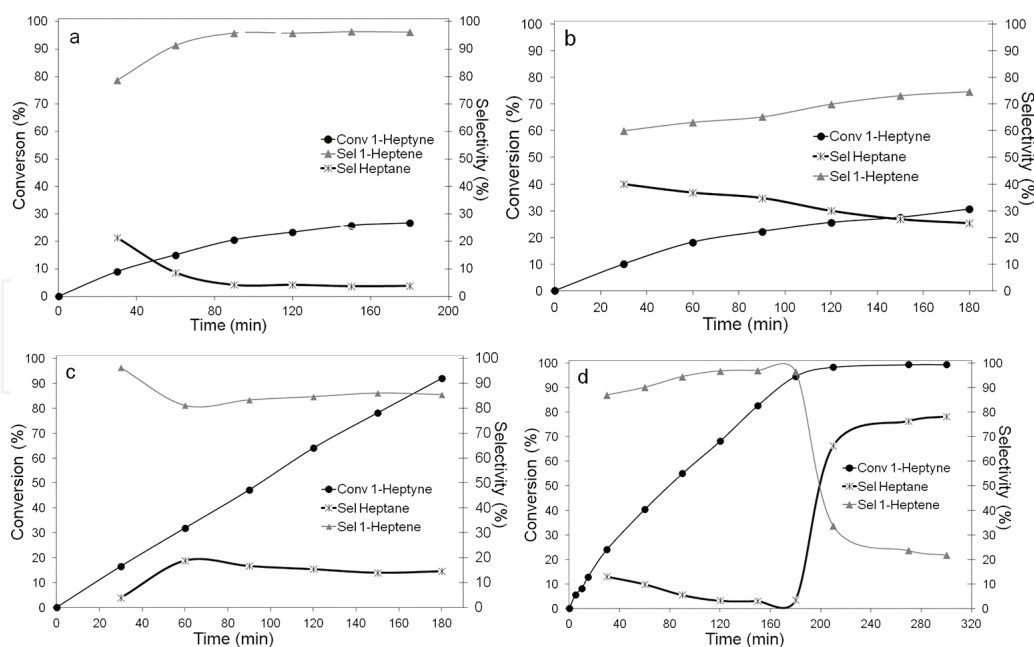


Figure 14. 1-heptyne hydrogenation. (a) 0.3PdAl, (b) 0.3PdCNR, (c) Lindlar, and (d) 0.3PdUTAl. Reaction conditions: toluene solvent, $C^0_{1\text{-heptyne}} = 0.350$ M, 0.15 MPa H_2 , 303 K, $W_{\text{Cat}} = 0.75$ g.

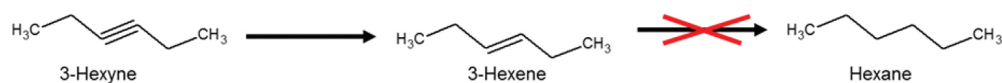


Figure 15. Scheme of the reaction of selective hydrogenation of 3-hexyne to 3-hexene.

The 0.3PdUTAl catalyst was also tried in the hydrogenation of 3-hexyne to 3-hexene. The results of total conversion of 3-hexyne ($X_{3\text{HI}}$) and selectivity to 3-hexene (S_{HE}) and n-hexane (S_{HA}) are plotted in **Figure 16**. Values of 99% and 94% selectivity at 180 min reaction time can be seen. Also, no deactivation of the catalyst was detected.

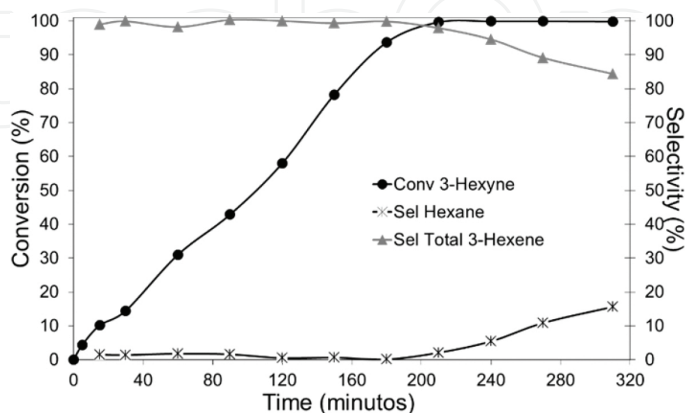


Figure 16. 3-hexyne hydrogenation. 0.3PdUTAl catalyst. Toluene solvent, $C^0_{3\text{-hexyne}} = 0.350$ M, 0.15 MPa H_2 , 303 K, $W_{\text{Cat}} = 0.75$ g.

5.2.3. 2,3-butanedione hydrogenation

Figure 17 shows the scheme of reaction for the selective hydrogenation of 2,3-butanedione to 3-hydroxybutan-2-one. In this reaction one of the carbonyl groups requires to be hydrogenated with an alcohol group.

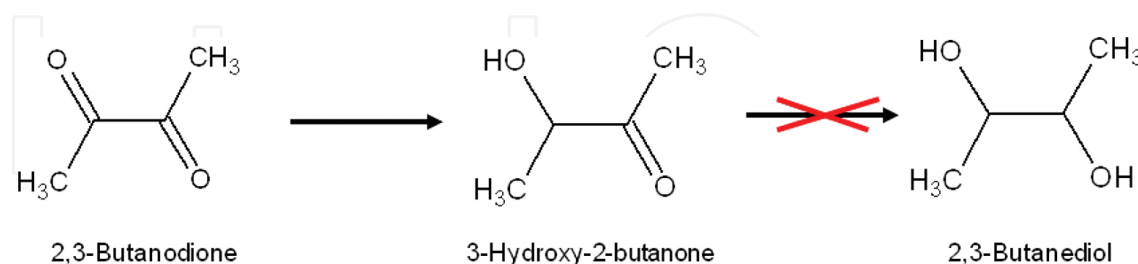


Figure 17. Scheme of reaction for the selective hydrogenation of 2,3-butanedione to 3-hydroxybutan-2-one.

The reaction of hydrogenation of 2,3-butanedione to 3-hydroxybutane-2-one is a reaction of interest for the industry of scents and fragrances [41–43]. **Figure 18** shows the graphs of total conversion of 2,3-butanedione ($X_{2,3BD}$) as a function of time for the catalysts 0.3PdUTAI, 0.3PdBTAl, 1.3PdUTAI, and 1.3PdBTAl. In all cases the selectivity to 3-hydroxybutane-2-one was higher than 98%.

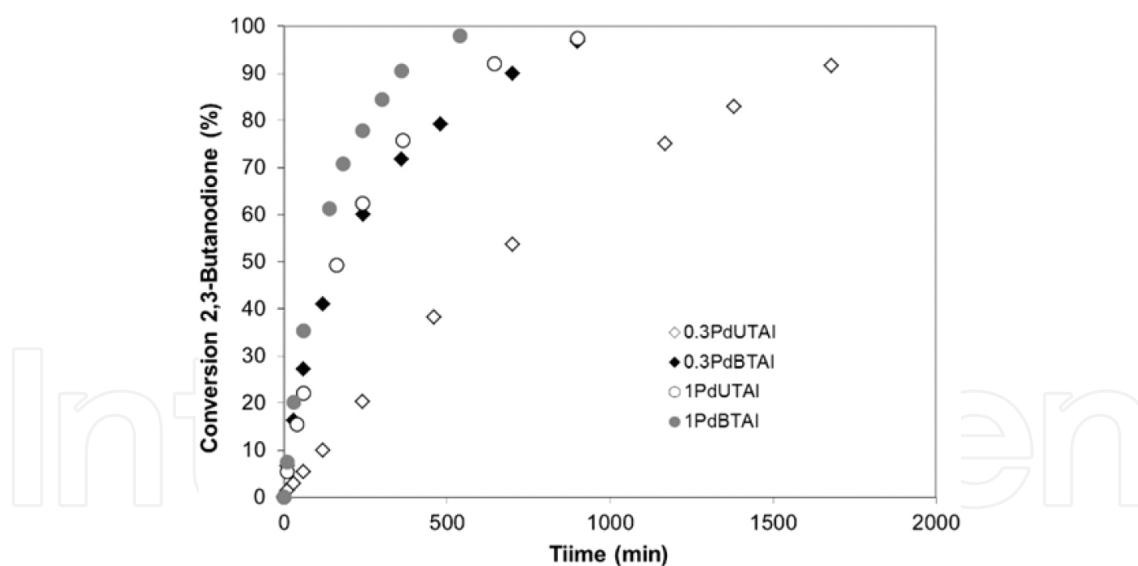


Figure 18. 2,3-butanedione hydrogenation. Reaction conditions: isopropyl alcohol solvent, $C_{2,3\text{-butanodione}}^0 = 0.057 \text{ M}$, 4.0 MPa H_2 , 368 K , $W_{\text{Cat}} = 2 \text{ g}$.

All catalysts of Pd supported over composite supports, independent of the kind of polymer used and of the metal content, were active and highly selective for the reaction of interest. Among the composite catalysts series, those based on the BTAl support were more active than those based on the UTAI. This was more evident in the case of the catalyst of low metal concentration.

The catalysts 1PtBTAl and 1PtUTAl (see **Figure 19**) were also tried in this reaction. In these catalysts a decrease is seen in the selectivity to 3-hydroxybutane-2-one due to the appearance of the product of consecutive hydrogenation of 2,3-butanediol. This pattern of lower selectivity of Pt as compared to Pd has already been reported in the literature [44].

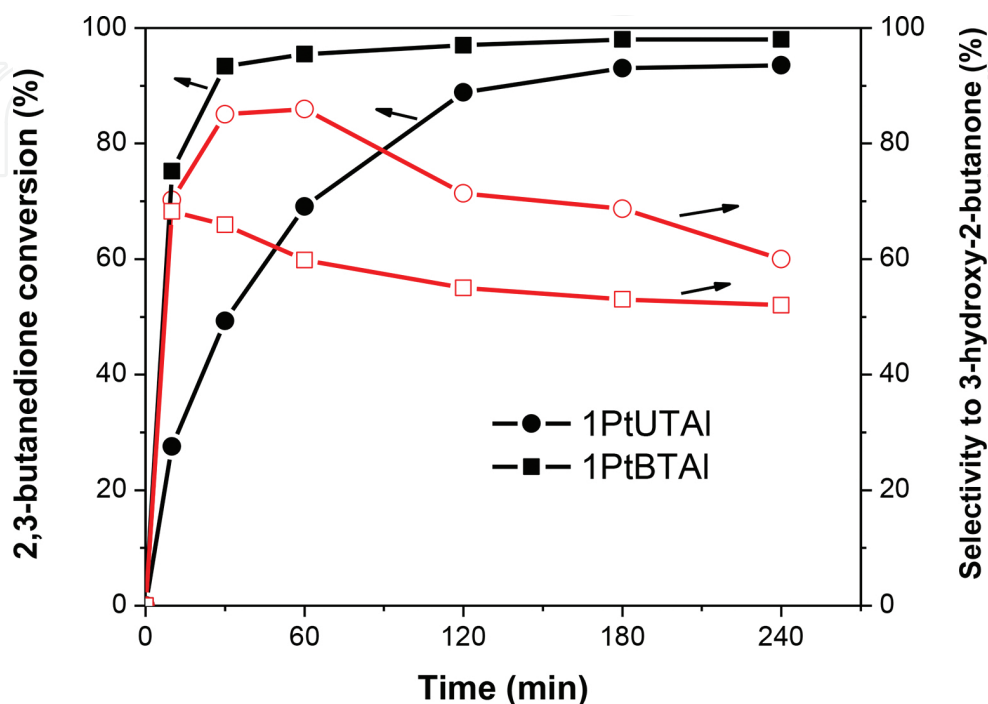


Figure 19. 2,3-butanedione hydrogenation. Reaction conditions: isopropyl alcohol solvent, $C^0_{2,3\text{-butanodione}} = 0.057\text{ M}$, 4.0 MPa H_2 , 368 K, $W_{\text{Cat}} = 2\text{ g}$.

5.2.4. Ethyl pyruvate enantioselectivity hydrogenation

The enantioselective hydrogenation of ethyl pyruvate has been an intensively studied research subject. It has been found that the Pt catalysts are the most appropriate for performing this reaction [45, 46], while the Ir, Ru, and Pd catalysts display lower yields [45, 47]. The Pt-cinchonidine catalysts favor the formation of (R)-ethyl lactate.

Figure 20 shows the scheme reaction for the selective hydrogenation of ethyl pyruvate to (R)-ethyl lactate (using cinchonidine as modifier). In this reaction the objective is to get an enantiomeric excess (ee) of the (R) form over the (S) form.

Figure 21 shows the results of catalytic activity obtained with the catalysts 1PtBTAl and 1PtUTAl employing cinchonidine as quiral modifier. The composite catalysts prepared were found to be active, showing conversion values higher than 90%. In both cases it can be seen that 1PtBTAl is more active than 1PtUTAl. This could be related to the higher availability of active sites. Also, when cinchonidine is used as chiral modifier the enantiomeric excess (ee) of (R)-ethyl lactate achieved was greater for the case of the 1PtBTAl catalyst. This could be related

to the size of the metal particles. A big size would permit a better interaction with the chiral modifier.

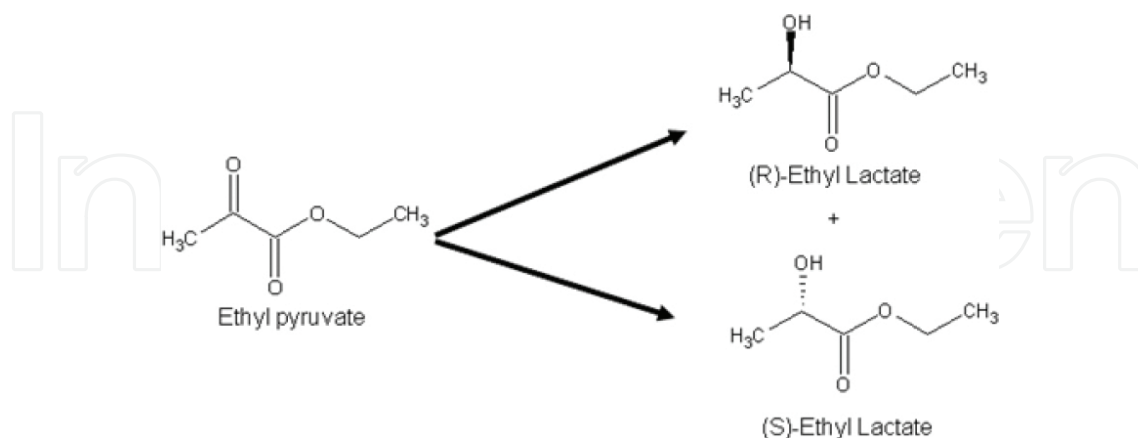


Figure 20. Scheme of reaction for the enantioselective hydrogenation of ethyl pyruvate to (R) or (S) ethyl lactate.

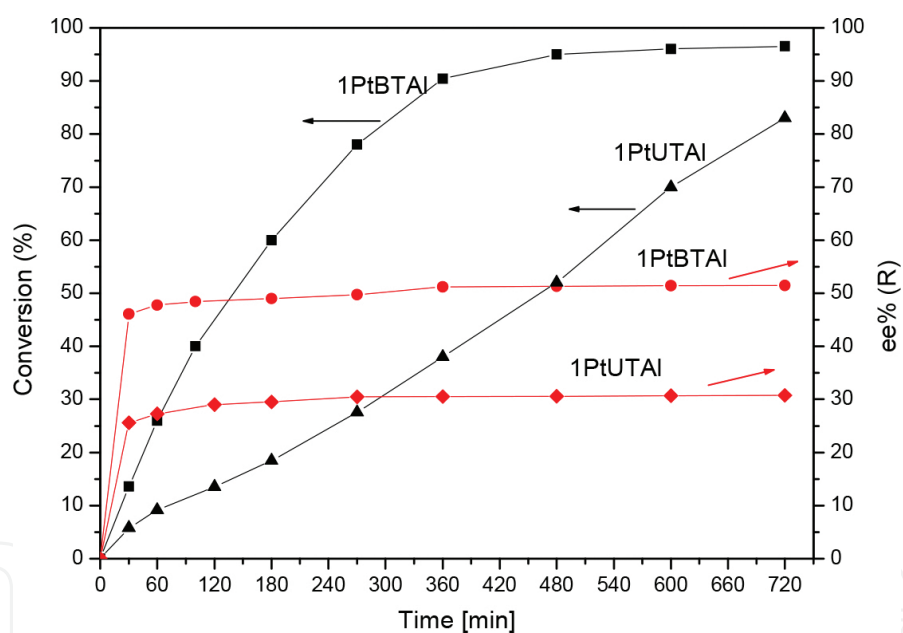


Figure 21. Ethyl pyruvate hydrogenation. Reaction conditions: isopropyl alcohol solvent, $C^0_{\text{Ethyl pyruvate}} = 0.346 \text{ M}$, $C^0_{\text{Cinchonidine}} = 0.002 \text{ M}$, 2.0 MPa H_2 , 298 K , $W_{\text{cat}} = 0.5\text{g}$.

6. Conclusions

In the present work a method was presented for the preparation of new organic-inorganic hybrid materials for being used as catalyst support, generally referred to in this work as “composites.” BTAI and UTAI composites are formed by a combination of inorganic material

(alumina) and an organic one (polymer). The organic phase was obtained by polymerization of organic molecules of functionality 2: bisphenol A glycerolated dimethacrylate, diurethane dimethacrylate, and triethylene glycol dimethacrylate. The inorganic phase in the form of a powder was mixed with the monomers and a heat starter of polymerization (benzoyl peroxide). The mixture was extruded and then polymerized by applying heat. Thus, the obtained rigid material was used as a support for the preparation of supported noble metal catalysts.

The composites display the combined action of a hydrophilic material (alumina) and a hydrophobic one (polymer). This is an ideal combination for the preparation of catalysts with small thicknesses of active metal surface layer. The combination of these dual properties makes the process of preparation of metal/composite catalysts easier, faster, cheaper, and more repetitive, in comparison to the preparation of catalysts of metals supported over common supports. Conventional methods using these common supports need a strict control over the viscosity, contact time, and pH of the impregnating solution, the temperature of impregnation, drying, and calcination. **Figure 22** shows a graphical description of composites catalysts synthesis procedure.

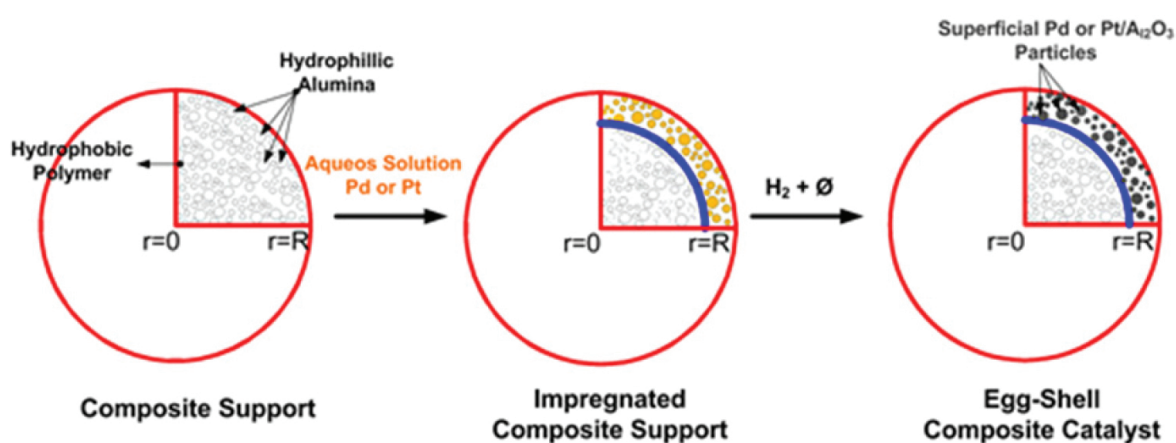


Figure 22. Graphical description of composites catalysts synthesis procedure.

Egg-shell supported metal catalysts have advantages over the catalysts with other metal distributions. They have a lower intraparticle mass diffusion resistance and enable a better control of the temperature on the surface of the catalyst, thus enabling an overall better control of the reaction and the reactor.

The results of hydrogenation of styrene using pellet catalysts and powder catalysts containing more than 1 wt% Pd showed that the composites UTAl and BTAl had higher values of the effectiveness factor (η) in comparison to the rest of the catalysts. These results can be attributed to the small thickness of the metal layer formed over the surface of the composite support, lower than the thickness in the other catalysts prepared using conventional supports as alumina or an activated carbon.

The Pd/composite catalysts of low metal content were compared to other commercial samples, LD265 (Axens) and ENGELHARD, in the reaction test of styrene hydrogenation. The Pd/

composite catalysts had slightly better catalytic properties than the commercial Pd catalysts, a fact pointing to the possibility of industrial use of these new materials.

In the tests of selective hydrogenation of terminal alkynes to terminal alkenes, the activity of the catalysts 0.3PdAl, 0.3PdCNR, 0.3PdUTAl, and Lindlar were evaluated using 1-heptyne as reactant. It was seen that at 180 min, Lindlar and 0.3PdUTAl achieved total conversion of the alkyne, with selectivity to 1-heptene of 85% in the case of the Lindlar catalyst and 97% in the case of 0.3PdUTAl. The 0.3PdAl and 0.3PdCNR catalysts suffered in this strong reaction deactivation. This was more noticeable from 1-heptyne conversion values of 10–20%. The 0.3PdUTAl catalyst had a similar activity as the commercial Lindlar catalyst. Some advantages of the new materials were evident. The Lindlar catalyst was available in powder form and was very expensive due to the high metal content (5 wt% Pd). The Pd/composites were pelletized and only had 0.25 wt% Pd content.

The good results of conversion and selectivity obtained during the reaction of hydrogenation of 3-hexyne, a nonterminal alkyne, to 3-hexene, over the 0.3PdUTAl catalyst, indicates that these composite catalysts can also be used in reactions comprising consecutive steps.

The reactions of hydrogenation presented were also favored by the use of composite supports because of their lower acid strength. This is an advantage for suppressing undesirable reactions, such as the oligomerization of alkenes and alkynes, leading to the formation of carbon deposits or gums over the catalysts. These and other reactions affect the selectivity and lifetime of the catalysts.

In the case of the reaction of synthesis of 3-hydroxybutane-2-one from 2,3-butanedione, which is of commercial interest for the perfume industry, it was seen that the Pd/composite catalysts could be used with values of conversion and selectivity close to 100%. The use of composites in the slurry reactors enabled sparing the filtering of the liquid phase at the end of the reaction. The difference in activity found between the PdBTAl and PdUTAl catalysts could be due to the differences in metal dispersion or to differences in the electronic properties of the surface Pd species.

During the enantioselectivity hydrogenation reaction of ethyl pyruvate using cinchonidine as a quiral modifier, both PtUTAl and PtBTAl composite catalysts were active and selective to (R)-Ethyl Lactate. PtUTAl catalyst had higher total conversion than PtBTAl but had less enantiomeric excess (ee). This activity and enantioselectivity behavior could be related, at least partly due to the electronic effects of the presence of chloride species that prevents the adsorption of the quiral modifier causing a decrease in the enantiomeric excess (ee), although geometrical effects of $\text{Pt}\delta^+\text{O}_x\text{Cl}_y$ species could not be discarded.

The advantage of the egg-shell catalysts that makes them to be preferred over other catalyst types is that they have smaller intraparticle mass transfer limitations. Having most of the metal phase on the outer surface layer, makes also the heat transfer more efficient, enabling a better control of the reaction and the reactor temperature.

A last advantage is related to the mechanical properties. The composites displayed higher values of diametrical and longitudinal resistance than alumina and silica and also suffered less

attrition. This translates into a higher crush resistance when used in packed beds and a lower tendency to the formation of fines when used in slurry stirred reactors.

In summary, it can be said that the composite catalysts synthesized in this work had an egg-shell metal distribution with very small metal surface layer thickness and proved to be superior to common metal catalysts prepared with commercial supports. This was attributed to a combination of the following properties: good mechanical resistance, simplicity of preparation procedure for support and catalyst, small thickness of the active phase, uniform distribution of the metal over the support surface, ease of preparation procedure scale-up, and possibility of achieving any desired pellet shape.

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References

- [1] Moulijn JA, van Leeuwen PWNM, van Santen RA, editors. *Studies in Surface Science and Catalysis*, Vol 79. 1st ed. The Netherlands: Elsevier; 1993, 465 p.
- [2] Hagen J. *Industrial Catalysis: A Practical Approach*. 3rd ed. Weinheim: Wiley-VCH Verlag GmbH&Co. KGaA; 2006, 513 p. DOI: 10.1002/3527607684.ch1
- [3] Patent US 3969273.Inv: Brown SM, Wallace DN; W.R. Grace & Co; 1976.
- [4] Patent US 4120826.Inv: Ebel RH, Spitzer DP, Bambrick WE; American Cyanamid Company; 1978.

- [5] Patent US 4810688.Inv: Ewert WM, Kubicek DH, Drake CA; Phillips Petroleum Company; 1989.
- [6] Patent US 5118901.Inv: Drake CA; Phillips Petroleum Company; 1992.
- [7] Patent US 5202298.Inv: Schubert PF, Bonnell RE, Freeman NL, Fentress DC, Mitchell KE, Lowrey RE, Kubicek DH, Ewert WM; Phillips Petroleum Company; 1993.
- [8] Patent US 4051072.Inv: Burton RE, Berg M; General Motors Corporation; 1977.
- [9] Patente US 7288686.Inv: Ryu JY; Catalytic Distillation Technologies; 2007.
- [10] Sheng-Yi L, Rutherford A. The distribution of active ingredients in supported catalysts prepared by impregnation. *Catal. Rev. Sci. Eng.* 1985; 27: 207–340.
- [11] Ismagilov IZ, Ekatpure RP, Tsykoza LT, Matus EV, Rebrov EV, de Croon MHJM, Kerzhentsev MA, Schouten JC. Optimization of anodic oxidation and Cu–Cr oxide catalyst preparation on structured aluminum plates processed by electro discharge machining. *Catal. Today* .2005; 105: 516–528. DOI: 10.1016/j.cattod.2005.06.053.
- [12] Gulková D, Kaluža L, Vít Z, Zdražil M. Preparation of MoO₃/MgO catalysts with eggshell and uniform Mo distribution by methanol assisted spreading: Effect of MoO₃ dispersion on rate of spreading. *Catal. Commun.* 2006; 7: 276–280. DOI: 10.1016/j.catcom.2005.10.017.
- [13] Zhuang YQ, Claeys M, van Steen E. Novel synthesis route for egg-shell, egg-white and egg-yolk type of cobalt on silica catalysts. *Appl. Catal., A*. 2006; 301: 138–142. DOI: 10.1016/j.apcata.2005.11.029.
- [14] Alves JA, Bressa SP, Martínez OM, Barreto GF. Kinetic study of the liquid-phase hydrogenation of 1-butyne over a commercial palladium/alumina catalyst. *Chem. Eng. J.* 2007; 125: 131–138. DOI: 10.1016/j.cej.2006.08.006.
- [15] Drelinkiewicz A, Pukkinen A, Kangas R, Laitinen R. Hydrogenation of 2-ethylanthraquinone over Pd/SiO₂ and Pd/Al₂O₃ in the fixed-bed reactor. The effect of the type of support. *Catal. Lett.* 2004; 94: 157–170. DOI: 10.1023/B:CATL.0000020540.90536.6d.
- [16] Lepage JE, Corty P, Freund E, Franck JP, Jacquin Y, Juguin B, Marcilly C, Martino G, Miquel J, Montarnal R, Sugier A, Landeghem HV. *Applied Heterogeneous Catalysis Design Manufacture Use of Solid Catalysts*. Institute Francais du Petrole, Editions Technip: Paris; 1987. 329 p.
- [17] Iglesia E, Soled SL, Baumgartner JE, Reyes SC. Synthesis and catalytic properties of eggshell cobalt catalysts for the Fischer-Tropsch synthesis. *J. Catal.* 1995; 153: 108–122. DOI: 10.1006/jcat.1995.1113.
- [18] Takehira K, Shishido T, Shoro D, Murakami K, Honda M, Kawabata T, Takaki K. Preparation of egg-shell type Ni-loaded catalyst by adopting “Memory Effect” of Mg–Al hydrotalcite and its application for CH₄ reforming. *Catal. Commun.* 2004; 5: 209–213. DOI: 10.1016/j.catcom.2004.02.004.

- [19] Takehira K, Kawabata T, Shishido T, Murakami K, Ohi T, Shoro D, Honda M, Takaki K. Mechanism of reconstitution of hydrotalcite leading to eggshell-type Ni loading on Mg single bond Al mixed oxide. *J. Catal.* 2005; 231: 92–104. DOI: 10.1016/j.jcat.2005.01.025.
- [20] Qiu Y, Chen J, Zhang J. Influence of nickel distribution on properties of spherical catalysts for partial oxidation of methane to synthesis gas. *Catal. Commun.* 2007; 8: 508–512. DOI: 10.1016/j.catcom.2006.08.003.
- [21] Galarraga C, Peluso E. Eggshell catalysts for Fischer–Tropsch synthesis: Modeling catalyst impregnation. *Chem. Eng. J.* 2001; 82: 13–20. DOI: 10.1016/S1385-8947(00)00352-1.
- [22] Lekhal A, Glasser BJ, Khinast JG. Impact of drying on the catalyst profile in supported impregnation catalysts. *Chem. Eng. Sci.* 2001; 56: 4473–4487. DOI: 10.1016/S0009-2509(01)00120-8.
- [23] Lin Q, Ji Y, Jiang Z-D, Xiao W-D. Effects of precursors on preparation of Pd/ α -alumina catalyst for synthesis of dimethyl oxalate. *Ind. Eng. Chem. Res.* 2007; 46: 7950–7954. DOI: 10.1021/ie070640b.
- [24] Patent WO 00/72961; Inv: Hu Y, Dent AL. 2000.
- [25] Patent US 6355596. Hu Y, Dent AL. 2002.
- [26] Patent US 4051072. Burton RE, Berg M. 1977.
- [27] Patent US 7288686. Ryu JY. 2007.
- [28] Patent US 7462751. Lowe DM, Molinier M. 2008.
- [29] L. Siqin, M. Xiaotang. Patent application publication US 2001/0056036 A1. 2001.
- [30] Gavriilidis A, Varma A, Morbidelli M. Optimal distribution of catalyst in pellets. *Catal. Rev. Sci. Eng.* 1993; 35: 399–456. DOI: 10.1080/01614949308013912.
- [31] Badano JM, Betti C, Rintoul I, Vich-Berlanga J, Cagnola E, Torres G, Vera C, Yori J, Quiroga M. New composite materials as support for selective hydrogenation; egg-shell catalysts. *Appl. Catal. A Gen.* 2010; 390: 166–174. DOI: 10.1016/j.apcata.2010.10.008.
- [32] Carrara N, Badano JM, Betti C, Lederhos C, Rintoul I, Coloma-Pascual F, Vera C, Quiroga M. Selective hydrogenation by novel composite supported Pd egg-shell catalysts. *Cat. Comm.* 2015; 61: 72–77. DOI: 10.1016/j.catcom.2014.12.012.
- [33] Carrara N, Badano J, Bertero N, Torres G, Betti C, Martínez-Bovier L, Quiroga M, Vera C. Kinetics of the liquid phase selective hydrogenation of 2,3-butanedione over new composite supported Pd catalysts. *Chem. Technol. Biotechnol.* 2014; 89: 265–275. DOI: 10.1002/jctb.4113.

- [34] Badano J, Quiroga M, Betti C, Vera C, Canavese S, Coloma-Pascual F. Resistance to sulfur and oxygenated compounds of supported Pd, Pt, Rh, Ru catalysts. *Catal. Lett.* 2010; 137: 35–44. DOI: 10.1007/s10562-010-0336-x.
- [35] Badano J, Lederhos C, Quiroga M, L'Argentièrè P, Coloma-Pascual F. Low metal loading catalysts used for the selective hydrogenation of styrene. *Quim. Nova.* 2009; 33: 48–51. DOI: 10.1590/S0100-40422010000100010.
- [36] Lederhos CR, L'Argentièrè PC, Fígoli NS. 1-heptyne selective hydrogenation over Pd supported catalysts. *Ind. Eng. Chem. Res.* 2005; 44: 1752–1756. DOI: 10.1021/ie040187t.
- [37] Lederhos CR, L'Argentièrè PC, Coloma-Pascual F, Fígoli NS. A study about the effect of the temperature of hydrogen treatment on the properties of Ru/Al₂O₃ and Ru/C and their catalytic behavior during 1-heptyne semi-hydrogenation. *Catal. Lett.* 2006; 110: 23–28. DOI: 10.1007/s10562-006-0085-z.
- [38] Lederhos CR, Badano JM, Quiroga ME, Coloma-Pascual F, L'Argentièrè PC. Influence of Ni addition to a low-loaded palladium catalyst on the selective hydrogenation of 1-heptyne. *Quim. Nova.* 2010; 33: 816–820. DOI: 10.1590/S0100-40422010000400010.
- [39] Lederhos CR, Maccarrone MJ, Badano JM, Coloma-Pascual F, Yori JC, Quiroga ME. Hept-1-yne partial hydrogenation reaction over supported Pd and W catalysts. *Appl. Catal. A.* 2011; 396: 170–176. DOI: 10.1016/j.apcata.2011.02.011.
- [40] Maccarrone MJ, Torres G, Betti C, Lederhos CR, Coloma-Pascual F, Quiroga ME, Yori JC. Partial hydrogenation of 3-hexyne over low-loaded palladium mono and bimetallic catalysts. *Appl. Catal. A.* 2012; 441: 90–98. DOI: 10.1016/j.apcata.2012.07.016.
- [41] Bartowsky EJ, Henschke PA. The 'buttery' attribute of wine-diacetyl-desirability, spoilage and beyond. *Int. J. Food Microbiol.* 2004; 96: 235–252. DOI: 10.1016/j.ijfood-micro.2004.05.013.
- [42] Calbert HE, Price WV. A study of the diacetyl in cheese. I. Diacetyl content and flavor of Cheddar cheese. *J. Dairy Sci.* 1949; 32: 515–520. DOI: 10.3168/jds.S0022-0302(49)92074-3.
- [43] Whittaker P, Clarke JJ, San RHC, Begley TH, Dunkel VC. Evaluation of the butter flavoring chemical diacetyl and a fluorochemical paper additive for mutagenicity and toxicity using the mammalian cell gene mutation assay in L5178Y mouse lymphoma cells. *Food Chem. Toxicol.* 2008; 46: 2928–2933. DOI: 10.1016/j.fct.2008.06.001.
- [44] Rylander PN. *Catalytic Hydrogenation in Organic Syntheses*. Academic Press Edition. New York. 1979. 90 p. DOI: 10.1016/B978-0-12-605355-5.50016-1
- [45] Blaser HU, Jalett HP, Monti DM, JReber JF, Wehrli JT. Modified heterogeneous platinum catalysts for the enantioselective hydrogenation of α -ketoesters. *Stud. Surf. Sci. Catal.* 1988; 41: 153–163. DOI: 10.1016/S0167-2991(09)60810-7.
- [46] Wehrli JT, Baiker A, Monti DM, Blaser HU. Enantioselective hydrogenation of α -ketoesters: Preparation and catalytic behavior of different alumina-supported platinum

catalysts modified with cinchonidine. *J. Mol. Catal.* 1990;61: 207–226. DOI: 10.1016/0304-5102(90)85156-C.

- [47] Meheux PA, Ibbotson A, Wells PB. Enantioselective hydrogenation: II. Variation of activity and optical yield with experimental variables in methyl pyruvate hydrogenation catalyzed by cinchona-modified platinum/silica (EUROPT-1). *J. Catal.* 1991;128: 387–396. DOI:10.1016/0021-9517(91)90297-H.

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