



Review

Hydrogenation of olefins over hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex immobilized on functionalized MCM-41 and SBA-15

Trissa Joseph^a, S.S. Deshpande^a, S.B. Halligudi^{a,*},
A. Vinu^b, S. Ernst^b, M. Hartmann^{b,*}

^a *Inorganic Chemistry and Catalysis Division, National Chemical Laboratory, Pune 411008, India*

^b *Kaiserslautern University of Technology, Department of Chemistry, Chemical Technology, Erwin-Schroedinger-Strasse 54, 67663 Kaiserslautern, Germany*

Received 7 February 2003; accepted 28 May 2003

Abstract

Hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ has been immobilized inside the pores of amine functionalized MCM-41 and SBA-15 materials. These grafted complexes were characterized by XRD, FTIR, N_2 adsorption measurements, XPS and tested as catalyst for the hydrogenation of olefins. Immobilization and pore size has marked effects on the catalytic activity in the hydrogenation of olefins and the complex immobilized on functionalized SBA-15 was found to be catalytically more active than the one immobilized on MCM-41.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex; MCM-41; SBA-15, immobilization; Hydrogenation

1. Introduction

Since the discovery of the M41S family of materials by Mobil Corporation scientists in 1992 [1,2], much attention has been paid to the synthesis and applications of mesoporous molecular sieves. In 1998, Zhao et al. [3] synthesized a new ordered hexagonal mesoporous silica with much thicker walls named SBA-15 using triblock co-polymer; poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) $[\text{EO}_n\text{–PO}_m\text{–EO}_n]$ as the structure directing agent. These mesoporous materials because of their high sur-

face area, tunable pore size and well modified surface properties [4,5] are finding use as adsorbents for the removal of toxic heavy metal ions from waste water [6], enzyme carriers [7], catalysts [8] and materials to sequester and release proteins [9].

The chemical reactivity of these mesoporous materials facilitates the covalent anchoring of various functional groups to its walls. The preparation of such inorganic–organic hybrid materials is of growing interest [10,11], especially for the attachment of various metal complexes. Sutra and Brunel [12] have reported the anchoring of Mn(III) Salpr complex through covalently linked organic moieties. Brunel et al. [13] has reported the grafting of TEMPO to organically modified MCM-41. Ruthenium(II) meso tetrakis(4-chloro phenyl) porphyrin

* Corresponding authors. Tel.: +91-20-589-3300/2000;

fax: +91-20-5411696/5893761.

E-mail address: halligudi@cata.ncl.res.in (S.B. Halligudi).

has been encapsulated in MCM-41 modified with 3-aminopropyl triethoxysilane (APTES) for alkene oxidation by Liu et al. [14]. Crudden et al. [15] anchored a bidentate rhodium phosphine complex onto MCM-41 and used as catalyst for hydrogenation of alkenes. We reported earlier, the catalytic activity of vanadium Schiff's base complex covalently anchored onto the walls of functionalized MCM-41 in the oxidation of adamantane using urea hydroperoxide [16].

In continuation of our work in this field, we report herein the synthesis of inorganic–organic hybrid materials and immobilization of an octahedral hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ on mesoporous materials like Si-MCM-41 and Si-SBA-15, and its catalytic activities in the hydrogenation of olefins.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS), cetyltrimethylammoniumbromide (CTAB), $[\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}]$ (Pluronic P123), triphenylphosphine (TPP), APTES, styrene, α -methyl styrene, trans-stilbene, cis-stilbene and limonene were procured from Aldrich Co. Tetramethylammonium hydroxide (TMAOH) was obtained from Merck. All the solvents were of AR grade and were procured from S.D. Fine Chemicals (India) and were distilled and dried before use.

2.2. Synthesis

2.2.1. Si-MCM-41

Si-MCM-41 was synthesized using a standard procedure. In a typical procedure, TMAOH (12.08 g) in 100 ml distilled water was added under constant stirring to 20.8 g of TEOS and the mixture was stirred for 1 h. To this solution, CTAB (27.33 g) in 98 ml water was added dropwise. The composition of the resultant gel was $\text{SiO}_2:0.33 \text{ TMAOH}:0.55 \text{ CTAB}:60 \text{ H}_2\text{O}$. This mixture was stirred overnight and the gel was transferred to a Teflon-lined autoclave and kept at 373 K for 5 days. The solid MCM-41 obtained was filtered, washed several times with distilled water, dried at 373 K in air, calcined at 823 K for 8 h in

nitrogen and then kept at this temperature for 6 h in air. X-ray diffraction (XRD) and TEM (Jeol model 1200 EX) have confirmed the hexagonal mesoporous MCM-41 structure.

2.2.2. Si-SBA-15

Si-SBA-15 was synthesized by following the standard procedure reported in [3]. The SBA-15 used in this work has been synthesized from a typical synthesis batch with the composition of 4 g Pluronic P123 $M_{\text{avg}} = 5800$ $[\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}]$, 120 g of 2 M HCl and 9 g TEOS. Typically, 4 g of triblock co-polymer was dispersed in 30 g distilled water and stirred for 3 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and finally 9 g of TEOS was added dropwise; the mixture was maintained at 40 °C for 24 h under stirring and then at 110 °C for 48 h under static condition in a teflon bottle. The crystallized product was filtered, washed with warm distilled water, dried at 383 K for 24 h, calcined at 813 K in nitrogen for 12 h and then maintained at 813 K in air for 5 h to completely remove the template. The structure was confirmed by XRD and N_2 adsorption measurements.

2.2.3. Synthesis of NH_2 -modified MCM-41 and SBA-15 ($\text{NH}_2\text{-MCM-41}/\text{NH}_2\text{-SBA-15}$)

$\text{NH}_2\text{-MCM-41}/\text{NH}_2\text{-SBA-15}$ was prepared by following the procedure reported in [12]. In a typical surface modification process, freshly activated Si-MCM-41 and Si-SBA-15 (3 g, 423 K) under vacuum was refluxed in toluene (50 ml; distilled over freshly cut sodium and dried over zeolite A) with APTES (3 g) for 3 h under argon atmosphere. The solid was washed with diethyl ether and Soxhlet extracted with 250 ml dichloromethane yielding covalently anchored APTES moieties $\text{NH}_2\text{-MCM-41}/\text{NH}_2\text{-SBA-15}$, Fig. 1a.

2.2.4. Synthesis of hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex— $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$

$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (Fig. 1b) was synthesized using the procedure described elsewhere [17]. A solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (2.61 g, 10 mmol) in 2-methoxyethanol (200 ml) and aqueous formaldehyde (200 ml; 40%, w/v) were added rapidly and successively to a vigorously stirred boiling solution of TPP (15.8 g, 60 mmol) in the same solvent (300 ml). The mixture was refluxed for 10 min, allowed to cool, filtered, washed

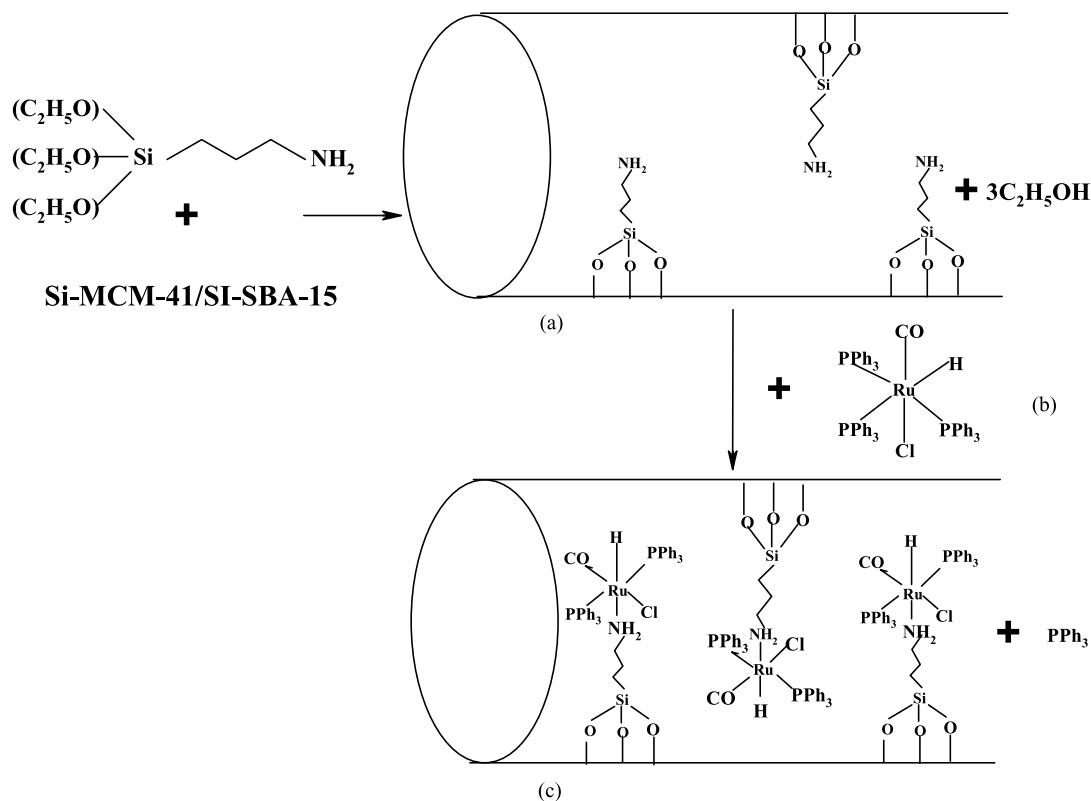


Fig. 1. Synthesis of NH_2 -MCM/SBA- $[RuHCl(CO)(PPh_3)_2]$.

with ethanol and hexane successively and dried in vacuum to obtain a light brown colored solid in good yield. The purity and structure of the complex was confirmed by melting point, elemental analysis and FTIR.

2.2.5. Immobilization of $[RuHCl(CO)(PPh_3)_3]$ over NH_2 -MCM-41/ NH_2 -SBA-15

To a suspension of freshly activated NH_2 -MCM-41/ NH_2 -SBA-15 (1 g) in dry toluene (40 ml), a solution of $[RuHCl(CO)(PPh_3)_3]$ (0.1 g) in anhydrous toluene (10 ml) was added and the resulting solution was refluxed for 3 h and the solid was Soxhlet extracted with anhydrous toluene and vacuum dried for 24 h. The ruthenium content in NH_2 -MCM-41- $[RuHCl(CO)(PPh_3)_2]$ and NH_2 -SBA-15- $[RuHCl(CO)(PPh_3)_2]$ (Fig. 1c) was estimated to be 0.88 and 1.3 wt.% by inductively coupled plasma optical emission spectrometer (ICP-OES). As shown in Fig. 1, the complex gets attached to the amine-modified Si-MCM-41 and Si-SBA-15 by displacement of a phosphine ligand.

The trans bond weakening effect of the hydride ligand in $[RuHCl(CO)(PPh_3)_3]$ accounts for the ready displacement of trans phosphine by strongly bonding amine (base). To the best of our knowledge, this is the first report on the anchoring of octahedral hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex onto mesoporous materials like Si-MCM-41 and Si-SBA-15, and study of their application in catalytic hydrogenation of olefins.

2.2.6. Characterization procedures

The C, H, N analysis of $[RuHCl(CO)(PPh_3)_3]$, NH_2 -MCM-41, NH_2 -SBA-15, NH_2 -MCM-41- $[RuHCl(CO)(PPh_3)_2]$ and NH_2 -SBA-15- $[RuHCl(CO)(PPh_3)_2]$ was done on a Carlo Erba (model EA 1108) elemental analyzer. The ruthenium content in the samples was estimated by ICP-OES. The crystallographic identifications of the MCM-41 samples were performed using X-ray powder diffraction with Cu $K\alpha$ radiation (Rigaku model D/MAXIII VC, Japan,

$\lambda = 1.5418 \text{ \AA}$). The powder XRD patterns of the SBA-15 materials were collected on a Siemens D5005 diffractometer using Cu K α ($\lambda = 0.154 \text{ nm}$) radiation. The textural properties of the immobilized complexes were determined from N₂ adsorption isotherms measured on an Omnisorb 100 CX Coulter instrument. The FTIR spectra of the samples were recorded on a Shimadzu (model 8201PC) spectrophotometer. X-ray photoemission spectra (XPS) measurements were made, at 298 K, on a VG Microtech Multilab-ESCA 3000 spectrometer, equipped with a twin anode of Al and Mg, and using Mg K α base pressure in the analyses chamber maintained at 3×10^{-10} to 6×10^{-10} Torr.

2.3. Catalytic tests

A known amount of substrate, catalyst and acetonitrile (30 g) were placed in a 300 ml Parr autoclave, pressurized with hydrogen (400 psig) and heated to the desired temperature (333 K). The progress of the reaction was monitored by withdrawing samples at different time intervals and analyzing by gas chromatograph (Shimadzu 14B, FID detector, SE-52 30 m capillary column). The identities of the products were confirmed by GC–MS (Shimadzu GCMS QP 5000).

3. Results and discussion

3.1. Characterization

3.1.1. XRD

Fig. 2a–e shows the XRD patterns of Si-MCM-41, NH₂-MCM-41, NH₂-MCM-41-[RuHCl(CO)(PPh₃)₂], physical mixture of Si-MCM-41 and [RuHCl(CO)(PPh₃)₃] and “neat” [RuHCl(CO)(PPh₃)₃]. The XRD pattern of Si-MCM-41 (Fig. 2a) shows a very intense peak assigned to reflections at (100) and two additional peaks with low intensities at (110) and (200) reflections, respectively, which can be indexed to hexagonal lattice. It is seen that upon functionalization with APTES, the intensities of all the peaks decrease marginally (Fig. 2b). No significant further loss in the intensity of peak assigned to reflections at (100) is observed after immobilization of the ruthenium complex (Fig. 2c). However, the peaks at (110) and (200) reflections were not observed upon immobilization of the complex. The XRD pattern of

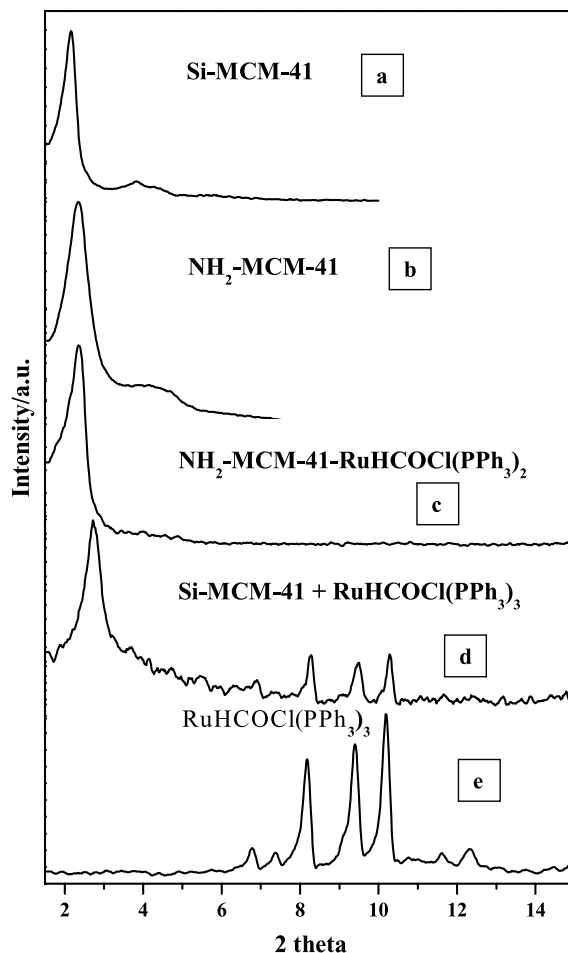


Fig. 2. XRD profiles of (a) Si-MCM-41, (b) NH₂-MCM-41, (c) NH₂-MCM-41-[RuHCl(CO)(PPh₃)₂], (d) Si-MCM-41 + [RuHCl(CO)(PPh₃)₃], and (e) “neat” [RuHCl(CO)(PPh₃)₃].

the physical mixture of Si-MCM-41 and the ruthenium complex shows some peaks other than that of MCM-41, which can be indexed to that of the neat complex on the surface of MCM-41 (Fig. 2d). XRD pattern of “neat” [RuHCl(CO)(PPh₃)₃] is depicted in (Fig. 2e).

The XRD patterns on Si-SBA-15, NH₂-SBA-15 and NH₂-SBA-15-[RuHCl(CO)(PPh₃)₂] are depicted in the Fig. 3a–c. XRD diffraction pattern of Si-SBA-15 shows a very intense peak (100) and four additional high order peaks with lower intensities (Fig. 3a), indicating a significant degree of long-range ordering of the structure and well formed hexagonal pore

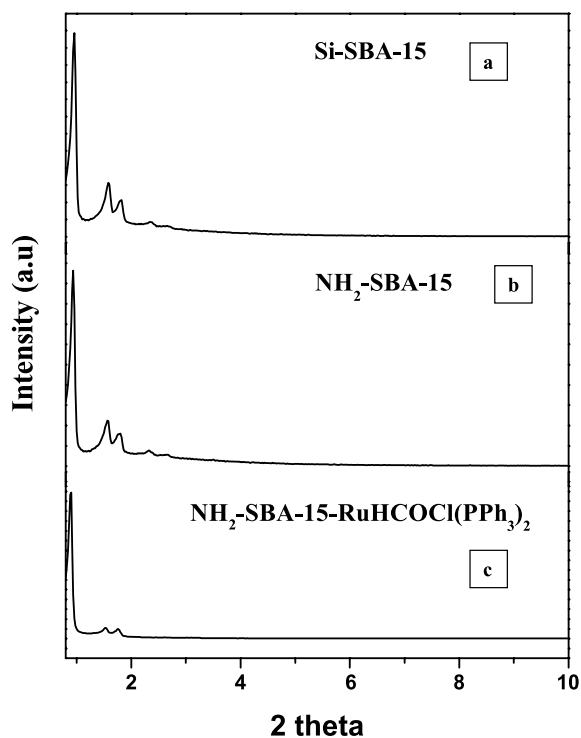


Fig. 3. XRD profiles of (a) Si-SBA-15, (b) NH_2 -SBA-15, and (c) NH_2 -SBA-15- $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$.

arrays. Some loss in the intensities of the peaks was observed upon modification with APTES revealing that silylation has indeed occurred inside the mesopores of Si-SBA-15 (Fig. 3b). However, it is evident from XRD that in addition to the very intense peak (100), four higher order peaks were still observed indicating that the silylation procedure did not diminish the structural ordering of Si-SBA-15 on immobiliz-

ing the ruthenium complex (Fig. 3c). This indicates that the structure of Si-SBA-15 is retained when the ruthenium complex is dispersed in the channels.

3.1.2. Sorption studies

The textural properties such as specific surface area and pore size of the support were followed throughout the different modification processes. The textural properties were determined by N_2 -sorption studies carried out at 77 K. The data on the specific surface area and pore size of the catalysts are present in Table 1. As reported earlier [18,19], a tremendous decrease in the specific surface area was observed (1000–600 m^2/g) upon modification of Si-MCM-41 with APTES. Reduction in the mesoporous diameter from 33 to 20 Å was also observed. Further decrease in the specific surface area from 600 to 260 m^2/g and pore size from 20 to 11 Å was observed upon immobilization of NH_2 -MCM-41 with the ruthenium complex, which suggests that the complex is present inside the channels of the support. In the case of SBA-15, a decrease in the specific surface area from 980 to 800 m^2/g and decrease in pore size from 90 to 80 Å was observed on modification with APTES. Further decrease in the specific surface area from 800 to 630 m^2/g and pore size from 80 to 73 Å was observed upon immobilization of NH_2 -SBA-15 with the ruthenium complex. The N_2 -adsorption measurements and XRD studies confirm the presence of ruthenium complex inside the channels of NH_2 -MCM-41 and NH_2 -SBA-15.

3.1.3. FTIR

The amine-modified and $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ -immobilized MCM-41/SBA-15 materials were characterized by IR spectroscopy. The FTIR spectra

Table 1
Characterization data of “neat” and immobilized $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$ complexes

Catalyst	FTIR bands (cm^{-1})				B.E. (eV) (Ru 3p)	Surface area (m^2/g) (N_2 -adsorption)	Pore size (Å)
	$\nu(\text{RuH})$	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{NH})$	$\nu(\text{CH}_2)$			
“Neat” $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$	2007	1919	–	–	464	–	–
MCM-41	–	–	–	–	–	1000	33
NH_2 -MCM-41	–	–	3365	2935	–	600	20
NH_2 -MCM-41- $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$	2045	1940	–	–	465	260	11
SBA-15	–	–	3298	2872	–	980	90
NH_2 -SBA-15	–	–	–	–	–	800	80
NH_2 -SBA-15- $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$	2045	1940	–	–	–	630	73

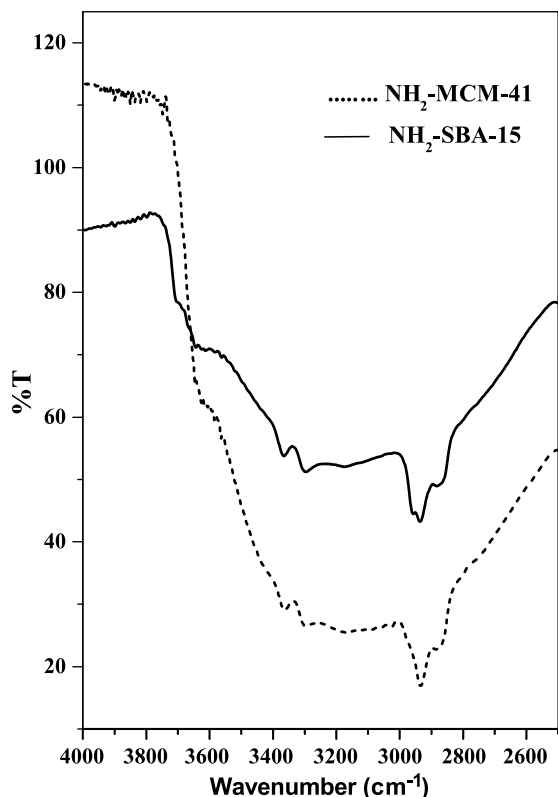


Fig. 4. FTIR spectra of (---) $\text{NH}_2\text{-MCM-41}$ and (—) $\text{NH}_2\text{-SBA-15}$.

of $\text{NH}_2\text{-MCM-41}/\text{NH}_2\text{-SBA-15}$ showed two bands at 3365 and 3298 cm^{-1} characteristic of the NH_2 groups (NH vibrations), and two bands at 2935 and 2872 cm^{-1} characteristic of asymmetric and symmetric vibrations of the CH_2 groups of the propyl chain of the silylating agent (Fig. 4). These results are quite consistent with the results previously reported [20].

FTIR spectra of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, $\text{NH}_2\text{-MCM-41-}[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$ and $\text{NH}_2\text{-SBA-15-}[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$ are shown in the Fig. 5. The spectra of immobilized complex showed characteristic peaks of the neat complex indicating the retention of structure of the complex upon immobilization. The neat complex showed a medium band for $\nu(\text{RuH})$ at 2007 cm^{-1} and a strong band due to $\nu(\text{C}\equiv\text{O})$ at 1920 cm^{-1} , which are shifted to 2045 and 1940 cm^{-1} , respectively, upon immobilization. The increase in the intensities of $\nu(\text{C}\equiv\text{O})$ could be attributed to the presence of a

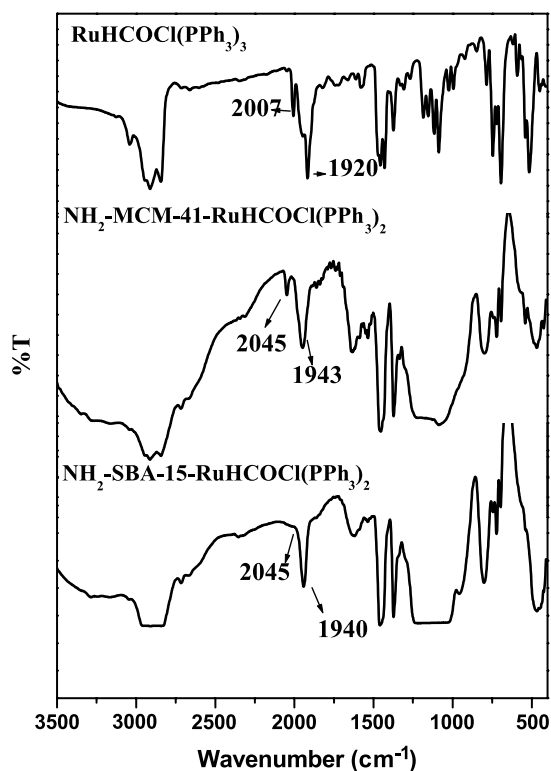
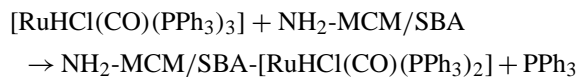


Fig. 5. FTIR spectra of (a) “neat” $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (b) $\text{NH}_2\text{-MCM-41-}[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$, and (c) $\text{NH}_2\text{-SBA-15-}[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2]$.

strong electronegative atom like nitrogen, which is a strong σ donor. In the immobilized complexes, the decrease in the intensity of bands due to phosphine at 3000 , 742 , 717 and 692 cm^{-1} indicates that one phosphine molecule has been knocked out during the coordination of ruthenium to nitrogen. The unusual trans bond weakening effect of the hydride ligand in $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ complex accounts for the ready displacement of trans phosphine by strong bonding Lewis base [21]. The nitrogen can easily replace trans phosphine giving an anchored $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ complex as shown below



3.1.4. XPS

The XPS of the Ru 3p core level of “neat” $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ and $\text{NH}_2\text{-MCM-41-}[\text{RuHCl}(\text{CO})$

(PPh₃)₂] are shown in the Fig. 6. The neat ruthenium complex exhibits Ru 3p core level peak at a binding energy of 464 eV consistent with the +2 oxidation state of ruthenium. In the case of the immobilized complex, a shift in the binding energy of the Ru 3p core level to 465 eV was observed, which could be due to coordination environment surrounding a metal of the complex in the mesoporous channels.

3.2. Catalytic activity

The hydrogenation of olefins was carried out with neat and immobilized catalysts. The data obtained on the catalytic activity (Table 2) TOF's were considerably higher in the case of immobilized catalysts than that of the neat complex with respect to all the substrate in the hydrogenation reaction. The improvement in the catalytic activity of the immobilized catalyst, upon functionalization of ruthenium complex, can be attributed to the coordination of the ruthenium complex to APTES over Si-MCM-41, Si-SBA15 and electron transfer from APTES to ruthenium.

The higher catalytic activity (TOF) in the case of the complex immobilized on functionalized SBA-15 than that of MCM-41 could be because of the easy access of the substrate molecules into the active sites of the complex in mesoporous channels, having large pore diameter in case of SBA-15 compared to MCM-41. It is well established fact that mesoporous supports pro-

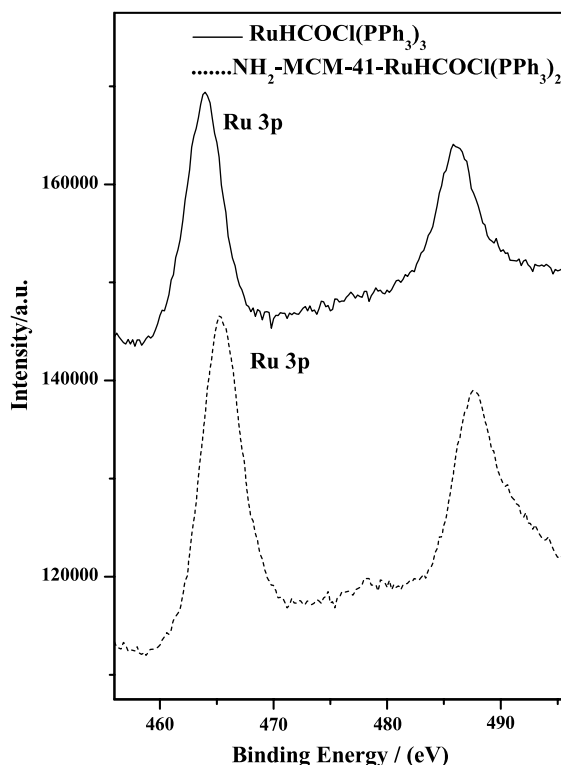


Fig. 6. XPS of (—) “neat” [RuHCl(CO)(PPh₃)₃], and (---) NH₂-MCM-41-[RuHCl(CO)(PPh₃)₂] from Ru 3p core level.

Table 2

Hydrogenation of olefins by “neat” and immobilized hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex

Catalyst (mg)	Substrate	Conversion (wt.%)	TOF ^a
“Neat” [RuHCl(CO)(PPh ₃) ₃] (4.1)	Styrene	9	16.7
NH ₂ -MCM-41-[RuHCl(CO)(PPh ₃) ₂] (50)	Styrene	43	80.0
NH ₂ -SBA-15-[RuHCl(CO)(PPh ₃) ₂] (33.9)	Styrene	66	122.8
“Neat” [RuHCl(CO)(PPh ₃) ₃] (4.1)	<i>t</i> -Stilbene	10	10.6
NH ₂ -MCM-41-[RuHCl(CO)(PPh ₃) ₂] (50)	<i>t</i> -Stilbene	82	87.2
NH ₂ -SBA-15-[RuHCl(CO)(PPh ₃) ₂] (33.9)	<i>t</i> -Stilbene	93	98.8
“Neat” [RuHCl(CO)(PPh ₃) ₃] (4.1)	<i>cis</i> -Stilbene	12	12.8
NH ₂ -SBA-15-[RuHCl(CO)(PPh ₃) ₂] (33.9)	<i>cis</i> -Stilbene	95	100.8
“Neat” [RuHCl(CO)(PPh ₃) ₃] (4.1)	α -Methyl styrene	18	29.6
NH ₂ -SBA-15-[RuHCl(CO)(PPh ₃) ₂] (33.9)	α -Methyl styrene	97	160.8
“Neat” [RuHCl(CO)(PPh ₃) ₃] (4.1)	Limonene	15	21.3
NH ₂ -SBA-15-[RuHCl(CO)(PPh ₃) ₂]	Limonene	89	126.0

Conditions: substrate = 1 g; mole ratio of Ru-complex (catalyst) to substrate (styrene = 4.5×10^{-4} , *t*-stilbene = 7.7×10^{-4} , *cis*-stilbene = 7.7×10^{-4} , α -methyl styrene = 5.12×10^{-4} , and limonene = 3.1×10^{-4}); acetonitrile = 30 g; temperature = 333 K; H₂ pressure = 2.758×10^3 kPa; and time = 12 h.

^a TOF = mole of substrate converted per mole of Ru per h.

vide added advantages of surface area, porosity and complex environment, which do not allow the metal complexes to undergo side reactions like dimerization and oligomerization, etc. leading to a decrease in catalytic activities in their neat forms.

3.3. Catalyst leaching and recycling studies

In order to check, leaching of the metal complex from immobilized catalyst into reaction medium, during hydrogenation of olefins, was carried in a few selected systems. The reaction mixture after a contact time of 12 h was filtered to separate the immobilized catalyst and the filtrate. The filtrate collected was placed into the reactor and the reaction was continued with the filtrate by charging fresh hydrogen for another 4 h. It was found that there was no absorption of H₂, and gas chromatographic analysis of the reaction mixture showed no further increase in the conversion of substrate. This ensured that the reaction was catalyzed heterogeneously in presence of immobilized catalyst. In addition to this, leaching of Ru in the filtrate was tested by ICP-OES, which showed the absence of Ru in solution after the hydrogenation reaction.

Immobilized catalysts recyclability experiments in hydrogenation of olefins were performed by separating the catalysts from the reaction mixture after a contact time of 12 h. The catalyst separated was washed with acetonitrile, dried and subjected to another cycle with a fresh reaction mixture, under the same hydrogenation reaction conditions. It was found that the conversion with the specific substrates was nearly the same. The above procedure was repeated for three cycles with the two immobilized catalysts, the specific substrate and we did not observe any loss in the catalytic activity of the immobilized catalyst.

4. Conclusions

Hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium(II) complex has been immobilized on amine functionalized MCM-41 and SBA-15 by the displacement of one PPh₃ group. Immobilization of metal complexes on supports having higher surface area and the pore sizes have marked effects on the activity of [RuHCl(CO)(PPh₃)₃] complex in the hydrogenation of olefins. The easy access of the active

site to the substrate molecules is perhaps responsible for the higher activity of the SBA-15 catalysts. In general, the complex immobilized on functionalized mesoporous materials are more active than the “neat” complex and these could be reused in repeated cycles. There was no leaching of the metal complex from the immobilized catalyst into the reaction medium and these immobilized catalysts can be recycled in the hydrogenation reactions.

Acknowledgements

This work was carried out under Indo-German Joint Collaboration in S & T, DST-DAAD PPP project. All the authors thank DST, New Delhi, India and DAAD, Bonn, Germany for financial support. Trissa Joseph acknowledges the CSIR, New Delhi for granting her SRF.

References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* 279 (1998) 548.
- [4] X. Feng, G.E. Fryxell, L.-Q. Wang, A.Y. Kim, J. Liu, K.M. Kemner, *Science* 276 (1997) 923.
- [5] L. Mercier, T.J. Pinnavia, *Adv. Mater.* 9 (1997) 500.
- [6] A.M. Liu, K. Hidajat, S. Kawi, D.Y. Zhao, *Chem. Commun.* (2000) 1145.
- [7] H. Takahashi, Bo Li, T. Sasaki, C. Miyazaki, T. Kajino, S. Inagaki, *Microporous Mesoporous Mater.* 44–45 (2001) 755.
- [8] C. Huber, K. Moller, T. Bein, *JCS Chem. Commun.* (1994) 2619.
- [9] Y.-J. Han, G.D. Stucky, A. Butler, *J. Am. Chem. Soc.* 121 (1999) 9897.
- [10] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, *Nature* 402 (1999) 867.
- [11] B.F.G. Johnson, S.A. Raynor, D.S. Shephard, T. Mashmeyer, J.M. Thomas, G. Sanker, S. Bromley, R. Oldroyd, L. Gladden, M.D. Mantle, *Chem. Commun.* (1999) 1167.
- [12] P. Sutra, D. Brunel, *Chem. Commun.* (1996) 2485.
- [13] D. Brunel, F. Fajula, J.B. Nagy, B. Deroide, M.J. Verhoef, L. Veum, J.A. Peters, H. van Bekkum, *Appl. Catal. A: Gen.* 213 (2001) 73.
- [14] C.-J. Liu, S.-G. Li, W.-Q. Pang, C.-M. Che, *Chem. Commun.* (1997) 65.

- [15] C.M. Crudden, D. Allen, M.D. Mikoluk, J. Sun, *Chem. Commun.* (2001) 1154.
- [16] T. Joseph, M. Hartmann, S. Ernst, S.B. Halligudi, *J. Mol. Catal. A: Gen.*, (2003), in press.
- [17] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, *Inorg. Synth.* 15 (1974) 48.
- [18] D. Brunel, A. Cauvel, F. Fajula, F. Di Renzo, *Stud. Surf. Sci. Catal.* 97 (1995) 173.
- [19] A. Cauvel, D. Brunel, F. Di Renzo, F. Fajula, in: *Proceedings of the 53rd International Meeting on Phys. Chem. 'Organic Coatings,' Am. Inst. Phys.* 354 (1996) 477.
- [20] M.J. Verhoef, J.A. Peters, H. van Bekkum, *Stud. Surf. Sci. Catal.* 125 (1999) 465.
- [21] S. Gopinathan, S.S. Deshpande, I.R. Unny, C. Gopinathan, *Ind. J. Chem.* 25A (1986) 1015.