Artigo

LOW METAL LOADING CATALYSTS USED FOR THE SELECTIVE HYDROGENATION OF STYRENE

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A series of Group VIII metal catalysts was obtained for the semi-hydrogenation of styrene. Catalysts were characterized by Hydrogen Chemisorption, TPR and XPS. Palladium, rhodium and platinum low metal loading prepared catalysts presented high activity and selectivity (ca. 98%) during the semi-hydrogenation of styrene, being palladium the most active catalyst. The ruthenium catalyst also presented high selectivity (ca. 98%), but the lowest activity. For the palladium catalyst, the influence of the precursor salt and of the reduction temperature on the activity and selectivity were studied. The following activity series was obtained: PdN-423 > PdCl-673 > PdCl-373> PtCl-673 > RhCl-673 >> RuCl-673. As determined by XPS, differences in activity could be attributed, at least in part, to electronic effects.

Keywords: selective hydrogenation; metal catalysts; styrene.

INTRODUCTION

In the last decade, around 35% of the gasoline consumed in USA came from cracking processes; moreover, ca. 20-40% of the gasoline consumed in the whole world was supplied by cracking processes.[1,2] The petroleum cracking process generate fractions rich in benzene, toluene, xylenes (BTX), and gasoline, known as C_{5+} streams, with high contents in olefins, diolefines and styrene (up to 15 wt%).[3-5] Due to their unstable character, diolefines and styrene should be eliminated to prevent the formation of gums in later processes or during storage.[1] The catalytic hydrogenation of olefins is the most used industrial process.[6,7] Styrene is a good model compound of BTX and gasoline fractions because it is one of the slower reacting components that should be removed.[1] Styrene may be hydrogenated to ethylbenzene, ethylciclohexane and also could polimerize deactivating the active sites of the catalysts. In Figure 1 it can be seen the possible reaction paths.
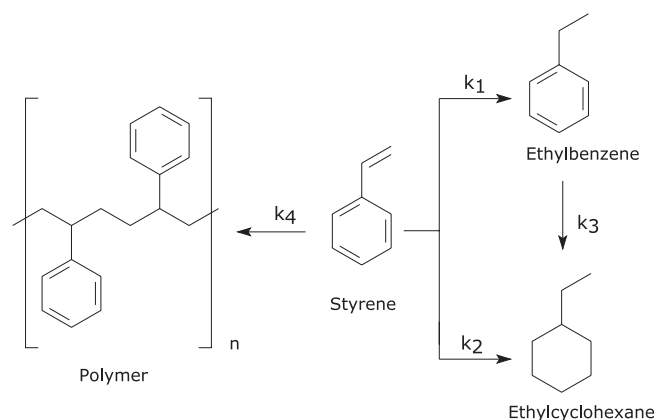

Figure 1. *Schematic reaction path for the styrene hydrogenation*

The hydrogenation must be selective without modification of the valuable aromatic nucleus. The group VIII metals such as Rh, Ru, Pt and Ir are well known as hydrogenation catalysts.[8] Among them, the platinum group metals catalysts allow carring out hydrogenations at milder conditions than other metals, like Ni, for industrial applications.[9] Styrene hydrogenation in particular has been studied with palladium and nickel catalysts using relatively mild conditions.[10,11]

The continuous increase of the petroleum raw's price and the variable price of Group VIII metals used as catalysts in the hydrogenation reactions, make interesting to investigate the influence of these metals on the activity and selectivity during the selective hydrogenation of exo-cyclic double bonds C-C.

The objective of the present work is to investigate the influence of the reduction temperature and of the precursor salt on the activity of several supported Group VIII catalysts with low metal loading, during the styrene semi-hydrogenation carried out in liquid phase.

EXPERIMENTAL

The catalysts were prepared by incipient wetness using γ-Al_2O_3 as support (CK-300, mesh 35-80, calcined 4 h at 823 K, 180 $m^2 g^{-1}$ BET surface area). To study the influence of the metals and of the precursor salts, different acidic solutions (pH=1) were prepared. The precursors employed were: $PdCl_2$ and $Pd(NO_3)_2.2H_2O$ (Fluka, Cat Nº: 76050 and 76070, respectively, purity > 99.98%), $RuCl_3.H_2O$, $RhCl_3.xH_2O$ and $H_2PtCl_6.H_2O$ (Strem Chemicals, Cat Nº: 44-5880, 45-1880 and 78-0200, respectively, purity > 99.9%). Different acidic solutions of the choride precursor salt were prepared using HCl at pH=1. For $Pd(NO_3)_2.2H_2O$ an acidic solution was prepared using HNO_3 at pH=1. The concentration of the solutions were calculated in order to obtain a metal loading, M/γ-Al_2O_3 (M = Pd, Ru, Pt, Rh), of 0.35 wt %. The γ-Al_2O_3 was impregnated with each solution following the incipient wetness technique.[12] The impregnated solids were dried during 24 h at 393 K, and then they were calcined under an air flow during 4 h at different temperatures: Pd at 673 K and Pt, Ru and Rh at 773 K. Prior to reaction, the catalysts were reduced with H_2 during 1 h at different temperatures: Pt, Ru and Rh at 673 K, Pd prepared from $PdCl_2$ at 373 and 673 K, and Pd prepared from $Pd(NO_3)_2$ at 423 K. For the most active catalyst, the influence of the precursor salt and of the reduction temperature were studied. The metal loading of the catalysts was obtained by spectrophotometric determinations.

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The dispersion and the Temperature Programmed Reduction (TPR) determinations for each metal catalyst were determined using a Micromeritics Auto Chem II equipment equipped with a thermal conductivity detector and cold water trap before the entering the thermal detector .

Dispersion values were obtained after reducing each sample at the above mentioned temperatures. The samples were degassed *in situ* for 2 h under an argon flow (AGA purity 99.99%), and then cooled at room temperature except palladium catalysts, which were cooled at 373 K where the formation of palladium hydride is negligible.[13] After that, the chemisorption with hydrogen was performed.

During the TPR analysis, the samples were dried *in situ* at 423 K for 1 h under an argon flow (AGA purity 99.99%). After that, the samples were cooled up to 250 K in the same atmosphere. Then the temperature was increased up to 1073 K at 10 K min^{-1} in a gas flow containig 5% (v/v) hydrogen/argon, at a total flow rate of 40 mL min^{-1}.

The superficial electronic state of each metal and of chlorine and their atomic ratios were studied by X-ray Photoelectron Spectroscopy (XPS) following the Pd 3d$_{5/2}$, Pt 4d$_{5/2}$, Rh 3d$_{5/2}$, Ru 3d$_{5/2}$.and Cl 2p$_{3/2}$ peaks position, respectively. As a consequence of the interference of the Al 2p line, the Pt 4d$_{5/2}$ peak position was followed instead of the most common Pt 4f$_{7/2}$.To correct possible deviations caused by electronic charge on the samples the Al 2p line was taken as an internal standard at 74.4 eV but also taking into account the low intense C 1s peak at 284.6 eV. Measurements were made using a VG-Microtech Multilab equipment, a MgK$_\alpha$ (hv: 1253.6 eV) radiation and a pass energy of 50 eV. The XPS system analysis pressure was kept at 5x10^{-7} Pa. Samples were treated *in situ* with H$_2$ following the same procedure as that for catalyst preparation. A careful deconvolution of the spectra was made. The areas under the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of 30-70% proportions.[14]

The styrene selective hydrogenation was carried out in a batch PTFE coated stainless steel stirred tank reactor fed with 200 mL of a solution of 10% (v/v) styrene (Aldrich, Cat. N° S497-2, purity > 99%) in toluene (Merck, Cat. N° TX0735-44, purity > 99%), using n-decane (Fluka, Cat. N° 30550, purity > 98%) as an internal standard. The reactor was operated at 353 K, 10 bar H$_2$ and 800 rpm. Runs were carried out in triplicate with an experimental error of 3%, using 0.2 g of catalyst and a styrene/M molar ratio equal to 2.6 10^4. Internal and external diffusional limitations were absent in the conditions of this work. Reactant and products were analyzed by GC equipped with a FID detector.

RESULTS AND DISCUSSION

Figure 2 shows the TPR profiles for the Pd (a), platinum and rhodium (b) and ruthenium (c) catalysts. As shown in Figure 2a, for both Pd precursor salts, a characteristic peak at 292 K was observed, corresponding to the reduction of PdO species weakly interacting with the support.[15] A desorption peak at approximately 339 K was attributed to the decomposition of β-PdH$_x$ species.[15,16] The catalyst prepared from PdCl$_2$ also presented a peak at 448 K, which could be attributed to the partial reduction of Pd-chlorine-containing species, such as Pd$_x$Cl$_y$O$_z$.[17] As shown in the curves depicted in Figures 2b and 2c, TPR results indicated that at 670 K Pt, Rh and Ru catalysts were reduced.

Table 1 presents the metal loading (w), metal dispersion (D), the XPS results for the metals and for chlorine and the activity results, expressed as Turn Over Frequencies (TOF) for the different catalysts. In Figure 3 are shown the XPS profiles of: palladium (a), platinum (b), rhodium (c) and ruthenium (d) catalysts. For the dispersion calculations a H/M= 1 ratio was adopted.[18-21] PdCl-673, PdCl-373 and PtCl-673 presented the higher dispersion values, probably due to the formation of Pd$_x$Cl$_y$O$_z$[17] and Pt$_x$Cl$_y$O$_z$[22] species. On the palladium and platinum
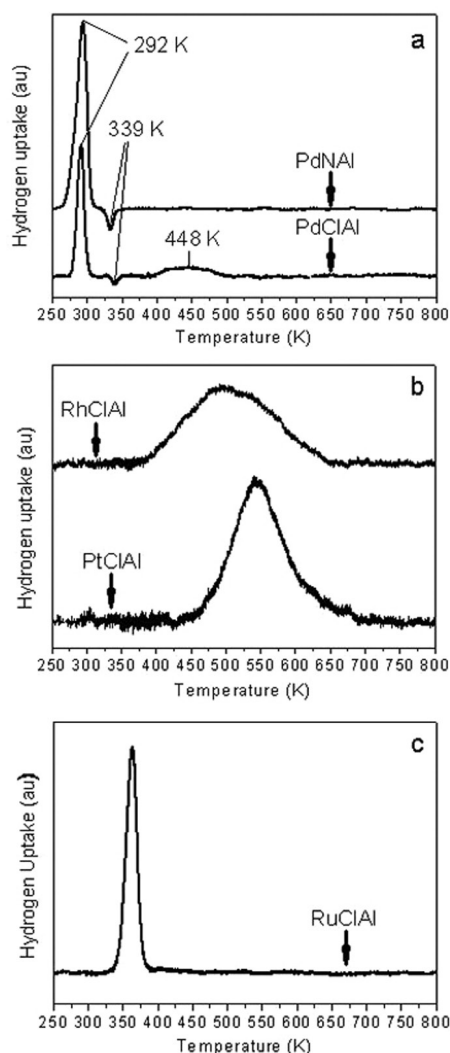
Figure 2. TPR profiles of: palladium (a), platinum and rhodium (b) and ruthenium (c) catalysts

catalysts prepared from chlorine precursors (PdCl-673, PdCl-373 and PtCl-673) the XPS results showed the presence of the Cl 2p$_{3/2}$ peak at ca. 198.5 eV, corresponding to superficial chloride species,[23] indicating that chlorine was not completely eliminated after reduction. As shown in Figure 3, the Pd 3d$_{5/2}$ peak position for PdN-423, 334.7 eV, could be assigned to Pd^0.[23] The Pd 3d$_{5/2}$ peak position for catalysts PdCl-673 and PdCl-373, 335.4 and 335.9 eV, respectively, could be assigned to electron-deficient species, Pd^{n+}, with *n* between 0 and 2.[23] It can also be seen for the last two catalysts that the hydrogen treatment temperature influenced the amount of superficial chlorine, as the Cl/Pd atomic ratio for PdCl-373 was almost seven times higher than that for PdCl-673. For the PtCl-673 catalyst, in Figure 3b, two peaks were observed: one at 313.8 eV, assigned to Pt^0, and another one at 315.8 eV, that could be assigned to electron-deficient species, Pt^{n+}, with *n* between 0 and 2.[23] The atomic proportions of each Pt species are also shown in Table 1. The XPS results obtained for Ru 3d$_{5/2}$ and Rh 3d$_{5/2}$ indicated the presence of superficial Ru^0 and Rh^0 species.[23]

The selectivity for all the catalysts was ca. 98%. Figure 4 shows the styrene total conversion as a function of time. It can be seen that initially the reaction order was 0 in styrene, and that it changed to 1 at high conversions. Then, a Langmuir-Hinshelwood-type kinetic model can be suggested.[1] As shown in Figure 4, the Pd catalyst presented the highest conversion vs. time values; hence, it appe-

Table 1. Reduction temperature (T_R), metal loading (w), metal dispersion (D), metals and chlorine binding energies and Cl/M atomic superficial ratio determined by XPS and TOF for the different catalysts evaluated

Catalyst	T_R (K)	w (%)	D (%)	M (eV)	Cl $2p_{3/2}$ (eV)	Cl/M (at./at.)	TOF (s^{-1})
PdN-423	423	0.31	26	334.7	-	0	61.9
PdCl-673	673	0.34	38	335.4	198.6	1.6	45.0
PdCl-373	373	0.34	37	335.9	198.5	10.9	41.0
PtCl-673	673	0.33	39	313.8[a]	198.5	2.4	27.9
				315.8[b]			
RhCl-673	673	0.32	20	306.9	-	0	23.3
RuCl-673	673	0.30	3	279.5	-	0	17.7

M: Pd $3d_{5/2}$, Pt $4d_{5/2}$, Rh $3d_{5/2}$ or Ru $3d_{5/2}$. [a] 28% atomic. [b] 72% atomic.
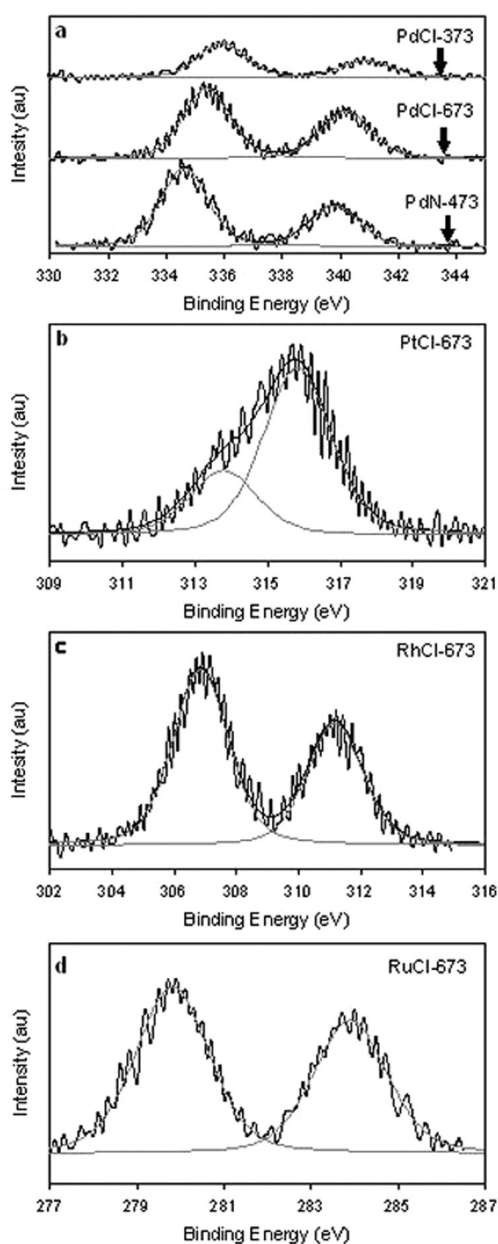

Figure 3. XPS profiles of: palladium (a), platinum (b), rhodium (c) and ruthenium (d) catalysts

ared interesting to study the influence of chlorine in its catalytic performance. For this reason, and only in the case of Pd, we used also a nitrate precursor.
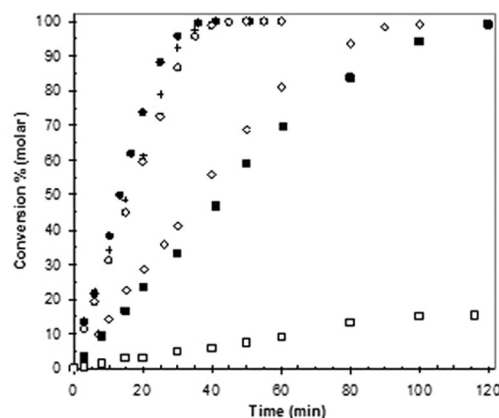

*Figure 4. Styrene total conversion as a function of time **for the different catalysts evaluated**, (●) PdCl-673 (+) PdCl-373 (○) PdN-423 (◊) PtCl-673 (■) RhCl-673 (□) RuCl-673*

TOF values were calculated from the conversion initial values. These results indicated the following order of activities: $Pd(NO_3)_2 > PdCl_2 > PtCl_6H_2 > RhCl_3 >> RuCl_3$. The bibliography lacks of papers comparing the activity and selectivity among metals of the VIII group used as monometallic catalysts in the same operational conditions during the selective hydrogenation of high molecular mass olefinic compounds, such as styrene. For other particular reaction systems, several relative activity series can be found in the literature; as reported in the review of Hagen, these series can widely differ.[24] The differences in activity between the catalysts prepared from the chloride salts could be attributed, at least in part, to differences in the electronic density of the external *d* orbitals of each metal: Pd, d^{10}; Pt, d^9; Rh, d^8 and Ru, d^7. For both palladium precursors, $Pd(NO_3)_2$ and $PdCl_2$, reduced at different temperatures, the following order of activities was observed: PdN-423 > PdCl-673 > PdCl-373. The differences in activity for the Pd catalysts could be attributed to the presence of Pd^0 or electron-deficient species, Pd^{n+}, on each catalyst. The higher activity (TOF value) was obtained for Pd^0. It is broadly accepted in the bibliography that the electron-deficient Pd^{n+} species are less active as they have less d electrons available for interacting with the substrate.[25]

CONCLUSIONS

Palladium, rhodium and platinum low metal loading prepared catalysts presented high activity and selectivity (ca. 98%) during the semi-hydrogenation of styrene. The ruthenium catalyst also presented high selectivity (ca. 98%), but the lowest activity. The following activity series was obtained: PdN-423 > PdCl-673 > PdCl-373> PtCl-673 > RhCl-673 >> RuCl-673. Differences in activity could be attributed, at least in part, to electronic effects.

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