EFFECT OF THE PREPARATION METHOD AND DISTRIBUTION PROFILES OF PDO AND PD SUPPORTED CATALYST IN THE ISOPROPYL ALCOHOL PARTIAL OXIDATION

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I. INTRODUCTION

The majorities of commercial reactions, in chemical industrial processes involve the participation of heterogeneous catalysts; these catalysts make possible develop chemical reactions in a more efficient way e. j velocity, selectivity, yield and conversion. For these reason, there are many research looking for the development of new catalyst for new synthesis route.

In heterogeneous catalysis, the catalyst is in a different phase of the reactants. The catalyst can be formed by a support and the active specie. The active specie may be an oxide or metal form.

The palladium as active component in catalysts has been used in different types of reactions, such as: hydrogenation and dehydrogenation, oxidation, partial oxidation (1). Palladium catalysts, have been used in reactions to form aldehydes and ketones, an example is the partial oxidation of isopropyl alcohol to obtain acetone (2). Other application of Palladium is in catalytic converters (3)

There are different methods for catalysts preparation, the most common are: impregnation co precipitation and precipitation. In the impregnation way of catalyst preparation, higher area materials such as silica, charcoal or alumina, (with a previous geometric form) are often used as carriers or supports for the active component of catalyst; the active component is usually deposited by soaking the carrier with a solution of the active specie precursor (4). The impregnation step is followed by drying calcination and activation by procedures such as oxidation or reduction. In a summary the impregnation method has three main parts (5, 6, 7):

1- To establish contact between the support and the active component precursor.
2- Drying of the support impregnated with the active component precursor.
3- Activation of the catalyst by a thermal or reactive process.

The effectiveness of supported catalyst, prepared by impregnation, is strongly affected by the distribution profiles of the active phase obtained on the carrier. The distribution profiles have influence in the activity, selectivity and the form in the catalysts would be poisoned or deactivated.

The variables that affect the distribution profiles are: impregnation time, concentration of the active specie solution, previous state of the support (dry or wet), pH and viscosity of the impregnation solution, impregnation protocols among other.

There are four distribution profiles and they are shown in the figure 1
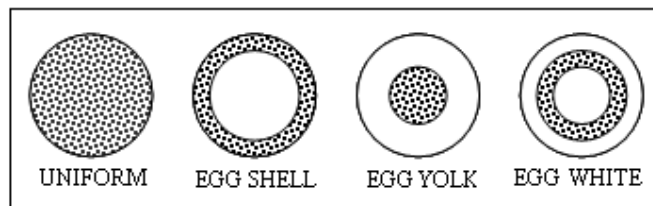

Fig 1 Distribution Profiles for Active Specie in Supported Catalysts

In this research palladium catalysts were prepared by impregnation, using different time of impregnation and support previous states. The catalysts were activated mean two forms: oxidation calcination and reduction. These catalysts were tested in a laboratory reactor varying the ratio of mass of catalyst over feed reactant flow (W/F) at 453 K and atmospheric pressure.

II. MATERIALS, EQUIPMENT AND METHODS

2.1. Materials:

Spherical Pellets of γ Al_2O_3 with 1.8 mm of diameter, supplied by SASOL were used as carrier. The active specie precursors were $NiCl_2$ and $PdCl_2$ analytical grade from Merck. Due the high cost of palladium salt the beginning catalysts were impregnated with Ni as a first approximation. As redactor agent $NaBH_4$ (Merck) was used.

In the reactor experiments, the catalysts were proved for the oxidation partial isopropyl alcohol (IPA), supplied by Merck.

2.2 characterizations:

The support pellets were characterized by superficial area determination BET, X ray diffraction (XRD), Thermo gravimetric analysis (TGA), Energy Dispersive X-ray analysis (EDX), and Scanning Electron Microscope (SEM). The catalysts prepared were characterized by this same techniques and Atomic Absorption Spectroscopy analysis. (AAS). The analysis of the compounds present in the exit stream of the reactor was detected by gas chromatography (GC)

2.3 Equipment:

The textural characterization of pellet and catalyst was determined by adsorption isotherms with Nitrogen at 77 K and area BET determination. These measures were made in a Quantachrome AUTOSORB 3B. The different crystalline structures were determined in a Diffractometer Miniflex Rigaku at 30 kV and 10 mA with a fixed heating speed of 1ª/min. and with direction angles between 2 and 80.

The thermal analysis, of support and catalyst s was made in NETZCH DSC STA 409PC equipment, fitting the speed heating in 15ª/min and 1473 K as higher limit of temperatures.

The amount of Ni and Pd, deposited on the support was measured by Atomic Absorption Spectroscopy, in a Perkin Elmer Analyst 300, using lamp of Ni and Pd at 232 and 244 nm, respectively.

The SEM and EDX analysis were carried on in FEI QUANTA 200 equipment. The FT-IR analyses were took place in a THERMO NICOLET Model Nexus. The quantification of the substances in the exit stream of the reactor was analyzed by GC in SHIMADZU GCMS QP2010S equipment.

2.4 **Experimental Section;**

The alumina supported Nickel a Palladium catalysts were prepared in the way shown in figure 2
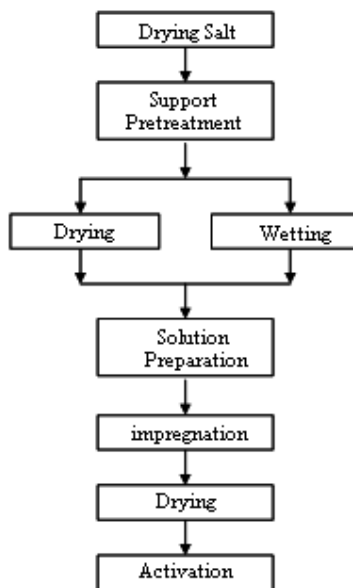

Fig 2 Technique of impregnation followed in this work.

The spherical pellets were soaked in a solution of palladium chloride $5*10^{-3}$ M, for the catalysts Pd/γ Al_2O_3; and in several solution of nickel chloride 0.25 M, 0.5 M y 1 M in the case of Ni/ γ Al_2O_3. The conditions of Temperature, wetting time for the support, and drying time for the active species precursors, carrier and impregnated support, were similar to other reported in the literature. (8-12). these conditions are shown in the table 1.

TABLE 1: Pretreatment and Drying Condition for Active specie precursor, carrier and catalysts

STEP	NiCl$_2$		PdCl$_2$	
	Time (H)	Temperature (K)	Time (H)	Temperature (K)
Salt Drying	4	398	3	393
Support Drying	24	398	24	398
Wetting Support	24	293	24	293
Drying Impregnated Support	4	398	3	393
Calcination	5	773	4	773

2.4.1 Preliminary Experiments with NiCl$_2$

Some preliminary test, for the impregnation step, were made using NiCl$_2$ as active specie precursor. The variables selected for this assay were concentration, impregnation time and support previous state. The values proved for these variables were taken of the literature (8, 9) and are shown in the table 2
.

Table 2 Values of Variables for Nickel impregnates catalysts-

VARIABLES	INTERVALS
Concentration	0.25 – 0.5 – 1 M
Time	1 -1.5 – 2 (h)
Previous State of Support	Wet or Dry

A total of 18 tests were done (PN1 to PN 18) and only 6 were chosen for the characterizations. They are reported in the table 3.
Table 3

Table 3: Conditions of the Nickel Catalyst taken for Characterization.

TEST	CONCENTRATION (M)	SUPPORT PREVIOUS STATE	TIME (h)
PN 2	0.25	Wet	2
PN 4	0.25	Dry	2
PN 6	0.25	Dry	1
PN 8	0.5	Wet	1.5
PN 10	0.5	Dry	1.5
PN 12	0.25	Wet	1.5

2.4.2 Palladium Catalysts:

For the palladium catalysts, the variables studied were exactly the same that the Nickel catalysts. The values of these variables are shown in the table 4.

Table 4 Values **of Variables for Palladium impregnates catalysts**

VARIABLES	INTERVALS
Concentration	$5*10^{-3}$ M
Time	1 - 5 (h)
Previous State of Support	Wet or Dry

The impregnation time and the concentration of active phase precursor solution were taken of previous results reported in the literature. (13, 14). A total of 6 tests were made and are reported in the table 5.

Table 5 Experimental Conditions for Palladium Catalysts

TEST	CONCENTRATION (M)	SUPPORT PREVIOUS STATE	TIME (h)
PN 2	$5*10^{-3}$	Wet	5
PN 4	5*10	Dry	1
PN 6	5*10	Wet	1
PN 8	5*10	Dry	5
PN 10	5*10	Dry	1
PN 12	5*10	Dry	5

Those identified as PP1 to PP4, are catalysts activated by calcinations. (PdO/ γ-Al$_2$ O$_3$)- The test called PA1 and PA2 correspond to catalysts activated by reduction. To reduce Pd^{+2} to Pd metallic, NaBH$_4$ were used a redactor agent.(Pd/ γ-Al$_2$ O$_3$) The reduced catalysts were prepared as follows: the impregnated pellet were soaked in a solution 1.2 M of NaBH$_4$ for 1 hour at 293 K, and then the pellet were retired and washed with acetone, finally the reduced catalysts were dried, during 3 hours at 393K.

To obtain a distribution different to uniform, two additional catalysts were prepared using Lactic acid as co-impregnate, as follows: the pellets of γ-Al$_2$O$_3$ were put in contact with a solution1M of lactic acid for 20 minutes and then they were soaked in a 0.1 M solution of PdCl$_2$. The conditions are shown in the table 6.

Table 6; Experimental conditions for Palladium Catalysts co impregnated with lactic acid

TEST	CONCENTRATION (M)	SUPPORT PREVIOUS STATE	TIME (h)
PAS1	0.1	Dry	1
PAS2	0.1	Dry	5

2.5 Reactor Test:

The catalysts were proved for the partial oxidation, in gas phase, of propyl alcohol to acetone.

$$2CH_3CH(OH)CH_3 + O_2 \rightarrow 2CH_3COCH_3 + 2H_2O$$
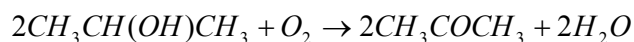
This procedure was carried on in a packed bed reactor (PBR) at 453 K and atmospheric pressure, the reactor was made stainless steel 316 with a diameter of 1.58 cm and 61 cm long. A schema of reactor is show in the figure 3.
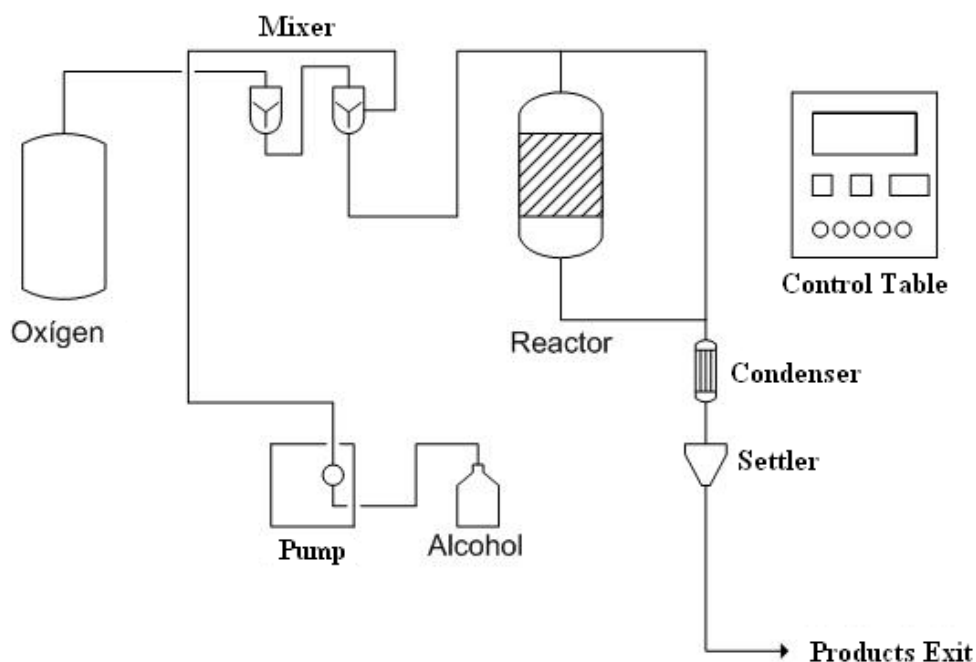

Figure 3: Schema of PBR Reactor Laboratory

In this reactor the bed was formed by 3 grams of catalysts diluted in quartz sphere in a ratio 1:3. Two different ratios of catalyst weight to molar flux of reactant (W/F$_{Ao}$) were used: 15 and 8 g/mol/L., A feed ratio 2:1 of IPA to Oxygen was used in all reactor tests. Three different catalysts were proved in the reactor, all with a uniform distribution of the active phase. (PP2, PP4 and PA1)

III RESULT AND CONCLUTIONS:

The characterization of support, catalysts and products obtained after the partial oxidation are reported in this section:

3.1 **Textural Characterization**

The isothermal adsorption for support and catalysts are presented in the figure 4. It show a typical mesoporous structure for the solids.
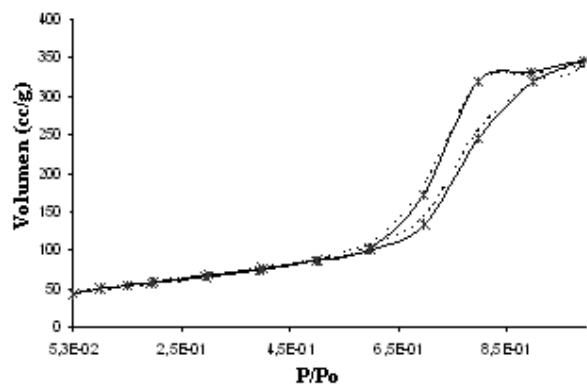
Fig. 4 Isothermal adsorption for Support and catalysts,

The areas of support and catalysts were calculated by BET equation, the results obtained are shown in the table 7.

Table 7: Superficial Areas of the Palladium Catalysts (A= without Burn, C= Burned)

TEST	SUPPORT PREVIOUS STATE	TIME (H)	AREA	C
PP1 - A´	Wet	5´	220´	129
PP1 - C´			217´	122
PP2 - A´	Dry	1´	217´	116
PP2 - C´			232´	120
PP3 - A´	Wet	1´	207´	133
PP3 - C´			222´	120
PP4 - A´	Dry	5´	226´	162
PP4 - C´			220´	159
PA1 - C´	Dry	1´	176´	202

This values show that the time and calcinations have some little effect in the area of solid materials.

3.2 XRD

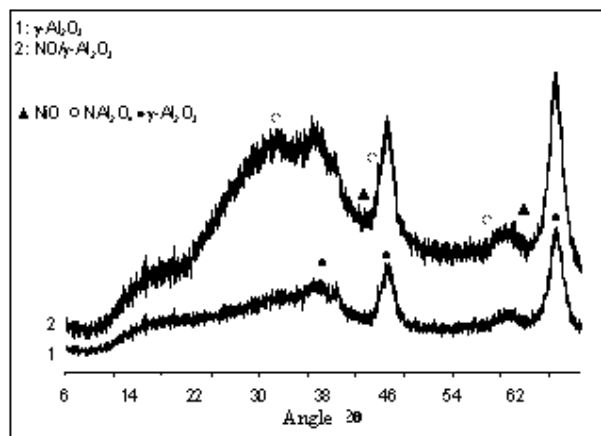The figures 5 and 6 show the diffractogram of support and Ni and Pd catalysts,
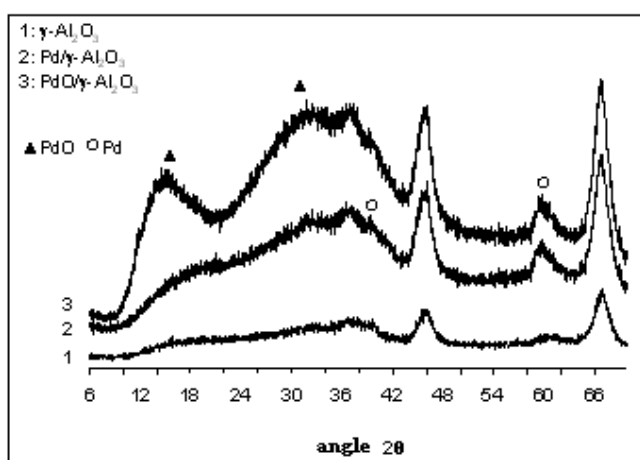
Fig 5. XRD for the support and Nickel Catalysts.

Fig 6. XRD for the support and Palladium catalysts-

3.3 Thermal analysis

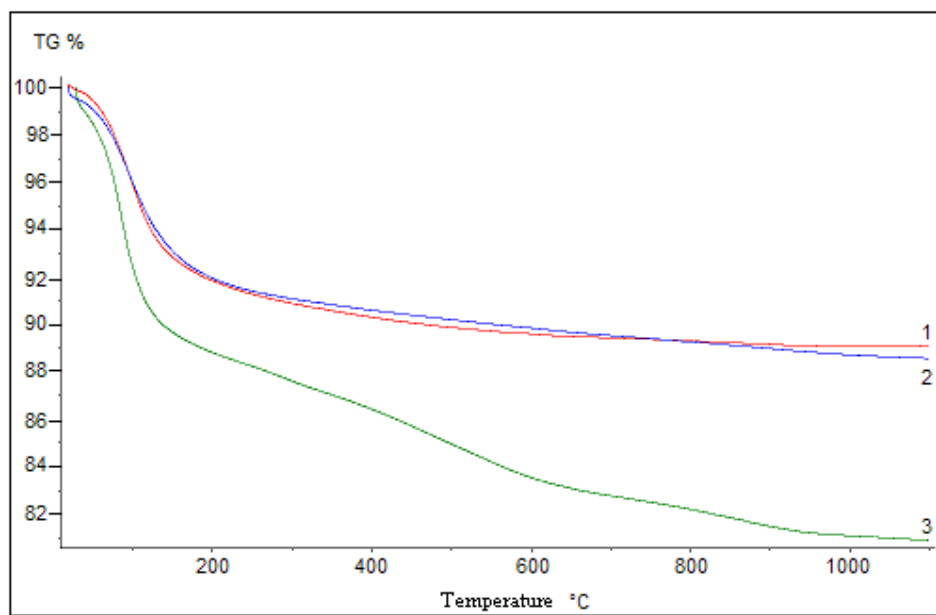In the figure 8 are shown the TGA for the support and PdO/γ-Al$_2$ O$_3$ fresh and used

Fig. 7. TGA analysis for 1) γ-**Al$_2$O$_3$ 2) PdO/** γ-**Al$_2$O$_3$ Fresco 3) PdO/** γ-**Al$_2$O$_3$ Used**

3.4 Atomic Absorption

The amount of Ni and Pd deposited in the support was evaluated by AAS analysis and the results are shown reported in the tables 8 and 9.
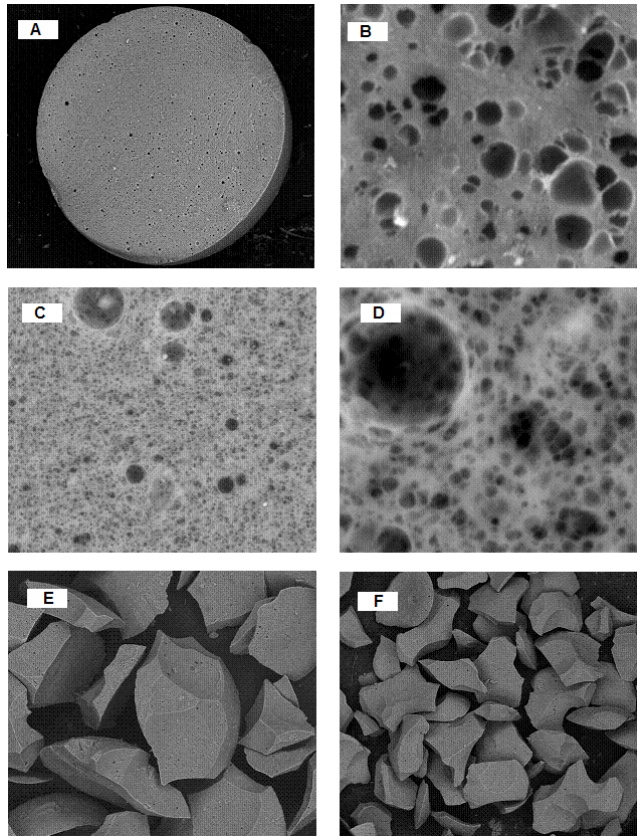
Table 8 Content of Ni in Nickel catalysts

TEST	mg Ni//g of catalyst
PN 2	2.53
PN 4	12.10
PN 12	3.26
PN 6	14.38
PN 8	29.08
PN 10	35.88

Table 9 Content of Pd in Palladium catalysts

TEST	mg Pd//g of catalyst
PP 1A	0.163
PP 1C	0.202
PP 2A	0.222
PP 2C	0.253
PP 3A	0.170
PP 3C	0.262
PP 4A	0.247
PP 4C	0.312
PA 1	0..227
PA 2	0.305

3.5 SEM analysis

The figure are represented the microscopic analysis of the support, PdO/ γ-Al$_2$O$_3$ and Pd/ γ-Al$_2$O$_3$ catalysts fresh and used.

Fig. 8 SEM Microphotographs for A) γ **-Al$_2$O$_3$ B)** γ **-Al$_2$O$_3$ C) PdO/** γ **-Al$_2$O$_3$ Fresh D) PdO/** γ **-Al$_2$O$_3$ Used E) Pd/** γ **-Al$_2$O$_3$ Fresh F) Pd/** γ **-Al$_2$O$_3$ Used.**

The figure 9 shows the EDX analysis for the Pd/ γ-Al$_2$O$_3$ and is clear that this protocols of preparation result in an egg shell distribution. R is the radio of pellet and r is a radial position inside the pellet.
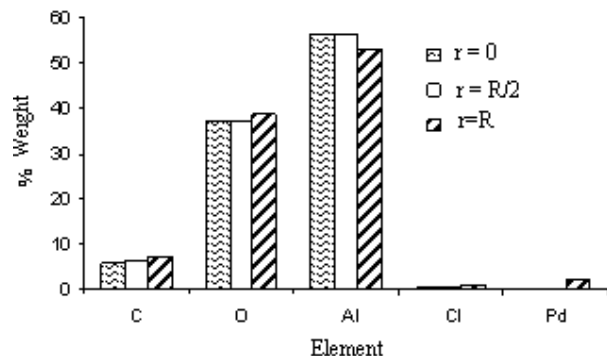
Fig 9 Composition of the catalyst prepared with coimpregnant,

3.6 REACTOR TEST:

The conversion and rate of reaction for the catalysts tested are reported in the table 10 and figure 10 .In this table and figure can be shown that catalysts prepared by calcinations give higher conversions and rates of reaction.

Table 10. Conversion and rate of reaction for the catalysts (1: W/F$_{AO}$=15gcat/mol/h, 2: W/F$_{AO}$=8gcat/mol/h

TEST	CONVERSION	RATE OF REACTION (mol/h/g cat)
PP 2-1	59%	0038
PP 2-2	40	0.053
PP 4 -1	58%	0.039
PP 4 2	39%	0.053
PA 1 1	45%	0.066
PA 1 -2	28%	0.073

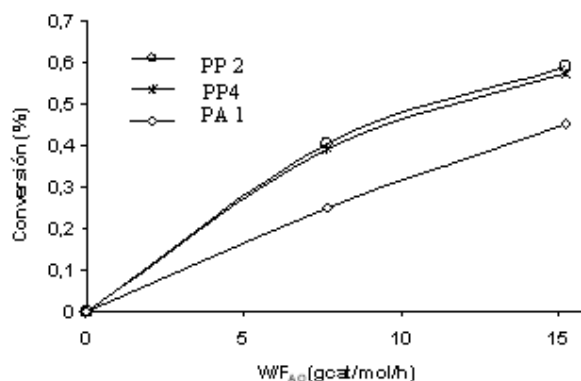**Fig 10 Conversion vs. W/F$_{A0}$ for the catalyst tested.**

IV CONCLUSIONS

The methodology proposed for the preparation of PdO/ γ-Al$_2$O$_3$ and Pd/ γ-Al$_2$O$_3$ may be used to obtain different distribution profiles for active specie on the support. The

previous state of the support affects the amount of metal deposited on the carrier. The metallic form of Palladium gives less conversion for IPA to acetone reaction

Referencies

[1]. Kirk, R.E. (1998) Encyclopedia of Chemical Technology (4 Ed.) New York: Wiley.

[2]. Bond, G. C. (1972). Principles of Catalysis. Monographs for Teachers Number 7 (2da Ed.). London, England: Chemical Society.

[3]. Heck, R.M., Farrauto, R.J. (1995). Catalytic Air Pollution Control, Commercial Technology. New York, United States: Van Nostrand Reinhold.

[4]. Droguett, S. (1983). Elementos de catálisis heterogénea. Secretaria general de la organización de los estados americanos. Washington, D.C.

[5]. Nelmark, A.V., Kheifez, L.I. & Fenelonov, V.B. (1981). Theory of Preparation of Supported Catalysts. *Ind. Eng. Chem. Prod. Res. Dev*. 20, 439-450

[6]. Perego, C. & Villa, P. (1997). Catalyst preparation methods. *Catalysis Today*. 34, 281-305

[7]. Toebes, M.L., Van Dillen, J.A.& De Jong, K.P. (2001). Synthesis of Supported Palladium Catalysts. *Journal of Molecular Catalysis A: Chemical.* 173, 75–98

[8]. Caro, D.K. (2006). Estudio de la Distribución de Níquel sobre Gama Alúmina γ-Al$_2$O$_3$: Efecto del pH, Protocolo de Impregnación y Tiempo de Impregnación. Tesis de Pregrado. Universidad de los Andes, Bogotá, Colombia.

[9]. Jackson, S.D., Willis, J., Kelly, G.J., Mclellan, G.D., Webb, G., Mather, S., Moyes, R.B., Simpson, S., Wells, P.B.&Whyman R. (1998). Supported nickel catalysts: Preparation and characterization of alumina-, molybdena-, and silica-supported nickel, and the identification of reactive oxygen on these catalysts by exchange with isotopically labelled carbon dioxide. *PCCP. Physical Chemistry Chemical Physics*. 1 (10), 2573-2580

[10]. Jerez, T.I. (2006). Estudio de la Distribución de Níquel sobre Gama Alúmina γ-Al$_2$O$_3$: Efecto del Estado Previo del Soporte, Concentración Inicial, Tiempo y Protocolo en la Impregnación. Tesis de Pregrado. Universidad de los Andes, Bogotá, Colombia.

[11]. Komiyama, M., Merrill, R.P. & Harnsberger, H.F. (1980). Concentration Profiles in Impregnation of Porous Catalysts: Nickel on Alumina. *Journal of Catalysis*. 63, 35-52.

[12]. Shuzhang, X., Zhiying, L., Guoguang, Z. & Zuhui, X. (2002). Modification effect of cerium in gas hydrogenation of acrylonitrile over Pd/Al$_2$O$_3$ catalysts. Department of Chemistry, Shanghai Normal University, Shanghai, China.

[13]. Lee Sheng Yi & Aris Rutherford. (1985). The distribution of active ingredients in supported catalysis prepared by impregnation. *Catalysis Review – Science Engineering.* 27 (2), 207-340.

[14]. Summers, J.C. & Ausen, S.A. (1978). Catalyst Impregnation: Reactions of Noble Metal Complexes with Alumina. Journal of Catalysis 52, 445 – 452