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Study of catalytic activity on hydrogenation reactions of 1-hexene by $RuCl_2(Py)_4$ and $RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$ supported on functionalized MCM-48

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Resumen

Estudio de la actividad catalítica en reacciones de hidrogenación de 1-hexeno por $RuCl_2(Py)_4$] y $RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$] soportado en MCM-48 funcionalizado. Se sintetizaron dos catalizadores híbridos: **(I)** a partir de diclorotetrakis(piridina)rutenio(II) [$RuCl_2(Py)_4$] y **(II)** cis-diclorobis(dimetilsulfóxido)bis(nicotinato de sodio)rutenio(II) [$RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$] 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 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 hibridos; hidrogenación; complejos de rutenio; quimioespecificidad

Abstract

Two hybrid catalysts were synthesized: **(I)** from dichlorotetrakis(pyridine)ruthenium(II) [$RuCl_2(Py)_4$] and **(II)** *cis*-dichlorobis(dimetylsulfoxide)bis(sodiumnicotinate)ruthenium(II) [$RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$] 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 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[1-3].

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[4-7]. Metal transitions complexes that have shown good results in homogeneous catalysis and mesoporous 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[8]. 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[9-12]. This work contributed in the development of two new hybrid catalysts to hydrogenation of 1-hexene, in which the complexes $RuCl_2(Py)_4$ and $RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$ 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[13]. 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 800ºC with a heating rate of 20ºC/min and Air flow of 100 mL/min. 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 µm 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.*[14] with the successive support of the different species like anchor and passivation ligands and coordination complexes.

$RuCl_2(Py)_4$ and $RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$ were synthesized following methods described by Wilkinson *et al*[15, 16] and Suárez *et al.*[9] respectively. MCM-48 was prepared using the method developed by Galarneau *et al*[17].

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 dichloromethane as a solvent; finally, the solid was dried in vacuum and labeled as NH_2-MCM-48 and NH_2-P-MCM-48, $RuCl_2(Py)_4$-NH_2-P-MCM-48 **(I)** and $RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$-$NH_2$-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 H_2 pressure. The reactor was placed in the heating oven and the starting time was taken when the reaction reached the established temperature[8].

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 ν(SiO-H) stretching at about 3450 cm^{-1} and 810 cm^{-1}, respectively, and a wide and intense band at 1106 cm^{-1} which is attributed to ν_s(O-Si-O) stretching. A new band about 2940 cm^{-1} is assigned to the symmetric ν(-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 ν(C=C) stretching at 1478 cm^{-1}; hybrid catalyst **(II)** showed two signals (1432 cm^{-1}, 696 cm^{-1}) corresponding to ν(C=O) and γ(=C–H) of sodium nicotinate ligand; these bands suggest the effective anchorage of the ruthenium(II) complexes on the functionalized support[18].

SEM/EDX: Table 1 shows chemical analysis of all prepared materials. MCM-48 contains only silicon and oxygen, NH_2-MCM-48 and NH_2-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				
NH_2-MCM-48	50.47	44.98	3.58	0.97		
NH_2-P-MCM-48	50.17	44.11	4.17	1.05		
(I)	43.72	38.42	11.63	1.39	2.22	2.62
(II)	42.46	39.37	12.13	0.73	2.80	2.51

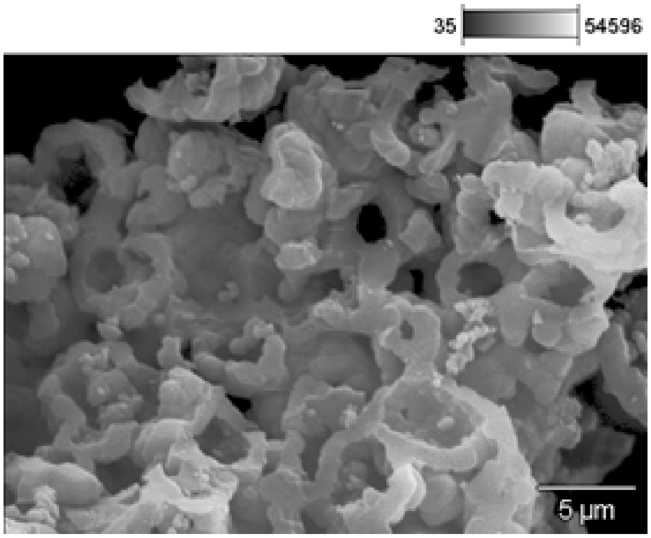

Fig. 1: SEM Micrograph of hybrid catalysts (**I**).

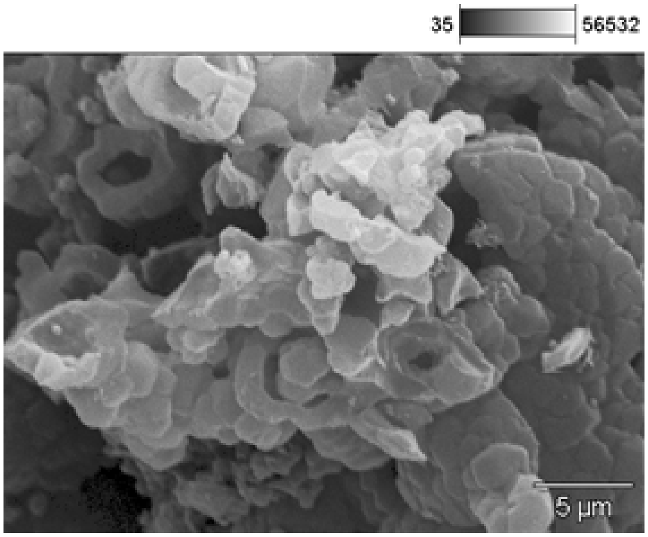

Fig. 2: SEM Micrograph of hybrid catalysts (**II**).

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[16]. 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*[20].

N_2 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[21]; 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[22,23].

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

Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
MCM-48	1080	0.8303	3.0235
NH_2-MCM-48	745	0.6296	2.8432
NH_2-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 materi-als. MCM-48 showed only one loss between 60 °C and 150 °C, it corresponds to lattice water[24]. 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[25]. 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[26, 27]. In the mass spectra of hybrid catalysts **(I)** and **(II),** a series of ions with unpaired electrons can be observed[28]. 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*"[29]. 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_2 loss of the remaining alkylic chain, followed by the loss of the two pyridine ligands.

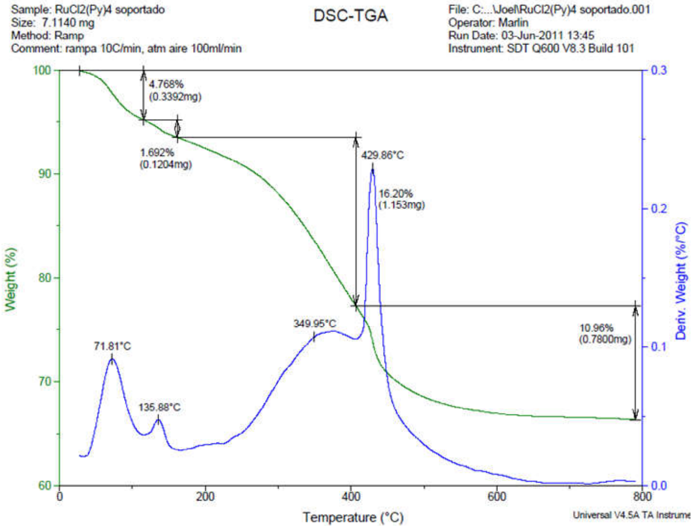

Fig. 3: Thermograms (TGA/DSC) of hybrid catalyst **(I)**.

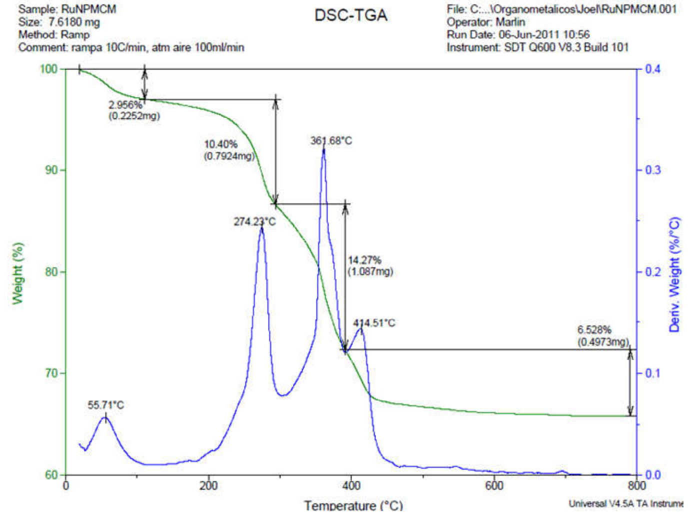

Fig. 4: **(II)** Thermograms (TGA/DSC) of hybrid catalyst **(II)**.

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 show in table 3. The conversion diminishes somewhat which is common for this type of system due to leaching of the metal complexes[30] and decomposition[31] 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.

(I)		(II)	
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_2 pressure: 600 psi. Catalyst **(II)**: reaction time: 16 h; T: 100°C; S/C ratio: 2000:1 and H_2 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^{-1} and the catalyst **(II)** 166 h^{-1}; if we compare this value with the reported catalyst in homogeneous phase[9] (TOF 150 h^{-1} for $RuCl_2(DMSO)_2(NC_5H_4CO_2Na)_2$), 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[32] offering more actively concentrated sites and increasing efficiency in the process.

Conclusions

The functionalization through the post synthesis method of the mesoporosous 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^{-1} for both catalysts, being better than the results obtained with a homogeneous catalyst.

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References

1. B Cornils, WA Herrmann. Concepts in homogeneous catalysis: the industrial view. **J. Catal.**, **216(1-2)**, 23-31 (2003).
2. W Mägerlein, C Dreisbach, H Hugl, MK Tse, M Klawonn, S Bhor, et al. Homogeneous and heterogeneous ruthenium catalysts in the synthesis of fine chemical. **Catal. Today**, **121(1-2)**, 140-150 (2007).
3. L Mercs, M Albrecht. Beyond catalysis: N-heterocyclic carbene complexes as components for medicinal, luminescent, and functional materials applications. **Chem. Soc. Rev.**, **39(6)**, 1903-1912 (2010).
4. J Vielma, RR Contreras, B Fontal, M Reyes, F Bellandi, Y Fonseca, et al. Complejos metálicos soportados sobre MCM-48 funcionalizado en reacciones catalíticas (Parte 1). Hidrogenación de 1-hexeno con el complejo $Re_2(CO)_8(\mu\text{-dffm})$. **Cienc. Ing.**, **35(2)**, 103-112 (2014).
5. V Vossoughi, AK Dalay, N Abatzoglou, YF Hu. Performances of promoted cobalt catalysts supported on mesoporous alumina for Fischer-Tropsch synthesis. **Appl. Cat. A: General**, **547**, 155-163 (2017).
6. A Romero, A Nieto-Márquez, E Alonso. Bimetallic Ru:Ni/MCM-48 catalysts for the effective hydrogenation of d-glucose into sorbitol. **Appl. Cat. A: General**, **529**, 49-59 (2017).
7. Q Peng, Y Yang, Y Yuan. Immobilization of rhodium complexes ligated with triphenyphosphine analogs on amino-functionalized MCM-41 and MCM-48 for 1-hexene hydroformylation. **J. Mol. Cat. A: Chem.**, **219(1)**, 175-181 (2004).
8. J Vielma, B Fontal, RR Contreras, M Reyes, F Bellandi, Y Fonseca, et al. $RhCl(CO)(TFFMS)_2$ y $RhCl(TFF)_3$ inmovilizados sobre MCM-48 funcionalizado y su estudio catalítico en reacciones de hidroformilación de 1-hexeno. **Avances en Química**, **9(2)**, 55-62 (2014).
9. T Suarez, B Fontal, J Vielma, M Reyes, F Bellandi, P Cancines, et al. Synthesis, characterization, and biphasic ionic liquid media 1-hexene hydrogenation reaction of $RuCl_2(DMSO)_2(NC_5H_4CO_2Na\text{-}3)_2$. **Trans. Met. Chem.**, **36(6)**. 617-620 (2011).
10. B Cornils, W Herrmann. Applied Homogeneous Catalysis with Organometallic Compounds. VCH, New York-EEUU (1996).
11. AP Wight, ME Davis. Design and Preparation of Organic−Inorganic Hybrid Catalysts. **Chem. Rev.**, **102**, 3589-3614 (2002).
12. NE Leadbeater, M Marco. Preparation of Polymer-Supported Ligands and Metal Complexes for Use in Catalysis. **Chem. Rev.**, **102**, 3217-3274 (2002).
13. W Armarego, B Chai. Purification of laboratory chemical. Butteworth-Heinemann, Kidlington-UK (2013).
14. T Soundiressane, S Selvakumar, S Ménage, O Hamelin, M Fontecave, AP Singh. Ru- and Fe-based *N*,*N'*-bis(2-pyridylmethyl)-*N*-methyl-(1*S*,2*S*)-1,2-cyclohexanediamine complexes immobilised on mesoporous MCM-41: Synthesis, characterization and catalytic applications**. J. Mol. Catal. A: Chem**, **270**, 132-143 (2007).
15. J Osborn, F Jardine, J Young, G Wilkinson. The preparation and properties of tris(triphenylphosphine)halogeno-rhodium(I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives. **Chem. Soc. A**, 1711-1732 (1966).
16. I Evans, A Spencer, G Wilkinson. Dichlorotetrakis(dimethylsulphoxide)ruthenium(II) and its use as a source material for some new ruthenium(II) complexes. **J. Chem. Soc. Dalt.**, 204-209 (1973).
17. A Galarneau, MF Driole, C Petitto, B Chiche, B Bonelli, M Armandi. Effect of post-synthesis treatment on the stability and surface properties of MCM-48 silica. **Micropor. Mesopor. Mat.**, **83**, 172-175 (2005).
18. L Alvila, TA Pakkanen, TT Pakkanen, O Krause. Comparative study of homogeneous catalytic activity of group 8–9 metal compounds in hydroformylation of 1-hexene. **J. Mol. Catal.**, **73**, *325*-334 *(1992).*
19. S Sahoo, P Kumar, F Lefebvre, S Halligudi. Enantioselective hydrogenation of olefins by chiral iridium phosphorothioite complex covalently anchored on mesoporous silica. **J. Catal.**, **254**, 91-100 (2008).
20. A Sakthivel, J Zhao, G Raudaschl-Sieber, M Hanzlik, A Chiang, FE Kuhn. Heterogenization of chiral molybdenum(VI) dioxo complexes on mesoporous materials and their application in catalysis. **Appl. Catal. A: General**, **281**, 267-673 (2005).
21. P Webb, C Orr. Analytical Methods in Fine Particle Technology. Micromeritics Instrument Corporation, Norcross-EEUU (1997).
22. R Antony, R Marimuthu, P Vishnoi, R Murugavel. Ethoxysilane appended M(II) complexes and their SiO_2/MCM-41 supported forms as catalysts for efficient oxidation of secondary alcohols. **Inorg. Chim. Acta**, **469**, 173-182 (2018).
23. A Sakthivel, M Abrantes, AST Chiang, FE Küng. Grafting of η^5-Cp(COOMe)MoCl$(CO)_3$ on the surface of mesoporous MCM-41 and MCM-48 materials. **J. Org. Chem.**, **691(5)**, 1007-1011 (2006).
24. ME Brown. Introduction to Thermal Analysis: Techniques and Applications, Kluwer Academic Publisher, Dordrecht-Nederland (2001).
25. F Adam, K Mohammed-Hello, SJ Chai. The heterogenization of l-phenylalanine–Ru(III) complex and its application as catalyst

in esterification of ethyl alcohol with acetic acid. **Chem. Eng. Res. Des., 90**, 633–642 (2012).

26. W Henderson, JS McIndoe. Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds: Tools-Techniques-Tips. John Wiley & Sons, New Jersey-EEUU (2005).
27. TV Kulik, LR Azizova, B Palyanytsya, A Zemlyakov, V Tsikalova. Mass spectrometric investigation of synthetic glycoside of muramyl dipeptide immobilized on fumed silica surface. **Mat. Sci. Eng. B.**, **169**, 114–118 (2010).
28. FW McLafferty, F Turecek. Interpretation of Mass Spectra. University Science Books, California-EEUU (1993).
29. P Atkins, T Overton. Química Inorgánica. Mc Graw Hill, México DF-México (2008).
30. R Xu, W Pang, J Yu, Q Huo, J Chen, Chemistry of zeolites and related porous materials: Synthesis and structure. John Wiley and Sons, Singapore (2007).
31. J Basset, F Lefebvre, C Santini. Surface organometallic chemistry: some fundamental features including the coordination effects of the support**. Coord. Chem. Rev.**, **178**, 1703-1723 (1998).
32. J Hagen. Industrial Catalysis. Wiley-VCH, Weinheim-Germany (1999).