

HYDROGENATION OF NITROBENZENE ON Au/ZrO₂ CATALYSTS

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ABSTRACT

The hydrogenation of nitrobenzene at 298K and pressure of 40 bar of H₂ over zirconia supported Au catalysts has been studied. Three different procedures were used to prepare 1wt% of Au/ZrO₂ catalysts: i) An impregnation method using HAuCl₄ as gold precursor ii) Deposition precipitation of Au nanoparticles generated in the presence of urea and iii) Deposition of Gold nanoparticles generated in presence of cetyltrimethylammonium bromide (CTMABR) as surfactant. The catalysts were characterized by nitrogen adsorption-desorption isotherms at 77 K, XRD, TEM and XPS techniques. The reactions were carried out in a stainless steel batch reactor using ethanol as solvent. The catalysts exhibits a higher selectivity to aniline, with low accumulation of intermediate products. The kinetic study displayed orders 1 respect to hydrogen pressure and to the substrate concentration (nitrobenzene), and the activation energy was 67.2 KJ/mol.

Keywords: Gold, nanoparticles, zirconia, nitrobenzene hydrogenation

INTRODUCTION

In the last few years, the selective hydrogenation of nitro compounds to produce amines has been the focus on interest of number of researchers in field of Fine Chemistry. It is commonly used to manufacture amines, which are important intermediates for dyes, urethanes, agro-chemicals and pharmaceuticals [1-3], for instance in the synthesis of sildenafil (Viagra) (4), the antibiotic linezolid (Zyvox) and the HIV protease inhibitor amprenavir (agenerase). Thus, exploring new catalysts or methods to achieve chemoselective hydrogenation of nitrocompounds has attracted considerable attention [5-9].

Generally, the process is approached by three methods: i) One is a stoichiometric reduction of the corresponding aromatic nitro compounds by using iron, tin, zinc or a metal sulfide such as Na₂S. However, this method displays low selectivity for nitro group, and large amounts of waste acids and residues are generated during the reaction. ii) The second is catalytic hydrogenation of nitro compounds with H₂ over supported noble metal catalysts, e.g. Pd, Pt, Ru and Ni catalysts [10-15], etc. Nevertheless, hydrogenation byproducts from other groups are often inevitable in most cases. iii) Another method is chemoselective hydrogenation of aromatic nitrocompounds catalysed by carbonyl or organic metals in the presence of CO and H₂O [16, 17]. It is therefore desirable to develop a more efficient and environmental process to achieve chemoselective hydrogenation for obtaining valuable functionalized anilines.

With regard to the hydrogenation of nitrobenzene, which is used to produce aniline, the reaction can be carried out in gas or liquid phase by using supported metal catalysts an organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions [9,18-20] and CO₂ under supercritical conditions [21]. The use of these solvents has some drawbacks owing to their toxicity, flammability, or environmental hazards. In addition, the solvent may play a crucial role in the stabilization of reactive intermediates and have a decisive influence on chemical reactions. Though many studies have been made, the efficient hydrogenation with high selectivity, as well as with high activity, for nitrocompounds has not so far been reported. The most frequently used nitro-group hydrogenation catalysts are palladium or platinum on carbon and Raney nickel [22-24]. The hydrogenation of aromatic nitro groups can be performed easily under mild conditions, while hydrogenation of aliphatic nitro groups is usually slower, requiring slightly elevated temperatures and pressures. In the hydrogenation of the former reactions, the nitroso compound and the hydroxylamine have been observed as intermediates, while a series of side reactions might lead to the formation of hydrazo compounds, which can be sometimes isolated.

In general, the activity and selectivity of this reaction depends on the catalysts as well as the reaction conditions [25]. Indeed, one of the intermediates or side products may become the dominant product, for instance, azoxy, hydrazo and hydroxylamines can be in high yields [4, 22, 24]. The accumulation of hydroxylamines is dangerous, explosive even at low levels, as these compounds are thermodynamically unstable [26]. The accumulation may be diminished by using iron or vanadium-modified catalysts [27, 28]. Recently, the reaction was studied with a using gold as hydrogenation catalyst [29] that gave high selectivity to substituted anilines, but showing lower activity. Nevertheless a catalyst with the same selectivity as gold but with a higher activity would be desired for industrial application [30]. Thus, there is a scientific and technological challenge to transform active but not selective noble metals (Pt, Pd, Ru) and a non noble metal (Ni) into highly active and chemoselective catalysts. Some recent studies have shown that the addition of cationic species or salts and presence of partially reduced may contribute to enhance the selectivity in these systems. Additionally, in principle the behaviour of gold catalysts, mainly in terms of activity may also be improved with appropriate preparation conditions.

Thus, in most of the researches, published before 2000, the used support for these kind of reactions was activated carbon and in minor extent alumina, silica, and MCM-41. It was been pointed out that activated carbons seems to be the most appropriate for this type of reactions because of it can provide more sites to produce a high dispersion of the metal component and because of the water produced in the hydrogenation reaction may affect the activity of the catalysts supported on oxides [22, 21-23]. Only few studies have been devoted to other oxides such as TiO₂ or Fe₂O₃ [24-25] which have shown interesting behaviour.

As was mentioned previously, the experimental conditions affect significantly, the catalytic behaviour. If the reaction is performed in liquid phase batch type reactors, usually the reaction temperature for this kind of reactions are in the range 80- 120°C, using mainly THF or ethanol as solvent and 10 bar of hydrogen pressure whereas [16,17], in gas phase the reactions are studied at temperature close to 250°C and 1 bar of hydrogen [5-8, 31].

In the present work, zirconia Au supported catalysts, with 1wt% Au and different procedures to obtain highly dispersed species gold with nanoparticle sizes were used. This is extremely important considering that gold, usually does not exhibit ability to chemisorb H₂ and therefore the hydrogenation capacity is quite low. However, small gold particles behave different, they chemisorb H₂ and they may be active in hydrogenation reactions [32,33]. The use of gold has been pointed out in preliminary researches and due to the well known ability to interact with NO₂ groups provide the catalysts the unique ability to produce a fast hydrogenation of the nitrocompounds to the corresponding anilines,

without accumulation of nitroso and hydroxylamines intermediates and their potential exothermic decomposition. See Fig. 1.

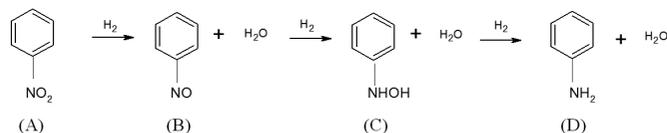


Figure 1. Proposed pathways for the reduction of nitro compounds.

EXPERIMENTAL

1. Reagents

Nitrobenzene (Fluka), absolute ethanol (Merck), TiO₂ (99.7% anatase, Alfa Aesar), SiO₂ ($S_{BET} = 287 \text{ m}^2/\text{g}$), gold(III) chloride trihydrate Sigma-Aldrich (99.9%) and H₂ by AGA. ZrO₂ used as support of gold catalysts was supplied by Alfa Aesar.

2. Catalyst Preparation

2.1 Impregnation.

The catalysts were prepared by impregnation (34) at 25 °C in a rotavapor evaporator under stirring using an aqueous solution H₂AuCl₄ in a necessary amount to get an Au content of 1 wt%. The obtained solid was calcined under air flow at 300 °C for 2 h and then reduced in H₂ flow at 500 °C for 2 h.

2.2 Deposition of Au nanoparticles generated by reduction *atmosphere* at 80 °C.

In a round bottom flask is placed the amount of support needed to prepare the catalyst, with 50 ml of an aqueous solution of the precursor containing the necessary amount needed to prepare the desired metal loading and the stoichiometric amount of urea in proportion of 100/1 respect to metal and it was connected to a system that allows flowing H₂ in the reaction medium at atmospheric pressure. Then the system was heated to 80 °C under continuous stirring until the color changes from yellow to violet. The obtained solid was filtered and washed with deionized water until constant conductivity.

1.3 Deposition of Au nanoparticles generated by reduction *in the presence of a surfactant*

The catalyst was prepared with CTMABR and ethanol under stirring into autoclave. In sequence an aqueous solution of the precursor containing the necessary amount needed to prepare the desired metal loading and the stoichiometric amount of NaOH was prepared. Both dissolutions were carried out in a batch reactor and then reduced to 40 bar for 30 minutes.

3. Characterization

N₂ adsorption-desorption isotherms were carried out in a ASAP 2010 Micromeritics apparatus. X-ray diffraction (XRD) studies were performed in Rigaku X-ray Geigerflex diffractometer using a Ni filter and Cu K α radiation, the range of study was 2θ 2-80°. TEM studies were carried out in a JEOL Model JEM-1200 EXII transmission electron microscope equipped with an emission source of electron at 200kV. The samples were prepared by replica extractive procedure. Chemical analysis by Atomic Absorption was performed on an UNICAM Solar spectrophotometer.

Photoelectron spectra (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyser operated in a constant pass energy mode and Mg K α X-ray radiation ($h\nu = 1253.6 \text{ eV}$) operated at 10 mA and 12 kV. The surface Au/Zr ratio was estimated from the integrated intensities of Au 4f_{7/2} and Zr 3d_{5/2} lines after background subtraction and corrected by the atomic sensitivity factors [35].

4. Nitrobenzene Hydrogenation Reaction.

The catalytic evaluation was carried out in liquid phase in a batch reactor Parr stainless steel at 298K, and in standard experiments the experimental conditions were: 100 mg of catalyst, 0.10 mol/L of nitrobenzene in ethanol, hydrogen pressure of 40 bar and all components (catalyst, solvent and substrate) under continuous stirring of 800 rpm. For kinetic studies changes in nitrobenzene concentration (5 to 20 mmol/l), hydrogen pressure (10 to 40 bar) and temperature (298 to 323 K) were performed. Liquid samples were taken periodically from the reactor and analyzed in GC-MS device (Shimadzu

GCMS-QP5050), using a chiral β -dex 225, 30 m column (SUPELCO) and helium as carrier gas.

RESULTS AND DISCUSSION

Figure 2 shows the nitrogen adsorption isotherms at 77K on the studied support. The isotherm corresponds to type IV in the classification of BDDT [36]. It displays a hysteresis loop indicative of transitional cylindrical bottle pores, mainly in the range 4 to 10 nm being the surface area of 96 m²/g.

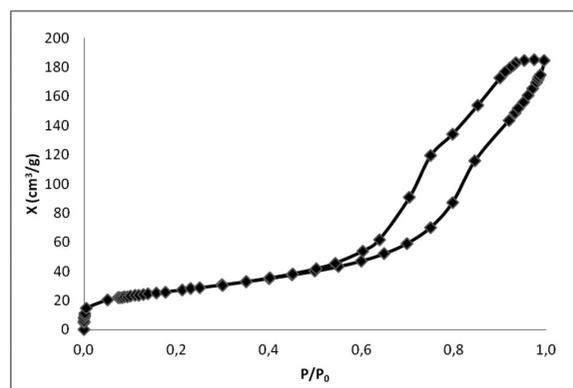


Figure 2. Nitrogen adsorption-desorption isotherms at 77 K on ZrO₂ support.

Figure 3 shows the X-ray diffraction patterns of the support and prepared Au/ZrO₂ catalysts. In all patterns appear the characteristic reflexions due to monoclinic and tetragonal phases of the ZrO₂ and Au catalysts displays also a small and broad line at $2\theta \approx 38.2^\circ$ assigned to Au.

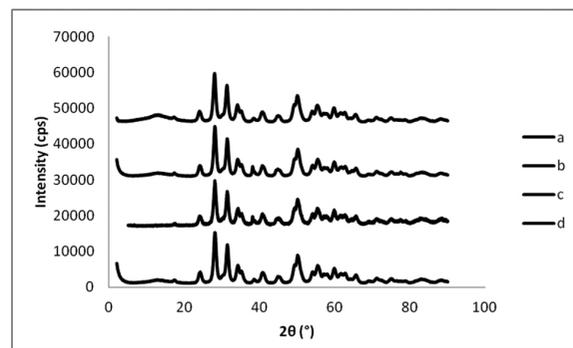


Figure 3. XRD patterns of Au/ZrO₂ catalysts. a) Au/ZrO₂- DP-urea b) Au/ZrO₂- I c) Au/ZrO₂- S and d) ZrO₂

Gold particle size were evaluated by TEM studies. Figure 4 compiles representative TEM micrographs of the prepared Au/ZrO₂ catalysts. It can be seen similar metal particle in all samples with a rather narrow distribution. The average particle size was obtained does not change significantly with the preparation procedure. Gold loading was lower than the nominal 1 wt%, mainly in the catalysts prepared by the surfactant procedure. In this later, the strong interaction between the surfactant and gold precursor may avoid in some extent the precipitation of the metal component after the addition of NaOH. Thus, in the following steps reduction in H₂ impregnation of the colloid dispersion on the support and washing, Au-surfactant entities may be removed from the ZrO₂ surface, leading to a lower Au content than the nominal.

Table 1. Metal content, gold particle size (d) and gold dispersion (D) of Au/ZrO₂ catalysts evaluated from TEM results.

Catalyst	Au loading, wt%	d, nm	D
Au/ZrO ₂ - I	0.94	6.7	0.18
Au/ZrO ₂ - DP-urea	0.91	5.8	0.21
Au/ZrO ₂ - S	0.46	6.9	0.17

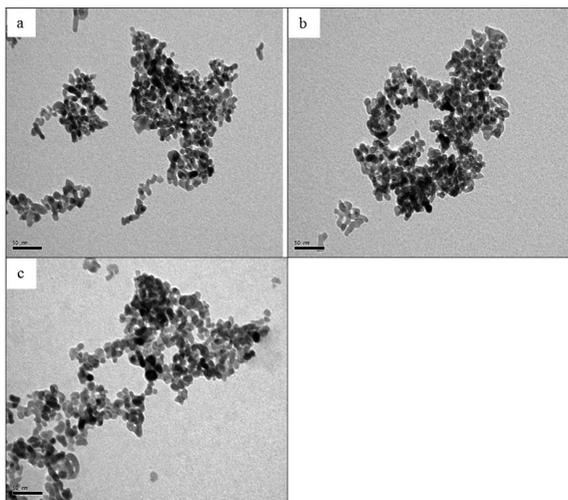


Figure 4. Transmission electron micrographs of Au/ZrO₂ catalysts a) Au/ZrO₂- DP-urea b) Au/ZrO₂- I c) Au/ZrO₂- S

Figure 5 shows the XPS core-level spectra of the catalysts. The peak corresponding to Au 4f_{7/2} has been analysed. Au⁰ should displays a BE of 84.0.0 eV. It can be seen slight shift in the BE to higher values, indicative of the presence of Au in higher oxidation states. Thus, the catalysts prepared by impregnation, the Au crystals remains mainly in a reduced state with small proportion of Au⁴⁺, whereas in those prepared by deposition in presence of urea and surfactant the higher BE values are indicative of a Au⁺ species. With regard to the Au/Zr surface ratios, no significant differences can be observed in the prepared catalysts, except in that prepared by the surfactant method which exhibit a lower ratio due to it lower Au content. Additionally, bulk and surface ratio of each catalyst are rather similar between bulk and surface ratio. The mentioned features suggest that the catalysts should posses similar metal particle sizes, in agreement with TEM results. Table 3 summarizes the BE of Au 4f_{7/2} and the corresponding bulk and surface Au/Zr atomic ratios of the prepared catalysts.

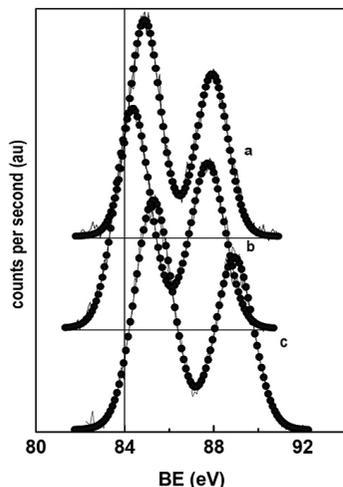


Figure 5.- XP spectra of Au 4f_{7/2} core level of Au/ZrO₂ catalysts a) Au/ZrO₂- DP-urea b) Au/ZrO₂- I c) Au/ZrO₂- S

Table 2. Au 4f_{7/2} core level spectra (eV), bulk and surface Au/Zr atomic ratios of Au/ZrO₂ catalysts.

Catalyst	B,E. Au 4f _{7/2} , eV	(Au/Zr) _b	(Au/Zr) _s
Au/ZrO ₂ - I	84.4	0,0536	0.0048
Au/ZrO ₂ - DP-urea	85.1	0.0571	0.0058
Au/ZrO ₂ - S	85.3	0.0281	0.0036

Catalytic activity in nitrobenzene hydrogenation

Figure 1 shows a scheme of the nitrobenzene hydrogenation. The catalytic activity was studied under the operating conditions mentioned above and the evolution of the conversion of nitrobenzene on time for the different prepared catalysts is shown in Fig. 6a. It can be seen in all curves an induction period which may be related to the creation of active sites, i.e. to get a significant metallic Au sites required to chemisorbs hydrogen molecules. Then, the hydrogenation of nitrobenzene increases as a pseudo first order reaction. Differences in the catalytic behavior can be observed in the studied catalysts. Taking into account that the solids possesses different metal loading and slight differences in metal dispersion is more appropriate to compare the corresponding activity per site.

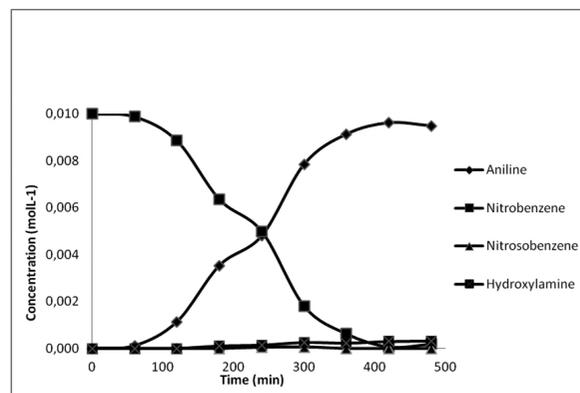
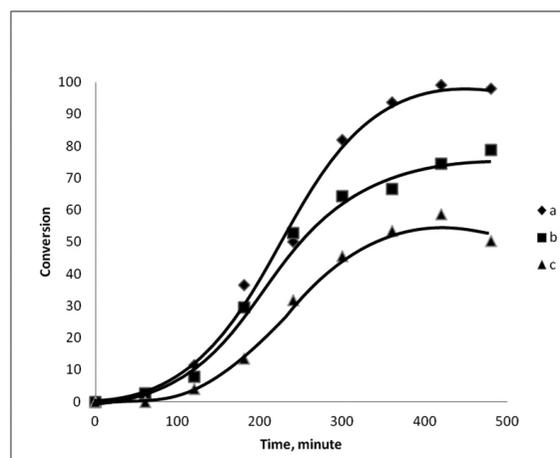


Figure 6. Nitrobenzene hydrogenation on Au/ZrO₂ catalysts . T= 25°C, P H₂= 40 bar, catalyst weight 100 mg and NB concentration= 0.01 molL⁻¹.

- a) Evolution of the conversion level with time
- b) Evolution of reactants and products concentration with time

Table 3 compare the turnover number at 200 min of reaction of the studied catalysts in the hydrogenation of nitrobenzene at 298 K. Almost no changes in the TOF in the studied catalysts can be noted. The fact that TOF remain constant can not necessarily be explained on the basis of an insensitive reaction, because the metal particle size of the studied catalysts differs only in a small extent. Fig. 6b displays the evolution of the products on time. In all the catalysts tested, aniline was the main product being nitroso and hydroxylamine intermediate products present at negligible amounts. This indicates that the reaction rate of the second and third steps are very high compared to the first

one, and therefore almost no accumulation of intermediate products occur. This feature is one of the main advantages of gold compares to other active phase for this kind of reactions.

Table 3. Turnover frequencies (s^{-1}) in the hydrogenation of nitrobenzene at 298K and 40 bar of hydrogen over Au/ZrO₂ catalysts.

Catalyst	TOF, s ⁻¹
Au/ZrO ₂ - I	1.58
Au/ZrO ₂ - DP-urea	1.70
Au/ZrO ₂ - S	2.37

Only a few reports dealing with the kinetic and mechanisms of hydrogenation of nitroarenes have been found. Rojas et al.[37] have studied the hydrogenation of m-dinitrobenzene over Pt/TiO₂ catalysts and they have proposed a Langmuir-Hinshelwood mechanism in which the surface hydrogenation reaction between m-nitroaniline and hydrogen is the rate limiting sep. Kotohiro [38] use Ru(CO)₂/N(Et)₃ as catalyst in the reduction of the nitroarene with CO/H₂O, occurs by hydrogen transfer from a cyclic adduct between the nitroso derived and the catalyst.

In order to provide more information dealing with the mechanism of reaction, a detailed kinetic study was performed over Au/ZrO₂-DP urea catalyst. After chosen the necessary conditions to avoid heat and mass transport limitations, serie of experiments in which reaction temperature or nitrobenzene concentration or hydrogen pressures were varied keeping the constant the other variables were performed in order to get the effect of each variable in the reaction rate. Thus, the reaction rate may be expressed as $r = k(T) C_{NB}^a P_{H_2}^b$

$$\text{or } \log r = \log k(T) + a \log C_{NB} + b \log P_{H_2}$$

Figure 7 a shows the conversion versus time for Au/ZrO₂-DP urea catalyst at 298 K, hydrogen pressure of 40 bar and different nitrobenzene concentrations. Taking the conversion values after the induction period the initial reaction rate was evaluated and plotted $\log r_0$ vs $\log C_{NB}$. The results can fit to a straight line being the slope 1.00 ± 0.05 (See Fig. 7b) corresponding this value to the dependence respect to the nitrobenzene concentration.

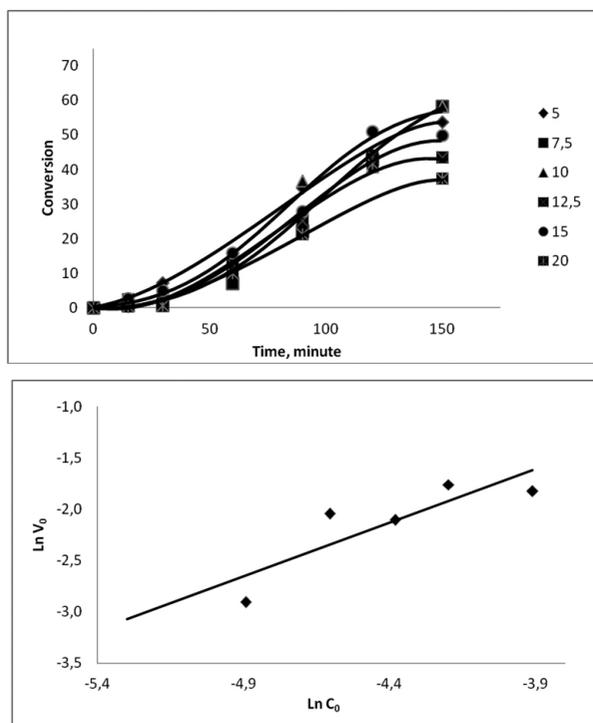


Figure 7 Nitrobenzene hydrogenation on Au/ZrO₂ catalysts . T= 25°C, P H₂= 40 bar, catalyst weight 100 mg. Effect of Concentration. .

- a) Evolution of the conversion level with time
b) Plot $\log r_0$ vs $\log C_{NB}$

Similarly, Fig. 8a shows the effect of the hydrogen pressure on the conversion level in the hydrogenation of nitrobenzene at 298 K and 0.1 mol/L of nitrobenzene in ethanol at different hydrogen pressures. Again a plot $\log r_0$ vs $\log P_{H_2}$ allow to get the dependence respect to hydrogen pressure. Fig. 8b displays these results, being the slope 1.00 ± 0.07 .

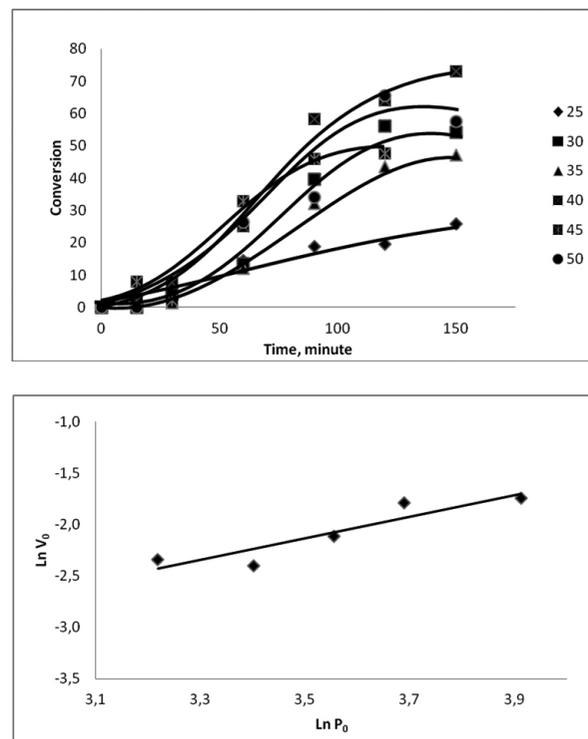
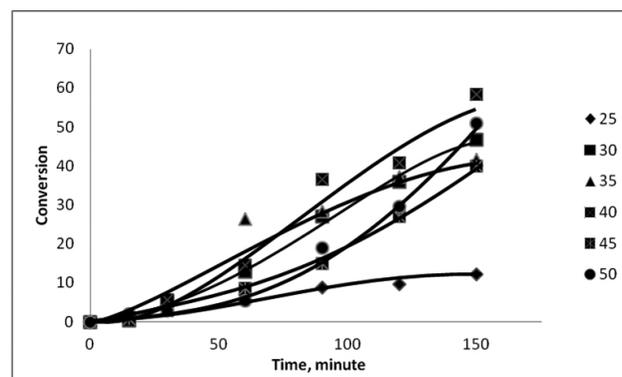


Figure 8 Nitrobenzene hydrogenation on Au/ZrO₂ catalysts. $C_{NB} = 0.01$ mol/L⁻¹, P H₂=40 bar, catalyst weight 100 mg. Effect of Hydrogen Pressure.

- a) Evolution of the conversion level with time
b) Plot $\log r_0$ vs $\log P_{H_2}$

In order to evaluate the apparent activation energy a series of experiments of hydrogenation of nitrobenzene at 40 bar of hydrogen, nitrobenzene concentration of 0.10 mol/L were performed in the temperature range 298 to 323 K (see Fig. 9a). A linear plot $\log r_0$ vs $1/T$ can be obtained. From the slope, an activation energy of 67.2 kJ/mol can be obtained (Fig.9b).



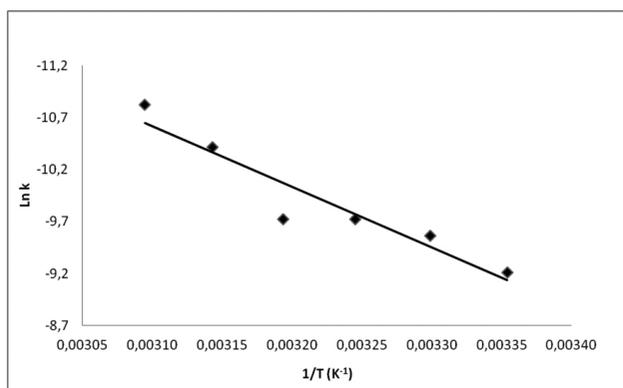


Figure 9 Nitrobenzene hydrogenation on Au/ZrO₂ catalysts. C_{NB} = 0.01 mol/L⁻¹, P H₂ = 40 bar, catalyst weight 100 mg. Effect of reaction temperature. a) Evolution of the conversion level with time b) Plot log r₀ vs log 1/T (K⁻¹).

If a Langmuir-Hinshelwood type mechanism is proposed in which A, B, C and D were defined in Fig. 1. It consist in a sequence of elementary steps in which only one is considered as a rate limiting step being the others in quasi-equilibrium.

- 1) A + S → A-S
- 2) H₂ + 2S → 2H-S
- 3) A-S + 2H-S → B-S + H₂O-S + S
- 4) B-S + 2H-S → C-S + 2-S
- 5) C-S + 2H-S → D-S + H₂O-S + S
- 6) D-S → D + S
- 7) H₂O-S → H₂O + S

By using the usual procedure seven rate equations can be obtained, depending on the step chosen as rate limiting step. Thus, the one derived considering the number 3 as a limiting step the following rate equation was obtained

$$r = k (C_A P_{H_2} - C_D / K_D) / (1 + K_A C_A + K_B P_{H_2} + K_C C_C + K_D C_D)^3$$

This equation may be simplified under initial conditions, thus the initial reaction rate is:

$$r_0 = k C_A P_{H_2} / (1 + K_A C_A + K_B P_{H_2})^3$$

if in the adsorption term $K_A C_A + K_B P_{H_2} \ll 1$ the equation is reduced to

$$r_0 = k C_A P_{H_2}$$

being the only rate limiting step that can appropriate fit the experimental values.

CONCLUSIONS

TEM studies indicate that 1 wt% Au/ZrO₂ catalysts prepared by different procedures allow to obtain gold nanoparticles close to 7 nm. The activity per site, TOF with similar values was displayed in the hydrogenation of nitrobenzene at 298K for all catalysts. It is noticeable that negligible amount of nitroso and hydroxylamine compounds were detected during the reaction. Kinetic studies, revealed order 1 respect to nitrobenzene concentration and hydrogen pressure, the results are compatible with a Langmuir-Hinshelwood mechanism, in which the rate limiting step is the surface reaction between the adsorbed nitrobenzene and adsorbed dissociated hydrogen.

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