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Enantioselective hydrogenation of olefins by chiral iridium phosphorothioite complex covalently anchored on mesoporous silica

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Abstract

Chiral monodentate phosphorous-based ligands have proven effective for the enantioselective hydrogenation of olefins. Binol-derived monodentate phosphorothioite (PS) ligand was synthesized from binol and thiopropyltriethoxysilane, and its iridium complex was covalently anchored to mesoporous silica supports like SBA-15, MCM-41, and MCM-48. These catalysts were characterized by different physicochemical techniques and assessed for their catalytic performances in the heterogeneous asymmetric hydrogenation of itaconic acid and its derivatives. It was found that the catalytic activities and enantioselectivities of the heterogenized iridium complex (IrPSSBA-15) in the hydrogenation reactions were comparable to its homogeneous analogue. Binol-derived monodentate phosphorothioite ligand in heterogeneously anchored form (iridium complex) is a more effective catalyst than the reported monodentate phosphorous ligand systems in the hydrogenation reactions, possibly due to the changes in electronic properties around the iridium metal center. The effects of substrate-to-catalyst molar ratio, solvents, and temperature on substrate conversions and enantioselectivities of the products were investigated in hydrogenation reactions.

Keywords: Binol; Monodentate ligand; Phosphorothioite ligand; Mesoporous silica SBA-15; Immobilization; Itaconic acid; Iridium complex; Enantioselective hydrogenation

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1. Introduction

The pioneering work [1–4] at the start of this century brought about a renaissance in the use of monodentate phosphorus ligands in the asymmetric hydrogenation reactions. The development of binol-derived monodentate phosphorus ligands is a research topic of increasing interest because of their easy preparation methods, higher stabilities, and excellent activities and enantioselectivities in asymmetric catalysis [5]. Because of the high cost of chiral ligands and noble metals used in catalyst preparation, catalyst recovery becomes an important issue for the application of enantioselective catalyst in large-scale processes. In recent years, enormous progress has been made in interdisciplinary research on the development of stereoselective solid-phase catalysis for asymmetric synthesis [6]. The heterogenization of a homogeneous catalyst would provide many advantages, including easy separation, efficient recycling, minimization of metal traces in the product, and process control, which would finally reduce the overall process cost. It has been reported that heterogeneous catalysts are even more selective than their homogeneous analogues in some reactions [7,8]. Moreover, the potential of heterogeneous chiral catalysts has been reported in recent reviews [9–14]. Simons et al. have reported the successful immobilization of rhodium complex of the monodentate ligand on silica support [15,16] and used in the asymmetric hydrogenation reactions. The covalent anchoring of ligands suffers from the lengthy process involved in functionalization of ligand and effective covalent anchoring onto the support [17,18]. Although inorganic material-immobilized catalysts have some advantages, they have attracted little attention [19–21] compared with immobilized catalysts prepared from

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organic polymeric supports. The immobilized chiral transition metal catalysts prepared from inorganic materials can prevent intermolecular aggregations of the active species because of their rigid structures. These catalysts often exhibit superior thermal and mechanical stabilities, and they do not swell or dissolve in organic solvents.

Recently, an iridium complex of monodentate phosphoramidite ligand has been reported for asymmetric hydrogenation reactions in homogeneous conditions [22]. Hydrogenation products like chiral 2-substituted succinic acids have attracted much recent interest for their utility as chiral building blocks [23,24]. In this paper, we report synthesis of a binol-derived monodentate triethoxysilyl phosphorothioite PS ligand (hereafter PS) and its iridium complex covalently anchored onto high-surface area mesoporous silica supports, along with their applications in the asymmetric hydrogenation of itaconic acid and its derivatives. The effects of reaction parameters such as substrate-to-catalyst molar ratio, temperature, hydrogen pressure, catalyst concentration, and solvents on the optimum substrate conversions and product enantioselectivities in the hydrogenation of olefinic substrates are explored.

2. Experimental

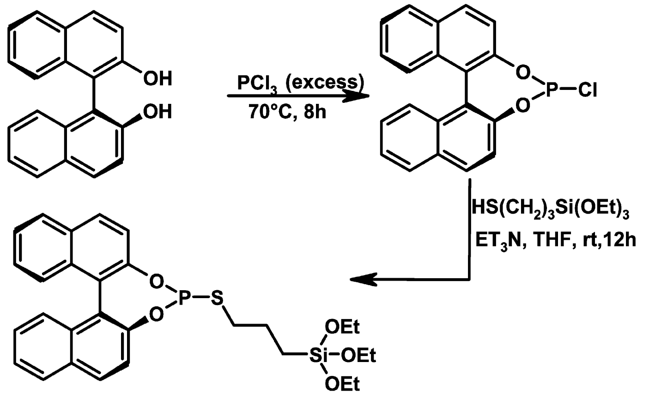
2.1. Chemicals

$[Ir(COD)Cl]_2$, S-binol, 3-thiopropyltriethoxysilane, TEOS, pluronic-123, dimethylitaconate, itaconic acid, and triethylamine were purchased from Aldrich. Diethylitaconate was prepared from itaconic acid by esterification with ethanol. Phosphorous trichloride and cetyltrimethylammonium bromide (CTAB) were procured from Loba Chemie, India and were used as received without further purification. Dichloromethane, ethyl acetate, toluene, methanol, tetrahydrofuran, and diethyl ether were purchased from Ranbaxy, India and distilled before their use following the standard procedure. For the quantitative estimation of enantiomers, the racemic products were obtained by Pd-charcoal-catalyzed reduction.

2.2. Catalyst preparation

2.2.1. Synthesis of triethoxysilyl phosphorothioite ligand (PS)

Scheme 1 depicts the synthesis of the monodentate PS ligand. S-binol (0.5 g) in 3 ml of phosphorous chloride (PCl_3) was heated under reflux for 8 h. Then excess PCl_3 was removed by evaporation under vacuum. The resultant solid was subjected to azeotropic distillation with toluene and dried under vacuum. The resulting residue was dissolved in toluene (10 ml) and added to a solution of 0.38 g (1.8 mmol) of thiopropyltriethoxysilane and 0.6 ml triethylamine in 5 ml of dry tetrahydrofuran at 0 °C. The resulting mixture was diluted with diethyl ether (12 ml), filtered over a plug of silica, and washed with 50 ml diethyl ether. The solvent was then removed under vacuum. Column chromatography on silica gave pure PS ligand. $[\alpha]_D = +57.53$ (C = 2.01, $CHCl_3$) ^1H NMR ($CDCl_3$): δ 0.64 (m, 2H), 1.25–1.33 (t, 12H), 1.65 (m, 2H), 1.93–1.97 (m, 2H), 3.40–3.52 (m, 6H), 7.08 (1H), 7.27–7.40 (m, 7H), 7.84–7.95(m, 4H) ^{31}P NMR ($CDCl_3$): δ 115. FTIR (cm^{-1}): 3059, 2942, 2839, 1460, 740, 809, 459.



PS

Scheme 1. Synthesis of the monodentate triethoxysilylphosphorothioite ligand.

2.2.2. Synthesis of homogeneous iridium complex of PS ligand (IrPS)

The homogeneous iridium phosphorothioite complex was synthesized as reported previously [22]. $[Ir(COD)Cl]_2$ (65 mg, 0.096 mmol) was placed in a 10-ml Schlenk flask, and the entire apparatus was evacuated and backfilled with N_2 three times to establish an inert atmosphere. Dry, degassed dichloromethane (1 ml) and PS ligand (100 mg, 0.192 mmol) were added, and the reaction mixture was stirred at room temperature for 10 min. The solvent was removed under vacuum to give a homogeneous IrPS complex. ^1H NMR (300 MHz, CDCl3): ^1H NMR ($CDCl_3$): δ 0.65 (m, 2H), 1.26–1.35 (t, 12H), 1.63 (m, 2H), 1.95–1.99 (m, 2H), 2.74–2.83 (m, 4H), 3.14–3.24 (m, 4H), 3.41–3.53 (m, 6H), 5.13–5.24 (m, 2H), 5.29–5.40 (m, 2H), 7.08 (1H), 7.27–7.40 (m, 7H), 7.84–7.95 (m, 4H) ^{31}P NMR ($CDCl_3$): δ 83.1. FTIR (cm^{-1}): 3059, 2942, 2839, 1460, 740, 809, 459.

2.2.3. Synthesis of siliceous support

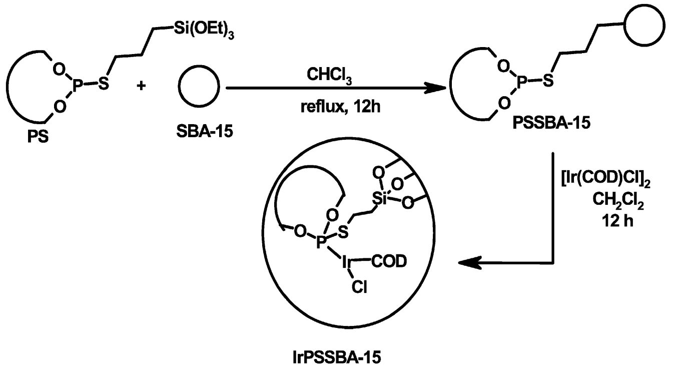
The pure siliceous supports, such as MCM-41, MCM-48, and SBA-15, were prepared as described previously [25–27].

2.2.4. Synthesis of ligand functionalized SBA-15

3 g of SBA-15 and 0.5 g of the PS ligand were mixed in 50 ml of chloroform and refluxed for 18 h (Scheme 2). The resulting material was filtered and washed with chloroform for several times and dried under vacuum at 50 °C to give ligand-functionalized SBA-15 (PSSBA-15). Ligand functionalization of MCM-41 and MCM-48 was carried out similarly to obtain PSMCM-41 and PSMCM-48, respectively.

2.2.5. Covalent anchoring of iridium complex onto ligand-modified SBA-15

$[Ir(COD)Cl]_2$ (0.05 g) dissolved in 50 ml of dichloromethane was slowly added to 3 g of the PSSBA-15, and the mixture was stirred at room temperature overnight. The resulting



Scheme 2. Covalent anchoring of the ligand onto the mesoporous silica SBA-15 support and complexation with iridium.

solid was filtered, washed repeatedly with dichloromethane, and then dried under vacuum at 40 °C to get an iridium complex covalently anchored onto SBA-15 (hereafter IrPSSBA-15). Similarly, IrPSMCM-41 and IrPSMCM-48 were prepared by following the above procedure.

2.3. Catalyst characterization

Iridium contents in the catalyst materials were estimated by inductively coupled plasma atomic emission spectrometry (ICP-AES). The elemental analysis (C and N) was carried out with Carlo Erba Instruments EA1108 elemental analyzer. The specific surface areas of the catalysts were measured by N_2 physisorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer. Samples were degassed in N_2 flow for 12 h at 100 °C before N_2 physisorption measurements. Low-angle powder XRD patterns of the samples were collected on a Philips X'Pert Pro 3040/60 diffractometer using Co$K\alpha$ radiation ($\lambda = 0.17890$ nm), an iron filter, and an X'celerator as a detector. Samples were prepared by placing the droplets of a suspension of solid in isopropanol on a polymer microgrid supported on a copper grid for TEM measurements. A ^{31}P MAS NMR spectrum of the catalyst was recorded using a Bruker DSX-300 spectrometer at 121.5 MHz with high-power decoupling using a Bruker 4-mm probe head. The spinning rate was 10 kHz, and the delay between the two pulses was varied between 1 and 30 s to ensure complete relaxation of the ^{31}P nuclei. The chemical shifts were measured taking 85% H_3PO_4 as the reference. A Shimadzu FT-IR-8201PC unit, in DRS mode, with a measurement range of 450–4000 cm^{-1}, was used to obtain the FT-IR spectra of solid samples.

2.4. Catalyst testing

In a typical reaction, olefin (10 mmol) and IrPSSBA-15 (0.20 g, 0.006 mmol of iridium) in 50 ml of dichloromethane were placed in a 300-ml Parr autoclave, which was purged with hydrogen five times and then pressurized with 20 bar H_2 and stirred at 40 °C. Samples were withdrawn at regular intervals and analyzed in a Shimadzu 14B gas chromatograph equipped with a flame ionization detector using HP-chiral capillary (30 m × 0.320 mm × 0.25 µm) column. The conversions of substrate and product enantioselectivities were estimated from gas chromatographic analysis following a standard method. After completion of the reaction, the reaction mixture was filtered to remove the catalyst, and the solvent was removed under reduced pressure. The resultant mixture was dried and purified by column chromatography on silica gel as the stationary phase (petroleum ether/ethyl acetate, 90/10). The optical rotation of products was measured using a Jasco P-1020 polarimeter; for example, dimethylmethylsuccinate: colorless liquid, enantiomeric excess was found to be 94% (GC condition: 90 °C isothermal, 60 min, minor isomer: 36.7, major isomer: 40.0) ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 3.61$ (s,1H), 3.63 (s, 1H), 2.66–2.74 (2H, m), 2.36–2.39 (1H, m), 1.13–1.17 (3H, d), GCMS m/z (relative intensity): 161 (0.05) [M^+], 129 (20.30), 100 (10.93), 87 (8.68), 69 (10.50), 59 (100), 41 (31.91), absolute configuration—R, optical rotation, $[\alpha]_D = +4.5°$, C = 3 in chloroform (literature value: $[\alpha]_D = +4.9°$, C = 2.9 in chloroform).

3. Results and discussion

Our main objective in this study was to achieve ready covalent anchoring of monodentate binol-derived ligands to mesoporous silica support through the phosphorous heteroatom in minimum number of steps. For the covalent anchoring of the phosphoramidite ligand through the nitrogen part of the ligand, the nitrogen precursor must be monoalkylated, because a secondary amine is needed as reported in literature. The monoalkylation of aminopropyltriethoxysilane was difficult, because it gave both monoalkylated and dialkylated product, making the procedure tedious. The precursor for covalent anchoring of the monodentate phosphite ligand is not readily available; we attempted it using readily available thiopropyltriethoxysilane. The use of this new ligand in covalent anchoring to the mesoporous support is reported here for the first time. The monodentate triethoxysilyl phosphorothioite ligand (PS) was easily synthesized from commercially available starting materials in few steps. The ^{1}H and ^{31}P NMR of the PS ligand confirmed the presence of the phosphorous-anchoring moiety in the ligand. The optical rotation data confirmed the retention of chirality of the ligand after functionalization with the thiopropyltriethoxysilane group. The homogeneous complex (IrPS) was synthesized from the iridium precursor, $[Ir(COD)Cl]_2$, with an iridium-to-ligand ratio of 1, as reported in case of the iridium monodentate complex [22]. Mesoporous silica supports, such as SBA-15, MCM-41, and MCM-48, were functionalized with the monodentate triethoxysilyl phosphorothioite ligand, after which complexation with iridium was carried out to obtain covalently anchored catalysts. These catalysts were characterized for their physicochemical properties by different techniques to establish their integrity and stability for use as heterogeneous catalysts in asymmetric hydrogenation reactions. The efficacies of these catalysts were assessed in the enantioselective hydrogenation of itaconic acid and its derivatives under different reaction conditions. The reaction conditions were optimized to get higher substrate conversions and enantioselectivities (ee) for products.

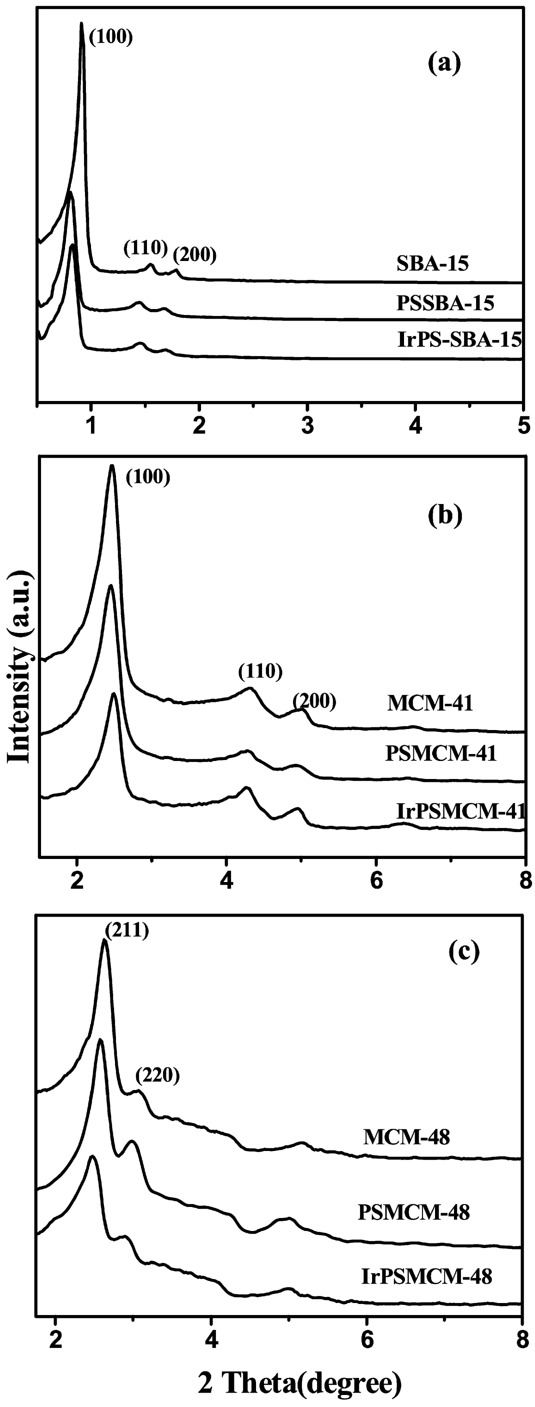


Fig. 1. Low angle powder XRD patterns of the materials (a) SBA-15, PSSBA-15, IrPSSBA-15, (b) MCM-41, PSMCM-41, IrPSMCM-41, (c) MCM-48, PSMCM-48, IrPSMCM-48.

Table 1
Physicochemical properties of the materials

No.	Catalyst	Surface area BET ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (Å)
1	MCM-41	1093	0.88	32.6
2	MCM-48	983	0.75	27
3	SBA-15	730	1.15	79
4	PSMCM-41	685	0.57	24
5	PSMCM-48	556	0.51	20
6	PSSBA-15	617	0.54	68
7	IrPSMCM-41	441	0.28	19
8	IrPSMCM-48	430	0.23	17
9	IrPSSBA-15	572	0.30	20

3.1. Catalyst characterization

3.1.1. Low-angle XRD

The powder XRD patterns of ligand-functionalized and complex immobilized supports and corresponding parent supports are shown in Fig. 1. The parent MCM-41 and SBA-15 supports exhibited three XRD peaks assigned to reflections at (100), (110), and (200), which are characteristic of 2D hexagonal lattice (Figs. 1a and 1b) and indicate a significant degree of long-range ordering in the structure. The XRD patterns of MCM-48 (Fig. 1c) showed an intense peak corresponding to the (211) reflection along with a shoulder peak at the (220) reflection, both typical of cubic cells. The phosphorothioite ligand-modified sample (PSSBA-15) showed decreased intensities of all peaks, with a marginal shift toward lower 2θ values, indicating silylation inside the mesopores of SBA-15. The peak intensities at the (100), (110), and (200) reflections of IrPSSBA-15 were further decreased, indicating immobilization of the iridium complex inside the mesoporous channels of SBA-15. But the mesoporous structure of the support remained intact under the conditions used for immobilization. Similar results were observed for MCM-41- and MCM-48-supported catalysts (Figs. 1b and 1c). These results indicate an ordered mesoporosity of the supports even after the incorporation of organic functional groups and iridium complexes.

3.1.2. N_2 sorption study

The specific surface area, pore volume, and pore diameters estimated from N_2 sorption studies of ligand-functionalized and iridium complex immobilized materials are presented in Table 1. BET surface areas and BJH pore size distributions were calculated using N_2 adsorption at −196 °C. Ligand functionalization and iridium complex immobilization affected the surface area and pore distribution of the modified samples. The samples displayed a type IV isotherm (as defined by IUPAC) with H_1 hysteresis and a sharp increase in pore volume adsorbed above a P/P_0 of 0.7 cm^3/g (Fig. 2), which is a characteristic of highly ordered mesoporous materials. The textural properties of SBA-15 were substantially maintained over ligand functionalization and on subsequent complexation of $[Ir(COD)Cl]_2$. The parent SBA-15 sample exhibited a maximum pore diameter (79 Å) and surface area (730 m^2/g), as shown in Table 1. Ligand functionalization of mesoporous silica resulted in a shift of the pore maximum to smaller diameters and a decrease in surface area (617 m^2/g). The complexation led to a further decrease in surface area and pore volume. The same trend was observed for the other two supports.

3.1.3. Microscopic analysis

SEM images of IrPSSBA-15 (Fig. 3) show that the rope-like micromorphology of SBA-15 remained intact even after functionalization with ligand and iridium complex. TEM measurements were carried out to study the morphology of the SBA-15 and IrPSSBA-15 catalysts (Fig. 4). TEM images of these catalysts showed retention of the periodic structure of the parent SBA-15 precursor, confirming that the hexagonally arranged mesopores of SBA-15 were retained after modification with ligand and iridium complex.

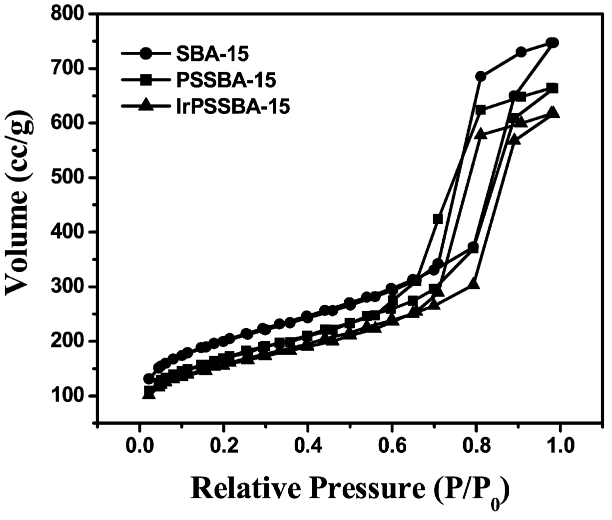


Fig. 2. Nitrogen adsorption desorption isotherms of SBA-15, PSSBA-15, IrPSSBA-15.

3.1.4. Nuclear magnetic resonance

MAS NMR is a good technique for investigating ligand functionalization and complex anchored onto the mesoporous support. Because the PSSBA-15 and IrPSSBA-15 samples contained small amounts of phosphorus, we used cross-polarization (^{1}H–^{31}P) MAS NMR to enhance the sensitivity of the ^{31}P signal. The ^{1}H–^{31}P coupled CP-MAS NMR spectra of the ligand functionalized SBA-15 (PSSBA-15) and iridium complex-anchored SBA-15 (IrPSSBA-15) are depicted in Figs. 5a and 5b, respectively. The ^{31}P peak corresponding to PSSBA-15 exhibits a marginal shift at δ 113.6 ppm, compared with that of neat ligand at δ 115 ppm, possibly due to the different ligand environments. IrPSSBA-15 exhibits a ^{31}P peak at δ 81.6 ppm, clearly indicating that the iridium complex has covalently anchored to the modified SBA-15 support, and the shift clearly confirms the presence of the iridium complex in a new environment [22].

3.1.5. FTIR

The FTIR spectra of PSSBA-15 and IrPSSBA-15 are given in Figs. 6a and 6b. SBA-15 showed characteristic FT-IR peaks at 2900–3800, 1080, and 450 cm^{-1} due to O–H of the silanols, adsorbed water molecules, and Si–O–Si stretching vibrations, respectively. PSSBA-15 showed an additional peak at 1460 cm^{-1} due to the C=C stretching of the aromatic ring and

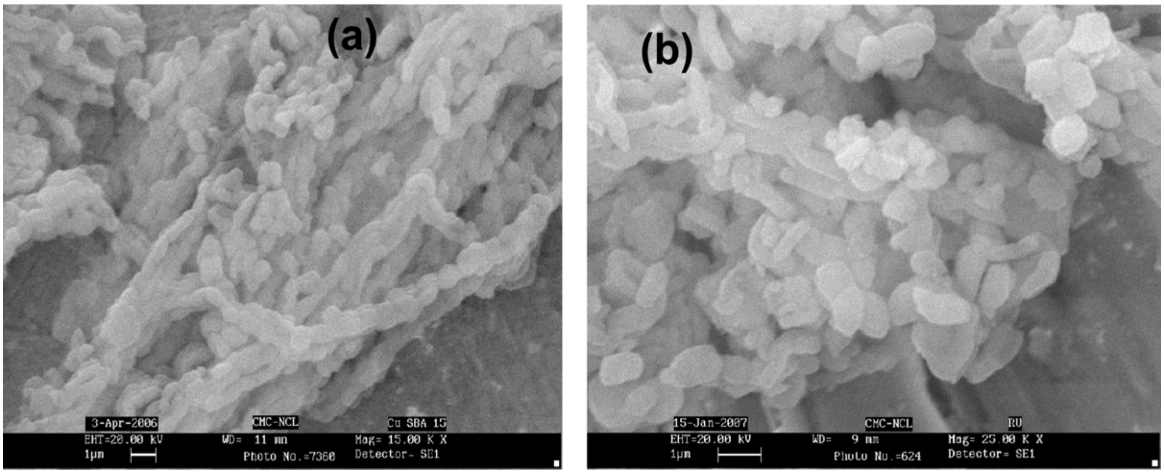


Fig. 3. SEM photographs of (a) SBA-15 and (b) IrPSSBA-15.

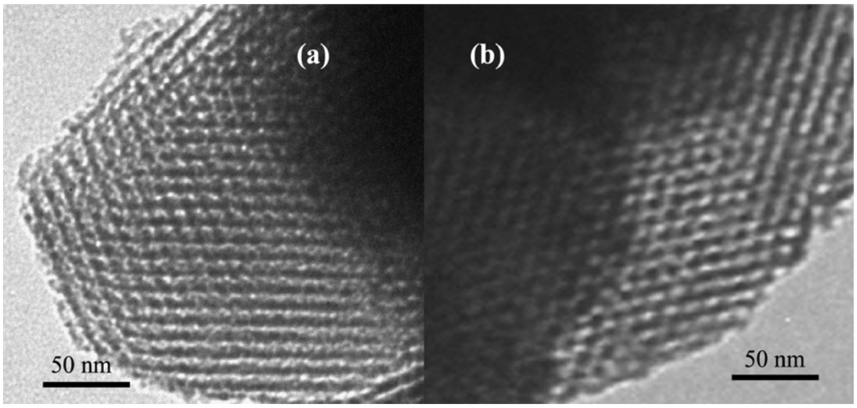


Fig. 4. TEM photographs of (a) SBA-15 and (b) IrPSSBA-15.

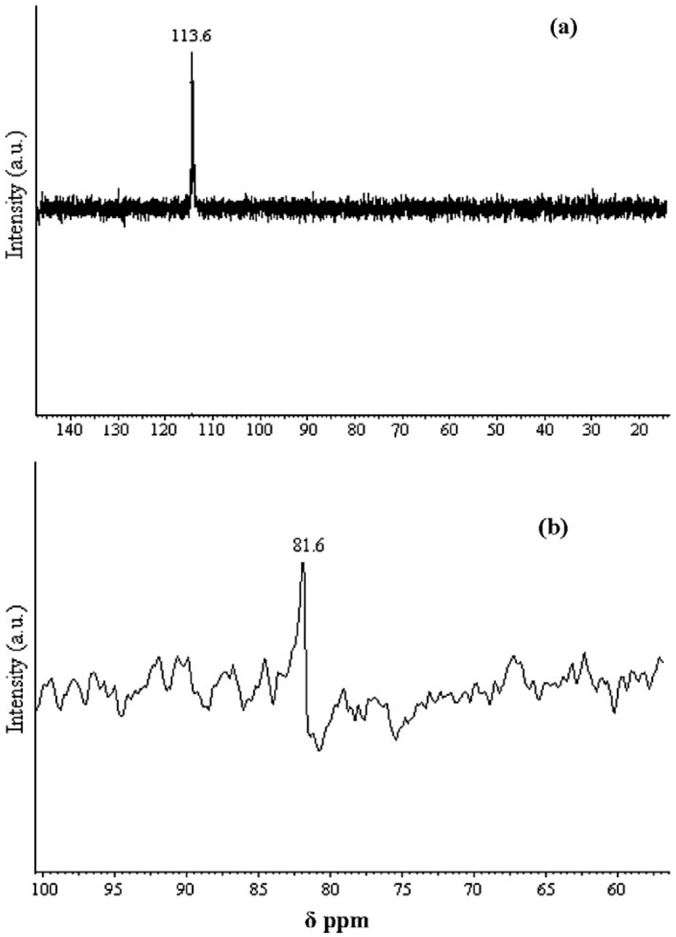


Fig. 5. ^{31}P MAS NMR spectra of (a) PSSBA-15 and (b) IrPSSBA-15.

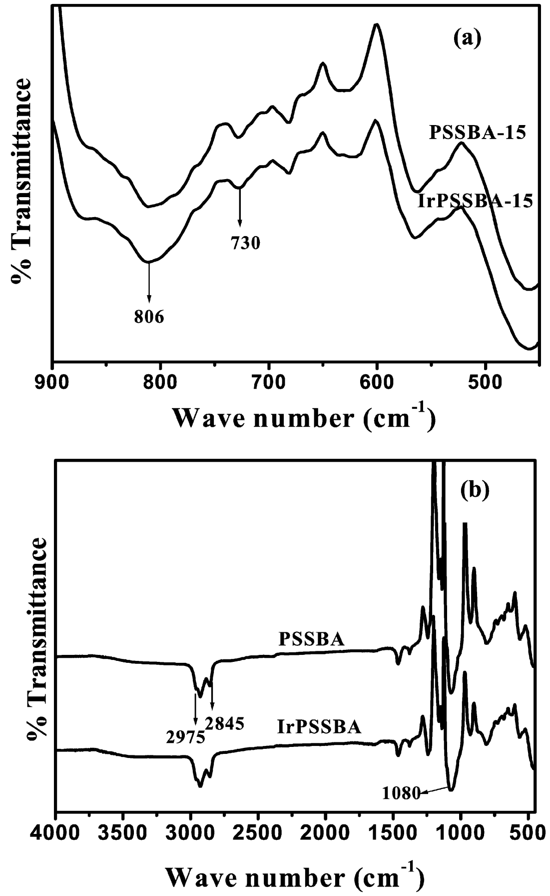


Fig. 6. FTIR spectra of PSSBA-15 and IrPSSBA-15, (a) wave number range (500–900 cm^{-1}), (b) wave number range (500–4000 cm^{-1}).

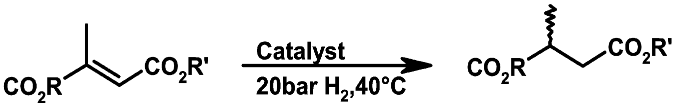
2975 and 2845 cm^{-1} due to C–H and C–C stretching modes of the propyl spacer, respectively. The bands observed in the range 730–800 cm^{-1} are due to the O–P–O stretching (Fig. 6a) and P–S stretching band (460 cm^{-1}) [28] merging with Si–O–Si stretching vibrations. Similar results were observed for the MCM-41 and MCM-48 supports. FT-IR results support the successful incorporation of the metal complex onto the surface of mesoporous silica.

3.2. *Catalytic results*

The efficiency of the three immobilized catalysts prepared was assessed in the enantioselective hydrogenation of itaconic acid and its derivatives. These results are summarized in Table 2. Dimethylitaconate was chosen as the test substrate, and the heterogeneous enantioselective liquid-phase hydrogenation was carried out with a substrate to catalyst molar ratio of 1660:1 in dichloromethane at 40 °C and 20 bar H_2. A homogeneous liquid phase reaction was also performed with neat iridium complex (IrPS) under similar conditions for comparative purpose. It was found that the activity (in terms of turnover number [TON], defined as mole of substrate converted per mole of iridium) of neat complex was twice as high as in the heterogeneous system. This could be due to a slower interaction between the substrate and the catalyst in heterogeneous triphasic gas–solid–liquid system compared with a homogeneous liquid system [29]. The results presented in Table 2 clearly demonstrate that dimethylitaconate was hydrogenated with very high conversion (up to 99%) and high product enantioselectivity (up to 94% ee), which are comparable with the homogeneous analogue (entry 2, Table 2). It has been reported that higher catalyst loadings (substrate: catalyst molar ratio = 50:1) are usually required to get higher enantioselectivity [30–32]. But, surprisingly, we have found excellent activity and enantioselectivity (ee) even with a substrate-to-catalyst molar ratio of 1660, which is nearly 30-fold higher than the reported iridium phosphoramidite complex [22] and the other rhodium monodentate phosphorous complexes. This can be attributed to an increase in electron density around the metal center [33,34]. Phosphorus-sulfur π-bond formation is less favored geometrically than phosphorus-oxygen π-bond formation [35]; thus, an increase in electron density may occur around the iridium metal center compared with the reported phosphite and phosphoramidite ligands, which favor the oxidative addition of hydrogen in the catalytic hydrogenation reaction cycle [36]. Thus, our catalyst reported here provides high enantioselectivity in asymmetric hydrogenation reactions under milder reaction conditions.

Increasing the substrate-to-catalyst molar ratio from 1660 to 3000 caused no significant decrease in the conversion of dimethylitaconate, but did produce a decrease in the enantiose-

Table 2
Asymmetric hydrogenation of Itaconic acid and its derivatives[a]



Entry	R	R	Conversion (mol%)	TON[b]	ee[c] (%)
1	Me	Me	99	1650	94
2[d]	Me	Me	99	1650	96
3[e]	H	H	98	1633	93
4	Et	Et	90	1500	91
5[f]	Me	Me	85	1416	94
6[g]	Me	Me	82	1366	94
7[h]	Me	Me	98	3005	57
8[i]	Me	Me	97	1981	73

[a] Reaction conditions: 10 mmol of the substrate, substrate to catalyst molar ratio = 1660:1, dichloromethane 50 ml, temperature 40 °C, 20 bar H_2, time 20 h;

[b] TON (turn over number) mole substrate converted per mole of Ir.

[c] % ee was calculated by GC analysis using HP-Chiral column.

[d] The reaction was carried out under homogeneous condition, which was completed within 12 h.

[e] The product was analyzed by converting the acid to the corresponding methyl ester.

[f] Using IrPSMCM-41 as catalyst.

[g] Using IrPSMCM-48 as catalyst.

[h] The substrate to catalyst molar ratio taken was 3000:1.

[i] The substrate to catalyst molar ratio taken was 2000:1.

lectivity of dimethylmethylsuccinate (Table 2, entries 7 and 8). Increasing the iridium-to-ligand molar ratio from 1:1 to 1:2 produced no significant changes in catalyst activity and selectivity in the hydrogenation of dimethylitaconate. Consequently, iridium complex with a single monodentate phosphorothioite ligand covalently anchored to mesoporous silica supports are the most active catalysts for enantioselective hydrogenation reactions—a significant and important finding of our studies.

All three siliceous mesoporous supports resulted in the same product enantioselectivity in the hydrogenation of dimethylitaconate, but with different TONs. IrPSSBA-15 proved to a more efficient catalyst (99% conversion and 1650 TON) compared with IrPSMCM-41 (conversion, 85%; TON, 1416) and IrPSMCM-48 (conversion, 82%; TON, 1366) (Table 2, entries 1, 5, and 6) in the foregoing reaction. IrPSSBA-15 was an efficient catalyst because the SBA-15 support afforded less diffusional resistance for the substrate molecules to interact with active sites of the complex in its mesoporous channels, having a larger pore diameter compared with the MCM-41 and MCM-48 supports [37,38].

Enantioselective hydrogenation of itaconic acid and diethylitaconate was carried out under similar conditions. Diethylitaconate was hydrogenated to the corresponding succinic acid derivative with 90% conversion and 91% ee (Table 2, entry 4), and, similarly, itaconic acid also was hydrogenated to the corresponding chiral product with higher conversion (98%) and optimum ee (93%) (Table 2, entry 3), indicating no significant influence of substitution over substrate molecules.

Table 3
Effect of solvent in the enantioselective hydrogenation of dimethylitaconate with IrPSSBA-15[a]

Entry	Solvent	Conversion (mol%)	TON[b]	ee[c] (%)
1	Dichloromethane	99	1650	94
2	Chloroform	99	1650	94
3	Acetone	95	1583	93
4	Ethyl acetate	99	1650	94
5	Methanol	94	1533	89
6	Toluene	25	416	–

[a] Reaction conditions: 10 mmol of the substrate, substrate to catalyst molar ratio = 1660:1, solvent 50 ml, temperature 40 °C, 20 bar H_2, time 20 h.

[b] TON (turn over number) mole substrate converted per mole of Ir.

[c] % ee was calculated by GC analysis using HP-Chiral column.

3.2.1. *Effect of solvent*

To investigate the effect of solvent on the substrate conversion and enantioselectivity, we carried out the hydrogenation of dimethylitaconate with the IrPSSBA-15 catalyst using different solvents. The results, along with the reaction conditions, are presented in Table 3. Dichloromethane, chloroform, and ethyl acetate were found to be the most effective solvent systems. The enantioselectivities varied within 1 to 2% and were excellent (up to 94%) in all the solvents studied. In protic polar solvent (methanol), a slight decrease in the product enantioselectivity was obtained, which is in consistent with previous reports [39]. The lack of activity in toluene might be due to the tendency of iridium to form stable η^6-arene complexes with aromatic compounds, as has been reported in rhodium complexes [40,41].

3.2.2. *Effect of reaction time*

The effect of reaction time over substrate conversion and enantioselectivity in the hydrogenation of dimethylitaconate is illustrated in Fig. 7. Fig. 7a shows that substrate conversion increased as a function of time for all of the catalysts, reaching optimum conversion in 20 h for IrPSSBA-15 (>99%), followed by the others. However, the ee values reached maximum from the very beginning of the reactions shown in Fig. 7b. No significant effect of reaction time on the product ee was seen; a maximum ee around 90% was obtained after 1 h of reaction with all three catalysts.

3.2.3. *Effect of temperature*

We used the various catalysts to study the effect of temperature (range, 30–50 °C) in the hydrogenation of dimethylitaconate. The results indicate that a critical temperature of 40 °C is required to acquire the activation energy for hydrogenation for the three immobilized catalyst systems. At this temperature, the maximum conversion of dimethylitaconate (up to 94%) was obtained by all of the catalyst systems under the reaction conditions studied. Raising the temperature above 40 °C produced no further change in substrate conversion for all the catalysts, as shown in Fig. 8a. Temperature did not affect the product ee; however, a slight decrease in enantioselectivity was observed with a temperature increase from 40 to 50 °C (Fig. 8b) under the reaction conditions specified here.

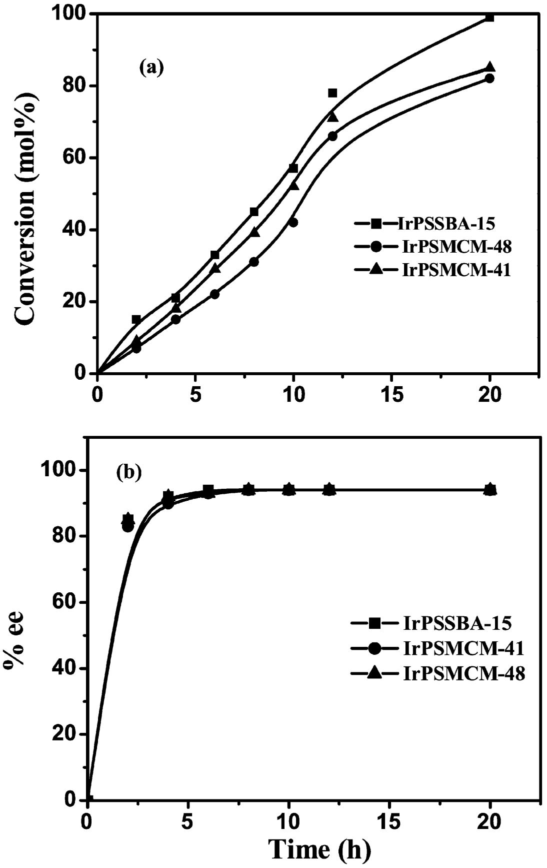


Fig. 7. Effect of reaction time (a) conversion of dimethylitaconate and (b) enantiomeric excess of dimethylmethylsuccinate. Reaction conditions: 10 mmol of the substrate, substrate to catalyst molar ratio = 1660:1, dichloromethane 50 ml, temperature 40 °C, 20 bar H_2.

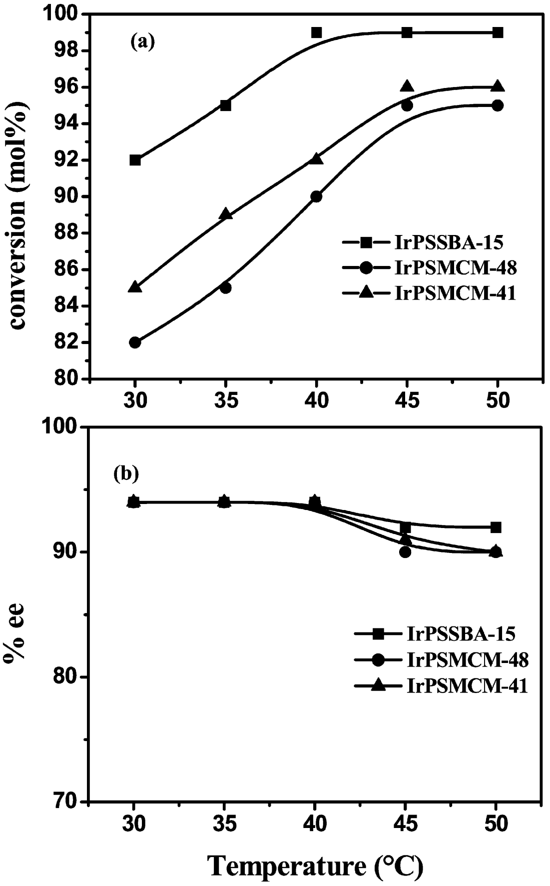


Fig. 8. Effect of reaction temperature (a) conversion of dimethylitaconate and (b) enantiomeric excess of dimethylmethylsuccinate. Reaction conditions: 10 mmol of the substrate, substrate to catalyst molar ratio = 1660:1, dichloromethane 50 ml, 20 bar H_2, time 20 h.

3.2.4. *Effect of hydrogen pressure*

The hydrogen pressure inside the reaction vessel had a pronounced effect on substrate conversion in the hydrogenation of dimethylitaconate, as shown in Fig. 9a. But the enantioselectivity of the heterogeneous catalyst did not significantly depend on a hydrogen pressure >10 bar, as shown in Fig. 9b. As shown in Fig. 9a, the conversion of dimethylitaconate increased markedly with increasing hydrogen pressure. The maximum substrate conversion and ee were achieved at 20 bar hydrogen pressure, beyond which no further enhancement in the conversion or ee was achieved.

3.2.5. *Catalyst stability*

To investigate whether any active species of the catalyst were leaching into the reaction medium, we carried out hydrogenation of dimethylitaconate to give dimethylmethylsuccinate under selected conditions with the IrPSSBA-15 catalyst. The reaction was stopped after 2 h, after which the autoclave was cooled to room temperature and conversion of dimethylitaconate was estimated. Then the catalyst was separated by filtration, the filtrate was added to the vessel, and the reaction was continued with fresh hydrogen pressure (20 bar) for another 20 h. No increase in substrate conversion was observed; it remained the same as was estimated in the presence of the catalyst. This observation confirms the complete absence of leaching of any active species of the catalyst into the reaction mixture; the catalyst truly acted as if it were heterogeneous.

We evaluated the recyclability of the IrPSSBA-15 catalyst in the hydrogenation of dimethylitaconate in five runs; the results are presented in Table 4. After each run, the catalyst (orange-colored) was washed repeatedly with dichloromethane, dried under vacuum at 70 °C for 2 h, and then used in the hydrogenation reaction with a fresh reaction mixture. Dimethylitaconate conversion was practically the same (99%) in all five cycles, with a marginal decrease at the fourth and fifth cycles with no change in the enantioselectivity of the product (94%). Thus, by recycling the immobilized catalyst five times, the substrate-to-catalyst ratio (s/c) of the whole reaction was increased to 8300, with the activity remaining the same with an enantioselectivity $>94\%$. In comparison, a homogeneous reaction at s/c 8300 gave lower enantioselectivity (49%). This finding demonstrates the successful immobilization of the iridium complex onto the support.

4. Conclusion

We have demonstrated a new, effective class of heterogeneous catalyst through synthesis of monodentate phosphorothioite iridium complex covalently anchored to mesoporous silica

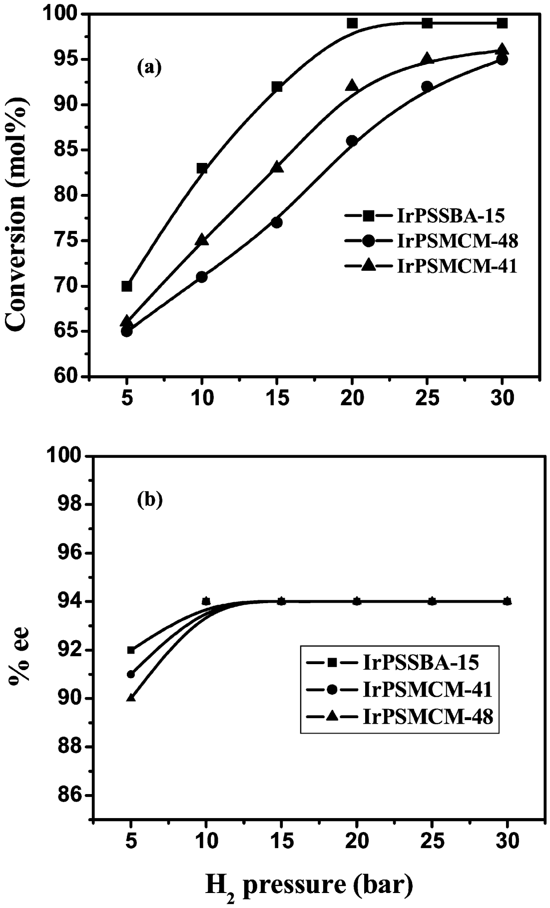


Fig. 9. Effect of H_2 pressure (a) conversion of dimethylitaconate and (b) enantiomeric excess of dimethylmethylsuccinate. Reaction conditions: 10 mmol of the substrate, substrate to catalyst molar ratio = 1660:1, dichloromethane 50 ml, temperature 40 °C, time 20 h.

Table 4
Recyclability of IrPSSBA-15 in the enantioselective hydrogenation of dimethylitaconate[a]

Entry	Cycle	Conversion (mol%)	ee[b] (%)
1	Fresh	99	94
2	1st	99	94
3	2nd	99	94
4	3rd	99	94
5	4th	97	94
6	5th	96	94

[a] Reaction conditions: 10 mmol of the substrate, substrate to catalyst molar ratio = 1660:1, dichloromethane 50 ml, temperature 40 °C, 20 bar H_2, time 20 h, after each cycle the catalyst was filtered and washed repeatedly with dichloromethane, dried under vacuum and used in the next cycle.

[b] % ee was calculated by GC analysis using HP-Chiral column.

from inexpensive S-binol in fewer steps. Catalyst diagnosis demonstrated the successful incorporation of ligand and metal complex onto the mesoporous silica. Among the catalysts investigated, iridium complex immobilized over SBA-15 (IrPSSBA-15) was found to be the ideal heterogeneous catalyst system for the enantioselective hydrogenation of itaconic acid derivatives. High conversions (99%) and excellent enantioselectivities (up to 94% ee) were observed under milder reaction conditions with a substrate-to-catalyst ratio 30 times higher than that used in the previously reported monodentate ligand-based catalytic systems. The catalyst was reused at least five times, and maintained the same activity and selectivity. Thus, we consider this protocol to be a readily accessible pathway to highly enantioselective immobilized hydrogenation catalysts.

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