Effect of the synthetic method of Pt/MgO in the hydrosilylation of phenylacetylene

Eulalia Ramírez-Oliva[a], Alejandro Hernández[a], J. Merced Martínez-Rosales[b], Alfredo Aguilar-Elguezabal[c], Gabriel Herrera-Pérez,[a] and Jorge Cervantes[a]*

[a]Facultad de Química, Universidad de Guanajuato, Guanajuato, Gto., 36050. México. [b]Centro de Investigaciones en Química Inorgánica, Universidad de Guanajuato, Guanajuato, Gto., 36050. México. [c]Centro de Investigaciones en Materiales Avanzados. Miguel de Cervantes Saavedra 120, Complejo Industrial Chihuahua. Chihuahua, Chih., 30110 México.
E-mail: jauregi@quijote.ugto.mx

Dedicated to Professor Edmunds Lukevics in honor of his productive academic life

---

Abstract

This work describes the synthesis and characterization of Pt/MgO (Pt/Mg(OH)$_2$, calcined Pt/MgO and agglomerated Pt/MgO) catalysts. The supports of the catalysts were obtained by the hydrolysis-precipitation method and the metallic phase of platinum was incorporated by impregnation. The characterization of the synthesized materials was made by means of DRX, FTIR, TGA-DTA and TPR techniques. The catalysts were applied to the hydrosilylation of PhC≡CH with three different silanes (Ph_3SiH, Ph_2MeSiH and $PhMe_2SiH$) as a model reaction. The activity of the proposed catalysts Pt/Mg(OH)$_2$, calcined Pt/MgO and agglomerated Pt/MgO had a reaction yield of 95 %. When the catalysts Pt/Mg(OH)$_2$ and agglomerated Pt/MgO were used in the reaction with Ph_3SiH, the selectivity to the *trans* isomer was favored (90%). A relationship was found between the increase in the reaction time and the increase of the kinetic volume of the silane radicals**.** The present results were compared to the previously obtained results using as a catalyst Pt/MgO obtained by the sol-gel method.

Keywords: Pt/MgO, impregnation, hydrosilylation, phenylacetylene, silanes, sol-gel.

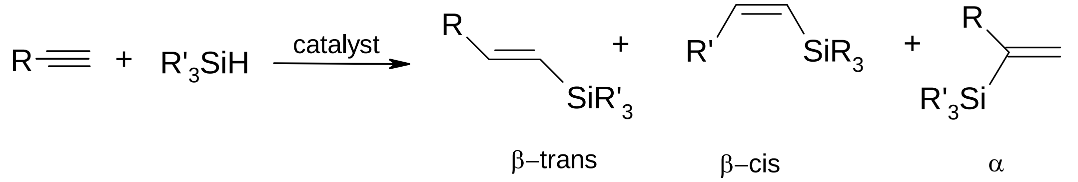
Introduction

The hydrosilylation reaction represents one of the most important routes in obtaining organosilicon compounds. The addition of Si-H bonds to unsaturated compounds can be carried out by free radical chain reactions, or more traditionally by the use of catalysts such as platinum or other transition metals. The hydrosilylation reaction of unsaturated compounds such as olefins, acetylenes, imines, allylamines and oxymes promoted by transition-metal catalysts is widely investigated for reduction of unsaturated groups or addition of Si-H bonds[1,2].

Catalytic hydrosililylation of olefins with soluble platinum complexes was first described by Speier *et al.*[3]. The hydrosilylation of alkynes is a very useful reaction because it is an alternative route in obtaining vinylsilanes which are very important precursors in organic synthesis[4,5].

Interest in metal supported catalysts has been a focal area of organosilicon chemists since the early 1970s. The development of catalysts with higher activity and selectivity toward hydrosilylation is a permanent demand. The important catalytic activity of platinum supported on carbon, silicates and silica in the hydrosilylation of ethylene, butadiene, acetylene and allyl chloride with trichlorosilane has been reported.[2] There are several examples that have been studied to reach this goal and more expensive catalysts have been employed for this purpose[6-9].

The hydrosilylation of a mono-substituted alkene has been proposed as a reaction model because it is possible to obtain a mixture of three isomers as a result of the Si-H addition[2] according to the following (Equation 1).



(1)

For the most part, magnesium oxide exhibits a high surface basicity because of the presence of O^{2-} ions. Such ions tend to easily capture protons. On the other hand, it has weak basic sites assigned to surface Mg^{2+} ions[10]. To avoid the surface basicity, there are several routes reported for obtaining magnesium oxides. One of the possible routes is the thermal decomposition of precursors[11-13], and another is the sol-gel method[14]. Originally, magnesium oxide was rarely used as support for metal catalysts due to the problem of its low specific area. The problem can be solved using some of the routes already mentioned. Since the 1990´s, magnesium oxide has been increasingly used as a support for catalysts. Platinum on MgO is an example of such a catalyst[15,16]. Some studies have been focused on the influence of the precursors or metal salt or solvent used in the synthesis of the catalysts[16]. Some examples of the application of Pt/MgO catalysts are, for example, the use in n-hexane conversion[10], and in the aromatization of alkenes[17,18]. More recent reports refer to the use of Pt/MgO on direct NO decomposition[19], and the CO_2 reforming of methane to syngas over highly active and stable Pt/MgO catalysts[20].

We have reported on the use of Ru/MgO and Pt/MgO obtained by the sol-gel method in the hydrosilylation of phenylacetylene as a model reaction[21]. We have extended the study of sol-gel catalysts to the activity of Pt/SiO_2 in the same model reaction[22]. Considering that the hydrosilyation of terminal acetylenes is one of our areas of interest in silicon chemistry, the synthesis and characterization of other Pt/MgO catalysts has been studied. Catalysts such as

$Pt/Mg(OH)_2$, calcined Pt/MgO and agglomerated Pt/MgO, were obtained and applied in the same hydrosilyation model reaction. We consider that it is important to compare the results of this work with the data previously reported using Pt/MgO obtained by the sol-gel method.

Results and Discussion

For the purpose of this study, three catalysts were identified: $Pt/Mg(OH)_2$, calcined Pt/MgO and agglomerated Pt/MgO. All of the samples were calcined at 500°C to periclase although the synthesis procedure of each catalyst will reflect some differences in the properties and also in the activity shown in the hydrosilyation reaction of phenylacetylene. The catalyst obtained by the sol-gel method will be called either the sol-gel catalyst or sol-gel Pt/MgO.

Support and catalyst characterization

In Figure 1 the TGA/DTA study is presented. There are two main signals related to the transformation process of $Mg(OH)_2$ to MgO. The first is the loss of H_2O in the temperature range from 320 to 420°C. The second one is the exothermic signal in the DTA profile related to the characteristic change in the crystalline phase from brucite to periclase[23].

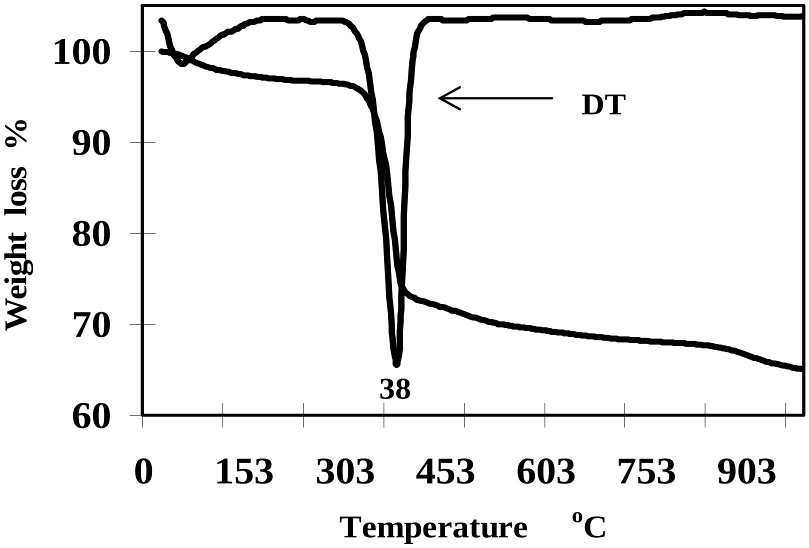


Figure 1. DTG/DTA profiles for the brucita to periclase transformation.

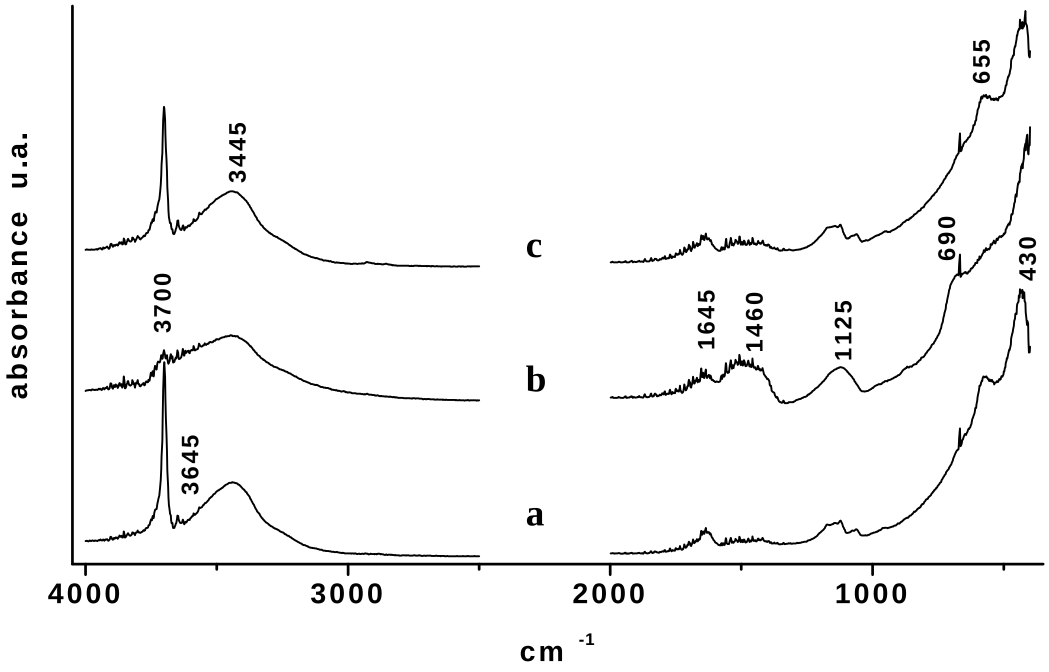


Figure 2. FTIR of supports: a) $Mg(OH)_2$, b) Calcined MgO, c) Agglomerated MgO.

In Figure 2 the FTIR study of the support and the precursor phase is presented. In Figure 2a a stretching frequency band at 3700 cm^{-1} is observed as well as in Figure 2c (agglomerated MgO). The band is associated with OH groups of $Mg(OH)_2$ and superficial OH groups of MgO[24,25]. Such a band is not present in the calcined MgO (2b).

XRD diffractograms of the supports and precursors are presented in Figure 3. In the case of $Mg(OH)_2$ (3a) the signals of the planes 101, 001, 102 are assigned to the crystalline hexagonal system. For the calcined MgO (3b) the signals of the cubic system corresponding to the planes 200, 111 and 220 are observed[23]. In Figure 3c, for agglomerated MgO, the signals of the planes are 001, 100, 101, 102, 111 and 103. As can be seen, the hexagonal phase of $Mg(OH)_2$ is present in agglomerated MgO. This information is consistent with the FTIR results.

Finally, Figure 3d shows the XRD pattern of the precursor PtO_x/MgO obtained after the calcinations at 500 °C of each impregnated support.

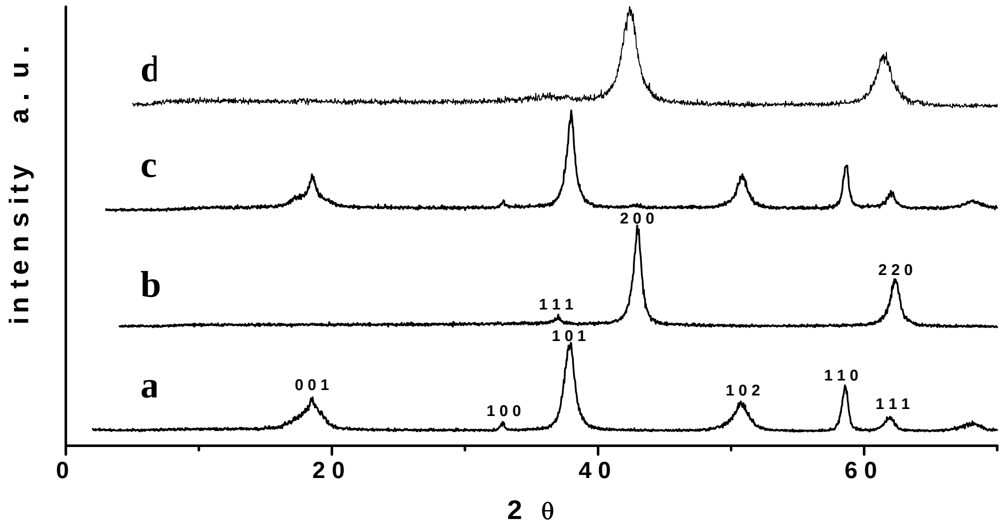


Figure 3. XRD patterns of supports and catalyst: a) $Mg(OH)_2$, b) Calcined MgO, c) Agglomerated MgO, d) PtO_x/MgO .

The textural properties of the supports and precursors as well as the dispersion of platinum is presented in Table 1.

Table 1. Textural properties, and metal dispersion of the solids and catalysts

Entry	Solid	S_{BET} (m^2/g)[a]	V_P (cm^3/g)	D_p (A)[b]	H/Pt atom ratio
1	$Mg(OH)_2$	30	0.18	245	-
2	MgO[b]	45	0.26	44	-
3	MgO[c]	20	0.12	190	-
4	PtO_x/MgO[a]	65	0.36	222	15.0
5	PtO_x/MgO[b]	70	0.26	144	6.5
6	PtO_x/MgO[c]	68	0.53	270	9.2
7	PtO_x/MgO[d]	55	0.14	123	27.0

[a]$Mg(OH)_2$, [b]calcinated, [c]agglomerated, [d]The catalyst was prepared by the sol-gel method

The surface area value obtained is small for the three supports. An increase in the surface area is observed in all cases as a result of the thermal treatment of the precursors [15]. A significant change in pore diameter is observed after the thermal treatment at 500 °C in the impregnated calcined MgO as well as in the impregnated agglomerated MgO. It has been reported that during the thermal treatment of MgO in the range 400-600 °C, there is one point when the pore diameter tends to decrease[15].

If a comparison is done with respect to the synthesis of the catalyst sol-gel Pt/MgO and the catalysts obtained by precipitation, it is possible to say that the difference in textural properties is not significant. However, the data presented in Table 1 illustrates a low platinum dispersion in the three catalysts. In this case, the sol-gel catalyst has the highest value of the H/Pt ratio. It is possible to correlate such data with the difference in the activity and the reaction time shown by the catalysts in the hydrosilyation reaction used as a model.

Evaluation of the catalytic activity in the hydrosilylation reaction of phenylacetylene

All the hydrosilylation reactions were performed using the same conditions previously established when the Pt/MgO obtained by sol-gel was used as catalyst. However, it was necessary to increase the reaction time to reach high conversions. The hydrosilylation reaction of phenylacetylene with Ph_3SiH, Ph_2MeSiH and $PhMe_2SiH$ in the presence of $Pt/Mg(OH)_2$, calcined Pt/MgO and agglomerated Pt/MgO gave as products the mixture of *trans* and *gem* isomers. In Table 2 the reaction conditions (temperature and reaction time) as well as the isomer-distribution are presented. The table shows the results previously reported when the catalyst used was Pt/MgO obtained by the sol-gel method[21]. The 100% conversion was reached at the reaction time described in Table 2.

Table 2. Hydrosilylation of phenylacetylene by R_3SiH

Entry	cat.	R_3SiH	Time h	% product		
				trans	*gem*	*cis*
1	PtO_x/MgO [a]	$HSiMe_2Ph$	3	65	35	---
2		$HSiMePh_2$	8	60	40	---
3		$HSiPh_3$	120	90	10	---
4	PtO_x/MgO [b]	$HSiMe_2Ph$	3	70	30	---
5		$HSiMePh_2$	8	70	30	---
6		$HSiPh_3$	120	65	35	---
7	PtO_x/MgO [c]	$HSiMe_2Ph$	3	65	35	---
8		$HSiMePh_2$	8	70	30	---
9		$HSiPh_3$	120	90	10	---
10	PtO_x/MgO [d]	$HSiMe_2Ph$	2	67	27	6
11		$HSiMePh_2$	2	65	35	---
12		$HSiPh_3$	2	82	18	---

[a] $Mg(OH)_2$, [b]calcined MgO, [c] agglomerated MgO, [d] sol-gel MgO[21].

In the hydrosilylation of phenylacetylene with either the Ph_2MeSiH or $PhMe_2SiH$ using the three catalysts, the main isomer obtained is the *trans* 65-70%, **2a-2b,** from 30-35% of the *gem,* **3a-3b**. No *cis* isomer was detected and this result makes a difference in respect to the hydrosilylation reaction using $PhMe_2SiH$ catalyzed by the sol-gel Pt/MgO. In the last case, 6% of the *cis* isomer was reported. It is well known that in some catalytic systems the stereochemistry of the reaction depends closely on the temperature and the amount of catalyst.

When the hydrosilyation using Ph_3SiH is catalyzed by $Pt/Mg(OH)_2$ and agglomerated Pt/MgO, the selectivity to the *trans* isomer is 90%, **2c** and 10% *gem*, **3c**. The same product distribution has been reported for the model reaction using Speier´s catalyst[26]. The tendency in product distribution is similar for the sol-gel catalyst: 82% *trans* and 18% *gem*. However, when calcined Pt/MgO is used, the product distribution is the same as observed for Ph_2MeSiH and $PhMe_2SiH$ (65% *trans*, **2a-2b** and 35% *gem,* **3a-3b**).

Although calcined Pt/MgO and sol-gel Pt/MgO have similar textural properties the platinum dispersion is very different (6.5 and 27 respectively. See Table 1).

As it has been mentioned before, the reaction time was modified according to the reaction performance in order to reach a 100% conversion. It has to be taken into account that the reaction time for the sol-gel Pt/MgO was 2h. The reaction times were 3 h for $PhMe_2SiH$, 8 h for Ph_2MeSiH and 120 h for Ph_3SiH, a very clear dependence of the volume of the silane radical on the reaction time. Another important factor that creates a difference in the catalysts performance is the platinum dispersion.

Conclusions

The three Pt/MgO catalysts obtained in this study show catalytic activity in the hydrosilylation reaction of phenylacetylene with the silanes $PhMe_2SiH$, Ph_2MeSiH and Ph_3SiH. The product distribution was mainly to the *trans* and *gem* isomers. There is no evidence of the *cis* isomer. In most cases, the isomers' ratio is similar, an exception is the hydrosilylation reaction of phenylacetylene with Ph_3SiH using calcined Pt/MgO as the catalyst.

The *trans*/*gem* isomer distribution is modified with respect to the results obtained when the sol-gel Pt/MgO catalyst is used in the reaction of Ph_3SiH using calcined Pt/MgO. Another difference with respect to the sol-gel catalysts is the absence of a *cis* isomer particularly in the hydrosilylation reaction with $PhMe_2SiH$.

The H/Pt ratio calculated for the three catalysts is lower than that obtained for the sol-gel catalyst. We can say that this is one of the main reasons that the reaction time of hydrosilylation is higher. The volume of the silane radical also has an effect on the reaction time.

Experimental Section

General Procedures. Supports preparation by the hydrolysis-precipitation method. The $Mg(OH)_2$ was obtained using the hydrolysis-precipitation route from $MgSO_4$•$7H_2O$ (PROVISI-PVS Chemicals) in an aqueous ammonia medium at a pH of 12 and at a reaction temperature of 70 °C with constant and vigorous stirring. The solid was recovered by vacuum filtration washing exhaustively with ammonia until the test for sulfate ions was negative. The $Mg(OH)_2$ was dried and calcined at 500°C for 2 h. In order to agglomerate the calcined MgO, it was put in a 2% aqueous solution of HNO_3 and located on a rotary disk that rotates at a constant rate. The spheres obtained were dried at room temperature and calcined at 350°C. The different supports ($Mg(OH)_2$, calcined MgO and agglomerated MgO) were milled and meshed before the incipient impregnating done using a $H_2PtCl_6.6H_2O$ solution in isopropanol. The impregnated samples were dried at 110°C and calcined in air at 500 °C for 2 h. The percentage of platinum was 0.5% in mass.

Supports and catalysts characterization

The characterization of the different supports as well as the catalyst precursors (PtO_x/support) were done using FTIR, XRD, TGA, DTA and TPR.

For the FTIR analysis, the samples were prepared in KBr and the spectra obtained in a FTIR Perkin Elmer 1600 using the Spectrum software V2.00. The resolution was 4 cm^{-1} and 32 scans.

The powder XRD studies were performed in an XRD diffractometer INEL model Equinox System 22102003 with ceramic cover tube and Cu filament (λ = 1.5458 Å) at a voltage of 40 KV and an intensity of 30mA.

The textural properties were measured from the nitrogen adsorption-desorption isotherm using a Micrometritic system model ASAP2010. The samples were degassed in a vacuum for 2 h at 200 °C.

The TGA/DTA analyses were done in a TA Instrument SDT 2960. The samples were cleaned and cooled in a flux of air (20 mL/min) and then heated-up to 110 °C for 30 min before cooling again at room temperature. The temperature ramp began at room temperature and increased in increments of 10°C/min until 850 °C was reached.

TPR studies were performed in a Micromeritic system AutoChem 2910 with electrical conductivity detector. The samples were cleaned under a dynamic atmosphere of helium (50 mL/min) at 50 °C for 1 h before cooling down to room temperature. Then the gas flux was changed to H_2/Ar at 10%. The temperature ramp began at room temperature and increased in increments of 10°C/min until 600 °C was reached.

Activation of platinum catalysts

The samples of catalysts were activated at 110 °C for 1 h in a nitrogen atmosphere. Then the platinum species PtO_x were reduced in a dynamic atmosphere of H_2 (99.99%) for 1 h.

Compounds preparation and characterization

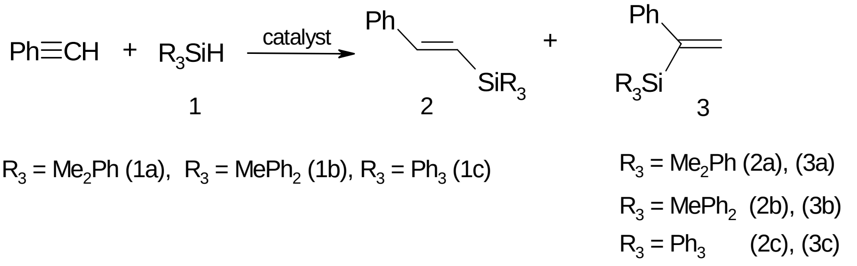
The general procedure of the hydrosilylation of phenylacetylene and Ph_3SiH, Ph_2MeSiH and $PhMe_2SiH$ in the presence of Pt/Mg(OH)$_2$. calcined Pt/MgO and agglomerated Pt/MgO catalyst systems is as follows:

All manipulations were carried out in a nitrogen atmosphere using Schlenk techniques. In a general reaction, in a 50 mL two neck round bottom flask connected to a reflux condenser in a nitrogen atmosphere, 25 mg of supported platinum catalyst were added to 4 mmols of the silanes, Ph_3SiH, Ph_2MeSiH or $PhMe_2SiH$, which were obtained from Gelest, Inc., and used as received. Subsequently, 4.5 mmol of PhC≡CH (Aldrich) were added. The reactants were stirred at 85 ^oC. The reaction time was dependent on the silane and catalyst used.

The reaction progress was monitored either by ^1H NMR or GC, taking samples every 30 min. The isomer distribution was calculated from the integration of vinyl protons in the case of NMR analysis and the corresponding area integration of signals obtained by GC.

^1H NMR spectra were obtained in a Varian Gemini 2000 spectrometer using $CDCl_3$ with 0.05 % TMS as the solvent. The GC chromatograms were obtained in an Agilent CG 6890 using a capillary column HP-5.5% phenylsiloxane of 30.0 m x 320 μm x 0.25 μm with a Flame Ionization Detector.

Product characterization. Reaction products shown in equation 2 were characterized mainly by ^1H NMR and the properties for all compounds prepared are compatible as those reported previously[26], with some remarks respect of compound 2c pointed out in the spectroscopic information. In the ^1H NMR spectrum two doubles are seen in 5.5-6.3 ppm region, which are typical signals of the AB spin system(J= 2.75–3.0 Hz) and correspond to protons in *geminal* position. The signals in the downfield region of 6.4-7.0 ppm are assigned to the AX spin system (J= 19-19.1 Hz) and indicate vicinal protons of the HC=CH fragment in the *trans* position.



(2)

(E)-1-(Dimethylphenylsilyl)-2-phenylethene (2a). ^1H NMR ($CDCl_3$, 200MHz): δ 0.43 (s, 6H, $SiMe_2$), 6.58 (d, J = 19 Hz, 1H, *trans* SiHC=), 6.94 (d, J = 19 Hz, 1H, *trans* PhHC=), 7.02 – 7.68 (m, 10 H, Ph).

1-(Dimethylphenylsilyl)-1 phenylethene (3a). ^1H NMR ($CDCl_3$, 200MHz): δ 0.41 (s, 6H, $SiMe_2$), 5.67 (d, J = 3 Hz, 1H, $=CH_2$), 5.99 (d, J = 3 Hz, 1H, $=CH_2$), 7.02 – 7.68 (m, 10, H, Ph).

(E)-1-(Diphenylmethylsilyl)-2-phenylethene (2b). ^1H NMR ($CDCl_3$, 200MHz): δ 0.70 (s, 3H, SiMe), 6.74 (d, J = 19 Hz,1H, *trans* SiHC=), 6.97 (d, J = 19.05 Hz, 1H, *trans* PhHC=), 7.02 – 7.62 (m, 15 H, Ph).

1-(Diphenylmethylsilyl)-1-phenylethene (3b). ^{1}H NMR ($CDCl_3$, 200MHz): δ 0.65 (s, 3H, SiMe), 5.58 (d, *J*= 2.75 Hz,1H, $=CH_2$), 6.14 (d, *J* = 2.75 Hz, 1H, $=CH_2$), 7.02 – 7.62 (m, 15 H, Ph).

(E)-1-(Triphenylsilyl)-2-phenyletene (2c). ^{1}H NMR ($CDCl_3$, 200MHz): δ 6.97 (In the characterization done in the equipment conditions (200 MHz), it was observed only a large singlet resonance. According to the literature[27], it is observed a doublet with J=2 Hz assigned to 1-trans). Also, it has been reported[26] that this compound has signals at 7.0 (H_A, $Ph_3SiCH=$) and 7.03 (H_B, PhCH=), *J*(H_A-H_B = 19.05 Hz). We were unable to make the same assignment, 7.18-7.62 (m, 20 H, Ph).

1-(Triphenylsilyl)-1-phenylethene (3c). ^{1}H NMR ($CDCl_3$, 200MHz): δ 5.69 (d, *J*= 2.75, 1H, $=CH_2$), 6.28 (d, *J*= 2.75, 1H, $=CH_2$), 7.09-7.62 (m, 20 H, Ph).

Acknowledgements

The authors want to thank Dirección de Investigación y Postgrado de la Universidad de Guanajuato (**DINPO-UG**) for financial support received through the grant **UG-QUI-23-04**.

References

1. Marciniec, B.; Gulinski, J.; Urbaniak, W. In: *Comprehensive Handbook on Hydrosilylation*; Marciniec B., Ed.; Pergamon: Oxford, **2002**.
2. Ojima, I. Li, Z. ; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; J. Wiley: New York, **1998**, pp 1479.
3. Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957,** *79*, 974.
4. Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998,** *120*, 1339.
5. Sudo, T.; Asao, N.; Gevorgyan, V.;Yamamoto, Y. *J. Org. Chem.* **1999,** *64*, 2494.
6. Hilal, H.; Abu-Ied, M.; Alsubu, M.; Khalaf, S. *J. Mol. Cat.* **1986,** *39*, 1.
7. Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 2909
8. Marinetti, A. *Tetrahedron Lett.* **1994**, *35*, 5861.
9. Takeuchi, R.; Natta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045.
10. Aramendía, M. A.; Benítez, J. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Porras, J. M.; Ruiz, J. R.; Urbano, F. J. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2003**, *225*, 137.
11. Aramendía, M. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Porras, A.; Urbano, F. J. *J. Mater. Chem.* **1996**, *6*, 1943.
12. Choudhary, V. R.; Rane, V. H.; Gadre, R. V. *J. Cat.* **1994,** *145*, 300.
13. Aramendía, M. A.; Benítez, J. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *J. Solid State Chem.* **1999**, *144*, 25.

14. López, T.; Gómez, R.; Navarrete, J.; López-Salinas, E. *J. Sol-Gel Sci. Tech.* **1998,** *13*, 1043
15. Aramendía, M. A.; Benítez, J. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *Langmuir* **1999,** *15,* 1192.
16. Aramendía, M. A.; Benítez, J. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2000**, 168, 27.
17. Davis, R. J.; Derouane, E. G. *Nature* **1991,** *349*, 313.
18. Clarke, J. K. A.; Bradley, J. A.; Garvie, J. A. L.; Graven, A. J.; Baird, T. *J. Cat.* **1993**, *143*, 122.
19. Wang, X.; Sigmon, S. M.; Spivey, J. J.; Lamb, H. H. *Catal. Today* **2004**, *96*, 11.
20. Yang, M.; Papp, H. *Catal. Today* **2006**, *115*, 199.
21. Jiménez, R.; López, J. M.; Cervantes, J. *Can. J. Chem.* **2000,** *78*, 1491.
22. Jimenez, R.; Martinez-Rosales, J. M.; Cervantes, J. *Can. J. Chem.* **2003,** *81*, 1370.
23. Yu, C. J.; Xu, A.; Zhang, L.; Song, R.; Wu, L. *J. Phys. Chem. B* . **2004**, *108,* 64.
24. Teramura, K.; Tanaka, T.; Ishikawa, H.; Kohno, Y.; Funabiki T. *J. Phys. Chem. B* **2004,** 108, 346.
25. Diwald, O.; Knözinger, E. *J. Phys. Chem. B* **2002,***106,* 3495.
26. Lukevics, E.; Sturkovich, R. Ya.; Pudova, O. A. *J. Organomet. Chem.* **1985,** *292*
27. Liepiņš, E.; Golderg, Yu.; Iovel, I.; Lukevics, E. *J. Organomet. Chem.* **1987**, *335*, 301.
28. Lewis, L. N.; Sy. K. G.; Bryant, G. L. Jr.; Donahue P. E. *Organometallics* **1991**, *10*, 3750.