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Abstract Pyrolysis gasoline (PyGas) is an unstable byproduct of the pyrolysis of naphtha and other hydrocarbons for the production of olefins. PyGas is stabilized by hydrogenation at mild conditions. The hydrogenation of styrene to ethylbenzene is considered a model test reaction for studying the selectivity of the catalysts because it has the slowest rate of conversion. The catalytic activity and selectivity of two bimetallic co-impregnated Pd–Ni catalysts supported on γ -alumina were assessed and compared to those of a commercial monometallic Pd catalyst (AXENS LD265). The laboratory-prepared catalysts had different metal content and Pd:Ni atomic ratios (1:1 and 1:7). Catalytic tests of selective hydrogenation of styrene to ethylbenzene were made in a batch stirred tank reactor and in a continuous fixed bed trickle bed reactor. The sulfur resistance of the bimetallic catalysts in semicontinuous condition, was assessed by means of the same operational conditions using thiophene as a model poison compound. The support, Pd–Ni co-impregnated catalysts and LD265 commercial catalysts were further characterized by N₂ chemisorption,

EPMA, OM, ICP elemental analysis, temperature programmed reduction, XPS and X-Ray diffraction. The results indicated the presence of different metal species: Pd⁰, Pd^{δ+}, Ni⁰ and NiO. The lab-prepared bimetallic catalysts were found to be active for the selective hydrogenation of styrene (both in the batch and continuous system). During the continuous evaluations, the commercial LD265 catalyst had an intermediate activity level that lied between the values corresponding to the Pd–Ni bimetallic catalysts: PdNi(1:1) ≫ LD265 > PdNi(1:7). During the poison free semicontinuous evaluations, the pattern of conversion as a function of contact time of co-impregnated Pd–Ni catalysts are quite similar to that of commercial LD265 catalyst, though the catalytic activity is slightly better for PdNi(1:1). After 90 min of contact time the order of conversion was: PdNi(1:1) > LD265 > PdNi(1:7). On the other hand, during the poison semicontinuous tests (with 300 pp of thiophene), the initial reaction rates of the co-impregnated catalysts decreased, pointing a poisoning of the active sites by thiophene. PdNi(1:1) had higher initial reaction rate than PdNi(1:7) during poison free or poisoned in both conditions. PdNi(1:7) was more sulfur resistant than PdNi(1:1). The higher activity of the PdNi(1:1) catalyst was attributed to the presence of Pd⁰ and Pdⁿ⁺/Ni^{m+} species that favored respectively, the homolytic cleavage of the H–H bond and the adsorption of styrene. The higher sulfur resistance of the PdNi(1:7) catalyst would be associated with the higher Cl/Al surface atomic ratio in this catalyst (electronic effect) and the presence of electrodeficient species of Pd (Pd_x^{δ+}O_yCl_z) that prevented the adsorption of thiophene by steric hindrance (geometrical effect of the large species) or by electronic effects.

Keywords (separated by '-') Styrene selective hydrogenation - Bimetallic catalysts - Sulfur resistance - Palladium - Nickel - LD265

Footnote Information



2 Activity and sulfur resistance of co-impregnated bimetallic 3 PdNi/ γ -Al₂O₃ catalysts during hydrogenation of styrene

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8 Abstract

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17 poison compound. The support, Pd–Ni co-impregnated catalysts and LD265 commercial catalysts were further characterized
18 by N₂ chemisorption, EPMA, OM, ICP elemental analysis, temperature programmed reduction, XPS and X-Ray diffraction.
19 The results indicated the presence of different metal species: Pd⁰, Pd ^{δ +}, Ni⁰ and NiO. The lab-prepared bimetallic catalysts
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31 Al surface atomic ratio in this catalyst (electronic effect) and the presence of electrodeficient species of Pd (Pd_x ^{δ +}O_yCl_z) that
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33 **Keywords** Styrene selective hydrogenation · Bimetallic catalysts · Sulfur resistance · Palladium · Nickel · LD265

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Introduction

Pyrolysis gasoline (PyGas) is a byproduct of the pyrolysis of naphtha and other hydrocarbons for the production of olefins (Reddy et al. 1992; Cheng et al. 1986). Steam cracking is the preferred method for the production of olefins of high petrochemical value, such as ethylene and propylene. The main subproduct of this process is a fraction of intermediate

boiling point known as pyrolysis gasoline or PyGas that has a high content of aromatics such as benzene, toluene and xylene (BTX) and unsaturated compounds such as diolefins and styrene (Zhou et al. 2006). PyGas is an unstable liquid due to the presence of great amounts of unsaturated or polyunsaturated species. With the objective of guaranteeing its stability for the subsequent downstream processes PyGas must be hydrotreated to saturate those reactive olefinic and vinylic bonds. Stabilized PyGas can then be either used for blending in the gasoline pool as a high octane additive or be treated for extracting C₆–C₈ BTEX aromatics of petrochemical value.

In the classical PyGas hydrotreating process the virgin naphtha is treated in two steps of catalytic hydrogenation (Cheng et al. 1986; Gaspar et al. 2008). Di-olefins and alkenyl aromatics are hydrogenated in the first step at mild hydrogenation conditions (Shell Development Co. 1982). Other unsaturated hydrocarbons are not reacted thus preserving most of the Research Octane Number (RON) of the virgin naphtha and making the product suitable for blending in the gasoline pool. The second step is performed at a higher temperature and involves deeper hydrogenation of more olefinic bonds and elimination of sulfur (Sze and Bauer 1969; Authayanun et al. 2008). The reaction of styrene hydrogenation to ethylbenzene is considered a model test reaction for studying the selectivity of the catalysts for the first reaction. Styrene is considered the most refractory compound of all other reactive species and it has the slowest rate of conversion. For optimizing this reaction alumina supported Pd and Ni catalysts are commonly used (Gaspar et al. 2008; Nijhuis et al. 2003). Pd is the most efficient metal for hydrogenation of PyGas and styrene but is rare and expensive. Ni catalysts are attractive because of their low cost and resistance to As and water (Hoffer et al. 2002). The PyGas streams have however great amounts of sulfur compounds (Nijhuis et al. 2003; Hatch and Matar 1981; Choi et al. 2004) especially thiophene, that poison the catalysts. The use of bimetallic catalysts is an interesting alternative for improving the sulfur resistance. From a practical point of view, the effect of the addition of a second metal has the following objectives: (i) augmenting the catalytic activity, (ii) modifying the selectivity, (iii) improving the stability of the catalyst. The positive effect of the addition of the second metal can involve simple actions like helping the reduction of the first metal or enhancing the spill-over of hydrogen, or it may involve more complex metal–metal interactions (geometrical effects, electronic effects, stabilizing effects, synergies, onset of bifunctional mechanisms) (Alonso et al. 2012).

In previous works of our group, we have found that Pd monometallic catalysts prepared from chlorinated precursor turned out to be more active and resistant to poisoning with sulfur and oxygenated compounds than Pd monometallic catalysts prepared from nitrogen precursor or other metals

(Pt, Ru and Rh) (Badano et al. 2010a; b). In another work, monometallic palladium catalysts prepared with novel composite materials (of mixed organic and inorganic nature) as supports, proved to be highly active for the selective hydrogenation of styrene (Carrara et al. 2015). The group also carried out kinetic studies of the selective hydrogenation of styrene to ethylbenzene, using a palladium catalyst supported on the new composite supports (Betti et al. 2016). Other studies of kinetic of the selective hydrogenation of pyrolysis gasoline were presented by Zhou et al. (2007). The group has already been studying the activity and sulfur resistance of Pd–Ni, Pt–Ni and Pt–W bimetallic catalysts, prepared by successive impregnations, in the selective hydrogenation of styrene to ethylbenzene (Betti et al. 2012a, 2018, b).

Most of the publications deal with catalytic evaluations of bimetallic catalysts prepared by successive impregnations, in this way one metal is more superficial and the other remains covered (Alonso et al. 2012; Gaspar et al. 2008; Betti et al. 2018). To our knowledge there are few studies using co-impregnated catalysts, where both metals are superficially exposed, so it would be interesting to characterize the active species, study the activity, selectivity and their sulfur resistance especially during the hydrogenation of styrene. On the other hand, most of the publications with successively impregnated bimetallic catalysts are under batch conditions, and it is interesting to carry out previous studies of evaluations of co-impregnated bimetallic catalysts in a trickle bed reactor. So, the objective of this work are (a) synthesize two Pd–Ni/ γ -Al₂O₃ catalysts of varying metal content by co-impregnation technique; (b) characterize the bimetallic prepared catalysts; (c) evaluate their catalytic performance in continuous and semicontinuous mode of reaction and compare them against a commercial palladium catalyst; and (d) to assess sulfur resistance of the Pd–Ni catalysts in batch conditions. Selective hydrogenation of styrene is used as a model test reaction as it is the most refractory compound in the PyGas stream. Commercial LD265 was used as a reference catalyst.

Experimental

Catalysts preparation

Two bimetallic catalysts were prepared and named PdNi(1:7) and PdNi(1:1), having a Pd–Ni atomic ratio of 1:7 and 1:1, respectively. The incipient wetness co-impregnation technique was used. The support was γ -Al₂O₃ Ketjen CK 300 (previously calcined 3 h in air at 823 K to stabilize its structure), with an impregnation volume of 0.7 mL g⁻¹. A solution acidified by the addition of HCl (Sigma-Aldrich, 320331, 37 wt %, pH 1) was used for the dissolution of the salts of the metals, PdCl₂ (Sigma-Aldrich, CAS Number:

144 2099324, purity > 99.9%) and NiCl₂ (Merck, CAS: 7718-
145 54-9, purity > 98%). The amount of each metal was reg-
146 ulated in order to obtain the desired Pd/Ni ratio. 5 g of
147 PdNi(1:7) were prepared using 3.5 mL of a solution of
148 0.044 g_{Ni} mL⁻¹ and 0.012 g_{Pd} mL⁻¹, determined by ICP.
149 Besides, 5 g of PdNi(1:1) were synthesized using 3.5 mL
150 of 0.0031 g_{Ni} mL⁻¹ and 0.0063 g_{Pd} mL⁻¹ (checked by ICP).
151 After impregnation, the samples were dried in a stove for
152 24 h at 373 K.

153 A Pd commercial catalyst was used as a reference. This
154 was an Axens LD265 (0.3 wt% Pd, spherical pellets) that
155 was ground to 180–500 μm in order to be used in the tests.

156 Characterization of the catalysts

157 A Micromeritics ASAP 2020 instrument was used to
158 obtain the nitrogen adsorption–desorption isotherms
159 between 0.02 and 0.98 relative pressures (P/P_0) and the
160 Brunauer–Emmett–Teller (BET) model was used to calcu-
161 late the specific surface area (S_{BET}), average pore volume
162 (V_p) and average pore diameter (d_p) of the support. Alumina
163 support was outgassed 2 h at 523 K under vacuum, and then
164 N₂ adsorption isotherms at 77 K were obtained.

165 LD265 catalyst was analyzed using scanning electron
166 microscopy (SEM) equipped with an energy dispersion
167 system (EDAX) that enables to analyze elementary chemi-
168 cal with an X-ray microbeam. This technique is known as
169 electron probe microanalyzer (EPMA) and it was allowed
170 to elucidate metal distribution and create elemental map-
171 pings. Before measure, LD265 catalyst pellets were coated
172 with thin carbon film in order to avoid influence of charge
173 effect during the SEM operation. The scanning speed was
174 0.02 mm min⁻¹ and the acceleration voltage of electron beam
175 was 20 kV.

176 The thickness of the metal surface of LD265 commercial
177 catalyst was also determined optically with the aid of micro-
178 graphs of the cross section of the pellets. Optical micro-
179 graphs (OM) were obtained with a Mitsubishi Microwatcher
180 VS-30H Microscope and a Sony Color Video Printer. To
181 obtain the OM images, the samples were encapsulated in a
182 thermoplastic resin. Then the surface of the resin was pol-
183 ished with sandpaper number 500, 1000 and 2000 in order to
184 expose the cross section of the catalysts. Finally, a sandpaper
185 number 2500 was used for preparation end of the surface.

186 The Pd and Ni metal contents were assessed by means of
187 inductively coupled plasma (ICP) analysis. A sampling was
188 carried out for each catalyst, taking 3 portions of it (three
189 weighings, 3 digestions and three determinations). The
190 results were obtained in triplicate giving consistent results.
191 The equipment used was a Perkin Elmer 2100. The catalysts
192 were digested in sulfuric acid and diluted before performing
193 the analysis.

194 The electronic state of the surface species of Pd and Ni
195 as well as the atomic ratios of the different elements were
196 determined by X-ray Photoelectron Spectroscopy (XPS).
197 The XPS analysis was performed in a VG-Microtech Multi-
198 lab 3000 spectrometer equipped with a hemispherical elec-
199 tron analyzer. The radiation source was a Mg anode operated
200 at 200 W, generating a K alpha line with a photon energy
201 of 1253.6 eV and a line width of 0.7 eV. The pre-reduced ex
202 situ (1 h at 473 K) powder catalysts were pressed into small
203 inox cylinders and then mounted on a sample rod placed in
204 a pre-treatment chamber and reduced in H₂ for 1 h at 473 K
205 before being transferred to the analysis chamber. Before
206 recording the spectra, the sample was maintained in the
207 analysis chamber until a residual pressure of 5×10^{-9} mbar
208 was reached. The spectra were collected at a pass energy
209 of 50 eV and the energy step for scanning was 0.1 eV. The
210 intensities were estimated by calculating the integral of each
211 peak, after subtraction of the S-shaped background, and by
212 fitting the experimental curve to a combination of Lorentz-
213 ian (30%) and Gaussian (70%) lines. Binding energies were
214 referenced to the C 1 s line at 284.6 eV, which provide values
215 with an accuracy of 0.2 eV.

216 X-ray diffraction spectra of the catalysts were acquired
217 in a Shimadzu XD-1 using CuKα ($\lambda = 1.5405 \text{ \AA}$) radiation
218 filtered with Ni, in the $25^\circ < 2\theta < 80^\circ$ range. A scanning
219 rate of 1° min^{-1} was used. The catalysts were first ground to
220 a powder and reduced ex situ in hydrogen. Then they were
221 cooled down to room temperature in nitrogen and placed in
222 the sample holder for taking the spectrum.

223 The study of the reducibility of the surface species was
224 done by temperature programmed reduction (TPR) in a
225 Micromeritics Auto Chem II apparatus with a thermal con-
226 ductivity detector. For the preparation of the calibration
227 curve, Ag₂O was used as calibration material, which has
228 a consumption of $95.0 \pm 0.3 \text{ cm}^3$ of H₂ per gram of oxide.
229 Before the detection a cold trap was used to condense water
230 vapor. Before each TPR test 100 and 500 mg of powdered
231 synthesized catalysts were calcined in situ in air in order
232 to eliminate the residual adsorbed water (1 h at 473 K,
233 10 K min^{-1} , at a flowrate of 40 mL min^{-1}). Then they were
234 cooled down in Ar at 308 K at a flowrate of 40 mL min^{-1} .
235 The argon flow was closed and the reducing gas H₂ in Ar
236 (5% vol/vol) at a flowrate of 40 mL min^{-1} was enabled. A
237 reasonable time was waited until the TCD detector signal
238 stabilized. Once the detector signal was stabilized, the heat-
239 ing ramp at 10 K min^{-1} up to 1173 K begun and conse-
240 quently the acquisition of the detector signal. In all cases
241 high purity H₂ and Ar (99.99%) were used.

242 **Catalytic tests**

243 The reaction of selective hydrogenation of styrene to ethylb- 294
 244 enzene was performed in a batch reactor in semicontinuous 295
 245 mode and in a trickle-bed reactor in continuous mode. Runs 296
 246 were carried out in triplicates with an average experimental 297
 247 error of 3%. 298

248 *Continuous system* A trickle-bed reactor with a packed 300
 249 bed and a cocurrent flow pattern for gas and liquid was used. 301
 250 The catalytic bed involved an adequate amount of catalyst 302
 251 (w_c) in order to keep the amount of Pd constant in all the 303
 252 tests. The catalyst was diluted with SiC in a ratio $w_c/w_{SiC} = 1$ 304
 253 for improving the wetting of the catalyst and preventing 305
 254 heat and mass transfer in the reactor (Sie 1991). The pellets 306
 255 were ground and sieved to a size of 180–500 microns in 307
 256 order to avoid external diffusional limitations. The catalysts 308
 257 were first reduced in situ for 1 h with pure H_2 at a reduc- 309
 258 tion temperature of 473 K and atmospheric pressure with 310
 259 a hydrogen flow rate of 60 mL min^{-1} (using a temperature 311
 260 ramp of 6 K min^{-1}). The catalyst activity was tested iso- 312
 261 thermally at a temperature of 353 K, a pressure of 0.7 MPa, 313
 262 $WHSV = 17.3 \text{ h}^{-1}$ (for catalysts LD265 and PdNi(1:1)) 314
 263 and a value of $WHSV: 38.3 \text{ h}^{-1}$ for catalyst PdNi(1:7) in 315
 264 order to keep the palladium metal content constant and a 316
 265 H_2 /hydrocarbon ratio of 6 in the feed. During the reactor 317
 266 start-up the feed flowrate was set at 5 mL min^{-1} for 2 min 318
 267 in order to accelerate the filling of the empty space of the 319
 268 reacting system. The liquid feed was a 5% (vol:vol) solution
 269 of styrene in toluene, at a flow rate of 0.05 mL min^{-1} and a
 270 hydrogen flow rate of 60 mL min^{-1} . The blank test with a
 271 packed bed containing only SiC gave negligible conversion
 272 and thus the effect of the reactor walls or the diluent was
 273 disregarded. According to the vapor pressure of the liquid
 274 feed and the pressure of the system practically all organic
 275 compounds remained in the liquid phase, the molar fraction
 276 of organic vapors in the gas phase being only 5.7% approxi-
 277 mately. Hydrogen gas comprised 94.3% of the gas phase.
 278 The length of the runs was 6–8 h.

279 *Semicontinuous system* This was a stainless steel stirred 320
 280 tank reactor, internally lined with PTFE. Reaction condi- 321
 281 tions were 333 K, 2 MPa hydrogen pressure, 1200 rpm stir- 322
 282 ring rate. In each test 0.3 g of the crushed catalyst (180–500 323
 283 microns) and 200 mL of a styrene solution (5% vol:vol in 324
 284 toluene) were used. The catalysts were reduced ex situ in a 325
 285 glass continuous reactor under hydrogen at 673 K for 1 h 326
 286 with a hydrogen flow rate of 110 mL min^{-1} (using a tem- 327
 287 perature ramp of 10 K min^{-1}). Immediately reduced, the 328
 288 catalysts were cooled down up to room temperature under 329
 289 nitrogen flow, were charged at room temperature in the 330
 290 batch reactor and were catalytically evaluated. There was 331
 291 no chance of Pd reoxidation by oxygen from air, although 332
 292 oxygen chemisorption is possible, oxidation begins only at 333
 293 much higher temperatures. The start-up involved heating 334

294 at an inert atmosphere and stirring at 1200 rpm the liq- 295
 296 uid mixture to the setpoint temperature. Finally, the reac- 297
 298 tor was purged and then the hydrogen was introduced, this 298
 299 was time zero of the reaction. At the operational conditions 299
 300 of this work, internal and external diffusional limitations 300
 301 were absent. Catalytic tests at chosen reaction conditions 301
 302 were run using the commercial catalyst (LD265) but with 302
 303 increasingly smaller size, starting from the catalyst in pel- 303
 304 let form. When no increase in conversion at the outlet of 304
 305 the reactor was detected, intraparticle mass transfer limita- 305
 306 tions were supposed to be eliminated (Cagnola et al. 2004). 306
 307 On the other hand, with the object to eliminate gas–liquid 307
 308 diffusional limitations, experiences were carried out using 308
 309 different stirring speeds. It was found that at stirring rates 309
 310 higher than 800 rpm styrene conversion values remained 310
 311 constant, indicating that external gas–liquid limitations 311
 312 were absent (Holland and Chapman 1976; Le Page 1978). 312
 313 Styrene (Aldrich, Cat. No. S497-2, purity > 99%) and tolu- 313
 314 ene (Merck, Cat. No. TX0735-44, purity > 99%) were used 314
 315 as is and without further purification. For the tests with a 315
 316 poisoned feed, 600 ppm of thiophene (Sigma-Aldrich, CAS 316
 317 Number: 110-02-1, purity $\geq 99\%$) were added to the reaction 317
 318 medium before the reaction. 318

319 Reactants and products were analyzed in a Shimadzu gas 319
 320 chromatograph equipped with a flame ionization detector 320
 321 and a capillary column (30 m J&W InnoWax 19091N-213). 321

320 **Results and discussion**321 **Characterization of the catalysts**

322 Alumina support showed a mesoporous structure with S_{BET} 322
 323 of $180 \text{ m}^2 \text{ g}^{-1}$, d_p of 9.6 nm and V_p of $0.53 \text{ cm}^3 \text{ g}^{-1}$. These 323
 324 results can give an idea of the exposed surface area of the 324
 325 alumina support and its interaction with the precursors 325
 326 metals. 326

327 The variation of the wetting volume of the synthesized 327
 328 catalysts was determined. The fresh alumina support has 328
 329 an impregnation volume of 0.7 mL g^{-1} . For PdNi(1:1) the 329
 330 percentage of reduction of the wet volume of the fresh cata- 330
 331 lyst with respect to the support was 7%, while for PdNi(1:7) 331
 332 fresh catalyst it was 17%. This reduction is originated by 332
 333 the deposition of Pd and Ni on the alumina surface, block- 333
 334 ing some pores. Due to the higher loadings of PdNi(1: 7) 334
 335 catalyst, the percentage of reduction is higher. 335

336 By EPMA, the average thickness of the metallic phase of 336
 337 LD265 catalyst of 10 samples determined at random gave 337
 338 greater than 150 μm . 338

339 The images obtained from Optical Microscopy (OM) for 339
 340 the commercial LD265 catalyst, allowed observing inhom- 340
 341 geneous film thickness in the pellets greater than 80 μm . In 341

Fig. 1 OM images of the LD265 catalyst pellet cross section (left) and region magnification (right)

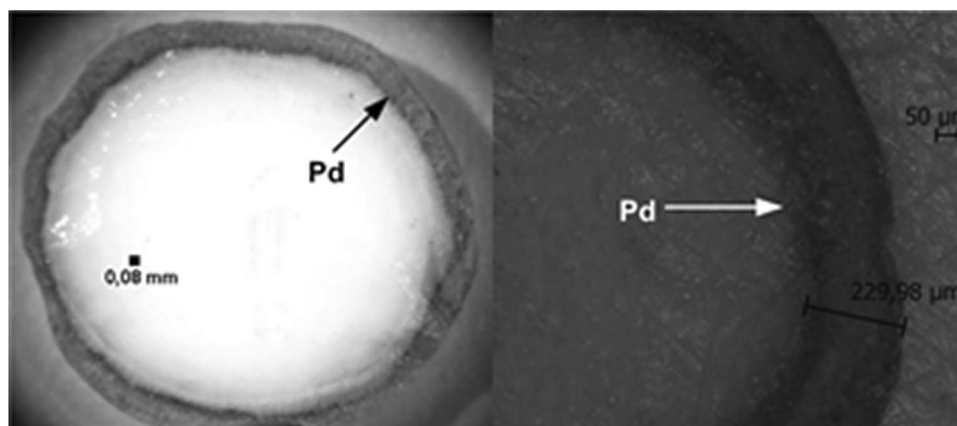


Table 1 Catalysts metal loadings as obtained by ICP

Catalyst	Mass concentration (%)	
	Pd (wt%)	Ni (wt%)
PdNi(1:7)	0.66	2.40
PdNi(1:1)	0.34	0.17
LD265	0.30	–

species (Hwang et al. 1999) that were not eliminated during the thermal pretreatment stages.

In the case of the PdNi(1:1) catalyst (see Fig. 2) the spectrum of Pd 3d was deconvoluted with two chemical components at 335.0 and 336.8 eV, that could be attributed to Pd⁰ (NIST 2012) and to palladium oxychloride species (Pd_xⁿ⁺O_yCl_z with n → 2) (Gaspar et al. 2008; Badano et al. 2010a, b). Besides in Fig. 3 for the same catalyst two peaks

Fig. 1 are shown the OM of the LD265 catalyst pellet cross section (Left) and a region magnification (Right). It can be observed a thickness of 229.98 μm.

Table 1 shows the noble metal contents as determined by ICP.

XPS analysis was used to obtain information on the chemical environment of the elements present on the surface of the catalysts. Table 2 shows values of the surface atomic ratios and the values of binding energy of Ni and Pd. The values of binding energy (BE) were determined by deconvolution of the XPS spectra of the Pd 3d_{5/2} and Ni 2p_{3/2} signals. Pd/Al and Cl/Al atomic ratios were also determined by computing the area under the XPS lines for each signal.

Figures 2, 3, 4 and 5 present the spectra obtained in the Pd 3d_{5/2} and Ni 2p_{3/2} regions for the synthesized catalysts. The Pd curves show the 3d_{5/2} and 3d_{3/2} peaks, separated by 5.2 eV. This coincides with literature reports (Wagner et al. 1978). The XPS spectra of the bimetallic catalysts show also a peak close to 198.5 eV that corresponds to Cl 2p_{3/2}. This signal was addressed to the presence of surface chlorine

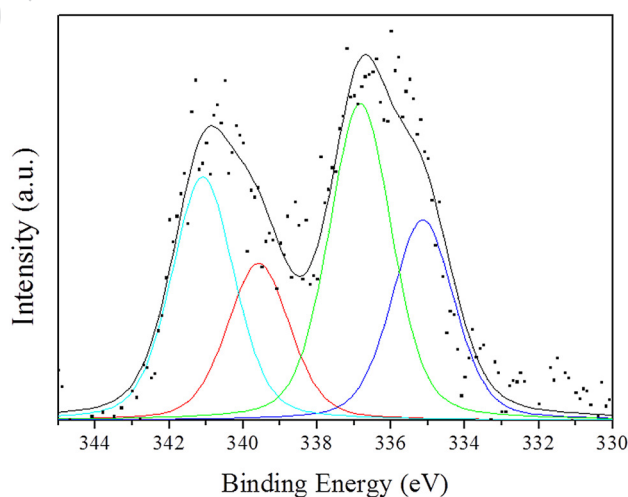


Fig. 2 XPS traces of Pd 3d of the PdNi(1:1) catalyst

Table 2 Values of binding energy (BE) of the Ni and Pd species

Catalyst	Pd 3d _{5/2} BE (eV)			Ni 2p _{3/2} BE (eV)		Atomic surface ratios	
	Pd ⁰	Pd ^{δ+}	Pd ⁺⁺	Ni ⁰	NiO	Cl/Al	Pd/Al
Pd:Ni(1:7)	–	335.9 (100%)	–	853.0 (59%)	856.0 (41%)	0.213	0.035
PdNi(1:1)	335.0 (39%)	–	336.8 (61%)	–	856.2 (100%)	0.022	0.001

Cl/Al and Pd/Al atomic surface ratios of the catalysts as measured by XPS

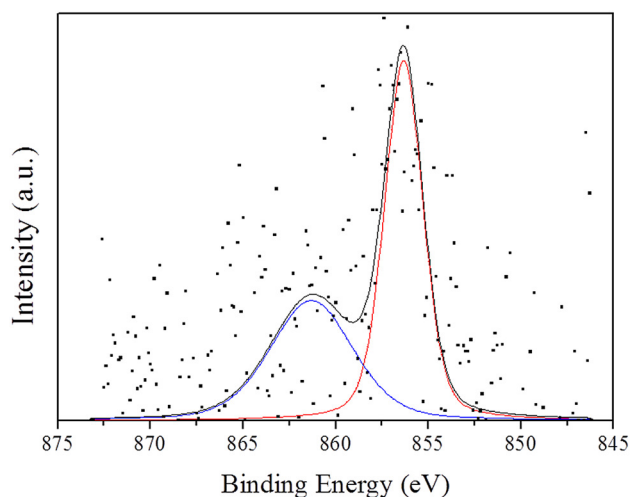


Fig. 3 XPS traces of the Ni $2p_{3/2}$ region of the PdNi(1:1) catalyst

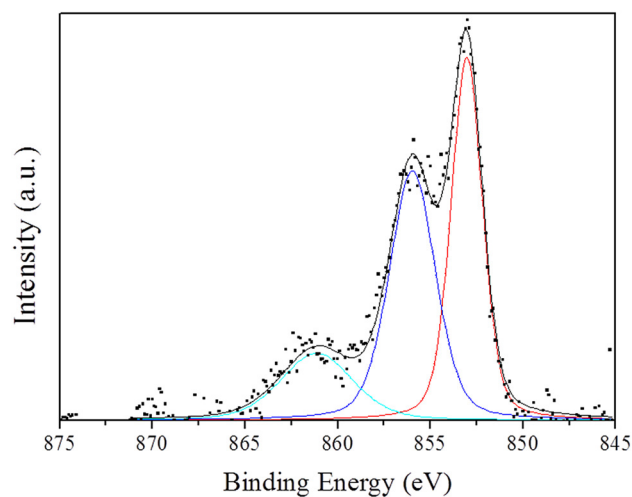


Fig. 5 XPS traces of the Ni $2p_{3/2}$ region for the PdNi(1:7) catalyst

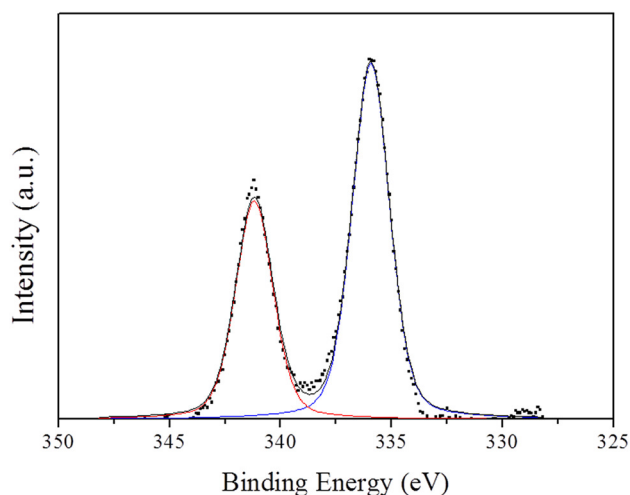


Fig. 4 XPS of the Pd $3d$ region in the case of the PdNi(1:7) catalyst

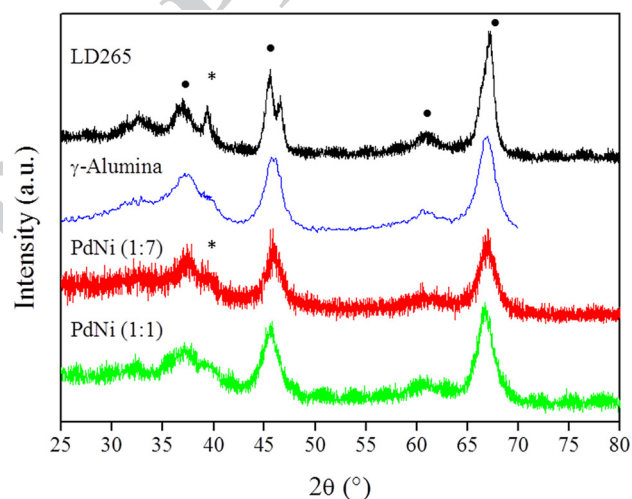


Fig. 6 X-ray diffractograms of the catalysts. (Filled circle) alumina, (asterisk) Pd

370 in the Ni $2p_{3/2}$ region were addressed to NiO (NIST 2012) (at
371 856.2 eV) and the shake up of Ni(II) (at 862.6 eV) (Benitez
372 et al. 1999; Heracleous et al. 2005; Ferrer et al. 2005).

373 With respect to the PdNi(1:7) sample Fig. 4 shows
374 that only a peak at 335.9 eV can be found in the Pd $3d_{5/2}$
375 region. This peak was attributed to oxychlorinated species
376 ($\text{Pd}_x^{\delta+}\text{O}_y\text{Cl}_z$, with $\delta \rightarrow 0$) (Gaspar et al. 2008; Badano et al.
377 2010a, b). Figure 5 shows that in the Ni $2p_{3/2}$ region three
378 peaks can be found. One at 853 eV due to Ni^0 and another
379 one at 856 eV due to electrodeficient Ni(II), in the form of
380 NiO (NIST 2012). There is also a third peak at 862.6 eV
381 corresponding to the shake up of Ni(II).

382 Table 2 shows that the PdNi(1:7) catalyst has higher Cl/
383 Al and Pd/Al atomic ratios than PdNi(1:1). When compar-
384 ing the BE of the electrodeficient species ($\text{Pd}^{\delta+}$ o Pd^{n+})

385 it is evident that the PdNi(1:1) catalyst had the highest
386 electrodeficiency.

387 Figure 6 shows the X-ray diffractograms of the PdNi(1:7),
388 PdNi(1:1) and commercial LD265 catalysts, and the
389 γ -alumina support. The resulting XRD pattern was that of
390 the alumina support. The diffractogram of PdNi(1:7) and
391 PdNi(1:1) had three main peaks of the γ - Al_2O_3 structure at
392 $2\Theta = 37.7^\circ$, 46.0° and 67.0° ($\langle 400 \rangle$ and $\langle 440 \rangle$ crystal planes)
393 (Huang et al. 2008). A small peak at 39.7° can be seen only
394 in PdNi(1:7), that would be related to the $\langle 111 \rangle$ planes of Pd^0
395 (Cobo et al. 2008). No peaks due to PdO nor NiO could be
396 found. This was attributed to the small size of the crystal-
397 lites and the relatively high limit of detection of the XRD
398 technique (Telkar et al. 2005). Heracleous et al. (2005) have

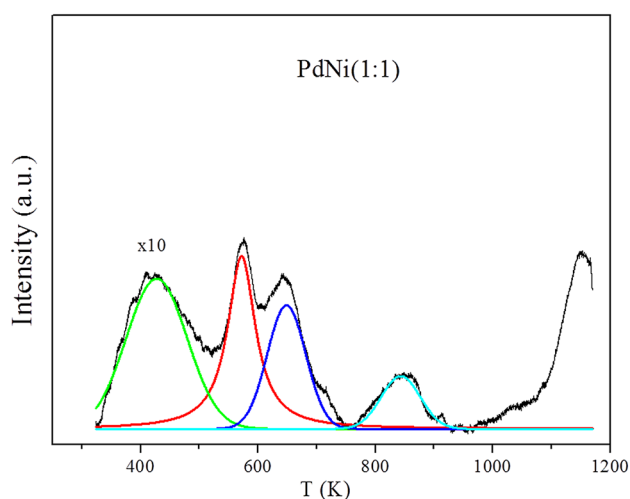


Fig. 7 TPR trace of the bimetallic PdNi(1:1) laboratory prepared catalyst sample

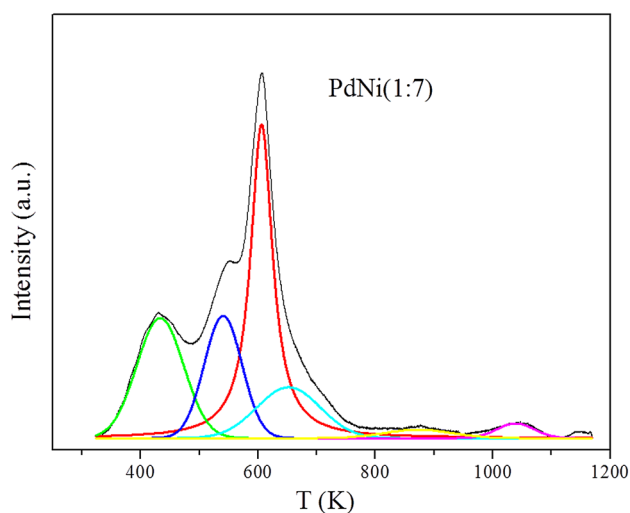


Fig. 8 TPR trace of the bimetallic PdNi(1:7) laboratory prepared catalyst sample

Table 3 Deconvoluted peaks, calculated area and peak temperature for Pd–Ni bimetallic catalysts

	PdNi(1:7)			PdNi(1:1)		
	Area (a.u.)	% Area	Peak temperature (K)	Area (a.u.)	% Area	Peak temperature (K)
Peak 1	0.934239	0.223496	432.4	0.377666	0.392751	427.3
Peak 2	0.833066	0.199292	541.4	0.301635	0.3136831	571.9
Peak 3	1.794290	0.429244	605.9	0.196963	0.2048301	648.5
Peak 4	0.419998	0.100475	650.9	0.0853277	0.088736	843.1
Peak 5	0.101715	0.024333	872.7			
Peak 6	0.096810	0.023160	1038.5			

informed that in the case of alumina supported Ni catalysts a minimum content of Ni of 15% is needed to detect the diffraction lines of NiO (bulk) at $2\theta = 43.3^\circ, 63.0^\circ, 75.5^\circ$ and 79.5° . Salagre et al. (1996) have informed that the diffraction lines of low intensity of the NiO particles of the Ni/Al₂O₃ catalysts can only be detected in amounts higher than 26.6%. In our case the crystallites cannot be detected. It is important to note that the diffractogram in Fig. 6 of the commercial catalyst only shows peaks corresponding to γ -Al₂O₃ (Huang et al. 2008) and Pd(111) planes of Pd⁰ (Cobo et al. 2008).

Figures 7 and 8 show the TPR traces of the laboratory prepared bimetallic Pd–Ni catalysts. These traces indicate the consumption of hydrogen during the reduction of different surface species. The TPR profiles obtained for PdNi(1:1) and PdNi(1:7) catalysts were deconvoluted from room temperature to 1000 K and the area under the curves were calculated. The obtained peaks and area are informed in Table 3.

According to literature reports the first peak at 427.3 and 432.4 K for PdNi(1:1) and PdNi(1:7), respectively, can be attributed to the reduction of Pd oxychlorinated species (Pd_xⁿ⁺O_yCl_z, 0 < n < 2) or the reduction of Pd_xⁿ⁺ ions that are stabilized by Cl⁻ remaining on the surface of γ -alumina (Noronha et al. 2000). As seen in Figs. 7 and 8, this peak was the most intense for PdNi(1:7) and shifted 5.1 K to higher T; this is due to the higher Pd content of the catalyst and suggest a higher interaction of Pd_xⁿ⁺ ions with the support. The peaks above 470 K can be attributed to the reduction of different Ni species. Some authors define three regions of reduction of Ni depending on the temperature range: (I) up to 600 K nickel oxides with null or weak interaction with the support are reduced (bulk NiO); (II) between 600 and 1000 K the reduction of the Ni oxides strongly interacting with the support occurs; (III) the region between 1000 and 1273 K in which the reduction of the Ni aluminates occurs (NiAl₂O₄) (Juan-Juan et al. 2006). In the spectra of Figs. 7 and 8, we can see that in the range from 400 to 1100 K the most intense signals are those of PdNi(1:7). This is due to the higher content of Ni of this catalyst. The observed peaks at 571.9 and 541.1 K for PdNi(1:1) and PdNi(1:7),

438 respectively, are attributed to bulk NiO with null or weak
439 interaction with the support. It is observed that this peak in
440 the PdNi(1:1) catalyst is shifted to higher temperatures com-
441 pared to the PdNi(1:7) catalyst (ca. 30.5 K). This could be
442 originated by a greater dispersion of nickel on the low load-
443 ing PdNi(1:1) catalyst, resulting a stronger interaction with
444 the support (Hilli et al. 2015). Besides, the peaks at 648.5
445 and 843.1 K for PdNi(1:1) and 605.9, 650.9 and 827.7 K for
446 PdNi(1:7), could be assigned to Ni oxides strongly interact-
447 ing with the alumina support.

448 Although the percent area of the deconvoluted peaks
449 informed in Table 3, as it is impossible to know the exact
450 stoichiometry of $\text{Pd}_x^{\text{n+}}\text{O}_y\text{Cl}_z$ and the oxidation state of Pd,
451 it is not possible to calculate the reduction degree of each
452 catalyst.

453 Catalytic tests

454 In all catalytic tests the selectivity to ethylbenzene was 100%
455 at the operational conditions used.

456 Continuous system

457 Figure 9 shows the curves of total conversion of styrene as a
458 function of time on stream for the two bimetallic Pd–Ni cata-
459 lysts and the reference commercial catalyst. These results
460 correspond to the test in the continuous flow system. In all
461 cases the systems had a period of catalyst “activation” or a
462 period to reach the steady-state during the continuous evalu-
463 ations, beginning to stabilize at about 120 min. PdNi(1:1)
464 was the most active catalyst all the stream time. After
465 120 min time on stream the activity of the PdNi(1:1) catalyst

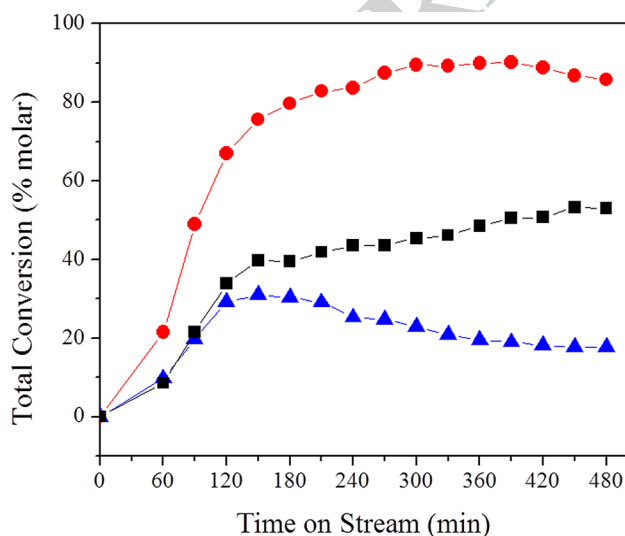


Fig. 9 Total conversion of styrene as a function of time on stream for the different catalysts. Reactions in the trickle-bed reactor. (Filled circle) PdNi(1:1), (filled triangle) PdNi(1:7), (filled square) LD265

466 increased smoothly from 75% to a value close to 90% at
467 360 min. Later at 450 min it decreased to about 85%. In the
468 case of the commercial LD265 catalyst the conversion of
469 styrene increased slightly from 120 to 480 min (from 36% up
470 to 45%). Meanwhile the PdNi(1:7) catalyst had a 30% con-
471 version at 120 min and kept this value up to 210 min. Then
472 the activity decreased gradually up to 20% at 480 min indi-
473 cating that the catalyst was deactivated. The order of cata-
474 lytic activity of the catalysts at 120 min time-on-stream was:
475 PdNi(1:1) \gg LD265 $>$ PdNi(1:7). This variation could be
476 associated to the presence of different active species on the
477 surface of the catalysts. The high activity of the PdNi(1:1)
478 catalyst would be explained by the presence of two type of
479 sites: totally reduced Pd^0 , and electrodeficient $\text{Pd}^{\text{n+}}$ and $\text{Ni}^{\text{m+}}$
480 species, as indicated by the XPS results. Species with higher
481 amount of available electrons in the external *d* orbital, as pal-
482 ladium, would favor the homolytic scission of the hydrogen
483 molecule. Pd^0 (d^{10}) rich in electrons would donate electrons
484 to the antibonding empty orbitals of the hydrogen molecule
485 (Shriver et al. 1994, Badano et al. 2010a, 2010b), promoting
486 the dissociative adsorption of H_2 . Furthermore, electrodeficient
487 $\text{Pd}^{\text{n+}}$ or $\text{Ni}^{\text{m+}}$ species (Lewis Acidic Sites, LA) would
488 favor the adsorption of styrene (Lewis Basic Sites, LB).
489 Besides the deactivation of the PdNi(1:7) catalysts during
490 the continuous flow reaction would be explained by the pres-
491 ence of surface $\text{Pd}^{\text{n+}}$ and/or $\text{Ni}^{\text{m+}}$ electrodeficient species
492 (LA) that favor the formation of green oil surface polymers.
493 The acidic function of any catalyst promotes the formation
494 of carbon deposits or gums over the surface because it cata-
495 lyzes the polymerization of olefinic $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds.
496 In a previous work we reported that during the hydrogena-
497 tion of alkynes over a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst the controlling step
498 was the dissociative adsorption of hydrogen over the metal
499 active sites (Maccarrone et al. 2012) while the active sites
500 promoted the adsorption of the substrate and the formation
501 of green-oil. In this sense Nikolaev et al. (2012) have stated
502 that the most probable mechanism of nickel deactivation is
503 the formation of green-oil. Hydrogenolysis reactions could
504 also be responsible for the modification of the activity of the
505 PdNi(1:7) catalyst (Tanabe et al. 1989; Gaspar and Dieguez
506 2000). Further work is necessary to elucidate this point.

507 Semicontinuous system

508 Figure 10 shows values of total conversion as a function
509 of contact time for the different catalysts as obtained in the
510 semicontinuous reactor. Figure 11 shows curves of total con-
511 version of styrene as a function of contact time but only for
512 the bimetallic catalysts. Figure 11 also includes a compari-
513 son of the tests with and without poisoning by thiophene.

514 In the tests with a sulfur-free feed (Fig. 10) the val-
515 ues of total conversion as a function of contact time were
516 quite similar for the three catalysts. For the bimetallic

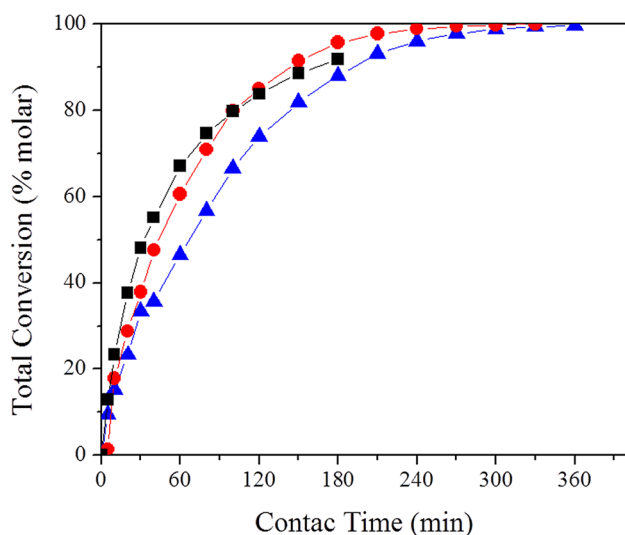


Fig. 10 Total conversion of styrene as a function of contact time for the different catalysts. Semicontinuous and sulfur free system. (Filled circle) PdNi(1:1), (filled triangle) PdNi(1:7), (filled square) LD265

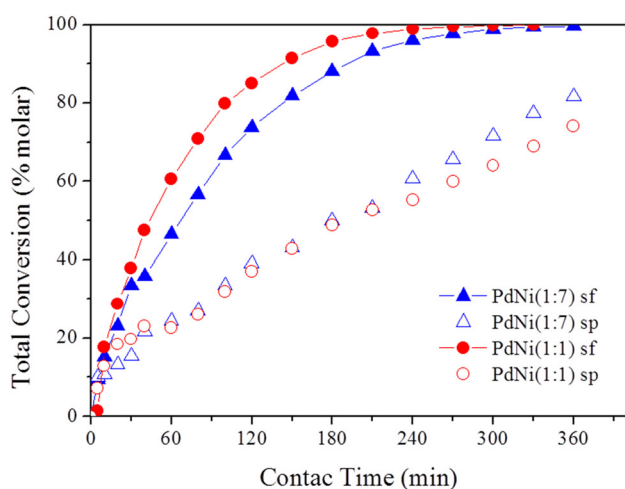


Fig. 11 Total conversion of styrene as a function of contact time for the bimetallic catalysts. Semicontinuous system using a sulfur-free feed (s_f) or a sulfur-doped feed (s_p)

co-impregnated and the commercial LD265 catalysts, the total conversion of styrene increase all the contact time, suggesting that no deactivation due to formation of green-oil on the catalysts surface occurred up to 360 min (Maccarrone et al. 2016). In these conditions the results indicated that initially the commercial LD265 catalysts was slightly more active than PdNi(1:1), with similar Pd loading, and both were more active than PdNi(1:7) with double palladium content. However from 90 min to the end of the run the PdNi(1:1) catalyst was more active. The order of conversion of styrene after 90 min was: PdNi(1:1) > LD265 > PdNi(1:7). At the conditions of

hydrogenation of pure styrene, the conversion of PdNi(1:1) is higher than that of PdNi(1:7). The presence of Pd⁰ and Pdⁿ⁺/Ni^{m+} species detected by XPS would explain the higher conversion of PdNi(1:1). These totally reduced metallic species would favor the dissociative adsorption of the hydrogen molecule (Badano et al. 2010a; b), while the electronefficient active sites (LA) would favor the adsorption of styrene (BL).

Figure 11 shows the evolution of the total conversion when thiophene is present (s_p) or absent (s_f) in the semi-continuous reaction medium. 600 ppm of thiophene were present in the sulfur containing feed. At short reaction contact times (< 50 min) the total conversion of styrene was slightly higher on the PdNi(1:1) catalyst than on the PdNi(1:7) catalyst. From 50 up to 210 min of contact time conversion levels became similar. At higher contact time values the conversion on the PdNi(1:7) (with double palladium content) was slightly higher. As both co-impregnated bimetallic Pd–Ni catalysts have different loading, initial reaction rates per gram of palladium were calculated (r^o) in order to compare them and the sulfur resistance of the different catalysts. The calculated rates were those obtained with the sulfur-free feed (r^o_{sf}) and the sulfur-containing feed (r^o_{sp}):

$$r^o = \frac{C^0}{w_{Pd}} \left(\frac{dX}{dt} \right)_{t=0} \quad (1)$$

r^o is the initial reaction rate of styrene [$\text{mol g}_{Pd}^{-1} \text{L}^{-1} \text{min}^{-1}$]. $(\partial X/\partial t)_{t=0}$ is the tangent value of the plot of styrene total conversion versus time at $t=0$. C^0 is the initial concentration of styrene [mol L^{-1}], w_{Pd} is the mass of Pd [g] and t is the reaction contact time [min]. From the values of r^o and considering a model of simple linear deactivation (zero order with respect to deactivation), the fraction of poisoned sites (α) can be calculated as in Eq. 2:

$$\alpha = 1 - (r^o_{sp}/r^o_{sf}). \quad (2)$$

Table 4 shows the values of r^o_{sf} , r^o_{sp} and α . As shown in Table 4 initial reaction rates of PdNi(1:1) are higher than those of PdNi(1:7), either in the sulfur free or sulfur-poisoned conditions. Also it is observed that the reaction rates decrease during the evaluations in the presence of

Table 4 Values of the fraction of poisoned sites (α) and the initial reaction rate (r^o)

Catalysts	Sulfur-free (s_f)	Sulfur-poisoned (s_p)	α
	r^o_{sf} ($\text{mol g}_{Pd}^{-1} \text{L}^{-1} \text{min}^{-1}$)	r^o_{sp} ($\text{mol g}_{Pd}^{-1} \text{L}^{-1} \text{min}^{-1}$)	
PdNi(1:7)	1.97	0.71	0.64
PdNi(1:1)	4.90	1.27	0.74

570 thiophene. The higher initial reaction rate of PdNi(1:1)
 571 could be attributed on the one hand to the presence of Pd⁰
 572 which promotes the dissociative adsorption of the hydro-
 573 gen molecule (Badano et al. 2010a; b), and to Pdⁿ⁺/Ni^{m+}
 574 electronefficient active sites (LA) that favor the adsorp-
 575 tion of styrene (BL). Otherwise, as seen in Table 4 the
 576 PdNi(1:7) catalyst is the one having the smallest fraction
 577 of poisoned sites.

578 In Fig. 12 is shown a Scheme of the electronic and geo-
 579 metric effects that promotes sulfur resistance of PdNi(1:7)
 580 catalyst. According to the most accepted model for deacti-
 581 vation of Group VIII metals by sulfur poison deactivation
 582 would occur by a donation of electrons from the sulfur atom
 583 (Lewis basic site, LB) to the metal (Lewis acid site, LA)
 584 (Badano et al. 2010a; b). Thiophene interacts with the pal-
 585 ladium 3d orbitals in a planar way through the π electrons of
 586 the aromatic nucleus (weak η₅ bond) (Badano et al. 2010a,
 587 b; Arcoya et al. 2003; L'Argentiére et al. 1995). During
 588 the poisoning tests, as some electrons of the d orbital are
 589 shared with the sulfur atom, the metal would have a lower
 590 amount of electrons available for promoting the cleavage of
 591 the hydrogen bond, diminishing the catalytic activity for all
 592 the catalysts after poisoning occurs. As seen in Table 4 the
 593 PdNi(1:7) catalyst is the one having the smallest fraction of
 594 poisoned sites. The higher sulfur resistance could be due to a
 595 higher surface Cl/Al atomic ratio as found by XPS (Table 2).
 596 This would make the Pd^{δ+} sites to be shielded by an elec-
 597 tron rich environment (geometrical effect) provided by the

598 chloride ions present in the Pd_xⁿ⁺O_yCl_z species, depending
 599 also on the surface amount of Cl⁻ remaining on the catalyst.
 600 This model would point to a repulsion (electronic effect) of
 601 the electron cloud of thiophene. This would preclude the
 602 approach of the electron pair of thiophene (LB) to the sur-
 603 face Pd^{δ+} (LA) and deactivation would be inhibited.

604 Conclusions

605 Two bimetallic supported Pd–Ni catalysts were prepared by
 606 co-impregnation using the incipient wetness technique and
 607 varying the atomic ratio of the metals. γ-Al₂O₃ was used
 608 as support. The effects of metal content and Pd:Ni ratio on the
 609 activity and sulfur resistance of the catalyst were assessed.
 610 The selective hydrogenation of styrene to ethylbenzene was
 611 used as test reaction, the most refractory compound in the
 612 PyGas stream. Both a semicontinuous reactor (stirred tank
 613 slurry reactor) and a continuous one (trickle-bed packed
 614 bed reactor) were used for the reaction. A monometallic Pd
 615 commercial catalyst was also tested for reference (Axens
 616 LD265).

617 Variation of the Ni/Pd atomic ratio yielded two catalysts
 618 (PdNi(1:1) and PdNi(1:7)) with different patterns of activity
 619 and sulfur resistance.

620 Tests at continuous flow conditions gave an activity
 621 order of: PdNi(1:1) ≫ LD265 > PdNi(1:7). The PdNi(1:7)
 622 catalyst had a progressive deactivation starting at 120 min.

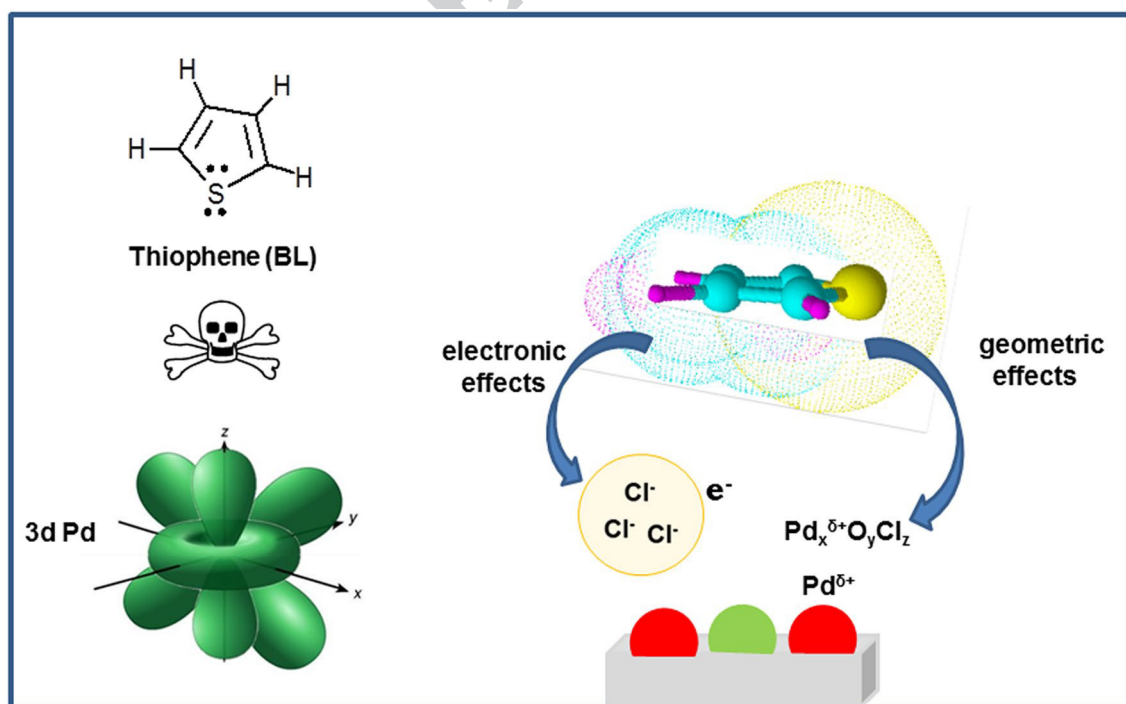


Fig. 12 Scheme of the electronic and geometric effects that promotes sulfur resistance of PdNi(1:7) catalyst

623 The highest activity of the PdNi(1:1) catalyst can be
 624 explained by the presence of Pd⁰ species (d^{10}) that favor
 625 the scission of the H–H bond due to the donation of elec-
 626 trons from the antibonding orbital of H₂ (electronic effect).
 627 Furthermore, electrodeficient Pdⁿ⁺ or Pd^{δ+} species would
 628 favor the adsorption of styrene, promoting its hydrogenation.
 629 The deactivation of the PdNi(1:7) catalyst during the
 630 reaction in continuous flow could be explained by the pres-
 631 ence of acidic surface Ni⁰ that would favor the formation
 632 of deactivating green oil.

633 In the case of the semicontinuous system the val-
 634 ues of total conversion of styrene as a function of con-
 635 tact time would be initially the commercial LD265
 636 catalysts was slightly more active than PdNi(1:1), both
 637 with similar Pd loading, and both were more active
 638 than PdNi(1:7) with double palladium content. But the
 639 order of activity from 90 min of contact time would be:
 640 PdNi(1:1) > LD265 ≫ PdNi(1:7). For the bimetallic Pd–Ni
 641 synthesized and commercial LD265 catalysts no deactiva-
 642 tion was detected due to the formation of green-oils on
 643 the surface.

644 On the other side the semicontinuous tests with the sul-
 645 fur doped feed showed a marked activity decrease that
 646 pointed to the presence of poisoning of the active sites
 647 by thiophene. As thiophene interacts with the palladium
 648 $3d$ orbitals in a planar way through the π electrons of the
 649 aromatic nucleus (weak η_5 bond), some electrons of the
 650 d orbital are shared with the sulfur atom, lowering the
 651 amount of electrons available for promoting the cleavage
 652 of the hydrogen bond, diminishing the catalytic activity for
 653 all the catalysts after poisoning occurs. The catalyst with
 654 the lowest metal load PdNi(1:1) was the most affected,
 655 showing a higher styrene conversion decrease in compari-
 656 son to the PdNi(1:7) catalyst. The better sulfur resistance
 657 of the latter could be explained by the higher Cl/Al surface
 658 atomic ratio. A cloud of chlorine electron in the vicini-
 659 ty of Pd_x^{δ+}O_yCl_z species would inhibit the nucleophilic
 660 attack by thiophene. Hence both electronic and geometric
 661 effects would be acting due to big size Pd_xⁿ⁺O_yCl_z species
 662 (geometric and electronic) and residual Cl⁻ (electronic).

663 In summary both co-impregnated PdNi(1:1) and
 664 PdNi(1:7) catalysts would be a recommendable for per-
 665 forming the selective hydrogenation of styrene during the
 666 first step of stabilization of PyGas. It had high levels of
 667 conversion (comparable to that of commercial LD265 cat-
 668 alyst) and moderate sulfur resistance in the semicontinu-
 669 ous flow runs, at the moderate temperature and pressure
 670 reaction conditions used.

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