



## Study of catalytic activity on hydrogenation reactions of 1-hexene by $\text{RuCl}_2(\text{Py})_4$ and $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2$ supported on functionalized MCM-48

Joel Eduardo Vielma-Puente<sup>1\*</sup>, José Guillermo Cárdenas Murillo<sup>1</sup>, Bernardo Fontal<sup>2</sup>, Ricardo Rafael Contreras<sup>2</sup>, Fernando Bellandi<sup>2</sup>, Marisela Reyes<sup>2</sup>, Yuraima Fonseca<sup>2</sup>, Eduardo Cardozo<sup>2</sup>, Cesar Araque<sup>2</sup>.

<sup>1</sup>Universidad de Guayaquil, Facultad de Ingeniería Química, Guayaquil-Ecuador.

<sup>2</sup>Universidad de Los Andes, Facultad de Ciencias, Departamento de Química, Laboratorio de Organometálicos, Mérida-Venezuela.

(\*) [joel.vielmap@ug.edu.ec](mailto:joel.vielmap@ug.edu.ec)

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### Resumen

**Estudio de la actividad catalítica en reacciones de hidrogenación de 1-hexeno por  $\text{RuCl}_2(\text{Py})_4$  y  $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2$  soportado en MCM-48 funcionalizado.** Se sintetizaron dos catalizadores híbridos: (I) a partir de diclorotetrakis(piridina)rutenio(II) [ $\text{RuCl}_2(\text{Py})_4$ ] y (II) *cis*-diclorobis(dimetilsulfóxido)bis(nicotinato de sodio)rutenio(II) [ $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2$ ] soportado en MCM-48 funcionalizado, usando el método post-síntesis con [3-(2-aminoetil-amino)propil]trimetoxisilano y trietoximetilsilano como ligandos de anclaje y pasivación, respectivamente. Los catalizadores se caracterizaron utilizando espectroscopia infrarroja (FTIR), espectrometría de masas (MS), análisis termogravimétrico (TGA-DSC), adsorción-desorción de nitrógeno, microscopía electrónica de barrido y análisis de rayos X de dispersión de energía (SEM-EDX). Se llevaron a cabo estudios de actividad catalítica en reacciones de hidrogenación y se optimizaron los parámetros de reacción (tiempo, temperatura, relación sustrato/catalizador y presión de  $\text{H}_2$ ). Los complejos soportados son quimioespecíficos para producir hexano y mostraron una conversión del 100% en condiciones óptimas. Los catalizadores se reutilizaron hasta cinco veces, con una disminución de aproximadamente el 30% de la actividad catalítica.

**Palabras claves:** catalizadores híbridos; hidrogenación; complejos de rutenio; quimioespecificidad

### Abstract

Two hybrid catalysts were synthesized: (I) from dichlorotetrakis(pyridine)ruthenium(II) [ $\text{RuCl}_2(\text{Py})_4$ ] and (II) *cis*-dichlorobis(dimethylsulfoxide)bis(sodiumnicotinate)ruthenium(II) [ $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2$ ] supported on MCM-48 functionalized, using post-synthesis method with [3-(2-aminoethylamino)propyl]trimethoxysilane and triethoxymethylsilane as anchoring and passivation ligands, respectively. The catalysts were characterized using infrared spectroscopy (FTIR), mass spectrometry (MS), thermogravimetric analysis (TGA-DSC), nitrogen adsorption-desorption, scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX). Studies of catalytic activity were carried out in hydrogenation reactions and the reactions parameters (time, temperature, substrate/catalyst ratio and  $\text{H}_2$  pressure) were optimized. Supported complexes are chemiospecific to produce hexane and showed 100% conversion under optimal conditions. Catalysts were reused up to five times with a decrease about 30% of catalytic activity.

**Keywords:** hybrid catalysts; hydrogenation; ruthenium complexes; chemoespecificity

### Introduction

Hydrogenation reactions are widely studied due to their important application in the chemical industry, not only in the hydrogenation of petroleum derivate compounds but also in synthesis of a great variety of fine chemicals used as agrochemicals, dyes, fragrances, foods, drugs, etc<sup>1-3</sup>.

In the last years, studies are leading to the development of new supported systems that can retain its selectivity in homogeneous systems and stability with easy separation like heterogeneous catalysts<sup>4,7</sup>. Metal transitions complexes that have shown good results in homogeneous catalysis and meso-

porous materials are being used in heterogeneous catalyst systems, to synthesize new 'hybrid catalysts' by different methods, such as sol-gel or in situ co-condensation and the post-synthesis method<sup>8</sup>. The intrinsic properties of mesoporous solids (zeolites, MCM, SBA) with high surface area, high thermal stability, and high mechanical strength, make these materials attractive for supporting metals complexes. Specifically, Mobile Crystallinity Materials (MCM) like MCM-41 and MCM-48, have been studied as support of ruthenium complexes for olefins hydrogenation reactions, showing high activity and selectivity, similar or better than their homologous homogeneous<sup>9-12</sup>. This work contributed in

the development of two new hybrid catalysts to hydrogenation of 1-hexene, in which the complexes  $\text{RuCl}_2(\text{Py})_4$  and  $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2$  were supported by post-synthesis method on MCM-48: using [3-(2-aminoethylamino)propyl]trimethoxysilane as anchor ligand, and triethoxymethylsilane as passivation ligand, both catalysts were characterized and studied in the hydrogenation of 1-hexene.

## Experimental

### Reagents and equipment

All reagents and solvents were obtained from Aldrich, Merck, Riedel de Haën, Fisher Chemicals and AGA of Venezuela; the reagents were used without previous purification and solvents were dried by methods described in the literature<sup>13</sup>. FTIR spectra were recorded with a Perkin Elmer 1725-X FTIR spectrometer; the samples were prepared by 5 wt. % KBr discs. Mass spectra were carried out on a Hewlett Packard System MSGC-5988 spectrometer, electronic impact ionization technique was used. Thermogravimetric analysis (TGA, DSC) were performed in an SDT Q600 equipment; measurements were realized from room temperature to 800°C with a heating rate of 20°C/min and Air flow of 100 mL/min.  $\text{N}_2$  adsorption-desorption measures were carried out on a Micrometrics ASAP 2010 sorptometer. SEM images were done on a FEI Quanta 200 FEG microscope with an EDX SDD EDAX Apollo X detector.

Analysis of catalytic tests were done by gas chromatography in a Perkin-Elmer Autosystem 900 GC with a methyl silicone Quadrex capillary column, 50 m. long, 2 mm diameter, 0.52  $\mu\text{m}$  thin film. Patterns of hexane, 1-hexene, cis- and trans-2-hexene were used as reference to detect its, and the percentage of products were calculated by turbochrom software.

### Preparation of hybrid catalysts

Hybrid catalysts were prepared by post-synthesis method described by Soundiressane *et al.*<sup>14</sup> with the successive support of the different species like anchor and passivation ligands and coordination complexes.

$\text{RuCl}_2(\text{Py})_4$  and  $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2$  were synthesized following methods described by Wilkinson *et al.*<sup>15, 16</sup> and Suárez *et al.*<sup>9</sup> respectively. MCM-48 was prepared using the method developed by Galarneau *et al.*<sup>17</sup>.

### Support of [3-(2-aminoethylamino)propyl] trimethoxysilane, triethoxymethylsilane and the ruthenium complexes

1.0000 g of MCM-48 was added to 50 mL of dry toluene, the solution was vigorously stirred during 15 min at room temperature. Subsequently, the anchor ligand [3-(2-aminoethylamino)propyl]trimethoxy-silane, the passivation ligand or ruthenium complexes was slowly added (0.1000 g of each of them), the mixture was refluxed during 24 h under argon atmosphere. The solids obtained were filtered and then it was purified by Soxhlet extraction for 6 hours using dichloro-

methane as a solvent; finally, the solid was dried in vacuum and labeled as  $\text{NH}_2\text{-MCM-48}$  and  $\text{NH}_2\text{-P-MCM-48}$ ,  $\text{RuCl}_2(\text{Py})_4\text{-NH}_2\text{-P-MCM-48}$  (**I**) and  $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_2\text{-NH}_2\text{-P-MCM-48}$  (**II**).

### Catalytic trials

The catalytic reactions were carried out in Parr batch reactors of 10 mL capacity. The temperature was provided by vertical heating ovens and monitored by PID temperature controllers and type K thermocouples. The reactions were performed as follows: 5 mL of dry THF were added in the reactor vessel, then 0.0050 g of hybrid catalyst and 1-hexene substrate were added; the reactor was closed and charged with an appropriate  $\text{H}_2$  pressure. The reactor was placed in the heating oven and the starting time was taken when the reaction reached the established temperature<sup>8</sup>.

The reuse of catalysts was carried out as follow: a catalytic test was carried out under optimal conditions, the solution that result was filtered and the solid obtained was dried and used again under the same conditions up to five times.

## Results and discussion

### Characterization of hybrids catalysts

**FTIR:** FTIR spectrums showed characteristic bands corresponding to symmetric and asymmetric  $\nu(\text{Si-O-H})$  stretching at about 3450  $\text{cm}^{-1}$  and 810  $\text{cm}^{-1}$ , respectively, and a wide and intense band at 1106  $\text{cm}^{-1}$  which is attributed to  $\nu_s(\text{O-Si-O})$  stretching. A new band about 2940  $\text{cm}^{-1}$  is assigned to the symmetric  $\nu(\text{-C-H})$  stretching of the alkylic chain, consistent with the structure of the anchor ligand. Hybrid catalyst (**I**) showed the occurrence of a new series of bands characteristics of the pyridine ligand: symmetric  $\nu(\text{C=C})$  stretching at 1478  $\text{cm}^{-1}$ ; hybrid catalyst (**II**) showed two signals (1432  $\text{cm}^{-1}$ , 696  $\text{cm}^{-1}$ ) corresponding to  $\nu(\text{C=O})$  and  $\gamma(\text{=C-H})$  of sodium nicotinate ligand; these bands suggest the effective anchorage of the ruthenium(II) complexes on the functionalized support<sup>18</sup>.

**SEM/EDX:** Table 1 shows chemical analysis of all prepared materials. MCM-48 contains only silicon and oxygen,  $\text{NH}_2\text{-MCM-48}$  and  $\text{NH}_2\text{-P-MCM-48}$  solids contain carbon and nitrogen additionally, indicating that the passivation and anchor ligands were supported. (**I**) and (**II**) ruthenium complexes, contain silicon, carbon, nitrogen and oxygen besides ruthenium and chloride. These results indicate that anchoring of the complexes on functionalized MCM-48 was probably obtained.

**Table 1.** EDX analysis.

Material	% Si	% O	% C	% N	% Ru	% Cl
MCM-48	55.22	44.78				
$\text{NH}_2\text{-MCM-48}$	50.47	44.98	3.58	0.97		
$\text{NH}_2\text{-P-MCM-48}$	50.17	44.11	4.17	1.05		
<b>(I)</b>	43.72	38.42	11.63	1.39	2.22	2.62
<b>(II)</b>	42.46	39.37	12.13	0.73	2.80	2.51

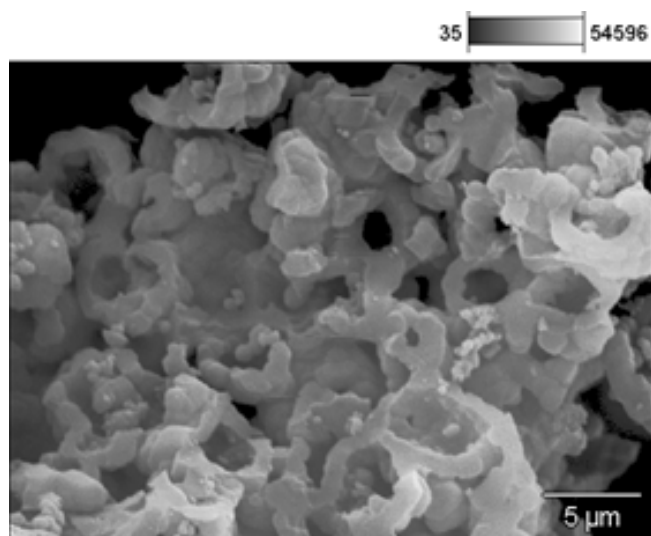


Fig. 1: SEM Micrograph of hybrid catalysts (I).

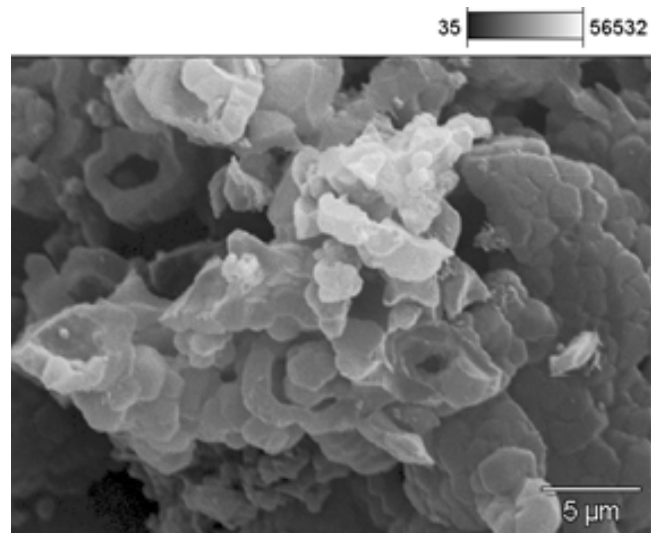


Fig. 2: SEM Micrograph of hybrid catalysts (II).

Figures 1 and 2 shows SEM photographs of hybrid catalysts (I) and (II), respectively. The morphology of the materials and agglomerates of particles with irregular appearance is observed. This morphology is typical, and it has been reported for different hybrids catalysts of coordination complexes on mesoporous MCM-48 and SBA-15 solids<sup>16</sup>. Therefore, incorporation of different species on the starting material, shows no changes in the morphology of the same; which is consistent with that reported by Sakthivel *et al.*<sup>20</sup>.

#### *N*<sub>2</sub> adsorption-desorption

All materials synthesized showed a type IV isotherm according to the IUPAC nomenclature corresponding to mesoporous materials. The surface area was obtained by applying the BET equation to the nitrogen adsorption isotherm and pore volume and pore diameter were calculated from the BJH model<sup>21</sup>; these values indicate that the pore diameters are in the medium porosity range (see table 2). Comparison of these values showed that new species were

incorporated on the MCM-48 solid, with a gradual decrease in all the parameters studied; it indicated that effectively anchor ligand, passivating ligand and ruthenium complexes were anchored on the surface and inside the pores<sup>22,23</sup>.

Table 2. Measurements of surface area, pore volume and pore diameter.

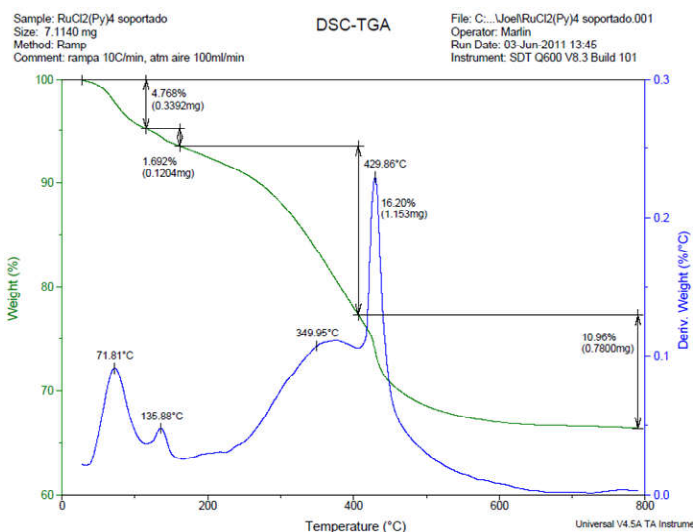
Material	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
MCM-48	1080	0.8303	3.0235
NH <sub>2</sub> -MCM-48	745	0.6296	2.8432
NH <sub>2</sub> -P-MCM-48	695	0.4761	2.7404
(I)	562	0.3386	2.1389
(II)	426	0.4015	2.5967

#### Thermogravimetric Analysis (TGA-DSC)

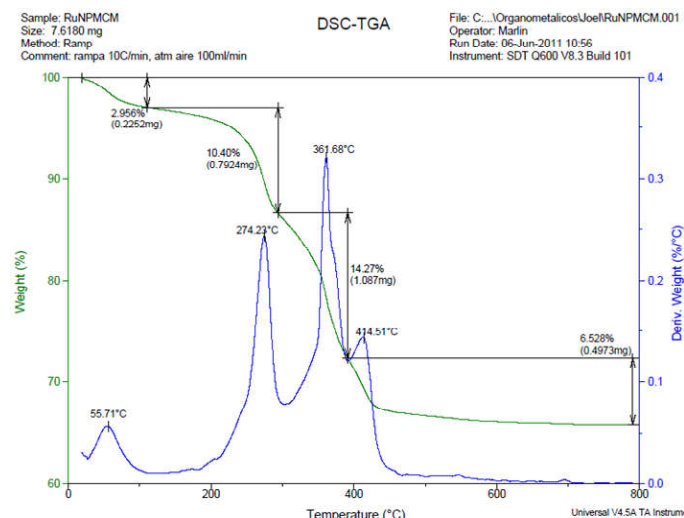
Thermogravimetric analysis was performed on all materials. MCM-48 showed only one loss between 60 °C and 150 °C, it corresponds to lattice water<sup>24</sup>. Functionalized materials showed changes in thermal stability, which has been associated with the presence of organic and inorganic compounds (anchor, passivation, and complex ligands), this behavior has been observed in similar hybrid catalysts<sup>25</sup>. In all thermograms (see figure 3 and 4) a mass loss between 60 °C and 120 °C was observed which corresponds to network water; between 120 °C and 800 °C, a series of losses (30 wt.%) was observed, which can be assigned to decomposition of organic material and metal complexes supported, indicating that the MCM-48 support has new species.

#### Mass Spectrometry

Under the experimental working conditions, only the organic fragments (anchor and passivation ligand, and the ligands of supported complexes) get to the ionization camera<sup>26, 27</sup>. In the mass spectra of hybrid catalysts (I) and (II), a series of ions with unpaired electrons can be observed<sup>28</sup>. These were formed by Si-C bond rupture from the alkylic anchor chain. The masses and isotopic patterns of these ions most probably indicated that the ruthenium complexes were linked to the anchor ligand chain through the nitrogen atoms, in a bidentate mode forming a five membered ring with the metal, which is consistent with the "chelating effect"<sup>29</sup>. The (I) catalyst shows a fragment ion at 419.30 m/z. This ion with odd electron number is observed that corresponds to a fragment coming from a C-C β bond breaking off from the silicon atom of the anchoring ligand; this ion indicates that a double substitution of the pyridine ligands in ruthenium(II) complex is coming from the nitrogen of the anchoring ligand; this reaction is thermodynamically favored because of the chelating effect of the diamine ligand. After the formation of the molecular ion, the consecutive CH<sub>2</sub> loss of the remaining alkylic chain, followed by the loss of the two pyridine ligands.



**Fig. 3:** Thermograms (TGA/DSC) of hybrid catalyst **(I)**.



**Fig. 4: (II)** Thermograms (TGA/DSC) of hybrid catalyst **(II)**.

The fragmentation pattern of the catalyst **(II)** shows an odd electron number fragment due to the breaking off from the Si-C on the anchoring ligand at 719.9 m/z which in this case corresponds to the fragment ion; this ion suggests the substitution of the two dimethylsulfoxide molecules by two nitrogen atoms from the anchoring ligands forming a chelating complex. Following the formation of the molecular ion, a loss of two fragments at 145 m/z is observed, this is consistent with the loss of two sodium nicotinate ligands bonded to the metal, releasing fragments at 574.15 m/z and 429.65 m/z.

#### Catalytic Tests

In order to optimize the parameters used in the catalytic assays using **(I)**, the reactions were carried out with the following variable conditions ranges: reaction time: 0 to 4 h, temperature: 60 °C to 140 °C; substrate catalyst ratio 400:1 to 2000:1; hydrogen pressure: 200 to 1000 psi. The optimal parameters for catalyst **(I)** were: Reaction time: 4 h; Temperature: 100 °C; substrate/catalyst ratio: 1000:1 and hydrogen

pressure: 600 psi. For the catalyst **(II)**, the reactions were carried at the following variable conditions ranges: reaction time: 0 to 24 h, temperature: 80 °C to 140 °C; substrate catalyst ratio: 400:1 to 2000:1; hydrogen pressure: 400 to 1000 psi. The optimal parameters for catalyst **(II)** were: reaction time: 16 h; temperature: 100 °C; substrate:catalyst ratio: 2000:1 and hydrogen pressure: 400 psi. The principal product is 1-hexene hydrogenation to n-hexane.

Under the optimal conditions the recycling of the catalysts was done. These results are shown in table 3. The conversion diminishes somewhat which is common for this type of system due to leaching of the metal complexes<sup>30</sup> and decomposition<sup>31</sup> of the metallic complexes. However, it is important to remark that after five runs, a high conversion percentage was still observed. The mercury assays were done in the fourth run and we found not to diminish the catalytic activity which showed that reaction occurs with the metallic complexes instead of metallic particles coming from metal complex decomposition.

**Table 3.** Recycling of the catalysts.

<b>(I)</b>		<b>(II)</b>	
Recycle	% conversion	Recycle	% conversion
1	99.98	1	99.98
2	95.72	2	98.72
3	90.89	3	97.48
4	81.85	4	83.53
5	70.17	5	75.76

**Reaction conditions:** Catalyst **(I)**: Reaction time: 4 h; T: 100°C; S/C ratio: 1000:1 and H<sub>2</sub> pressure: 600 psi. Catalyst **(II)**: reaction time: 16 h; T: 100°C; S/C ratio: 2000:1 and H<sub>2</sub> pressure: 400 psi

Initially catalyst **(I)** and **(II)** showed 99.98% conversion, but catalyst **(I)** is more efficient than catalyst **(II)**, considering that it has 2.22% of supported ruthenium, while complex **(II)** has 2.80%.

Catalyst **(I)** showed a TOF of 300 h<sup>-1</sup> and the catalyst **(II)** 166 h<sup>-1</sup>; if we compare this value with the reported catalyst in homogeneous phase<sup>9</sup> (TOF 150 h<sup>-1</sup> for RuCl<sub>2</sub>(DMSO)<sub>2</sub>(NC<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Na)<sub>2</sub>), the hybrid catalyst showed better catalytic activity, this can be explained by the synergic effect between the ruthenium complex and the MCM-48 support, in this case the pores of the support acts as microreactors<sup>32</sup> offering more actively concentrated sites and increasing efficiency in the process.

#### Conclusions

The functionalization through the post synthesis method of the mesoporous MCM-48 and its immobilization of the Ru complexes **(I)** and **(II)** were done successfully, obtaining the hybrid catalysts. Both were characterized and their catalytic activity in the 1-hexene hydrogenation reaction was carried out showing high catalytic activity. Catalyst **(I)**

showed more catalytic activity than complex (II) considering its lower content of supported metal percentage. TOF was higher than 150 h<sup>-1</sup> for both catalysts, being better than the results obtained with a homogeneous catalyst.

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