LIQUID-PHASE HYDROGENATION OF *m*-DINITROBENZENE OVER PLATINUM CATALYSTSHUGO ROJAS¹*, GLORIA BORDA¹, PATRICIO REYES², MARÍA BRIJALDO^{1,3}, JESÚS VALENCIA³¹ Escuela de Química, Grupo de catálisis (GC-UPTC), Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia² Departamento de Fisicoquímica, Universidad de Concepción, Casilla 160-C, Concepción, Chile³ Centro de Catálisis Heterogénea, Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia

(Received: March 7, 2011 - Accepted: August 3, 2011)

ABSTRACT

The *m*-dinitrobenzene hydrogenation to *m*-phenylenediamine in liquid phase was studied with platinum supported on SiO₂, TiO₂, Al₂O₃ and Nb₂O₅ catalysts. Incipient impregnation method was used to prepare the catalysts with 1wt% of Pt. The effect of the support and the reduction temperature (473 K or 773 K) were analyzed. The materials were characterized by X-ray diffraction (XRD), nitrogen physisorption (77 K), hydrogen chemisorption (298 K), transmission electron microscopy (TEM), temperature programmed reduction (H₂-TPR) and temperature programmed desorption of ammonia (NH₃-TPD). The results showed that Pt/TiO₂ (HT) catalyst had a higher yield (60%) toward *m*-phenylenediamine and conversion level (98.2%) of *m*-dinitrobenzene. This behavior can be attributed to the reduction of PtO_x crystallites to metallic Pt, small particle size and the strong metal-support interaction due to the migration of TiO_x species on the Pt crystallites.

Keywords: *m*-dinitrobenzene; *m*-phenylenediamine; hydrogenation; fine chemical.

INTRODUCTION

Hydrogenation of nitro compounds to amines has wide range applications in the synthesis of several intermediate and fine chemicals. The conventional process for reduction of nitro compounds (commonly known as Béchamp process) employed stoichiometric amounts of Fe-acid as the reducing agent producing almost equivalent amount of Fe-FeO sludge as a byproduct¹. Apart from the serious waste disposal problems, the Béchamp process also suffered from the difficulties in the separation of desired products from the reaction mass and use of corrosive reagents as acids. The catalytic hydrogenation using supported metal catalysts (gas-liquid-solid multiphase catalytic reactions) has emerged as a cleaner alternative to the conventional Béchamp process with better activity and selectivity^{2,3}. Although, these novel catalytic reactions have been employed in several instances, there is still a wide scope for their extension to several other products.

One example is the hydrogenation of *m*-dinitrobenzene (*m*-DNB) to *m*-phenylenediamine (*m*-PDA), which proceeds via formation of *m*-nitroaniline (*m*-NA). *m*-PDA is an important intermediate for the synthesis of some polymers, aramid fibers, and the production of dyes for textiles, leather and other materials. Additionally, it is also an important component in manufacture of hair dyes, epoxy resins and polyurethane⁵.

The hydrogenation of the intermediate *m*-NA to *m*-PDA is difficult due to the presence of nitro group in meta position which deactivates the benzene ring⁶ and hence the development of a catalyst to achieve a high selectivity to *m*-PDA is highly desirable.

Usually, the hydrogenation is carried out over Raney Ni catalyst⁷. Although Raney Ni has a high catalytic activity, a large amount of the catalysts is need in the course of the reaction because it is crushed under intense agitation. Moreover, noticeable environmental pollution can be caused during the preparation of the catalyst. Besides Raney Ni catalyst, some supported noble metal catalysts such as Pd/C have been used for this reaction, and they also exhibit high activity and selectivity^{8,9}.

In this work, supported platinum catalysts have been attempted for the hydrogenation of *m*-DNB. In view of the importance of carriers in supported catalyst, SiO₂, TiO₂, Al₂O₃ and Nb₂O₅ have been used to support platinum catalysts and evaluated in this reaction in order to find an effective catalyst. Furthermore, the effects of the support on the physical-chemistry properties of the platinum catalysts were studied based on the characterization results of X-ray diffraction (XRD), nitrogen physisorption at 77 K, hydrogen chemisorption at 298 K, temperature-programmed reduction of hydrogen (H₂-TPR) and temperature-programmed desorption of ammonia (NH₃-TPD).

EXPERIMENTAL

Catalysts preparation

Pt/SiO₂, Pt/TiO₂, Pt/Al₂O₃ and Pt/Nb₂O₅ catalysts were prepared by one-step incipient impregnation method^{10,11} of a SiO₂ (Syloid-266-Grace

Davidson.), TiO₂ (Degussa P-25), γ-Al₂O₃ and Nb₂O₅ (Aldrich) with an aqueous solution of H₂PtCl₆ (analytical grade) to give a Pt loading of 1% wt. The metal concentration was defined according to several researches reported^{12,13}, which affirmed that the platinum present high hydrogenate powder and because it is noble metal with high cost. The impregnated solids were dried at 393K for 6 h, calcined in air at 673 K for 2 h.

Catalysts characterization

Nitrogen physisorption was performed in Micromeritics ASAP 2020 equipment. The surface areas were evaluated by the Brunauer-Emmett-Teller (BET) method at liquid nitrogen temperature using N₂ as the adsorbent at 77 K and samples were degassed at 573 K for 6h prior to analysis. The pore size distribution data were calculated by the ASAP 2020 software from the N₂ desorption isotherms. The Barrett-Joyner-Halender (BJH) method with cylindrical pore size calculated from the Kelvin equation was used in the data processing. The same equipment was also used to measure the dispersion of Pt on the supports using hydrogen chemisorption 298 K.

The morphology and particle size of the supported platinum were observed by transmission electron microscopy analysis employed a JEOL Model JEM-1200 EXII equipped with an emission source of electrons at 200 kV. The samples for analysis were prepared by dispersion in ethanol and deposited on a holey carbon/Cu grid (300 Mesh). Up to 250 individual metal particles were counted for each catalyst and the surface area-weighted mean Pt diameter (dp) was calculated from;

$$dp = \frac{\sum n_i d^3}{\sum n_i d^2}$$

Where n_i is the number of particles of diameter d_i .

X-ray powder diffraction (XRD) of the catalysts obtained only to characterize the phases of the obtained powders. The characterization of the samples was carried out on the Rigaku instrument using Cu K_α radiation (λ = 0.154 nm) at 40 kV and 30 mA. The diffraction patterns were recorded over the range of 10-84°. The scanning speed was 40 min⁻¹.

H₂-TPR was carried out in a quartz reactor and 100 mg of catalyst sample was filled into reactor for each experiment. Prior to the reduction, the sample was pretreated in a Ar stream at room temperature for 30 min, later the circulating gas was swap by 95 % argon and 5 % hydrogen mixture, at flow rate of 50 ml min⁻¹. After, the temperature was increased from 298 to 1173 K at the rate of 283 K min⁻¹. The H₂ consumption in the reactant stream was detected by a thermal conductivity cell.

Adsorption of NH₃ was studied by a pulse method in a Micromeritics TPD/TPR 2900 apparatus. The samples were heated up to 383 K and maintained at this temperature for 1 h under He flow. Then, pulses of NH₃ were sent to the samples up to complete saturation. Later, the samples were cooled to room temperature, and once the base line was restored, the temperature was increases linearly at a heating rate of 283 K min⁻¹ up to 800 K.

Activity test

Prior the activity evaluation, Pt supported catalyst was obtained by reduction in a hydrogen flow for 2 h at 473 K (LT: low temperature) and 773 K (HT: high temperature), respectively. Catalytic reactions were conducted in a batch reactor at a constant stirring rate (1000 rpm). For all reactions, hydrogen partial pressure was of 0.82 MPa, catalyst weight of 100 mg, 50 mL of a 0.10 M solution of *m*-DNB in ethanol (Aldrich) and reaction temperature of 343 K. The absence of oxygen was assured by flowing He through the solution, as well as when the reactor was loaded with the catalyst and reactants at atmospheric pressure during 30 min. Prior the experiment, all catalysts were reduced *in situ* under hydrogen flow of 20 mL min⁻¹ at atmospheric pressure and temperature of 343 K. Samples were withdrawn at appropriate intervals and analyzed using gas chromatograph Varian 3400 furnished with an HP5 (30 m x 1,0 µm) and a flame ionization detector (FID), using He as carrier. Under these analytical conditions, the retention time of the reported reactants and products were: *m*-DNB: 13 min; *m*-NA: 17 min and *m*-PDA: 8 min.

RESULTS AND DISCUSSION

The diffractograms of Pt/TiO₂, Pt/SiO₂, Pt/Al₂O₃ and Pt/Nb₂O₅ catalysts reduced at high temperature (HT) are showed in figure 1. It can be observed that the Pt/SiO₂ catalyst exhibits signals near to 2θ = 39.5° y 46°, 66° y 81° due to the presence of crystallites of platinum¹⁴. These signals also are displayed by the Pt/Nb₂O₅ catalysts; the observed diffraction lines corresponding to 22.5°, 28.5°, 37° and 46° are characteristic of the crystalline niobia TT.

The peaks of Pt/TiO₂ showed a typical anatase (2θ = 25.2°, 38.2°, 48.3°, 55°, y 63.1°) phase TiO₂ with small fraction of rutile (2θ = 27.4°, 36°, 41°, 54°, 56° y 69°) according to the related literature^{15,16}. These results are in agreement with reports of Montes *et al.*¹⁷. The peaks of Pt/Al₂O₃ (2θ=37.8°, 47.3° and 67°) were mainly assigned to the γ-Al₂O₃ phase¹⁸. The results of X-ray powder diffraction not showed diffraction lines of platinum, which presumably is attributed to the highly dispersed on the support.

Figure 1. X-ray patterns of the supported Pt catalysts; (a)

Pt/SiO₂, (b) Pt/Nb₂O₅, (c) Pt/Al₂O₃, (d) Pt/TiO₂ (*): Pt.

The results of textural properties (surface area, pore diameter, pore volume), hydrogen chemisorption and particle size of supported Pt catalysts are reported in Table 1. In the textural properties no significant differences occur if the catalysts are reduced at high or low temperature, indicating that almost no sintering of the catalysts takes place as a consequence of H₂ treatment at high temperatures. It is possible to observe that the Pt/SiO₂ (LT-HT) catalysts possess the highest surface area (225 and 222 m² g⁻¹). On the other hand, the Pt/Nb₂O₅ (LT-HT) catalysts possess a low surface area (7.4 and 6.8 m² g⁻¹), which is agreement with its high crystallinity and absence of micropores.

Table 1. Surface area, pore volume, average pore diameter, ratio H/Pt and particle size (TEM) of the Pt supports catalysts.

Catalysts	S _{BET} (m ² g ⁻¹)	Pore size (Å)	Pore Volume (cm ³ g ⁻¹)	H/Pt	TEM (nm)
Pt/Nb ₂ O ₅ LT	7.4	151	0.040	0.02	9.6
Pt/Nb ₂ O ₅ HT	6.8	153	0.036	0.009	9.8
Pt/SiO ₂ LT	225	78	0.67	0.18	8.1
Pt/SiO ₂ HT	222	80	0.63	0.20	8.1
Pt/TiO ₂ LT	53	108	0.41	0.25	3.2
Pt/TiO ₂ HT	50	110	0.33	0.16	3.3
Pt/Al ₂ O ₃ LT	188	54	0.45	0.76	1.7
Pt/Al ₂ O ₃ HT	185	55	0.36	0.85	1.7

The nitrogen adsorption-desorption isotherms of platinum catalysts (series HT) are shown in figure 2. It can be seen that of the isotherms are similar and can be identified as type IV, with the exception of the Pt/Nb₂O₅ catalyst isotherm, which show type V behavior. Type IV isotherms are characteristic of mesoporous solids, whereas type V isotherm correspond to microporous solids. Type H2 hysteresis loops were detected in Pt/TiO₂, Pt/SiO₂ and Pt/Al₂O₃ catalysts. This type of loop is characteristic of bottleneck pores and of solids composed by small spherical particles. The Pt/Nb₂O₅ catalyst showed Type H4 hysteresis that corresponds to crack pores.

Figure 2. N₂ isotherms of Pt support catalysts (HT).

The Pt/SiO₂ and Pt/Al₂O₃ catalysts show similar chemisorption values when they are reduced at low or high temperatures, as expected because under this temperature range 473-773 K, due to the inert characteristic of the supports. The chemisorption values of Pt/Nb₂O₅ and Pt/TiO₂ HT catalysts are lower compared to the LT counterpart. This behavior is explained by the SMSI effect (strong metal-support interaction)¹⁹. This occurs because niobia and titania are partially reducible oxides and at high temperature reduction a slight reduction may take place leading to partially reduced species (Nb₂O_{5-x} and TiO_{2-x}) which can easily migrate over small metal particles. Similar results have been reported by Rojas²⁰ and Reyes²¹ in Ir/TiO₂ and Ir/TiO₂-SiO₂ catalysts using FTIR, where the electronic metal-support interaction was observed only for samples with the higher titanium content, after being submitted to HT treatment.

The results of particle size of platinum catalysts no significant differences in the systems reduced at high or low temperatures were observed. Representative TEM images (a) and Pt particle size distributions (b) associated with (1) Pt/Nb₂O₅, (2) Pt/SiO₂, (3) Pt/TiO₂ and (4) Pt/Al₂O₃ catalysts are given in figure 3.

The TEM images reveal a pseudo-spherical morphology for the Pt particles in all the samples. A particle size distribution of Pt/Nb₂O₅ HT showed a wider size distribution with particles varied in width from 1 to 22 nm giving an average Pt particle size of 9.8 nm, as show in figure 3 (b₁). This higher value is due to the lower surface area of niobia, therefore the formations of clusters or agglomerates of platinum particles are likely. The Pt/SiO₂ HT catalyst displays a wider distribution with platinum particle size 8.2 nm (figure 3b₂). The high particle sizes obtained in the Pt/Nb₂O₅ and Pt/SiO₂ catalysts, consistent with the platinum signals were observed in the X-ray patterns, as average particle sizes for these systems exceeded 5 nm. Studies performed by transmission electron microscopy (TEM) confirm that the platinum is highly dispersed in Pt/TiO₂ HT and Pt/Al₂O₃ HT catalysts, showing metal particle size close to 3.3 nm and 1.7 nm respectively. X-ray diffraction studies only showed the lines due to the support, indicating that the dispersion degree of metallic species of Pt is high on the titania and alumina surface.

Figure 3. (a) Representative TEM images, (b) particle size distributions of platinum support catalysts.

The reducibility of the catalysts was studied by TPR under H₂/Ar flow in the temperature range from 298 K to 1173 K. In figure 4 and 5, the TPR profiles for the Pt/SiO₂, Pt/Nb₂O₅, Pt/TiO₂ and Pt/Al₂O₃ catalysts are displayed. For the prepared catalysts, the profiles show differences in the reducibility of platinum particles.

The profile of Pt/Nb₂O₅ presented reduction peaks at 400 K that usually ascribed to an oxochloroplatinum surface complex (PtO_xCl_y)²². The broad peak at 650 K is related to partial reduction of the support²³. The reduced species (NbO_x) are probably responsible for the changes in catalytic and chemisorptive properties of the catalysts after reduction at high temperatures²⁴. Pt/SiO₂ system present a peak at 500 K, it may be related to the PtO_xCl_y complex, as described in literature²⁵. In this catalyst no showed signals of reduction peaks may be ascribed to the reduction of the support. The reduction temperature of PtO_xCl_y species in the Pt/Nb₂O₅ catalyst was lower than in the Pt/SiO₂ catalyst which may be attributed to the fact that niobia is a partially reducible supports. Other characteristic in these catalysts was their higher metal particle size and lower dispersion, which were determined by TEM and hydrogen chemisorption, respectively. This behavior may be related to the low hydrogen consumptions for these catalysts.

Figure 4. Temperature programmed reduction profiles Pt/Nb₂O₅ (a) and Pt/SiO₂ (b).

Figure 5. Temperature programmed reduction profiles Pt/TiO₂ (a) y Pt/Al₂O₃ (b).

Pt/TiO₂ catalyst exhibits a maximum peaks at 350, 560 and 640 K. The peak at 350 K is ascribed to the presence of surface oxochloroplatinum complex; the peak at 560 K is related with the reduction of surface PtO_x to metallic platinum²⁴.

In the TPR profile of the Pt/Al₂O₃ catalyst, the PtO_xCl_y complex reduced at 460 K, also a hydrogen uptake near at 523 K is observed, which is assigned at reduction of PtO₂ particles to PtO. The small peak at 640 K may be attributed to the reduction of PtO to Pt⁰. A similar behavior was reported by Reyes *et al.*²⁵, and Arteaga *et al.*²⁶. They prepared Pt/Al₂O₃ catalysts using H₂PtCl₆ as precursor. The peak at 640 K corresponds to surface oxygen of the TiO₂²⁷⁻²⁹. These results suggest that presence of Pt facility the reduction oxygen species on the surface of the TiO₂. Similar effect produced by noble metals (Au, Pt, Rh and Pd) has been reported on CeO₂³⁰. The partially reduced titania lead to surface TiO_{2-x} species after hydrogen at high temperatures (above 673 K), according at the following equation³¹:

The oxychloroplatinum surface complex (PtO_xCl_y) would be formed during drying and calcination, due to the residual chloride ions on the supports after prepared by incipient wetness with H₂PtCl₆ solution²¹. The presence of this species also was observed by Hwang *et al.*³², they reported that reduces in the range of 400 and 573 K.

In addition, the Pt/TiO₂ and Pt/Al₂O₃ catalysts presented as well as (PtO_xCl_y) complex, platinum oxide species, the presence of these last can be attributed to a higher dispersion and narrower particle size distribution. These facts facilitate a higher elimination of chlorine during the calcination and reduction treatments. At the same time, in the reduction step occurs the formation of platinum oxide that transforms later on at metallic platinum.

The surface acidity of the catalysts was evaluated from TPD of ammonia. The order of surface acidity of studied samples was following; Pt/SiO₂ > Pt/Al₂O₃ > Pt/TiO₂ > Pt/Nb₂O₅ catalysts. Figure 6 shows the TPD profiles of the catalysts. The position and maximum temperature of each profile is a qualitative indication of relative acidity strong of the particular site. The profiles of the Pt/Nb₂O₅ and Pt/Al₂O₃ catalysts showed two desorption peaks; one at 350 K correspond at weak acidity type and the others at 500 K and 610 K in Pt/Nb₂O₅ and Pt/Al₂O₃ respectively. These later peaks are attributed at intermediate acidity. The profiles of ammonia desorption of the Pt/TiO₂ and Pt/SiO₂ catalysts exhibited a similar behavior; these systems showed an intermediate acidity type.

Figure 6. The TPD of ammonia over Pt catalysts

Table 2. Surface acidity NH₃ (molec. g⁻¹) of the studied samples.

Catalysts	TPD-NH ₃ Molec. g ⁻¹ × 10 ¹⁹
Pt/Nb ₂ O ₅	3.2
Pt/SiO ₂	7.2
Pt/TiO ₂	5.4
Pt/Al ₂ O ₃	6.8

Figure 7 shows the evolution of the conversion level with time at 343 K and 0.82 MPa in *m*-dinitrobenzene hydrogenation over supported Pt catalysts (HT series). All the catalysts exhibited similar trends. The conversion increased with the time of reaction.

Table 3 summarizes the conversion level at the same reaction time (1 h) as well as the initial activity for *m*-DNB hydrogenation, expressed as micromole converted per second per gram of catalysts and the initial turnover frequency

(TOF) at the 10% of conversion for Pt supported catalysts for both studied series (HT and LT). It can be seen lower conversion level, initial activity and TOF by the LT series compared with the HT counterpart. Among them, Pt/TiO₂ HT catalyst possess higher activity, whereas, Pt/Nb₂O₅ LT catalyst showed low activity, initial activity and TOF.

Figure 7. *m*-dinitrobenzene hydrogenation at 343 K and 0.82 MPa. Conversion level in function of time. HT series.

Table 3. Conversion at 1h of reaction, initial activity, TOF at conversion 10 %, for the *m*-dinitrobenzene hydrogenation at 343 K and 0.82 MPa over Pt supported catalysts.

Catalysts	X (%) t=1h	Initial activity (μmols g ⁻¹ cat)	TOF (s ⁻¹)
Pt/TiO ₂ LT	4.9	6.94	2.15
Pt/TiO ₂ HT	48.1	9.92	2.54
Pt/Al ₂ O ₃ LT	31.2	1.74	0.22
Pt/Al ₂ O ₃ HT	43.4	5.57	0.72
Pt/SiO ₂ LT	14.5	4.34	0.96
Pt/SiO ₂ HT	17.5	8.17	1.91
Pt/Nb ₂ O ₅ LT	8.0	0.050	0.09
Pt/Nb ₂ O ₅ HT	12.5	4.63	0.44

X: Conversion

With regard to the HT series the highest initial activity is shown by the Pt/TiO₂ followed of Pt/Al₂O₃ catalyst. These results suggest that are catalysts with sites very active for the reaction nitro groups hydrogenation. The highest activities exhibited might result from the particle size; the catalysts that showed small particle size and higher metallic dispersions development a great number of exposed sites at molecules of *m*-DNB and atomic hydrogen. The Pt/SiO₂ and Pt/Nb₂O₅ catalysts showed lower initial activity. These catalysts presented particles higher at 5 nm and metallic aggregates were formatted. This fact indicated the presence of less number of active sites, which was calculated for the H/metal ratio.

The TOF results exhibited the same behavior of conversion and initial activity. The catalysts presented values in the following order: Pt/TiO₂ > Pt/Al₂O₃ > Pt/SiO₂ > Pt/Nb₂O₅. The TOF decreased with increased of the particle size was observed. The reaction probably is structure sensitive.

In the reaction of *m*-DNB hydrogenation, *m*-NA was detected as main intermediate besides final product *m*-PDA. The results of selectivity and yield at 1, 3 and 5 h of reaction for Pt/TiO₂ and Pt/Al₂O₃ (LT-HT) catalysts in Table 4 were presented. The products obtained in term of yield or percentage product are expressed. This is due at that are consecutive reactions.

Table 4. Comparison of yield to *m*-nitroaniline and *m*-phenylenediamine over Pt/TiO₂ and Pt/Al₂O₃ catalysts.

Catalysts	Y (%) (1h)		Y (%) (3 h)		Y (%) (5h)	
	<i>m</i> -NA	<i>m</i> -PDA	<i>m</i> -NA	<i>m</i> -PDA	<i>m</i> -NA	<i>m</i> -PDA
Pt/TiO ₂ LT	46.9	0.0	65.7	4.6	73.6	7.0
Pt/TiO ₂ HT	43.0	5.0	59.2	18.7	47.1	39.5
Pt/Al ₂ O ₃ LT	31.2	0.0	54.7	2.7	67.6	4.6
Pt/Al ₂ O ₃ HT	43.4	0.0	68.2	3.4	65.6	16.4

Y: yield

These results suggest a higher yield of *m*-NA at 1h of reaction and only Pt/TiO₂ HT exhibited a slight quantity of *m*-PDA; as course the reaction (3h), increased the formation of *m*-NA. At 5 h of reaction the yield of *m*-NA decreased. This fact can be attributed to that *m*-NA is consumed and *m*-PDA is formed. In those catalysts can affirm that the polynitroaromatics hydrogenation is consecutive reaction; first occurs the reduction of -NO₂ to NH₂ and after the hydrogenation of the other -NO₂ group is performed. The activity and selectivity of the catalysts were strongly affected by the types of supports. In the conversion of *m*-DNB, Pt/TiO₂ HT and Pt/Al₂O₃ HT delivered the higher level. In themselves catalysts exhibited the *m*-PDA formation. These results suggest that the *m*-PDA formation depends of particle size. Generally with smaller Pt particles (< 5 nm) exhibited the aromatic amine formation. The hydrogenation *m*-DNB reaction is structure sensitive. The PtO_x species are more active than PtO_xCl_y complex, and easy reduction.

The evolution of the reactive (*m*-DNB), intermediate (*m*-NA) and final product (*m*-PDA) with the Pt/TiO₂ catalyst in the figure 8 is observed. The concentration of *m*-dinitrobenzene decreases with the reaction course, whereas, the concentration of *m*-NA increases to reach a maximum concentration (0.062 M approx.) and later on decreases. The concentration of *m*-PDA continually increases. This behavior is attributed to the presence of PtO_x species reduced smaller particle size and intermediate acidity. In the Pt/Al₂O₃ catalyst the behaviour is similar.

Figure 8. Evolution of reactive and products in the *m*-dinitrobenzene hydrogenation with Pt/TiO₂ HT catalyst.

In the Pt/Nb₂O₅ and Pt/SiO₂ catalysts the partial reduction of nitro groups of *m*-DNB was observed, with 99.9% to *m*-NA (figure 9). They had low activity for hydrogenation.

Figure 9. Evolution of reactive and products in the *m*-dinitrobenzene hydrogenation with Pt/SiO₂ HT catalyst.

As all the catalysts not produce the aromatic amine, a more appropriate comparison is to know the rate constants for all systems. The formation of *m*-NA and *m*-PDA are considered the first step (*k*₁) and second step (*k*₂), respectively.

The rate constants of the first step (*k*₁) of hydrogenation of *m*-DNB in all the catalysts reduced at 773 K was greater than the rate constants of the first step (*k*₁) of the catalysts were reduced at 473 K. In the HT series, the *k*₁ exhibited the following order: Pt/TiO₂-Al₂O₃ > Pt/TiO₂ > Pt/Al₂O₃ > Pt/SiO₂ > Pt/Nb₂O₅. This order is according to the tendency showed regarding the particle size, surface acidity and reduced PtO_x species. Also, with decreasing average particle size, the rate constants are increased. The catalysts with intermediate acidity and reduced PtO_x species showed higher rate constants (table 5).

Table 5. Rate constants in the *m*-dinitrobenzene hydrogenation.

Catalysts	<i>k</i> ₁ (mol·g ⁻¹ ·s ⁻¹)	<i>k</i> ₂ (mol·g ⁻¹ ·s ⁻¹)
Pt/TiO ₂ LT	2.2 × 10 ⁻³	2.40 × 10 ⁻⁴
Pt/TiO ₂ HT	3.4 × 10 ⁻³	7.60 × 10 ⁻⁴
Pt/Al ₂ O ₃ LT	6.0 × 10 ⁻⁴	1.80 × 10 ⁻⁴
Pt/Al ₂ O ₃ HT	2.5 × 10 ⁻³	3.80 × 10 ⁻⁴
Pt/SiO ₂ LT	4.0 × 10 ⁻⁴	-
Pt/SiO ₂ HT	7.3 × 10 ⁻⁴	-
Pt/Nb ₂ O ₅ LT	3.0 × 10 ⁻⁴	-
Pt/Nb ₂ O ₅ HT	5.0 × 10 ⁻⁴	-

The Pt/TiO₂ and Pt/Al₂O₃ catalysts formed *m*-PDA. In these systems, the rate constants (*k*₂) were lower than the rate constants (*k*₁). Therefore the reaction of *m*-NA to *m*-PDA is the limiting step of the reaction. These results are according to the literature; For such polynitroaromatics, the rate of reduction of the first nitro group is generally much more rapid than the rate of reduction of the remaining nitro groups; in most cases, the rate of subsequent reduction is so slow that the process is effectively stopped after the first nitro group is reduced³³.

CONCLUSIONS

- Activity and selectivity of supported platinum catalysts for *m*-dinitrobenzene hydrogenation reaction were strongly affected by the physico-chemical properties of supports.

- The highest activity and selectivity towards *m*-phenylenediamine observed over the Pt/TiO₂ catalyst in solvent ethanol, suggesting that the Pt/TiO₂ HT catalyst is a promising catalyst for the synthesis of *m*-phenylenediamine.

This result is attributed to the smaller particle size, intermediate acidity and reduced PtO_2 species.

- In this study was possible to obtain regioselective catalysts in the hydrogenation of substituted nitroaromatics from metal little studied in such reactions, with $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/TiO_2 catalysts reduced at high temperature better performance in the hydrogenation of *m*-dinitrobenzene.

ACKNOWLEDGMENT

The authors acknowledge to DIN-UPTC for financial support (SGI 683). We also thank to RECIEND COMPANY, by supplied TiO_2 P-25.

REFERENCES

- 1.- A. Bechamp. *Annales de Chimie*. Paris 42, 186, (1854).
- 2.- K. Westerterp, E. Molgal, K. Van Gelder. *Chem. Eng. and Proc.* 36, 54, (1997).
- 3.- C. Rode and R. Chaudhari. *Ind. Eng. Chem. Res.* 33, 1645, (1994).
- 4.- M. Telkar, J. Nadgeri, C. Rode, R. Chaudhari. *Appl. Catal. A: Gen.* 295, 23, (2005).
- 5.- L. Yingxin, C. Jixiang, Z. Jiyan, *Chin. J. Chem. Eng.* 15, 63, (2007).
- 6.- V. Belousov, T. Palchevskaya, L. Bogutskaya. *React. Kinet. Catal. Lett.* 36, 369, (1988).
- 7.- K. Shimazu, Y. Tateno, M. Magara, JP: 09132536 (1997).
- 8.- Z. Yu, S. Liao, Y. Xu, B. Yang, D. Yu. *J. Mol. Catal. A: Chem.* 120, 247, (1997).
- 9.- H. Mizuta, T. Nishimura, M. Wada and T. Nagata. JP Patent 0609551 (1994).
- 10.- P. Reyes, J.L.G. Fierro, H. Rojas. *J. Chil. Chem. Soc.* 52, 1155, (2007).
- 11.- C. Maldonado, J.L.G. Fierro, J. Coronado, B. Sánchez, P. Reyes. *J. Chil. Chem. Soc.* 55, 404, (2010).
- 12.- P. Reyes and H. Rojas. *React. Kinet. Catal. Lett.* 88, 363, (2006).
- 13.- H. Rojas, G. Borda, P. Reyes, J.J. Martínez, J. Valencia, J.L.G. Fierro. *Catal. Today*. 133, 699, (2008).
- 14.- D. Hoang, S. Farrage, J. Radnik, M. Pohl, M. Schneider, H. Lieske, A. Martin. *Appl. Catal.* 333, 67, (2007).
- 15.- V. Rodríguez, R. Zanella, G. Angel, R. Gómez. *J. Mol. Catal. A: Chem.* 281, 93, (2008).
- 16.- C. Maldonado, J.L.G. Fierro, G. Birke, E. Martínez, P. Reyes. *J. Chil. Chem. Soc.* 55, 506, (2010).
- 17.- F. Montes, P. Getton, W. Vong, A. Sermon. *J. sol-gel Science and Technology*. 8, 131, (1997).
- 18.- J. Choi, J. Kim, K. Sang, T. Gyu. *Powder Technology*. 18, 83, (2008).
- 19.- H. Rojas, G. Borda, P. Reyes, J. Castañeda, J.L.G. Fierro. *J. Chil. Chem. Soc.* 53, 1464, (2008).
- 20.- P. Reyes, H. Rojas, G. Pecchi, J.L.G. Fierro. *J. Mol. Catal. A: Chem.* 179, 293, (2002).
- 21.- P. Reyes, H. Rojas and J.L.G. Fierro. *J. Mol. Catal. A: Chem.* 203, 203, (2003).
- 22.- H. Lieske, G. Lietz, H. Spindler, J. Völter, *J. Catal.* 81, 8, (1983).
- 23.- D. Aranda, F. Noronha, M. Schmal, F. Passos. *Appl. Catal.* 100, 77, (1993).
- 24.- D. Aranda, F. Noronha, M. Schmal F. Passos. *Catal. Today*. 16, 397, (1993).
- 25.- P. Reyes, M. Oportus, G. Pechi, R. Frety, B. Moraweck. *Catal. Lett.* 37, 193, (1996).
- 26.- G. Arteaga, A. Medina, O. Colina, D. Rodríguez, F. Domínguez, J. Sánchez. *Ciencia*. 16, 354, (2008).
- 27.- N. Resende, J. Eon, M. Schmal. *J. Catal.* 183, 6, (1999).
- 28.- W. Epling, P. Cheekatamarla, A. Lane. *Chem. Eng. J.* 93, 61, (2003).
- 29.- R. Pérez, A. Gómez, J. Arenas, S. Rojas, R. Mariscal, J.L.G. Fierro, G. Diaz. *Catal. Today*. 107, 149, (2005).
- 30.- A. Trovarelli, G. Dolcetti, C. De Leitenburg, J. Kaspar, P. Finetti, A. Santoni. *J. Chem. Soc. Faraday Trans.* 88, 1311, (1992).
- 31.- L. Wang, M. Sakurai, H. Kameyama. *J. Hazard. Matt.* 167, 399, (2009).
- 32.- C. Hwang, C. Yeh. *J. Mol. Catal. A: Chem.* 112, 295, (1996).
- 33.- S. Arrows, C. Cramer, D. Truhlar, M. Elovitz, E. Weber. *Environ. Sci. Technol.* 30, 3028, (1996).