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Immobilized chiral diamino Ru complex as catalyst for chemo- and enantioselective hydrogenation

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Abstract

Chiral cyclohexyldiamine based Ru triphenylphosphine complex has been immobilized over mesoporous silica SBA-15 and used in the chemo- and enantioselective hydrogenation of prochiral and α,β-unsaturated ketones and imines to corresponding products. ^{31}P NMR, SEM, TEM, XRD, N_2 sorption measurements and FTIR analysis supported the retention of the complex over mesoporous silica. This catalyst was found to catalyze preferentially the hydrogenation of C=O over coexisting conjugated C=C linkages in the hydrogenation of α,β-unsaturated ketones with high turnover frequencies (TOF = mole of substrate converted per mole of Ru complex per hour) and gave excellent enantioselectivities in the hydrogenation of prochiral ketones compared to its homogeneous analogue. It also showed good activity in the hydrogenation of less reactive imines to secondary amines.

Keywords: Ruthenium(II) complex; Functionalized SBA-15; Chiral cyclohexyldiamine; Immobilization; Hydrogenation; Prochiral ketones; α,β-Unsaturated ketones; Imines; Enantioselectivity; Chemoselectivity

1. Introduction

Asymmetric hydrogenation is a core technology in fine chemicals synthesis particularly for pharmaceuticals, agrochemicals, flavours, and fragrances, which requires a high degree of stereochemical precision [1]. Asymmetric hydrogenations of C=C, C=O, and C=N functionalities have found important applications in organic synthesis and in the fine chemical business [2]. Hydrogenative reduction of prochiral ketones to chiral alcohols is a powerful tool for precise stereocontrolled organic synthesis. A high turnover frequency (TOF) can be obtained by designing suitable molecular catalysts and reaction conditions. Preferential reduction of a C=O function over a coexisting C=C linkage is an important and difficult task. Its versatility is manifested by the asymmetric synthesis of some biologically significant chiral compounds [3]. Although there are many examples of highly efficient catalysts for olefin and ketone reduction, imine hydrogenation is still a challenge in terms of both the turnover frequency and the lifespan of the active catalyst. This is due to the fact that C–N double bonds have certain traits, such as their preferred mode of binding and the strong donor character of the nitrogen, that are unfavorable for homogeneous catalytic hydrogenation [4,5]. One of the best transition-metal complexes for ketone hydrogenation that has been discovered is the chiral Ru(II)–diphosphine/1,2-diamine complex, which was developed by Noyori and Ohkuma [6]. This system was found to be active in the chemoselective hydrogenation of carbonyl over olefin functional groups and in the reduction of imines [2,6].

The immobilization of metal complexes enables the long-term use of expensive or toxic catalyst and provides a clean and straightforward separation of the product [7]. Compared to organic polymers, inorganic material-immobilized catalysts possess some advantages, though they attract little attention [8]. For example, they prevent the intermolecular aggregations of the active species because of their rigid structures, do not swell or dissolve in organic solvents, and often exhibit superior thermal and mechanical stability under the catalytic conditions. A recently discovered pure silica phase material,

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designated SBA-15, has long-range order, large monodispersed mesopores (up to 50 nm), and thicker walls (typically between 3 and 9 nm), which makes it more thermally and hydrothermally stable than the M41S-type materials [9–11]. There are reports on the immobilization of Ru catalyst on different supports for the hydrogenation of ketones [12], but very few reports on the chemoselective hydrogenation of α,β-unsaturated ketones and the hydrogenation of imines.

We have synthesized the novel heterogeneous catalysts by directly grafting a chiral 1,2-diaminocyclohexane (dach) based Ruthenium triphenylphosphine complex onto the surface of mesoporous silica SBA-15 that was very successful in the heterogeneous asymmetric hydrogenation of a series of ketones. This high activity of the Ru amine immobilized catalysts (here after [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15)) comes with high selectivity for the hydrogenation of ketones over olefin functional groups and promising activity in the imine hydrogenation.

2. Experimental

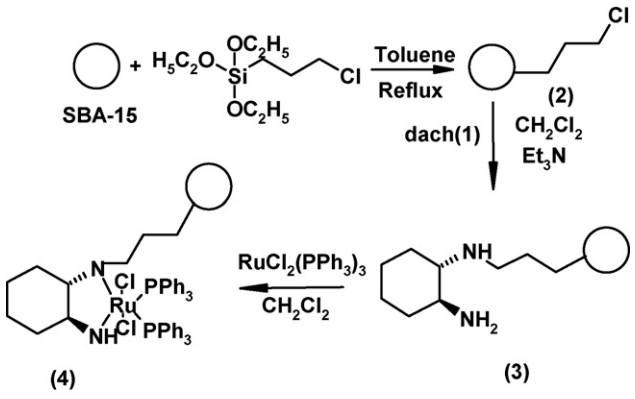
2.1. Chemicals

All the solvents procured from Merck, India were of AR grade and were distilled and dried prior to their use. All the ketones and α,β-unsaturated ketones were purchased from Aldrich chemicals and used as received. The (1*S*,2*S*)-1,2-diaminocyclohexane was purchased from Aldrich chemicals. All the imines were freshly prepared by the condensation of requisite amine and ketone in toluene in the presence of 4 Å molecular sieves according to literature [14]. $RuCl_2(PPh_3)_3$ was synthesized according to published paper [15]. Si–SBA-15 was synthesized using a similar procedure reported in the literature [9].

2.2. Catalyst preparation

2.2.1. Chloro functionalization of SBA-15

Surface functionalization of SBA-15 was carried out by post synthesis method. SBA-15 (3 g), chloropropyltriethoxysilane (3 mL) was refluxed overnight in toluene (50 mL) (Scheme 1). After that it was filtered and washed with toluene for several times. It was soxhelt extracted with toluene to remove the ungrafted chloropropyl triethoxysilane group.



Scheme 1. Synthesis of immobilized chiral ligand dach–SBA15 (3) and immobilized complex [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15 (4).

2.2.2. Ligand functionalization of SBA-15 (dach–SBA-15)

The chloro functionalized SBA-15 (2 g) was treated with (*S*,*S*)-diaminocyclohexane (0.3 g) in the presence of catalytic amount of triethylamine in dichloromethane under nitrogen atmosphere. It was refluxed at 313 K for 24 h and then filtered, washed with dichloromethane for several times and soxhelt extracted with dichloromethane to remove the unreacted amine.

2.2.3. Anchoring of the complex inside the ligand functionalized mesoporous material ([Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15)

One gram of ligand functionalized SBA-15 was added to a solution containing 38 mg (0.04 mmol) of the $RuCl_2(PPh_3)_3$ complex dissolved in 30 mL of dry dichloromethane, and the mixture was stirred at room temperature for 12 h under inert atmosphere, filtered, washed and soxhelt extracted with dry dichloromethane, and dried under vacuum.

2.3. Characterization

Elemental analyses were done for carbon and hydrogen and nitrogen in Carlo Erba (Model EA1108) elemental analyzer. The powder small angle X-ray scattering patterns of the SBA-15 materials were collected on a SIEMENS D5005 diffractometer using Cu Kα (λ = 0.154 nm) radiation. The FTIR spectra of the samples were recorded on a Shimadzu (Model 8201PC) spectrophotometer. The structure of the complex inside the mesopores of silica supports was characterized by MAS NMR spectroscopy (Bruker DSX-300 spectrometer). The specific surface areas of the samples were determined by the BET method from N_2 adsorption isotherms at 77 K using an Omnisorb CX-100 Coulter instrument. The reaction mixture was analysed by a gas chromatograph (Shimadzu 14B) equipped with a cross linked 5% diphenyl–95% dimethylpolysiloxane capillary column (30 m) and a flame ionization detector and the identity of the product was confirmed by GCMS (Shimadzu GCMSQP 5000) equipped with an identical column and a mass selective detector and by ^{1}H and ^{13}C NMR. The enantiomeric excess of the product was found out by HPLC using chiracel OD-H column. The ruthenium content in the catalyst before and after reaction was estimated by a Perkin-Elmer 1200 inductively coupled plasma spectrophotometer.

2.4. Catalytic experiments

2.4.1. General procedure for the hydrogenation of ketone

Synthesis of 1-(naphthalen-2-yl) ethanol (entry 1, Table 2): to a test tube, the precatalyst, Ru complex immobilized over mesoporous silica SBA-15 (0.2 g, 0.00039 mmol of Ru) and 1 M tBuOK (potassium *tert*-butoxide) in isopropyl alcohol (0.3 mL, 0.02 mmol) was added under nitrogen and stirred at room temperature for 30 min before 2-methylnaphthyl ketone (10 mmol, 1.70 g) and isopropyl alcohol (40 mL) was introduced. The contents of the test tube was transferred to 300 mL autoclave and

then sealed. After purging with hydrogen for five times, the final H_2 pressure was adjusted to 27 atm. After stirring at 343 K for 20 h, the reaction was stopped. The conversion was determined by GC to be 90%. The reaction mixture was filtered and washed several times with isopropyl alcohol. The filtrate was removed under reduced pressure and purified by column chromatography on silica as the stationary phase (pet ether:ethyl acetate, 85:15) to give 1-(naphthalene-2-yl) ethanol (85 and 76% ee), white solid, the enantiomeric excess was determined from HPLC (chiracel OD-H column, mobile phase: isopropyl alcohol:pet ether, 10:90; wave length: 254 nm; flow rate: 0.5 mL/min; minor isomer, 19.74; major isomer, 20.45), ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.73–7.78 (m, 4H), 7.37–7.46 (3H, m), 4.95–5.05 (1H, q), 1.49–1.53 (3H, d), ^{13}C NMR ($CDCl_3$): δ = 133.5 (C), 131.2 (C), 128.0 (CH), 127.6 (CH), 127.5 (CH), 127.3 (CH), 126.9 (CH), 126.1 (CH), 124.9 (CH), 123 (C), 76.1 (CH), 22.6 (CH_3).

2.4.2. General procedure for the hydrogenation of α,β-unsaturated ketone

Synthesis of (*E*)-1,3-diphenylprop-2-en-1-ol (entry 1, Table 3): It is same as in the case of hydrogenation of ketone. Reactions were carried out at 343 K and 27 atm. H_2 using 10 mmol of the substrate (α,β-unsaturated ketone, (*E*)-1,3-diphenylprop-2-en-1-one). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.15–7.33 (10H, m), 6.27 (1H, s), 6.06 (1H, s), 5.19 (1H, s), 4.59 (1H,s), ^{13}C NMR ($CDCl_3$): δ = 141.4 (C), 135.1 (C), 129.5 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.0 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 126.4 (CH), 126.3 (CH), 126.1 (CH), 77.0 (CH).

2.4.3. Hydrogenation of imines

Synthesis of *N*-(1-phenylethyl)benzenamine (entry 1, Table 4): it is same as in the case of hydrogenation of ketones. Reactions were carried out at 348 K and 27 atm. H_2 using 2.5 mmol of the substrate (imine, (*E*)-*N*-(1-phenylethylidene) benzenamine) substrate/catalyst/base ratio of 6410/1/30 in 20 mL of 2-propanol. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.24–7.30 (m, 3H), 7.08–7.12 (m, 4H), 6.94 (1H,m), 6.48 (m, 2H), 4.08 (1H, m), 1.5 (3H,d) ^{13}C NMR ($CDCl_3$): δ = 147.6 (C), 143.5 (C), 129.6 (CH), 129.6 (CH), 128.6 (CH), 128.6 (CH), 126.9 (CH), 126.9 (CH), 126.8 (CH), 117.2 (CH), 113.5 (CH), 113.4 (CH), 56.5 (CH), 21.5 (CH_3).

3. Results and discussions

As shown in Scheme 1, the reaction of 1,2-diaminocyclohexane (1) with the chloropropyl functionalised SBA-15 (2) in CH_2Cl_2 with triethylamine as base smoothly gave the supported ligand (3). Subsequent elemental analysis of ligand based on the wt.% of N demonstrated that the loading ratio of the chiral ligand was 0.003 mmol g^{-1}. Complexation of the functionalized ligand was carried out with $RuCl_2(PPh_3)_3$ to give the covalently anchored chiral Ruthenium complex (4).

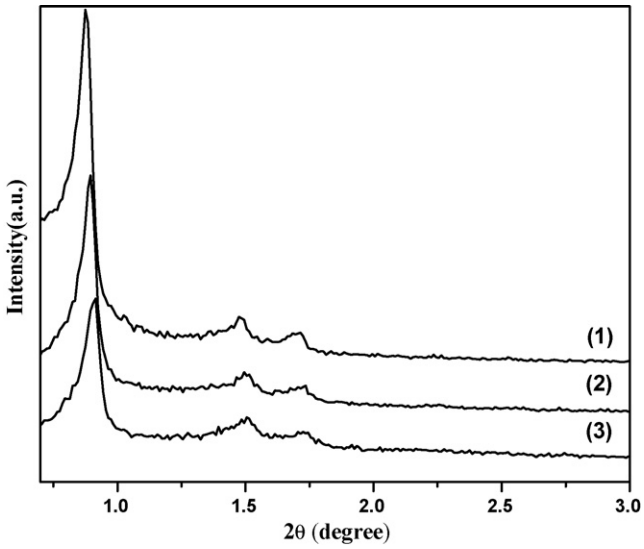


Fig. 1. Low angle XRD patterns of (1) SBA-15, (2) dach–SBA-15 and (3) [Ru(dach)$(PPh_3)_2(Cl_2)$]–SBA-15.

3.1. Catalyst characterization

3.1.1. Low angle XRD

The low angle XRD patterns of the siliceous SBA-15 showed hexagonal structure characteristic of this material and a well-resolved pattern with a prominent peak at 0.8° and two peaks at 1.4° and 1.6° 2θ, which matches well with the pattern reported for SBA-15. In low angle XRD of the material, the intensities of the reflections essentially did not change after the ligand functionalization and complexation over SBA-15 (Fig. 1). Low angle XRD peaks can be indexed to a hexagonal lattice with a $d(1\,0\,0)$ spacing of 110 Å, corresponding to a large unit cell parameter, a_0 = 127 Å ($a_0 = 2d(1\,0\,0)/\sqrt{3}$).

3.1.2. N_2 sorption study

N_2 sorption isotherms were measured for the pure support and for the immobilized complex. Table 1 represents a comparison of sorption isotherms and textural characteristics of pure and immobilized catalyst samples. The sample displayed a type IV isotherm with H_1 hysteresis and a sharp increase in pore volume adsorbed above $P/P_0 \sim 0.7$ cm^3/g, which is a charac-

Table 1
Physicochemical properties of the materials

Materials	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
SBA-15	780	1.34	9.1
Dach–SBA-15	576	1.14	8.8
[Ru(dach)$(PPh_3)_2(Cl_2)$]–SBA-15	418	0.92	7.9

Note. Dach–SBA-15, ligand functionalized SBA-15; [Ru(dach)$(PPh_3)_2(Cl_2)$]–SBA-15, anchored Ru complex inside the ligand functionalized mesoporous material.

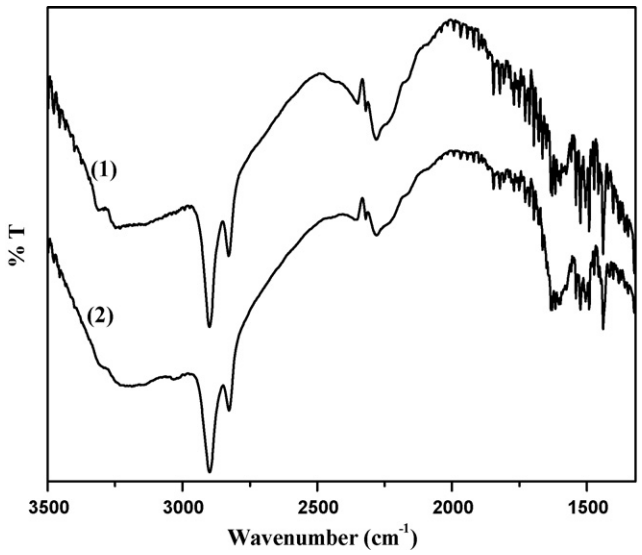


Fig. 2. FTIR spectra of (1) dach–SBA-15 and (2) [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15.

teristic of highly ordered mesoporous materials. It is seen that N_2 adsorbed or desorbed volumes were higher in the case of pure support than complex immobilized catalysts. BET surface area was found to decrease from 780 m^2/g for the pure support to 418 m^2/g for [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15, with corresponding decrease in mesopore volume from 1.34 to 0.92 cm^3/g. These results indicate that the complex is most likely anchored inside the mesopore channels of SBA-15.

3.1.3. FTIR

FTIR spectra of the dach-SBA-15 (Fig. 2) showed two low broad bands at 3325, 3245 cm^{-1} which are the characteristic bands of $–NH_2$ moiety. The sharp bands at 2902, 2828 cm^{-1}, are the corresponding bands for asymmetric and symmetric $–CH_2$ group vibrations, respectively, which belong to the propyl chain of the silylating agent. The vibrational bands at the same frequency were observed in the case complex anchored SBA-15 ([Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15) also. This was attributed towards the presence of the complex inside the channels of SBA-15.

3.1.4. CP-MAS NMR

The ^1H–^{31}P coupled CP-MAS NMR spectra of the [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15 (Fig. 3) revealed two peaks at 37.9 and 47.6 which is a slight shift compared to the corresponding ^{31}P spectra of neat metal complex [16].

3.1.5. TEM

Fig. 4 represents the TEM images of (1) SBA-15, (2) [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15. TEM images of the parent SBA-15 and of the grafted samples provided strong evidence of the retainment of mesoporous structure of the supports. The characteristic hexagonal silicate structures shown on TEM, supports the observation made by low angle XRD.

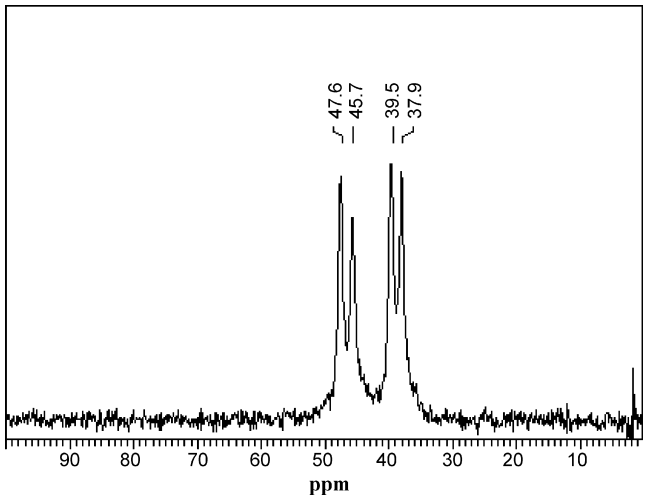


Fig. 3. ^{31}P MAS NMR of [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15.

3.1.6. SEM

SEM images of (1) SBA-15, (2) [Ru(dach)(PPh_3)$_2$(Cl_2)] –SBA-15 samples are depicted in Fig. 5. SEM image of the RuPN–SBA-15 sample revealed well distributed hexagonal particles organized into rope-like structures. This observation suggests that the mesoporous matrices retained their morphological integrity (shape and size) after functionalization by organic groups, but small agglomeration occurred in immobilized catalyst.

3.2. Catalytic activity

3.2.1. Enantioselective hydrogenation of ketones

The efficacy of the [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15 catalyst was assessed in the hydrogenation of prochiral ketones using a protocol similar to that developed for the homogeneous complex and is expressed in turnover frequencies (TOFs). 2-Methylnaphthyl ketone was chosen as the substrate and potassium *tert*-butoxide as base for initial testing, and the reaction was carried out with a substrate/catalyst/base (*S*/*C*/*B*) ratio of 25640/1/30 at 343 K and 27 atm. H_2. 1-(Naphthalen-2-yl)ethanol was obtained in 90% yield (TOF 961) and 76% ee in 20 h. In comparison, the homogeneous catalyst, [$RuCl_2$(PPh_3)$_2$((*S*,*S*)-CYDN)] gave 92% yield (TOF 982) and an ee of 75% under the same reaction conditions. The hydrogenation of 2-methylnaphthylketone with [Ru(dach)(PPh_3)$_2$(Cl_2)–MCM-41 (Ru(II)–diphosphine/1,2-diamine complex grafted over mesoporous silica MCM-41 by a similar procedure) resulted in the same enantioselectivity but the turnover frequency (TOF) was low as compared to the SBA-15 supported one (961 versus 569) (entry 9, Table 2). This could be because of the less diffusional resistance faced by the substrate molecules to interact with the active sites of the complex in mesoporous channels, having large pore diameter in case of SBA-15 compared to MCM-41 [13].

With the above results in hand, the asymmetric hydrogenation was then extended to other ketone substrates under the conditions of *S*/*C*/*B* = 25640:1:30, 343 K and 27 atm. H_2. As seen in

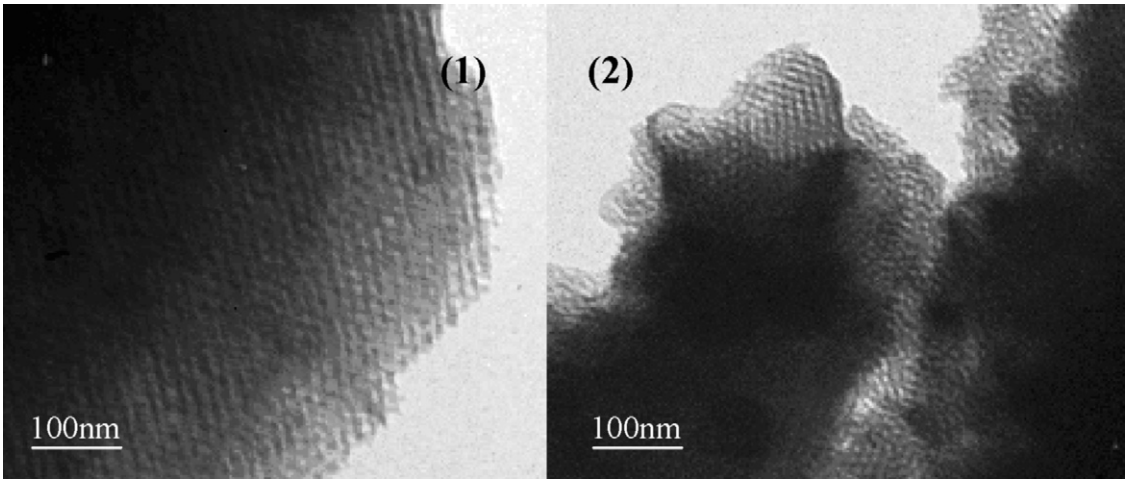


Fig. 4. TEM images of (1) SBA-15 and (2) [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15.

the Table 2, the immobilized [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15 exhibited high activity in terms of TOF and good enantioselectvities for various aromatic ketones, like actophenone, propiophenone, *p*-methoxyactophenone, *p*-chloroacetophenone, *p*-bromoacetophenone, and *o*-hydroxyacetophenone. The higher activity (TOF = 1310) (entry 4, Table 2) and good enantioselectivity (75%) was obtained in the hydrogenation of *p*-chloroacetophenone. In case of *o*-hydroxy acetophenone it afforded low conversion (TOF-641) and low ee (15%) (entry 7, Table 2). Results with the substituted acetophenones suggested that electron-withdrawing groups show higher substrate conversions and *o*-substitution with electron-donating groups tends to afford both low conversion and low ee. These observations are reminiscent of those made with the parent homogeneous analogue.

3.2.2. Chemoselective hydrogenation of α,β-unsaturated ketones

The chemoselective hydrogenation of α,β-unsaturated ketones were carried out with a substrate/catalyst/base (*S*/*C*/*B*) ratio of 25640/1/30 at 343 K and 27 atm. H_2, (*E*)-1,3-diphenyl-2-en-1-one was converted to the corresponding allyl alcohol in high conversion (TOF 2519) and high selectivity (>99%) (entry 1, Table 3). The reduction of 1-phenylbut-2-ene-1-one occurred with a TOF of 2435 and >99% selectivity for the corresponding allyl alcohol (entry 2, Table 3). In case of the chemoselective hydrogenation of cyclohex-2-enone, the major product was cyclohexanone and the selectivity of the corresponding allyl alcohol was only 10%, but when one methyl group is present in the third position, the major product was the corresponding allyl alcohol (entries 3 and 4, Table 3).

3.2.3. Hydrogenation of imines

[Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15 was also active in the hydrogenation of imines to the corresponding secondary amines. Here, no enantiomeric excess of the product was obtained as in case of its homogeneous analogue [17] but it showed good activity as compared to its homogeneous analogue. The hydrogenation of imines was carried out with a substrate/catalyst/base (*S*/*C*/*B*) ratio of 6410/1/30 at 348 K and 27 atm. H_2. Hydrogenation of *N*-(1-phenylethylidine) benzenamine to corresponding secondary amine has a TOF of 349 h^{-1} (entry 1, Table 4).

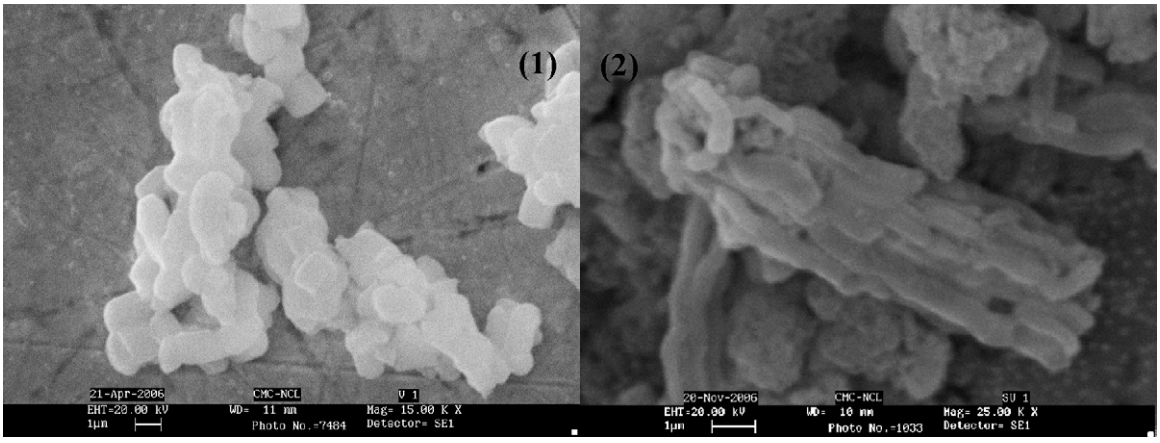
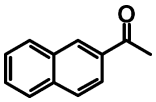
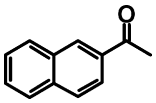
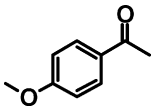
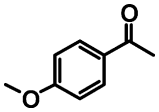
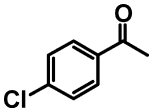
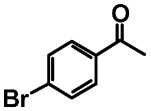
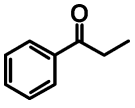
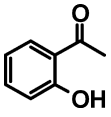
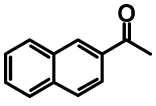


Fig. 5. SEM images of (1) SBA-15 and (2) [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15.

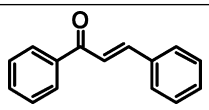
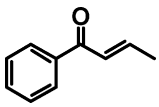
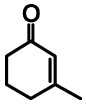
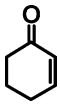
Table 2
Hydrogenation of prochiral ketones[a]

Entry	Substrate	Time (h)	Conversion (%)	ee (%)	TOF
1		24	90	76	961
2[b]		24	92	75	982
3		20	90	52	1153
4		20	82	34	1051
5		18	92	75	1310
6		20	91.5	30	1173
7		24	90	35	961
8		24	60	14	641
9[c]		36	80	74	569

[a] Reactions were carried out at 343 K and 27 atm. H_2 using 10 mmol of the prochiral ketones and a substrate/catalyst/base ratio of 25640/1/30 in 40 mL of 2-propanol.
[b] In the homogeneous condition.
[c] Reaction was carried out using MCM-41 as a support. Turnover frequency (TOF = mole of substrate converted per mole of Ru complex per hour).

Phenyl-*N*-(1-phenylethylidine)methanamine was converted to corresponding secondary amine with 97% conversion (entry 2, Table 4). The 2,5-dimethyl-*N*-(1-phenylethylidine)benzenamine showed less reactivity (entry 3, Table 4) in its hydrogenation, which may be due to steric effect caused by the adjacent methyl groups in the aniline ring. Hydrogenation of *N*-(1-*p*-tolylethylidine)benzenamine showed activity of 90% conversion (with a TOF of 288 h^{-1}) to secondary amine. Since imines are generally derived from the corresponding aldehydes or ketones, the overall reaction in one-pot constitutes a method for direct reductive amination, which would be an attractive synthetic route to secondary and tertiary amines.

Table 3
Chemoselective hydrogenation of α,β-unsaturated ketones[a]

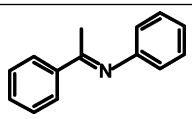
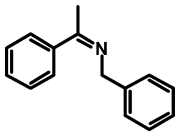
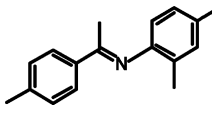
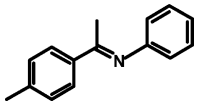
Entry	Substrate	Time (h)	Conversion (%)	Selectivity (%)	TOF
1		14	98	>99	1794
2		10	95	>99	2435
3		20	70	>90	897
4		22	100	10	1165

[a] Reactions were carried out at 343 K and 27 atm. H_2 using 10 mmol of the prochiral ketones and a substrate/catalyst/base ratio of 25640/1/30 in 40 mL of 2-propanol.

3.2.4. Catalyst recycling

An attractive feature of this catalytic system lies in the fact that the catalyst from the product can be easily removed by

Table 4
Hydrogenation of imines[a]

Entry	Substrate	Time (h)	Conversion (%)	TOF
1		18	98	349
2		20	97	311
3		24	60	160
4		20	90	288

[a] Reactions were carried out at 348 K and 27 atm. H_2 using 2.5 mmol of the substrate (imine); Substrate/catalyst/base ratio of 6410/1/30 in 20 mL of 2-propanol.

Table 5
Recyclability of the catalyst in the hydrogenation of methylnaphthalene ketone

Entry	Cycle	Time (h)	Conversion (%)	ee (%)	TOF
1	Fresh	24	90	76	961
2	First	24	90	75	961
3	Second	24	89	75	950
4	Third	24	74	69	801

Reactions were carried out at 343 K and 27 atm. H_2 using 10 mmol of the prochiral ketones and a substrate/catalyst/base ratio of 25640/1/30 in 40 mL of 2-propanol.

filtration and reused for the next cycles. Thus, when the hydrogenation was completed, the reaction mixture was filtered over a G-4 crucible; the used catalyst was thoroughly washed with 2-propanol and dried in vacuo. After this treatment, the catalyst was ready for the next cycle. For example, in each following runs, the amounts of methylnaphthylketone, 2-propanol, and base were the same as in the first run. In three consecutive runs, the following conversions (ee's in parenthesis) were observed: 90% (75%), 89% (75%), and 74% (69%) (Table 5). These data suggest that it is possible to recycle the [Ru(dach)(PPh_3)$_2$(Cl_2)]–SBA-15 catalyst.

4. Conclusions

In summary, we have synthesized easily accessible immobilized chiral 1,2-diaminocyclohexane ligand covalently anchored onto the mesopores of SBA-15. Ruthenium amine complex immobilized on SBA-15 was found to be the most active immobilized multifunctional catalyst system for the enantioselective hydrogenation of prochiral ketones and in the chemoselective hydrogenation of carbonyl group over olefin group in α,β-unsaturated ketones and in the hydrogenation of imines. The activities are comparable with that of homogeneous analogues in all the reactions studied. Most importantly this catalyst could be recyclable.

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