Catalysis Letters Vol. 107, Nos. 3–4, March 2006 (© 2006)
DOI: 10.1007/s10562-005-0011-9

Organometallic rhodium complexes encapsulated in mesoporous molecular sieves

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Received 2 November 2005; accepted 14 December 2005

Rh(III) complexes both dimmer $[Cp^*RhCl]_2(\mu\text{-}Cl)_2$ and monomer ($[RhCp^*(S)_3]^{2+}$) were encapsulated into MCM-41 channels. All silica MCM-41 molecular sieve and aminosililated MCM-41 matrix were used for rhodium complexes accommodation. Reactivity of Cp^* rhodium complexes encapsulated in meso structure was estimated on the grounds of their susceptibility to interaction with CO molecules resulting in the formation of carbonyl complexes. Formation of Cp^*Rh carbonyls was recorded by means of FTIR spectra. It was found that accommodation of Rh(III) complexes in MCM-41 molecular sieves activated the complex and led to the formation of $Rh(III)Cp^*$ carbonyls as a result of contact with CO. Contact of rhodium (III) complexes encapsulated in MCM-41 matrix with CO did not result in rhodium (III) reduction, whereas in the presence of amine groups in aminosililated MCM-41 the reduction of Rh(III) to Rh(I) occurred relatively easily and formation of $Cp^*Rh(CO)_2$ complex containing Rh(I) was noted.

Encapsulated rhodium complexes showed some activity in methanol carbonylation reaction carried out under heterogeneous conditions. For the most active catalyst the amount of methyl acetate reached about 8 mol.%, however, deactivation of catalyst occurred and after 2 h on stream methyl acetate was not found in the product.

KEY WORDS: rhodium complexes; carbonyl complexes; encapsulation; RT-IR spectroscopy; methanol carbonylation; mesoporous material.

1. Introduction

Encapsulation of transition metal complexes into channels or cages of molecular sieves offers an attractive method of immobilization of homogeneous catalysts with aim to prepare stable, solid catalysts for processes performed in a liquid phase. However, the use of zeolites as a matrix for large metalloorganic complexes accommodation suffered from the channel's entrance limitation. Therefore, the disclosure of mesoporous materials with pores diameter in the range of 2–10 nm by researchers from Mobil Oil [1] and Toyota [2] has opened a new and attractive perspective for the immobilisation of bulky active complexes inside the M41S channels. Rhodium complexes are known as active catalysts enable to activate small molecules such as CO or H_2 and therefore they were applied for such processes as hydroformylation or hydrogenation, which were performed under homogeneous conditions. Inconveniences of homogeneous conditions (necessity of separation of products, unreacted reagents and catalysts) are commonly known, therefore, possibility of immobilization of homogeneous catalysts by means of encapsulation into solid matrix has been widely searched.

In the presented study the rhodium (III) complex, {di-μ-chloro-dichloro-bis(pentamethylocyclopentadienyl) dirhodium; $[Cp^*RhCl]_2(\mu\text{-}Cl)_2$} known as a homogeneous catalyst for hydrogenation and carbonylation processes [3] has been used. The earlier attempts of immobilization of rhodium Cp^* complexes in Y zeolite matrix have shown that the interaction of these complexes with exchangeable cations present in zeolitesα-cages influenced their reactivity towards CO significantly [4,5]. The strong interaction of $Rh(III)Cp^*$ complexes with zeolite cations and zeolite structure leading to stabilization of carbonyl complexes inside theα-cages was proved. Considering the narrow entrance into faujasiteα-cage the number of bulky$[Cp^*RhCl]_2$ $(\mu\text{-}Cl)_2$ molecules introduced into the cage was rather limited, therefore, the use of mesoporous molecular sieves with channels diameter larger than 2 nm seemed very promising. All silica molecular sieves were used as a pure "protonic" form or as previously aminosililated matrix. The last one was deprived of OH groups during aminosililation process. The influence of MCM-41 structure containing weakly acidic OH silanol groups and also aminosililated MCM-41 matrix on reactivity of complexes introduced into MCM-41 channels towards CO molecules was estimated. Considering the ability for activation of CO molecules, the encapsulated complexes were used as catalysts for carbonylation of methanol performed under heterogeneous conditions.

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2. Experimental

MCM-41 was synthesised according to the literature data [6] using CTMABr as a template with the following reagents ratio: 1 TEOS:0.21 CTMABr:0.08 TMAOH:0.11 Na_2O:125 H_2O. Crystallization was carried out at 90 °C for 72 h. After template removal (calcination at 540 °C) mesoporous material was treated with NH_4NO_3 in methanol solution to remove sodium cation and subsequently calcined at 400 °C. Aminosililation procedure was performed according to [7–9] using (3-aminopropyl)-triethoxysilane (APTS) as a reagent. Mesoporous material was treated with boiling solution of APTS in toluene for 5 h under reflux. Separated solid was dried under vacuum first at RT and finally at 140 °C.

Rh(III) complex,$[Cp^*RhCl]_2(\mu\text{-}Cl)_2$ was impregnated into silica MCM-41 (Si-MCM-41) and aminosililated MCM-41 (MCM-41/Asil) by stirring of 1.5 g of mesoporous molecular sieve with 30 mL of 3.25×10^{-4} M solution of rhodium complex in CH_2Cl_2 for 18 h with following Soxhlet extraction. Monomeric complex was prepared by means of reaction of$[Cp^*RhCl]_2(\mu\text{-}Cl)_2$ with stoichiometric amount of $Ag(PF_6)$ in CH_2Cl_2 solution according to reaction presented in Equation 1:

$$[Rh(C_5Me_5)Cl_2]_2 + 4AgPF_6 + 6CH_2Cl_2 \rightarrow 2[Rh(C_5Me_5)(CH_2Cl_2)_3]^{2+} + 2(PF_3)_2^{2-} + 4AgCl\downarrow \quad (1)$$

After AgCl removal, the solution of monomeric complex of concentration 6.5×10^{-4} M was used for mesoporous material impregnation according to procedure described above.

Mesoporous material was characterised by means of XRD patterns recorded on Brucker diffractometer, adsorption/desorption isotherm of N_2 (ASAP 2000 from Micromeritics) and diffusive reflectance spectra (Spectrophotometer *Cary 100* from Varian). Amount of rhodium complexes introduced into mesoporous structure was estimated by means of ICP method (expressed as rhodium concentration).

Reactivity of rhodium complexes encapsulated into mesoporous materials towards CO molecules was estimated on the grounds of FTIR spectra. Modified MCM-41 pressed as wafer and located in vacuum cell was contacted with CO at different temperature after previous evacuation.

It was established on the grounds of TG measurements that dehydration of MCM-41 occurs at about 100 °C, therefore, evacuation of the samples before their contact with CO was performed at the temperature not higher than 150 °C.

Catalytic activity of $RhCp^*$ complexes immobilised in MCM-41 matrix for methanol carbonylation was estimated in heterogeneous conditions under atmospheric pressure, using 0.2 g of catalyst and reagents loading about 8 g/g cat/h.

3. Results and discussion

The correctness of meso structure of unmodified MCM-41 and the modified ones was established on the grounds of XRD measurements. XRD patterns of free MCM-41 and MCM-41 modified by means of aminosililation as well as the samples with $RhCp^*$ complexes encapsulated inside meso pores are presented in figure 1. Modification of MCM-41 resulted in some decrease in the intensity of [100] reflex. However, the diminution of [100] reflex intensity should not result from the lowering of pseudocrystallinity of meso structure but rather from subsequent filling up of the channels. This interpretation was consistent with the results of low temperature adsorption of nitrogen. The pore diameter decreased from 25 Å for free MCM-41 to 22 Å for aminosililated sample and to 19 Å for the samples modified with $RhCp^*$ complex. Similar change in XRD patterns (diminution of intensity of [100] peak) was observed as a result of introduction of large molecules of heteropoly acids into MCM-41 channels. Removal of heteropoly acids (with polar solvent) resulted in restoration of XRD patterns intensity [9].

$Rh(III)Cp^*$ complexes, both dimmer and monomer, were introduced into MCM-41 matrix by means of impregnation from CH_2Cl_2 solution. Excess of complex was removed by Soxhlet extraction with the same solvent. Samples after extraction showed bright yellow colour of different intensity. Concentration of rhodium in complex modified mesoporous material, estimated on the grounds of ICP measurements, was very near for all the samples (table 1).

UV–Vis reflectance spectra of rhodium complexes encapsulated into MCM-41 matrix presented in figure 2 indicated some interactions of rhodium complex with molecular sieve structure. Diffuse reflectance spectra recorded for supported complexes were shifted when compared to the bands of free complex (269 nm, 354 nm and broad band at about 440 nm). Nature of support influenced clearly the UV–Vis bands shift. Both dimmer and monomer complexes accommodated in aminosililated MCM-41 showed the band at 357 nm and very weak band at about 440 nm, which were located at the same position as in free complex. Additionally, two weak bands at 234 and 265 nm were also recorded. Accommodation in MCM-41 resulted in appearance new bands, a distinctive one at 252 nm and a broad one at about 410 nm. These results indicate the interaction between rhodium Cp^* complexes and applied supports.

The analysis of IR spectra recorded for free and supported $RhCp^*$ complex (in KBr) has also confirmed the interaction of encapsulated complexes with MCM-41 matrix (figure 3). The bands characterising of C–H bond in $-CH_3$ group recorded for free complex at 2998, 2968, 2916 and 2854 cm^{-1} were slightly shifted for the supported samples. The bands attributed to cyclopentadienyl ring [10] were only partly observable because of

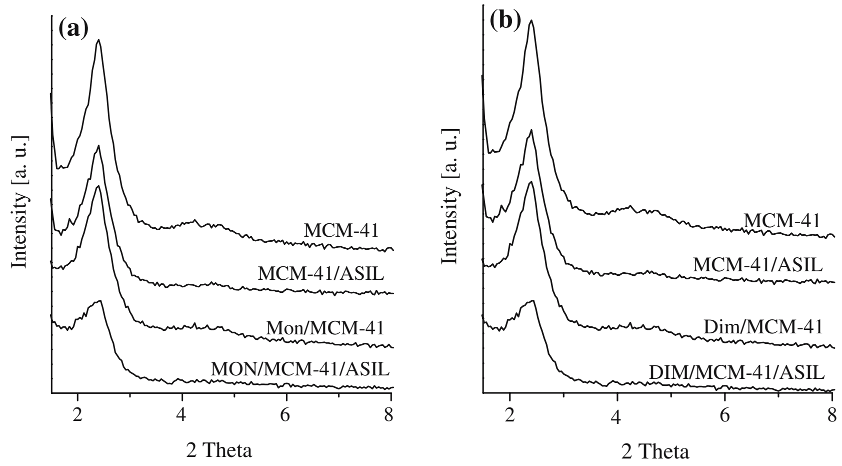


Figure 1. XRD patterns of MCM-41 and MCM-41/ASIL matrix and the samples modified with RhCp* complexes applied as monomer (a) and dimmer (b).

Table 1
RhCp* complexes concentration in mesoporous matrix expressed as rhodium wt.%

Samples	Samples (abbreviation)	Rh concentration in complex modified MCM-41 (wt.%)
$[Cp^*RhCl]_2(\mu\text{-}Cl)_2$/MCM-41	DIM/MCM-41	1.68
$[Cp^*RhCl]_2(\mu\text{-}Cl)_2$/MCM-41/ASIL	DIM/MCM-41/ASIL	1.67
$Cp^*Rh(Solvent)_3(PF_6)_2$/MCM-41	MON/MCM-41	1.61
$Cp^*Rh(Solvent)_3(PF_6)_2$/MCM-41/ASIL	MON/MCM-41/ASIL	1.67

overlapping with broad band of hydrogen bonded OH groups and strong bands originating from MCM-41 structure. The band at 1380 cm^{-1} was recorded for RhCp* complexes accommodated in MCM-41 and only slightly visible for the complex encapsulated in aminosililated matrix, while the band recorded for free complex at 1473 cm^{-1} was not observed in the supported system. It indicates, consistently with UV–Vis spectra, the interaction of Cp* ring with MCM-41 structure.

Reactivity of rhodium complexes accommodated in meso structure was estimated on the grounds of their ability of reacting with CO to form carbonyl complexes. Neither free dimmer nor monomer dissolved in CH_2Cl_2 and contacted with CO (many hours of bubbling of CO stream through the complex solution) did show any interaction resulting in carbonyls formation (no IR bands characteristic for CO group were recorded). On the contrary, both dimeric and monomeric rhodium complexes immobilised in MCM-41 matrix reacted with CO already at room temperature and after short contact time (10 min) two pairs of distinctive IR bands (at 2084 and 2010 cm^{-1} or 2094 and 2023 cm^{-1} for dimmer and monomer respectively) were recorded (figure 4). Prolongation of the contact time up to 20 h led to increase in intensity of the IR bands. Further evacuation at 100 °C for 1 h brought about the slight diminution of the bands intensity. Evacuation at 150 °C resulted in disappearance of CO bands observed in Dim/MCM-41 (2084 and 2010 cm^{-1}), whereas the carbonyl complexes formed in Mon/MCM-41 were stable even after evacuation at 200 °C. The longer contact with CO at RT resulted in appearance of rather weak band at about 2060 cm^{-1} accompanying earlier mentioned pairs of bands. However, complex which was characterised by this band was thermally unstable and the band disappeared after treatment at 150 °C. The IR bands of Rh carbonyl complexes characterised by frequencies higher

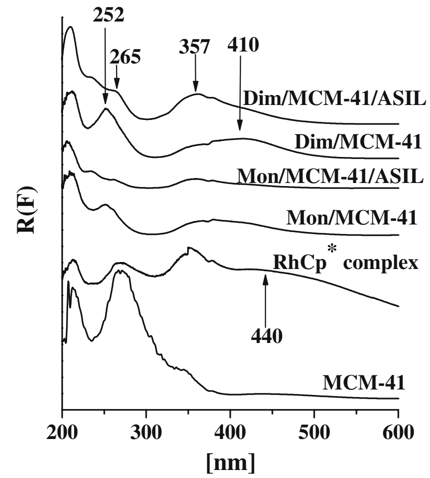


Figure 2. UV–Vis reflectance spectra of free RhCp* complex, MCM-41 and RhCp*/MCM-41 and RhCp*/MCM-41/ASIL samples.

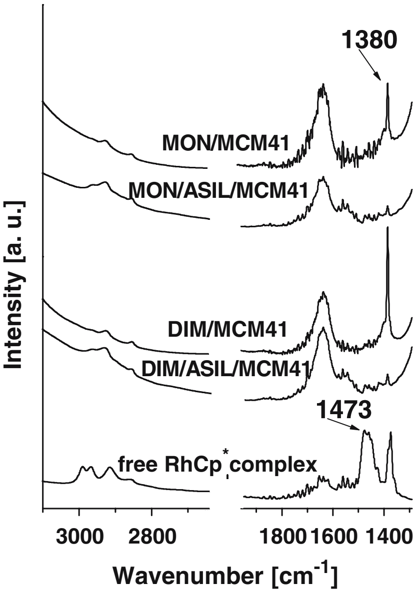


Figure 3. FTIR spectra of free RhCp* complexes and $RhCp^*$/MCM-41 and $RhCp^*$/MCM-41/ASIL samples.

than 2000 cm^{-1} should be attributed to Rh(III). The carbonyl Rh(III) complexes characterised by the bands at about 2084 and 2010 cm^{-1} or 2094 and 2023 cm^{-1} were reported earlier as being a result of CO interaction with Cp^*Rh complexes (dimmer$[Cp^*RhCl]_2(\mu\text{-}Cl)_2$ and monomer $[Cp^*Rh(S)_3]^{2+}$]) introduced in zeolite Y cages. These bands were attributed to one nuclear Rh(III) carbonyls of formula $Cp^*Rh(CO)_3{}^{2+}$ [5].

The question arises what kind of interaction is possible between silica mesoporous material MCM-41 containing only weakly acidic silanol groups and Rh(III) Cp^* complexes. It was shown in the earlier study [5] that strongly acidic protons present in α cage of HY did not activate $RhCp^*$ complexes towards reaction with CO at room temperature. It was surprising that dimeric complex encapsulated in faujasite showed only weak and easily removable carbonyl complexes at temperature not lower than 100 °C, while interaction of Rh Cp^* complexes with MCM-41 matrix allowed to form stable carbonyls already at RT. This difference may result from different geometry of a large cage of Y zeolite and the channel of MCM-41. A large cage of Y zeolite shows a diameter equal about 12 Å. Considering the size of Cp^* ligand (7.14 Å) the distance of π-electrons of Cp^* ring to proton located very near to the wall of HYα-cage is about 1.1 Å (Scheme 1). The interaction between these species is, therefore, very weak and can be observed only at temperature not lower than 100 °C. In consequence the formed carbonyl groups might be easily removed already after evacuation at room temperature. Considering the diameter of MCM-41 channel of 25 Å, distance between silanol group and π-electron from the Cp^* ring is much shorter (about 0.6 Å) and interaction should be easier. It allows to believe that interaction of $RhCp^*$ complex both with silanol OH groups and with MCM-41 structure activates the complex resulting in its higher activity towards CO molecules. The activating effect of silanol groups located in all silica meso structures on hydrocarbons reagents was reported in series of papers [11,12]. Choudhary *et al.* [11] on the grounds of TPD of different aromatic compounds (toluene, *p*-xylene, mesitilene and naphthalene) confirmed the interaction between π-electrons of aromatic ring and terminal silanol groups of all silica MCM-41. They have also found the energy site distribution on silica MCM-41. Seddegi *et al.* [12] have found that acidity of silanol groups present in all silica MCM-41 results in carbenium ion mechanism in polyethylene cracking reaction. It allows us to believe that OH silanol groups of Si-MCM-41 may interact both with Cp^* ring, which activates $RhCp^*$ complex and with CO carbonyl groups, resulting in higher stability of generated carbonyl complexes.

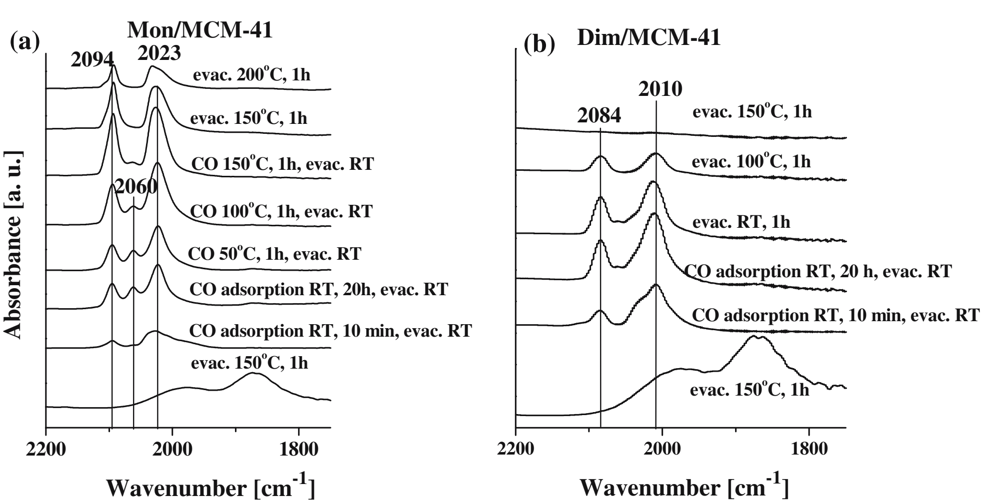
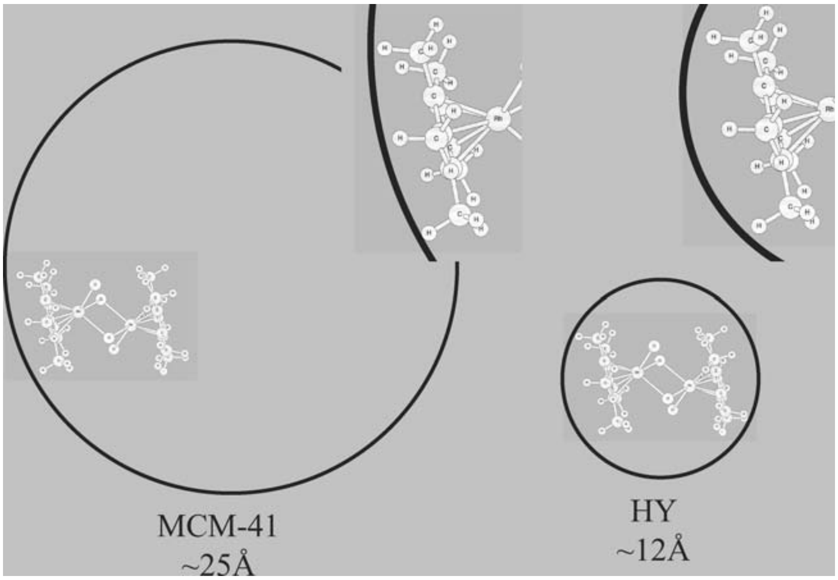


Figure 4. FTIR spectra (subtracted) recorded after interaction of CO with $RhCp^*$/MCM-41 under different conditions (a – monomeric complex, b – dimeric complex).



Scheme 1. The view of RhCp* complex location in the channel of MCM-41 molecular sieve and in the super cage of Y zeolite presenting a different distance between Cp* ring and OH groups situated at the wall of molecular sieves resulting from different pores diameter.

Interaction both dimeric and monomeric rhodium (III) complexes accommodated in MCM-41 matrix with CO did not result in rhodium (III) reduction even after interaction with CO at 150 °C.

Encapsulation of RhCp* complexes (both dimer and monomer) in aminosililated MCM-41 with following carbonylation resulted also in the formation of carbonyl complexes already at room temperature (figure 5). However, after 10 min contact with CO at RT only very weak IR bands were recorded. Prolongation of contact with CO up to 20 h resulted in an appearance of the distinct bands at 2090 and 2012 cm^{-1}. Simultaneously, the weak band at 1964 cm^{-1} has also been formed. The appearance of this band indicates a partial reduction of Rh(III) to Rh(I) with formation of Cp*Rh(CO)$_2$ complex [4]. Analysing of carbonyl IR bands (blue shifted when compared to the free Cp*Rh(CO)$_2$ complex) one can conclude that the Cp*Rh(I) carbonyl complex may be stabilised by the formation of donor – acceptor adduct between metal and amine group, which play a role of additional ligand (Scheme 2). IR band of Cp* Rh(I) carbonyls have appeared already at RT and they were still present after evacuation at 200 °C. Contact of Mon/MCM-41/Asil with CO at 150 °C resulted in the formation of additional band at 1862 cm^{-1}, which, on the grounds of literature [5,13] could be attributed to the presence of bridging CO group. Simultaneously with this band appearance, the intensity of the band at 1964 cm^{-1} diminished. Herrmann and co-workers [13] have found that Cp*Rh(I)(CO)$_2$ may be

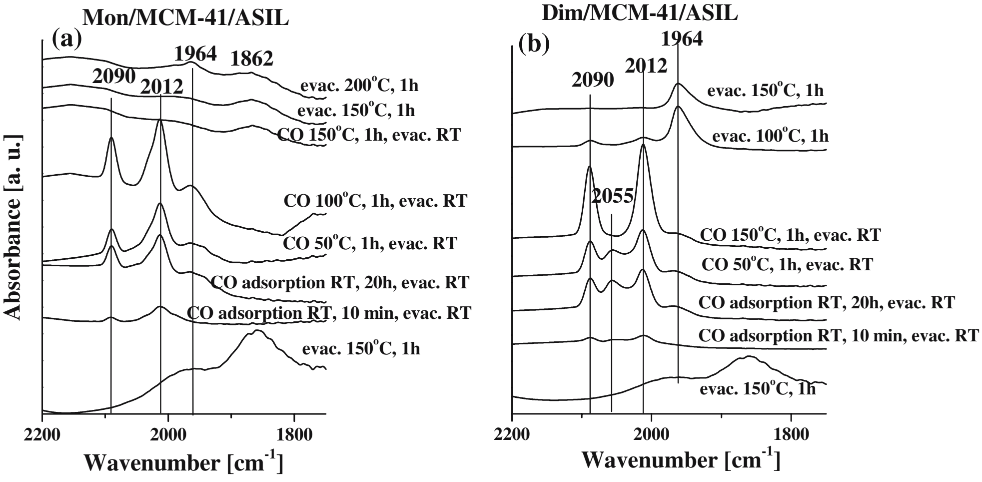
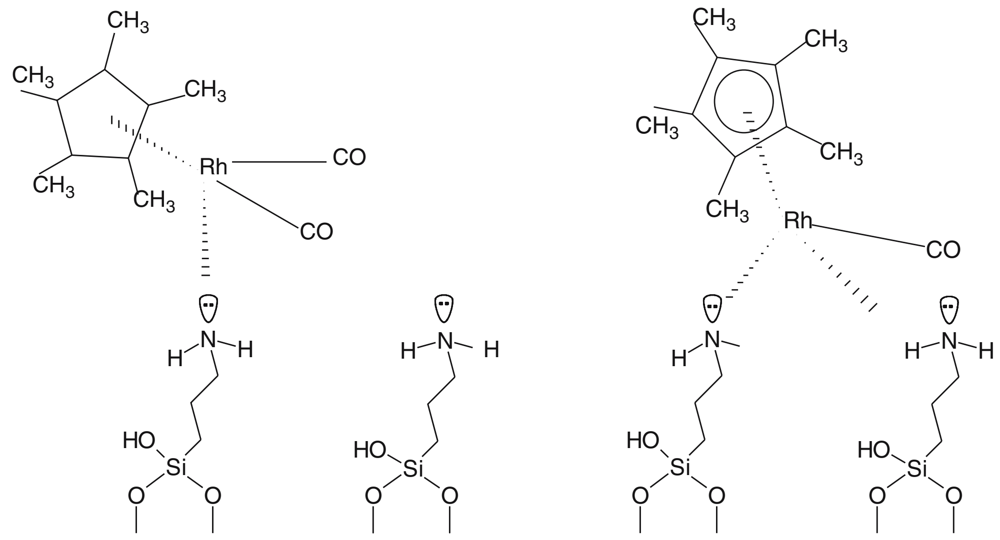
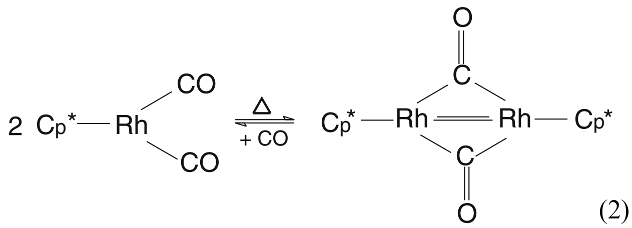


Figure 5. FTIR spectra (subtracted) recorded after interaction of CO with RhCp*/MCM-41/ASIL under different conditions (a – monomeric complex, b – dimeric complex).



Scheme 2. The possible interaction of amine groups in aminosililated MCM-41 molecular sieves with RhCp* carbonyl complexes.

transformed to di-nuclear Rh(I)Cp* carbonyls containing bridging CO group (Equation 2).



$$2\,\mathrm{Cp^*{-}Rh(CO)_2} \xrightleftharpoons[+\,\mathrm{CO}]{\Delta} \mathrm{Cp^*{-}Rh(\mu\text{-}CO)_2Rh{-}Cp^*} \qquad (2)$$

The formation of this complex as a result of carbonylation of RhCp* complexes encapsulated in Y zeoliteα-cage was postulated also in our earlier report [5].

From IR spectra one could conclude that rhodium complexes encapsulated into meso structure showed high reactivity towards CO molecules. It encouraged us for using these system as catalyst in the reaction involving CO. We have applied all the encapsulated rhodium complexes as catalysts for methanol carbonylation reaction carried out in heterogeneous conditions. Methanol was saturated with stream of CO and both reagents were introduced into catalyst layer at temperature 150, 200 and 250 °C. Products were analysed by GC technique. We have found some activity for carbonylation reaction performed at 200 and 250 °C only for the complexes accommodated in Si-MCM-41 (figure 6). The initial activity was even relatively high on Dim/MCM-41 catalyst (about 8 mol.% of methyl acetate was found in the product), however, deactivation of catalyst occurred and after 2 h on stream methyl acetate was not found in the product. Nevertheless, the catalytic results are in agreement with the results of IR spectra indicating the activating effect of meso structure on encapsulated RhCp* complexes.

4. Conclusions

(1) Accommodation of Cp*Rh(III) complexes in Si-MCM-41 molecular sieves activates these complexes (both dimmer and monomer) towards reaction with CO resulting in carbonyls formation.
(2) Both dimmer and monomer of Cp*Rh(III) complexes accommodated in Si-MCM-41 matrix and contacted with CO were not reduced to rhodium (I) complexes even at 150 °C.
(3) Rh(III) in Cp*Rh complexes encapsulated in aminosililated MCM-41 underwent reduction to Cp*Rh(I) carbonyls as a result of contact with CO already at RT.
(4) Rh(III)Cp* complex encapsulated in silica MCM-41 showed some activity in methanol carbonylation under heterogeneous conditions.

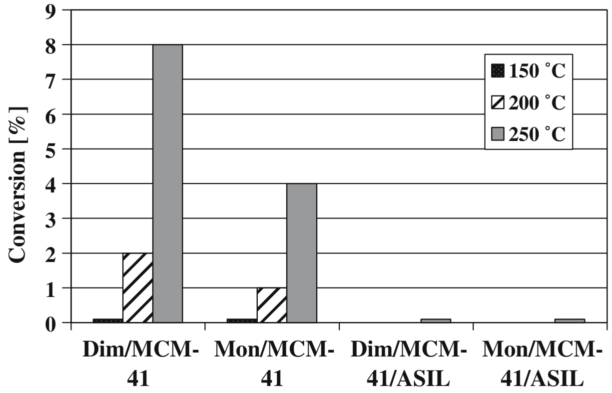


Figure 6. Catalytic activity of RhCp* complexes encapsulated in MCM-41 and MCM-41/ASIL for carbonylation of methanol in heterogeneous conditions under atmospheric pressure.

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