

Synthesis and Characterization of NiPdCe/ γ -Al₂O₃ Catalyst for Selective Hydrogenation of 1,3-Butadiene. Impregnation Conditions Study.

Luis Lozano^{1,2}, Julia Guerra^{1,2}, Susana Curbelo², Joaquín L. Brito¹ and Claudio Olivera²

¹Laboratorio de Fisicoquímica de Superficies, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 20632, Caracas 1020-A, Venezuela

²Grupo TADiP, Departamento de Termodinámica y Fenómenos de Transferencia, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela.

In this work, we propose a method of synthesis to obtain an egg-shell type catalyst for the selective hydrogenation of 1,3-butadiene. The procedure considers the influence of acidity and temperature on the final metal distribution on the support (γ -Al₂O₃). Three catalysts were prepared at the same impregnation and drying conditions in order to verify the reproducibility of this technique. The co-impregnation of precursor salts was achieved by a pore-volume method in a rota-vapor device which controls temperature and velocity; the solution containing the precursor salts was put in contact with the carrier during two hours at 25 °C and pH=10. The drying was done in two stages: free moisture was dried under vacuum at 100 °C, and bound moisture at 1 atm and 150 °C in a N₂ atmosphere. The solids were calcined at 400 °C during 4 hours. The catalysts were characterized by SEM-EDX, TPR and BET surface area. The surface area analysis indicates that the impregnation of metals does not considerably reduce the specific area of the original support, which is 176 m²/g. On the other hand, SEM-EDX demonstrates that the method succeeds in producing egg-shell type catalysts. Since all characterization techniques give similar results for all three sets of solids, it can be concluded that the method offers an effective and reproducible way of synthesizing egg-shell catalysts.

1. Introduction

One of the most important reactions in petroleum refining and in heterogeneous catalysis studies is the selective hydrogenation of unsaturated compounds. Noble metal catalysts supported over alumina or silica are employed for this reaction; although transition metals such as nickel, cobalt and copper can also be employed due to their hydrogenating properties, noble metals such as palladium and platinum are preferred because of their higher activity and selectivity to the desired products.

Recent studies have shown that a mixed phase Ni-Pd precursor leads to a metal alloy that exhibits synergistic effects on the activity and selectivity of hydrogenation reactions (Galiasso et al., 2008). Also, acidity control of the support through incorporation of a lanthanide metal such as cerium, and the influence of such a dopant over the dispersion of Pd have been demonstrated in several papers (e.g., de Souza Monteiro et al., 1995).

Selective hydrogenation of diolefins in the presence of olefins, e.g. 1,3-butadiene in the presence of 1-butene, is the archetype of these reactions. Although commercial catalysts are currently available for this particular reaction, there is still a large ongoing research effort to develop catalyst formulations that offer a highly dispersed active phase and maximize the selectivity of the reaction. Since this reaction is exothermic, the reactants can easily polymerize under normal conditions, leading to a variety of operational problems such as selectivity loss, hot spot generation, coke and gum formation and complete saturation of the reactants. The solution to these problems has been studied in terms of the catalyst synthesis. Some authors (Lekhal et al., 2001) have recommended incorporating the metal phase only on the external surface of the pellet, in order to avoid the resistances for mass and heat transfer into the center of the solid. This particular metal profile is known as “egg-shell”. Figure 1 illustrates several metal profiles on a carrier.

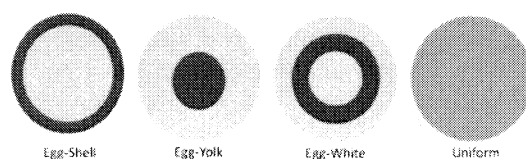


Figure 1. Possible metal distributions in a carrier

When preparing an egg-shell type catalyst, the active phase is usually incorporated by the incipient wetness impregnation method, because this prevents long-range migration of the metal particles. However, this is not the only requirement to be fulfilled in synthesizing this kind of catalyst. It is imperative also to control the metal-carrier interactions. In this paper, drying temperature and pH of the solution have been selected as the key variables to control the migration of the metal particles. The materials were characterized by scanning electron microscopy including energy dispersive X-Ray spectroscopy (SEM-EDX) to determine the type of profile that is obtained in the solids; we also implemented thermal gravimetric analysis (TGA) in a reductive atmosphere and surface area study to determine synergistic interactions between Ni-Pd metals and integrity of the structural features of the carrier.

2. Experimental

2.1 Selection of the Synthesis Method

The main objective of this work is to find a reproducible method to synthesize NiPdCe egg-shell catalysts for selective hydrogenation of 1,3-butadiene. Even though the pore-filling method was chosen as the most appropriate technique to obtain the solids (Cukic et al., 2009) by incipient wetness, several batches were prepared at different temperatures and pH to select the most suitable preparation conditions. Since the metal profile of the catalyst particles depends on drying temperature and pH of the solution (Lekhal et al., 2004), two drying temperatures were tried for the bound moisture, 100 °C and 150 °C maintaining the same pH. According to direct visual inspection (figure 2),

drying at 100 °C tends to place the metal particles at the center of the pellets generating an egg-yolk profile, instead of the egg-shell profile which can be observed at 150 °C. After the drying temperature of the bound moisture was set, the influence of pH impregnating solution was investigated. Experiments were carried out at pH=8, 9 and 10. Once again, simple inspection (figure 2) of the images showed that raising the pH level attracts metal particles to the edge of the pellets, so it was decided to set the impregnation conditions at pH=10.

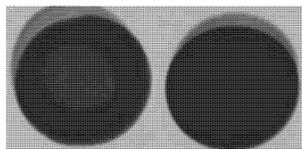


Figure 2. Metal profiles in catalysts pellets, according to synthesis protocol. Left: pH=8, T= 100 °C. Right: pH= 10, T= 150 °C

2.2 Materials

Nickel nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; tetraamine palladium (II) chloride hydrate, $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$; and ammonium cerium (IV) nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ were used in the impregnating solution for depositing Ni, Pd and Ce respectively on the support. The final catalyst has mass contents of 0.572% Ni, 0.518% Pd and 0.1% Ce (nominal contents). A commercial high surface area gamma alumina ($\gamma\text{-Al}_2\text{O}_3$ Alfa Aesar) was used as the carrier in the form of 1/8 in pellets.

2.3 Synthesis

The entire lot of catalyst pellets was prepared in three different batches, which were treated by the same synthesis technique. The co-impregnation of precursor salts was undertaken by pore volume filling in a rota-vapor device which controls temperature and velocity. The solution containing the precursor salts was put in contact with the carrier during two hours at 25 °C keeping the pH at 10, with a spin velocity of 90 rpm. The drying was done in two stages. First, the drying of free moisture was carried out under vacuum in the same rota-vapor device at 100 °C for 20 minutes. The solids were then transferred to a glass reactor to continue with the drying of bound moisture at 1 atm and 150 °C in a N_2 100 ml/min flow overnight. Finally, the solids were calcined at 400 °C for 4 hours in static air.

2.4 Catalyst Characterization

Metal composition in the edge and in the center of the pellets and also metal content in either region was observed using a scanning electron microscope JEOL JSM-6390; the samples were set in Bakelite, cut through the longitudinal axis of the pellets and polished before the analysis in order to expose the internal face of the pellets. The reduction of the solids was studied by thermal gravimetric analysis with a flow of 100ml/min of H_2 (15 vol%)- N_2 mixture; the test was carried out in the range of 40 – 900 °C, giving results comparable to those that should be obtained with conventional temperature-programmed reduction. The BET surface area of the $\gamma\text{-Al}_2\text{O}_3$ support and

the NiPdCe/ γ -Al₂O₃ catalysts were determined by N₂ adsorption at 77 K using a Micromeritics ASAP-2010 instrument.

3. Results and Discussion

3.1 SEM-EDX

Figure 3 shows the micrographies related to the metal profile and the atomic composition of Ni and Pd on the NiPdCe/ γ -Al₂O₃ solids. It is important to mention that Ce content could not be measured because the loading of this metal is lower than the limit of detection of the equipment. The remaining percentage is associated to Al₂O₃.

Table 1. Atomic proportions

	Center		Edge	
	Ni	Pd	Ni	Pd
Catalyst: 100 °C, pH= 8	0.96	11.31	3.29	10.34
Catalyst: 150 °C, pH= 8	0.00	0.00	4.91	7.01
Catalyst: 150 °C, pH= 9	0.00	0.00	5.24	3.99
Catalyst: 150 °C, pH= 10	0.00	0.00	9.41	8.70

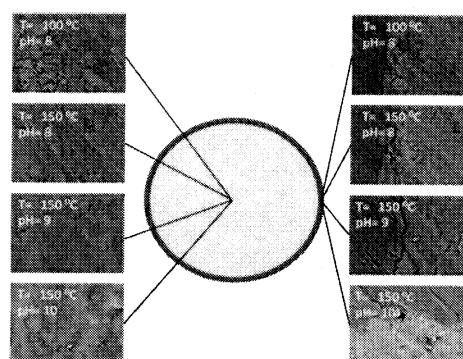


Figure 3. Micrographies of samples of the catalysts in different synthesis conditions. The diagram shows the approximate positions of the analyzed spots.

At the lower drying temperature, 100 °C, there is evidence of Ni and Pd present both at the center of the pellet and (in closer proportion) at the edge. After raising the temperature to 150 °C there is no evidence of either Pd or Ni at the center of the pellet. The Ni proportion at the edge of the pellets is seen to increase with the value of pH.

It is widely reported that the interaction between Ni and Al₂O₃ is stronger than that between Pd and Al₂O₃. According to the model proposed by Lekhal et al. (2001), for stronger metal-support interactions the metal profile in the pellet depends chiefly on the pH of the impregnating solution, thus it makes sense that the Ni metal particles tend to accumulate increasingly at the border of the pellet with increasing pH. On the other hand, the profile obtained by weaker metal-carrier interactions depends mainly on the

drying process, which is controlled in this work only by temperature. Therefore, the uneven behavior of the Pd concentration can be attributed to convection phenomena, because the flow of drying gas is not equal through the entire bed.

3.2 TGA analysis

The test was applied on samples from three catalyst batches synthesized at 150 °C drying temperature and pH = 10. Results were the same for all three samples, so we show only one of them. Figure 4 illustrates the relationship between mass loss and the temperature of treatment. The most important loss occurs in fact around 100 °C, outside the range of the plot, but it corresponds to the evaporation of unbound moisture from the carrier; only the subsequent mass changes, shown in Figure 6, can be related to reduction of the catalyst. The solid line represents the rate of mass decrease, obtained as the negative of the first derivative of the TGA curve. Once again, all samples behaved very similarly, and their curves are superimposed on the scale of the graph. The most important inflection, common to the three samples, occurs between 200 °C and 250 °C, which can be associated to the presence of a Ni-Pd solid solution. Another peak is observed at 600 °C that can be attributed to the reduction of Ni aluminate.

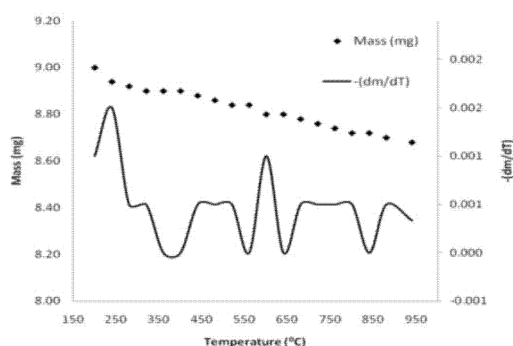


Figure 4. Typical TGA plot and first derivative of the reduction in 15vol% H_2 in N_2 of $NiPdCe/\gamma-Al_2O_3$ catalyst samples.

3.3 BET surface area

Table 2 reports the BET surface area obtained by N_2 physisorption. The three samples showed similar surface area, with very little decrease with respect to the carrier. This was to be expected, due to the small proportions of the supported metals and because the solids were not exposed to any extreme temperature treatment.

Table 2. BET surface area of the solids

Catalyst	Surface area (m^2/g)
Set 1	167
Set 2	156
Set 3	158
Carrier ($\gamma-Al_2O_3$)	176

Figure 5 presents an example of the adsorption isotherm obtained for the three cases. All the solids exhibited isotherms of the IV type, behavior associated with mesoporous solids such as alumina with cylindrical internal channels.

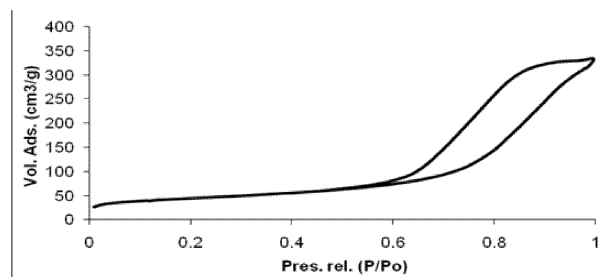


Figure 5. Typical adsorption isotherm of NiPdCe/ γ -Al₂O₃ catalyst samples.

4. Conclusions

A study has been conducted of the synthesis conditions for obtaining a specific metal profile on a solid support. The experiments reveal that increasing drying temperature helps the NiPd/ γ -Al₂O₃ system to generate profiles of the egg-shell type. Higher pH values induce Ni to aggregate in the edge of the particles. These results are in agreement with models proposed in literature, according to which increasing drying temperatures and pH values promote the formation of an egg-shell profile.

Finally, the analysis of structural features as well as reduction behavior demonstrate the reproducibility of the synthesis protocol proposed; in all cases, evidence is found of the reduction at 200-240 °C which agrees with the existence of a Ni-Pd mixed phase; also, all the catalysts presented the same kind of adsorption isotherm, proving (within the reproducibility of the technique) that neither the metal take-up nor the thermal treatment changes the structural characteristics of the alumina carrier.

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