KINETIC STUDY OF THE HYDROGENATION OF CITRAL ON Ir PROMOTED Au/TiO₂ CATALYSTJOSÉ J. MARTÍNEZ^{1,2}, HUGO ROJAS¹, PATRICIO REYES^{3*}¹Escuela de Ciencias Químicas, Universidad Pedagógica y Tecnológica de Colombia UPTC, Avenida Central del Norte, Vía Paipa, Tunja, Boyacá – Colombia.²Departamento de Química, Universidad Nacional de Colombia. Sede Bogotá. AA 14490, Bogotá, Colombia.³Universidad de Concepción, Facultad de Ciencias Químicas. Edmundo Larenas 129, 160-C, Concepción, Chile.

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ABSTRACT

A kinetic study of citral hydrogenation over an Au-Ir/TiO₂ catalyst was performed with the aim to understand the effect of iridium on gold in this catalytic system. Au-Ir/TiO₂ catalyst was prepared by co-deposition precipitation in an atomic ratio of 3/1. The effect of citral concentration, hydrogen pressure and temperature effect were also studied. The product distribution obtained is related with the proportion of Me⁶⁷/Me⁰ sites. The deactivation of the catalyst occurs in the whole studied temperature range, 363 to 403 K, being more drastic as temperature increases due to the irreversible adsorbed CO blocks principally Ir⁰ sites. From initial reaction rates treatment an apparent global order close to 1 was determined. A Langmuir-Hinshelwood-type kinetic model involving the surface reaction as the rate limiting step between adsorbed citral and hydrogen on active sites with different nature shows good agreement with experimental initial reaction rates.

Keywords: Citral, Au- Ir catalyst, kinetic study.

1. INTRODUCTION

Supported gold catalysts can show very high selectivity to unsaturated molecules in the hydrogenation reactions¹⁻⁶. The relationship between particle size and activity has been widely investigated experimentally and also theoretically⁶⁻⁸. Both activity and TOF increase as the gold particle size decreases⁸, however there is no agreement on the reason for this effect. It seems be that electronic effects based on particle size are necessary to explain the behavior catalytic of gold in hydrogenation reactions⁹. It has been proposed that the dissociation of hydrogen occurs on the low-coordinated sites of gold particles (edges and corners)⁶, however, any effect of the support on the intrinsic activity of the catalyst could reflect the ability of the support to aid in the activation of hydrogen¹⁰. Therefore, it is difficult to get experimental evidences of the catalytic activity of gold toward hydrogen dissociation and to distinguish between particle size and support effects¹¹. In all case, in hydrogenation reactions, the activity of gold catalysts is often much lower than those of the platinum-group metals^{6,12}.

The modification of gold particles by a second metal has been used for increases the rate of H₂ dissociation obtaining a more active catalyst than the monometallic catalyst of Au. A contribution to this approach has been presented by Corma *et al.*¹³ in Pt-Au catalysts, in which the activation of the nitroaromatic compounds was shown to take place at Au/Ti boundaries, and the reduction process occurs on the gold nanoparticles after H₂ dissociation. Sun *et al.*¹⁴ using a small amount of fully dispersed Pt entities loaded on Au NPs showed that it led to dramatic activity enhancement of the Au NPs (up to 70-fold) for the chemoselective hydrogenation of α , β -unsaturated carbonyl compounds, without changing the selectivity of Au NPs. A synergic effect between Pt and Au was proposed to explain this observation, in which the Pt sites function to activate the H₂ molecules whereas the Au sites help to activate the unsaturated substrate molecules by chemisorption. The synergy depends critically on the dispersion of Pt nanoparticles and the Pt-Au proximity, but it hardly affected by the temperature and H₂ pressure of the reaction¹⁵.

This same type of catalysts has been used over nanostructured supports, obtaining similar results. Pd-Au catalysts supported on mesoporous silica nanoparticles promote the hydrogenation of cinnamaldehyde¹⁶. The activity of bimetallic system was up to four times higher than that of Pd monometallic and eight times higher than that of commercial Pd/C catalyst. Similarly, the explanation has been attributed to the synergistic effect of Pd with the added Au, the highly dispersed active components and the possibility of that the addition of Au may modify the electronic properties of Pd. Similarly, the use of Pt-Au on CNT also leads to higher selectivity than that obtained with monometallic systems in the citral hydrogenation¹⁷, which is a model reaction for catalytic tests in the field of selective hydrogenation of α , β -unsaturated carbonyl compounds¹⁸.

In this reaction, Díaz *et al.*,¹⁹ indicates that Ir-Au/TiO₂ catalysts are more

actives and selective towards the unsaturated alcohol that Ir/TiO₂ or Au/TiO₂. It is likely that the iridium contributes to the dissociation of hydrogen and besides facilitates the preferential reduction of the carbonyl group. Some kinetic studies over gold catalysts in hydrogenation reactions indicates that the rate limiting step is the activation of H₂^{6,13}, and other authors indicate that is the surface reaction between the adsorbed molecule and adsorbed dissociated hydrogen²⁰. Sun *et al.*¹⁵ over Pt-Au/SiO₂ reported that cinnamaldehyde and H atoms are adsorbed on active sites of different nature, thus the active sites responsible for the H₂ activation are different from those for molecules adsorption on this type of catalysts. In the present work, a study of the citral hydrogenation over an Au-Ir/TiO₂ has been carried out with the aim of clarifying the kinetic behavior and a possible reaction mechanism.

2. EXPERIMENTAL

2.1. Chemicals

TiO₂ (Degussa P-25) with a specific surface area (S_{BET}) of 50 m²g⁻¹ was used as support. It was previously activated under vacuum at 423 K. H₂IrCl₆ (Aldrich>99%), HAuCl₄ (Aldrich> 99%), and Urea (JT-Baker), citral and heptane were used without further purification.

2.2. Preparation of catalyst

Au-Ir/TiO₂ sample was prepared by co-deposition precipitation using urea (DPU) as previously described²¹. Briefly, 1g of TiO₂ was mixed with 100 mL solution of H₂IrCl₆ and HAuCl₄ (wt.% (Ir + Au) = 1.0) in a atomic ratio of 3/1 of Au/Ir with an urea aqueous solution (0.66 M) and heated at 353 K for 16 h, after washed with water, centrifugation, dried under vacuum at 373 K and calcined at 673 K for 4 h. The reduction was carried out under H₂ flow at 573 K for 2 h.

2.3. Characterization techniques

BET surface area and porosity measurements were carried out by N₂ adsorption at 77 K using a Micromeritics ASAP 2020 instrument. The metal dispersion of catalysts was evaluated by H₂ chemisorption at 308 K performed with a Micromeritics Autochem 2920 apparatus.

Temperature programmed desorption (TPD) experiments of spent catalyst were carried out using the protocol proposed by Mäki-Arvela *et al.*²². The catalyst was heated under Argon (99.996%) with a flow rate of 50 cm³/min and temperature programmed at 10 K/min up to 900 K by using Micromeritics (Autochem 2920) apparatus and analyzing the CO (m/z = 40) desorbed by a mass spectrometer (Pfeiffer).

2.4. Kinetic study

Catalytic reactions were carried out in a stainless steel batch reactor at a constant stirring rate (1000 rpm). To carry out the kinetic study over the catalysts only one variable was modified in each experiment, keeping constant all the others. The effect of citral concentration was studied in the concentration range 0.025 to 0.2 M. The hydrogen partial pressure was studied in the range 0.48 MPa to 0.84 MPa. The temperature was varied in the range 363 up to 403K and the catalyst weight, ranged from 0.1 to 0.3 g. Prior the experiment, all catalysts were treated *in situ* under hydrogen flow of 20 cm³/

min at atmospheric pressure and temperature of 363K to remove possible surface oxide species generated during handling. To avoid the presence of oxygen, once the reactor was loaded with the reactant mixture and catalyst, the system was flushed with He at atmospheric pressure during 30 min. Analysis of the reaction mixture and products was carried out using a Varian 3800 gas chromatograph furnished with a β -Dex column of 30 m length and 0.53 mm ID. The GC analysis was performed using a flame ionization detector, using He as carrier. In all experiments, reactant and product concentrations were measured at different time intervals.

To avoid intraparticle mass-transfer resistance, it was used smallest catalyst particles sizes (100 μ m) and a stirring rate of 1000 rpm. Under these conditions it was demonstrated the absence of heat and mass limitations.

3. RESULTS AND DISCUSSION

3.1 Characterization

The textural properties of the TiO_2 support not were modified by the presence of gold or iridium particles as can be observed from the results in Table I. The nitrogen adsorption-desorption isotherm corresponds to type IV in the BDDT classification's showing a hysteresis loop typical of cylindrical pores. No significant change in the support surface area, neither the average pores size, occurs after the deposition of the metallic components. H_2 chemisorption at 308 K showed high dispersion of the metallic phase (estimated from the H/Me ratio). Metal particle size evaluated from chemisorption and by TEM studies revealed similar values, close to 4.0 nm. These results are compiled in Table I

Table I. Textural properties of TiO_2 and Au-Ir/ TiO_2 catalysts, H/Me ratio and metal particle size (d_p) obtained from H_2 -chemisorption and TEM studies.

Solids	S_{BET} , m^2g^{-1}	Pore size, nm	H/Me	d_{pCHEM} , nm	d_{pTEM} , nm
TiO_2	57	13.8	--	--	--
Ir-Au	62	13.2	0.27	3.7	4.0

Fig. 2 displays the temperature programmed reduction (H_2 -TPR) profile of Au-Ir/ TiO_2 calcined sample. It has been reported for Au/ TiO_2 catalysts, that the reduction to metallic gold takes place around 460K²¹ and the reduction of $[\text{AuCl}(\text{OH})_2]^-$ species at 570K²³ and those are only the two signals detected, whereas for Ir/ TiO_2 the reduction peaks commonly observed at 373K and 523 K are associated to the reduction of some large and dispersed IrO_2 particles, respectively²¹. In the profile obtained for Au-Ir/ TiO_2 , it can be observed four peaks at about 375 K (a), 466 (b) and 570 K (g). Both a and b peaks could be assigned to the reduction of gold species²¹ whereas, the g peak could be attributed to the reduction of IrO_2 species^{21, 24-26}. The shift at higher temperatures of this peaks could be associated to a higher formation of surface oxychlorometal complex (MeO_xCl_y , where Me: Au or Ir) that inhibits the reduction of metal species²⁷. Consequently, gold species spreads over the iridium surface due to that Au has lower surface free energy than Ir²⁸, which increases the temperatures of reduction of the IrO_2 species. The TPR profile of the Ir-Au/ TiO_2 catalyst apart from the peaks already described, exhibits a continuous increases in the baseline at temperatures higher than 773K which can be ascribed to a partial reduction of the support²¹.

Figure 1. TPR profile of Au-Ir/ TiO_2 catalyst.

With regard to the catalytic behavior, Au-Ir/ TiO_2 catalyst display an important hydrogenation of citral occurring in the first few minutes, with a rapid deactivation after this earlier period being more evident at high concentrations of citral. Thus, for 0.2M y 0.1M the reaction stopped completely when the conversion level was ca. 10% as can be clearly observed in Fig. 2 This behavior is attributed to a possible decarbonylation reaction either the aldehyde or the unsaturated alcohol yielding to irreversible adsorbed CO that blocked metallic active sites as has been previously discussed²². An important enhancement in the initial reaction rate as citral concentration decreases is observed. This may be explained taking into account that the reaction takes place on the active sites of the catalyst, in which the coverage by hydrogen and citral occurs. At higher citral concentration, most of the substrate molecules remain in the solution, and consequently the conversion is lower.

Figure 2. Conversion level as function of time of reaction in the citral hydrogenation at 363K, 0.62 MPa and 0.2 g de IrAu/ TiO_2 . (a) Effect of citral concentration: ($\square$) 0.025 M; ($\blacktriangle$) 0.1 M and ($\circ$) 0.2 M.

Figure 3 shows the evolution of the concentration of citral and their hydrogenation products on time for the study at 0.10 M of citral. It can be seen that the reaction takes place mainly during the first minutes leading to geraniol and nerol as main products and citronellal in a minor extent. Similar trends were observed at the other citral concentrations, however, the concentrations varied upon the initial substrate concentration. This catalytic behavior, in which the main products are the unsaturated alcohols revealed that the catalyst surface possesses active sites with two types of metallic sites (Me^0 and $\text{Me}^{\delta+}$). It has been widely reported that if the active phase is present essentially as zero valent state, the favored reaction is the hydrogenation of the C=C bond in the α , β unsaturated aldehyde leading to saturated aldehyde, meanwhile, as the proportion of $\text{Me}^{\delta+}$ increases, the pathway shift to the reduction of the carbonyl bond due to this later species contributes to polarize the C=O bond making easier its hydrogenation²⁵⁻²⁷.

Figure 3. Evolution of the concentration of ($\blacksquare$) citral and ($\square$) geraniol + nerol and ($\circ$) citronellal with time for the study at 0.10 M of citral

The formation of CO also has been considered to explain the behavior of deactivation of gold catalysts in hydrogenation reactions of nitroaromatics when the reaction is carried out using CO_2 as solvent under supercritical conditions²⁹. Additionally, it has been described the use of citral and geraniol TPD to identify the responsible of the deactivation in $\text{Pt}/\text{Al}_2\text{O}_3$, the authors suggests that especially unsaturated alcohols are active for decarbonylation²². To add more evidence of this poisoning a spent $\text{Au-Ir}/\text{TiO}_2$ catalyst was investigated by temperature programmed desorption technique²² under argon as a carrier gas (Fig. 4). Broad desorption of CO confirms that decarbonylation occurs on the catalyst surface. The desorption peak is centered at 430 K and it is almost complete at temperatures close to 600K.

Figure 4. Desorption of CO of spent $\text{Au-Ir}/\text{TiO}_2$ catalyst followed by TPD.

The evolution of the selectivity to the products with the conversion level is given in Fig. 5. For $\text{Au-Ir}/\text{TiO}_2$ the selectivity to unsaturated alcohol (geraniol and nerol) increases as conversion increases, while the selectivity to saturated aldehyde (citronellal) decreases. No other reaction products were detected. The absence of a further hydrogenation of citronellal is due to catalyst deactivation²², which suggests that the decarbonylation process poisons mainly the $\text{C}=\text{C}$ hydrogenation sites and therefore it modifies the $\text{C}=\text{C}/\text{C}=\text{O}$ adsorption competition, changing the obtained selectivity, in this case favoring an isomer in particular (nerol), this is clearly more evident with the modification of pressure of H_2 .

3.2 Kinetic study using initial rates.

To avoid any interference of deactivation caused by the products the data kinetic treatment was obtained at low conversions ($< 10\%$). On the basis of the amount of reactant consumed, the initial rates were calculated graphically using a third-order polynomial equation.

Effect of catalyst mass: The effect of catalyst loading on the initial rate of catalytic hydrogenation of citral is shown in Figure 6. The initial rate of reaction was found to increase linearly with the catalyst mass. This is an evidence of the absence of mass and heat transfer limitations.

Figure 5. Selectivity percentage to (○) nerol (Δ) geraniol and (◻) citronellal as a function of conversion of citral. (a) At distinct concentrations of citral, (b) at distinct relative pressures of H_2 .

Figure 6. Effect of catalyst mass on the initial rate of hydrogenation of citral on $\text{Au-Ir}/\text{TiO}_2$ catalyst at 363 K, 0.62 MPa of hydrogen partial pressure, 0.1 M of citral dissolved in heptane.

Effect of hydrogen partial pressure: The effect of hydrogen partial pressure was studied in the range 0.34 to 1.02 MPa. The effect of hydrogen partial pressure on the initial rate of reaction is shown in Figure 7 in which $\log r_0$ vs $\log P_{\text{H}_2}$ were plotted. From the slope the dependence of the reaction rate with the hydrogen pressure was obtained given a value of 0.50.

Figure 7. Effect of hydrogen partial pressure on the initial rate of hydrogenation of citral on Au-Ir/TiO₂ catalyst at 363 K, 0.1 M of citral dissolved in heptane and 0.2 g of catalyst.

Effect of citral Concentration. Citral concentration was varied from 0.025 to 0.2 M at constant pressure of H₂ of 0.62 MPa and temperature (363 K). The results expressed as log r_0 vs log Citral concentration are displayed in figure 8. The dependence calculated for initial rate was 0.40.

Figure 8. Effect of concentration of citral on the initial rate of hydrogenation of citral on Au-Ir/TiO₂ catalyst at 363 K, 0.62 MPa of H₂ and 0.2 g of catalyst.

Kinetic model: Two types of kinetic equations were employed in the quantitative description of the experimental results: first, empirical power-law equations based on initial rates and a second, equations based on the Langmuir-Hinshelwood mechanism. Power-law equations for the hydrogenation of citral on Au-Ir/TiO₂ obey the equation $r_0 = \text{mmol}_{\text{citral}}^{0.4} p_{\text{H}_2}^{0.5}$. Thus, for Au-Ir/TiO₂ the apparent global order is close to 1.

In order to evaluate the activation energy of the reaction, different experiments at 0.62 MPa and a citral concentration of 0.10 mole/L and temperatures in the range 363 up to 403 K were performed. Fig. 9 shows pseudo first order plots. It can be seen that the slope decreases as temperature increases, in principle an anomalous Arrhenius type behavior, which can be attributed to the fact that apart from the hydrogenation in parallel (and consecutive reactions), deactivation occurs in an import extent a of the active sites by surface poisoning by decarbonylation, which extent increases significantly compared with the former as temperature increases. Similar observation was previously described by Mäki-Arvela²² in the citral hydrogenation reaction over Pt/Al₂O₃ catalysts.

Figure 9. Kinetic data treatment of pseudo first order in the hydrogenation of citral at 0.1 M, 0.62 MPa of H₂ and 0.2 g of catalyst at distinct temperatures: (Δ) 363 K, (■) 383 K and (○) 403 K

Taking into account that the dependence respect to concentration of citral and pressure of hydrogen are both fractional, it should be convenient to obtain insight into the kinetics via Langmuir-Hinshelwood models.

A typical Langmuir-Hinshelwood model (LH) can be developed to describe the hydrogenation of citral based on the following assumptions general:

1. The hydrogenation surface reaction is irreversible.
2. The diffusional limiting steps can be neglected
3. The contribution of the coverage of the active sites by the products at the beginning of the reaction can also be neglected.

The variations of the L-H model are presented in the Table II, which were taken of the reference¹³. These models are based on the assumption that one of the three elementary steps (adsorption of citral, adsorption of hydrogen, surface reaction between adsorbed citral and hydrogen) is rate limiting step being the others in quasi-equilibrium and that the adsorption of hydrogen occurs dissociatively both competitive or non-competitive with the organic molecules.

In order to select a suitable rate equation, a nonlinear least-squares regression analysis was used for each rate equation to obtain the best values of the parameters using a non-linear regression program with an iterative Gauss-Newton method. The objective function to be minimized is residual sum of squares, $RSS = \sum (r^* - r_{\text{calc}})^2$ where r^* is the experimental relative rate, r_{calc} is the relative concentration calculated with the model.

The equation involving the surface reaction as the rate limiting step between adsorbed citral and hydrogen on active sites with different nature and that the H₂ is also adsorbed on the same type of active site as citral, shows good agreement between the model predictions and the observed values in the initial rates (figure 10). Thus, the reaction rate constant of the surface reaction obtained was of 0.58 min⁻¹ and the adsorption constants obtained for this model were $K_{\text{Citral}} = 0.90$ and for $K_{\text{H}_2} = 1.42$.

Figure 10. Parity plot of calculated initial rates with experimental initial rate.

Table II. Rate equation derived for citral hydrogenation over Ir-Au/TiO₂ (adopted of the reference)¹³.

Rate equations	Features
$r_0 = \frac{k_1 p H_2}{(1 + K_R C_{Citral})^2}$	Citral and H ₂ react on active sites with the same nature (competitive adsorption), but the H ₂ dissociation is the limiting step of the reaction
$r_0 = \frac{k_{Citral} C_{Citral}}{1 + K_{H_2}^{1/2} p H_2^{1/2}}$	Citral and H ₂ react after adsorbing on active sites with different nature (noncompetitive adsorption), but the citral adsorption of citral is the limiting step of the reaction
$r_0 = \frac{k_1 K_{Citral} K_{H_2} C_{Citral} p H_2}{(1 + K_{Citral} C_{Citral} + K_{H_2}^{1/2} p H_2^{1/2})^3}$	Citral and H ₂ react on active sites with the same nature (competitive adsorption), but the surface reaction is the limiting step of the reaction
$r_0 = \frac{k_1 K_{Citral} K_{H_2} C_{Citral} p H_2}{(1 + K_{Citral} C_{Citral})(1 + K_{H_2}^{1/2} p H_2^{1/2})^2}$	Citral and H ₂ react after adsorbing on active sites with different nature (non-competitive adsorption), but the surface reaction is the limiting step of the reaction
$r_0 = \frac{k_1 K_{Citral} K_{H_2} C_{Citral} p H_2}{(1 + K_{Citral} C_{Citral} + K_{H_2}^{1/2} p H_2^{1/2})(1 + K_{H_2}^{1/2} p H_2^{1/2})^2}$	Citral and H ₂ react after adsorbing on active sites with different nature (non-competitive adsorption), the surface reaction is the limiting step of the reaction and besides H ₂ also adsorbs on the same active site as citral.
$r_0 = \frac{k_1 K_{Citral} K_{H_2} C_{Citral} p H_2}{(1 + K_{Citral} C_{Citral})(1 + K_{H_2}^{1/2} p H_2^{1/2} + K_{Citral} C_{Citral})^2}$	Citral and H ₂ react after adsorbing on active sites with different nature (non-competitive adsorption), the surface reaction is the limiting step of the reaction and besides citral also adsorbs on the same active site as H ₂ .

* k_1 = kinetic constant of the surface reaction; k_{H_2} = kinetic constant of the H₂ dissociation; k_{Citral} = kinetic constant of the citral adsorption; K_{H_2} = adsorption constant of H₂ in the equilibrium; K_{citral} = adsorption constant of citral in the equilibrium.

Although in this model is not possible to distinguish the nature of active sites, it can be assumed that the citral is preferentially adsorbed on the surface of gold, while the hydrogen dissociation occurs on the surface of segregated iridium atoms and iridium atoms partially covered by gold, in these latter, the adsorption of citral is much difficult due to that citral is a larger molecule compared with hydrogen. Thus, the proposed model is in agreement with the TPR results. Besides, it also explains the catalyst deactivation due to that the adsorbed CO species strongly adsorbs on iridium sites more than on gold ones²¹, which causes an inhibition in the H₂-dissociation.

4. CONCLUSIONS

The hydrogen dissociation is facilitated by the presence of iridium atoms on the gold surface, however, an strong deactivation occurs due to the irreversible adsorption of CO, mainly on Ir⁰ sites, which is more evident as temperature increases. This observation is in agreement with TPR and TPD results. A Langmuir-Hinshelwood model that involve the surface reaction between adsorbed citral and hydrogen on different types of active sites as the rate limiting step, allowed a better agreement between the kinetic equation obtained from the proposed mechanism and the experimental results

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REFERENCES

1. P. Claus, H. Hofmeister, C. Mohr, *Gold Bulletin*. **37**, 181 (2004).
2. P. Claus, *Appl. Catal. A*. **291**, 222 (2005).
3. P. Claus, A. Bruckner, C. Mohr, H. Hofmeister, *J. Amer. Chem. Soc.* **122**, 11430 (2000).
4. C. Milone, R. Ingoglia, S. Galvagno, *Gold Bulletin*. **39**, 54 (2006).
5. C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia, S. Galvagno, *Chem. Commun.* 868 (2002).
6. R. Zanella, C. Louis, S. Giorgio, R. Touroude, *J. Catal.* **223**, 328 (2004).
7. T. Fujitani, I. Nakamura, T. Akita, M. Okumura, M. Haruta, *Angew. Chem. Int. Ed.* **48**, 9515 (2009).
8. E. Bus, R. Prins, J. A. van Bokhoven, *Catalysis Communications*. **8**, 1397 (2007).
9. H. Rojas, G. Díaz, J. J. Martínez, C. Castañeda, A. Gómez-Cortés, J. Arenas-Alatorre, *J. Mol. Catal. A*. **363**, 122 (2012).
10. U. Hartfelder, C. Kartusch, M. Makosch, M. Rovezzi, J. Sa, J. van Bokhoven, *Catal. Sci. & Technol.* doi: 10.1039/C2CY20485A In-Press (2012)
11. M. Manzoli, A. Chiorino, F. Vindigni, F. Boccuzzi, *Catal. Today*. **181**, 62 (2012).
12. M. Okumura, T. Akita, M. Haruta, *Catal. Today*. **74**, 265 (2002).
13. P. Serna, P. Concepción, A. Corma, *J. Catal.*. **265**, 19 (2009).
14. Y.-C. Hong, K.-Q. Sun, G.-R. Zhang, R.-Y. Zhong, B.-Q. Xu, *Chem. Commun.* **47**, 1300 (2011).
15. K.-Q. Sun, Y.-C. Hong, G.-R. Zhang, B.-Q. Xu, *ACS Catal.* **1**, 1336 (2011).

16. X. Yang, D. Chen, S. Liao, H. Song, Y. Li, Z. Fu, Y. Su, *J. Catal.* **291**, 36 (2012).
17. V. N. S.A. Ananthan, *Int. J. Modern. Chem.* **1**, 45 (2012).
18. A. Stolle, T. Gallert, C. Schmoger, B. Ondruschka, *RSC Advances*. doi: 10.1039/C2RA21498A. *In-Press* (2012).
19. G. Díaz, A. Gómez-Cortés, O. Hernández-Cristobal, J. Murcia, G. Borda, H. Rojas, *Top. Catal.* **54**, 467(2011).
20. S. Gómez, C. Torres, J. L. García Fierro, C. R. Apesteguía, P. Reyes, *J. Chil. Chem. Soc.* **57**, 1194 (2012).
21. A. Gómez-Cortés, G. Díaz, R. Zanella, H. Ramírez, P. Santiago, J. M. Saniger, *J. Phys. Chem. C* **113**, 9710 (2009).
22. P. Mäki-Arvela, N. Kumar, K. Eränen, T. Salmi, D. Y. Murzin, *Chem. Eng. J.* **122**, 127 (2006).
23. H. Rojas, J. Martínez, S. Mancípe, G. Borda, P. Reyes, *React. Kin. Mechan. Catal.* **106**, 445 (2012).
24. W. Zhang, Y. Huang, J. Wang, K. Liu, X. Wang, A. Wang, T. Zhang, *Int. J. Hydr. Energy* **35**, 3065 (2010).
25. P. Reyes, D. Salinas, C. Campos, M. Oportus, J. Murcia, H. Rojas, G. Borda, J. L. G. Fierro, *Quím. Nova* **33**, 777 (2010).
26. H. Rojas, G. Borda, P. Reyes, J. C. Castañeda, J. L. G. Fierro, *J. Chil. Chem. Soc.* **53**, 1464 (2008).
27. H. Rojas, G. Borda, P. Reyes, M. Brijaldo, J. Valencia, *J. Chil. Chem. Soc.* **56**, 793 (2011).
28. R. J. Chimentão, G. P. Valença, F. Medina, J. Pérez-Ramírez, *Appl. Surf. Sci.* **253**, 5888 (2007).
29. Y. Hao, R. Liu, X. Meng, H. Cheng, F. Zhao, *J. Mol. Catal. A* **335**, 183 (2011).