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Highly efficient solid catalysts for asymmetric hydrogenation fabricated via facile adsorption of Rh-MonoPhos on porous silicas

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Via a very simple and facile adsorption, Rh-MonoPhos was successfully immobilized on mesoporous silicas with channel-like and cage-like pores. The resulting solid catalyst showed higher activity (TOF 4800 vs 936 h⁻¹) and enantioselectivity (96.0% vs 94% ee) than its homogeneous counterpart in the asymmetric hydrogenation of itaconic acid dimethyl ester under similar conditions, probably due to the high dispersion of Rh-MonoPhos on mesoporous silicas. Significant rate enhancement was observed while Rh-MonoPhos immobilized on mesoporous silicas with cage-like pores in comparison with channel-like pores, reflecting that cage-like pores could facilitate the mass transport. The solid catalyst could be recycled for several times without obvious decrease in both activity and enantioselectivity.

Introduction

Asymmetric hydrogenation of prochiral olefins is an important methodology for the production of optically active molecules which could be used as intermediates for pharmaceuticals and agrochemicals. Among various chiral transition metal complexes developed for asymmetric hydrogenation of olefins, the chiral catalysts based on Binol-derived monodentate phosphorus ligands such as phosphoramidites (MonoPhos), phosphites and phosphonites have attracted much attention because of their easy preparation, high stability and efficiency. Considering the high cost of chiral ligands and noble metals for the catalyst preparation and the difficulty in purification of the product, the immobilization of chiral catalyst on solid supports becomes an important issue for practical applications because of the advantages of heterogeneous asymmetric catalysis, such as easy purification of the product, recovering and recycling of the catalyst.

So far, several strategies have been developed for the immobilization of Binol-derived monodentate phosphorus ligand based metal complex catalysts, such as covalent tethering, electrostatic interactions, self-supported strategy and so on. Sheldon and co-workers reported the immobilization of Rh-MonoPhos ([([MonoPhos]Rh(cod)]) on a Bemsted acidic aluminosilicate support (AiTUD-I) by ionic interactions and the resulting heterogeneous catalyst showed excellent enantioselectivity and activity in the asymmetric hydrogenation of methyl-2-acetamidoacrylate. Ding and co-workers demonstrated successful immobilization of Rh-MonoPhos via a self-supported strategy for enantioselective hydrogenations of α-dehydroamino acid and enamide derivatives. Halligudi and co-workers described a covalent anchoring of chiral iridium phosphorothioite complex on mesoporous silicas. Although the methods mentioned above are efficient, these strategies often involve multiple steps of synthesis and modification of the parent catalyst or the support, consequently making them less accessible for general use.

Comparing the strategies above, the adsorption method is the most facile. However, it generally faces the problem of catalyst leaching during the catalytic process. For improving the stability of the immobilized catalysts, the interaction strength between the molecular catalysts and supports should be enhanced and a solvent that is immiscible with the molecular catalyst should be chosen. Recently, Yang and co-workers reported the synthesis of solid catalysts for olefin metathesis by adsorption of the second generation Hoveyda-Grubbs catalyst on mesoporous silicas. They found that the solid catalyst could be stably recycled using hexane as solvent due to the fact that Hoveyda-Grubbs catalyst has low solubility in hexane.

Inspired by this work, we herein report the fabrication of highly efficient solid catalysts for asymmetric hydrogenation via facile adsorption of Rh-MonoPhos catalyst on porous silica supports considering the high affinity of silica towards the metal complex catalyst and the low solubility of Rh-MonoPhos in hexane. By using hexane as solvent, the prepared solid catalysts exhibit high activity, enantioselectivity and reusability in the asymmetric hydrogenation of itaconic acid dimethyl ester. Moreover, the influence of mesostructure of the mesoporous silicas on the catalytic performance of immobilized Rh-MonoPhos was investigated.

Experimental

Chemicals and materials

All chemicals were used as received unless otherwise stated. Pluronic P123 copolymer (EO₉₀PO₇₀EO₉₀), pluronic F127 (EO₆₀PO₇₀EO₆₀) and itaconic acid dimethyl ester were purchased from Sigma Aldrich. Tetraethylorthosilicate (TEOs,
Anhydrous dichloromethane and hexane were purchased from Beijing InnoChem Science and Technology Company. Metal precursor bis(norbordanediene)rhodium(I) tetrafluoroborate and silica gel (BET surface area 85–115 m²/g) was purchased from Alfa Aesar. The ligand monodentate phosphoramidite (MonoPhos) was synthesized according to the literature method. SBA-15 and FDU-12 were synthesized according to the reported method.

**Preparation of the solid catalysts**

1.0 g of silica based support (evacuated at 120 °C for 3 h) was dispersed in 6 ml of anhydrous CH₂Cl₂ containing Rh-MonoPhos (M/L=1/2, bis(norbordanediene)rhodium(I) tetrafluoroborate as metal precursor) catalyst (0.05 or 0.10 or 0.15 or 0.20 mmol).

After stirring at 40 °C for 6 h under Ar atmosphere, the solvent was volatilized slowly, and the resulted solid was dried under vacuum. The obtained pale yellow solid catalysts are designated as Rh-MonoPhos/X, where X refers as the type of silica based support. For example, Rh-MonoPhos/SiO₂ and Rh-MonoPhos/SBA-15, were synthesized using SiO₂ and SBA-15 as support, respectively.

**Characterization**

Nitrogen physical adsorption measurement was carried out on a Micrometritics ASAP2020 volumetric adsorption analyzer. Before taking the measurements, the samples were out gassed at 393 K for 5 h. The BET surface area was evaluated from the data in the relative pressure range P/P₀ of 0.05 to 0.25. The total pore volume was estimated from the amount adsorbed at the P/P₀ value of 0.99. The pore diameter was determined from the adsorption branch by the BJH method. UV-Vis spectra were recorded on a SHIMADZU UV-vis spectrophotometer. Diffuse-reflectance UV-Vis spectra were also recorded on the SHIMADZU UV-vis spectrophotometer using BaSO₄ as the reference. XRD patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system by using CuKα radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MK2 system, using aluminium Kα X-ray source at 250 W and 12.5 kV. The bonding energies were calibrated by using the contaminant carbon (C₁s=284.6 ev) as a reference. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV.

**General procedure for the asymmetric hydrogenation reaction**

Anhydrous hexane (5 ml) and itaconic acid dimethyl ester (0.5 mmol, 79 mg) were added to a test tube containing desired amount of Rh-MonoPhos/X (2.5 umol Rh, 50, 25, 17 or 12.5 mg) under nitrogen. The test tube was transferred into a stainless steel autoclave and sealed. After purging with H₂ for several times, the pressure was adjusted to 5 bar and left to stir at 25 °C in a constant temperature bath. After reaction, H₂ pressure was released and the solid chiral catalyst was separated with centrifugation. The conversion and enantiomeric excess were analyzed by chiral gas chromatography using a Supelco γ-DEX 225 capillary column (30 m × 0.25 mm × 0.25 mm). For the catalyst recycling, the solid chiral catalyst obtained after centrifugation (in a glovebox under N₂) was used directly for the next catalytic reaction.

**Results and discussion**

**Synthesis and characterization of the solid chiral catalysts**

Silica based porous materials with different porous structures, such as silica gel, SBA-15 with channel-like pores and FDU-12 with cage-like pores, were used as support materials for the immobilization of Rh-MonoPhos. During the immobilization process, the ligand/Rh molar ratio was kept at 2 based on the previous findings that this ratio exhibits better activity and enantioselectivity for monodentate phosphorus ligand based catalysts in the asymmetric hydrogenation. Rh-MonoPhos was immobilized onto solid support via a facile adsorption method.

As shown in Fig. 1, the XRD pattern of parent SBA-15 exhibits three diffraction peaks assigned to (100), (110), and (200), which are characteristics of mesoporous materials with 2-D hexagonal mesostructure. The XRD pattern of FDU-12 shows an intense peak corresponding to (111) reflection along with a shoulder peak assigned to (311) reflection, showing FDU-12 has cubic Fm3m symmetry. The XRD characterizations suggest that mesoporous silicas with SBA-15 and FDU-12 porous structure have been successfully synthesized. After immobilization of Rh-MonoPhos, the obtained solid catalysts show similar reflection patterns to their corresponding silica supports, indicating that the periodic mesopore structure is retained after including the molecular catalysts.

**Table 1. Textural parameters of the porous silica supports and solid chiral catalysts**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Materials</th>
<th>Rh content (mmol/g)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh-MonoPhos/SiO₂</td>
<td>0.05</td>
<td>70 (85-115)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>Rh-MonoPhos/SBA-15</td>
<td>0.05</td>
<td>440 (672)</td>
<td>0.69 (1.24)</td>
<td>7.3 (7.5)</td>
</tr>
<tr>
<td>3</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.05</td>
<td>260 (580)</td>
<td>0.40 (0.67)</td>
<td>16.0 (16.6)</td>
</tr>
<tr>
<td>4</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.10</td>
<td>158</td>
<td>0.26</td>
<td>20.0</td>
</tr>
<tr>
<td>5</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.15</td>
<td>133</td>
<td>0.20</td>
<td>20.4</td>
</tr>
<tr>
<td>6</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.20</td>
<td>38</td>
<td>0.07</td>
<td>20.1</td>
</tr>
</tbody>
</table>

* Data in the parenthesis refer to the parent porous silica supports. * BET surface area. * Single point pore volume calculated at relative pressure P/P₀ of 0.99. * BJH method from adsorption branch. * Textural parameters of their parent silica supports are same with entry 3.

The textural parameters of porous silica supports and solid chiral catalysts are summarized in Table 1. All mesoporous silica...
supports have high specific surface area, large pore volume and pore diameter, which might be beneficial for the dispersion of the immobilized molecular catalyst and the fast diffusion of the substrates and products during the catalytic process. After immobilization of Rh-MonoPhos, the BET surface area and pore volume decrease obviously, probably due to the pore occupation by Rh-MonoPhos. This suggests that Rh-MonoPhos catalysts are mainly dispersed in the nanopore of porous silica supports. The solid chiral catalysts exhibit similar adsorption isotherm curves and hysteresis loops with their parent supports, showing that the porous structure does not change after Rh-MonoPhos immobilization. This was also confirmed by the XRD results. Using FDU-12 as model support, the content of Rh-MonoPhos could be controlled in the range of 0.05 to 0.20 mmol/g by varying the concentration of Rh-MonoPhos during the adsorption process. As the content of Rh-MonoPhos increases from 0.05 to 0.20 mmol/g, the BET surface area and pore volume of the solid chiral catalysts decrease sharply from 266 to 38 m²/g and from 0.40 to 0.07 cm³/g, respectively.

To further investigate the electronic state of the catalytic center rhodium, X-ray photoelectron spectroscopy (XPS) of the homogeneous and heterogeneous catalysts (Rh-MonoPhos/FDU-12 as model) were performed and the results are shown in Fig. 3. In comparison with that of Rh-MonoPhos, the Rh3d5/2 bonding energy of Rh-MonoPhos/FDU-12 presents a slight deviation (307.9 eV versus 308.1 eV). This slightly deviation might further demonstrate the weak interaction between the catalyst and the support.

In order to investigate the dispersing degree of Rh-MonoPhos on silica supports, we treated Rh-MonoPhos/FDU-12 at 300 °C under air and then at 400 °C under H₂. Through the above treatment, Rh-MonoPhos should be converted into Rh nanoparticles. The TEM characterization shows that Rh nanoparticles with particle size of 4 nm are dispersed uniformly throughout FDU-12, further demonstrating that most of the molecular catalysts Rh-MonoPhos are distributed in the nanopores of FDU-12.

The catalytic performance of the solid chiral catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Rh content (mmol/g)</th>
<th>Reaction time (min)</th>
<th>Conv. (%)</th>
<th>Ee (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh-MonoPhos</td>
<td>--</td>
<td>15</td>
<td>&gt;99</td>
<td>91</td>
<td>1260</td>
</tr>
<tr>
<td>2</td>
<td>Rh-MonoPhos</td>
<td>--</td>
<td>15</td>
<td>50</td>
<td>94</td>
<td>956</td>
</tr>
<tr>
<td>3</td>
<td>Rh-MonoPhos/SiO₂</td>
<td>0.05</td>
<td>15</td>
<td>79</td>
<td>93</td>
<td>2400</td>
</tr>
<tr>
<td>4</td>
<td>Rh-MonoPhos/SBA-15</td>
<td>0.05</td>
<td>15</td>
<td>&gt;99</td>
<td>93</td>
<td>3240</td>
</tr>
<tr>
<td>5</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.05</td>
<td>10</td>
<td>&gt;99</td>
<td>96</td>
<td>4800</td>
</tr>
<tr>
<td>6</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.10</td>
<td>10</td>
<td>&gt;99</td>
<td>96</td>
<td>4250</td>
</tr>
<tr>
<td>7</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.15</td>
<td>10</td>
<td>98</td>
<td>95</td>
<td>3360</td>
</tr>
<tr>
<td>8</td>
<td>Rh-MonoPhos/FDU-12</td>
<td>0.20</td>
<td>10</td>
<td>80</td>
<td>94</td>
<td>2830</td>
</tr>
</tbody>
</table>

* Reaction conditions: S/C=200, 5 bar H₂, 5 ml hexane, [S]=0.1 M, 0.5 mmol substrate, 25 °C. Dichloromethane as solvent. Analysis by GC. Calculated with the conversion at 1 min.

The catalytic performance of the solid catalysts is investigated in the asymmetric hydrogenation of itaconic acid dimethyl ester (Table 2). Hexane is chosen as solvent because of its poor solubility toward the metal complex which will be favourable to avoid leaching of Rh from the solid material during the catalytic process. All the solid catalysts could catalyze the reaction to the desired product with high activity and enantioselectivity (>93% ee). For example, Rh-MonoPhos/silica gel and Rh-MonoPhos/SBA-15 could afford 79% and >99% conversion within 15 min, respectively (entries 3–4). Rh-MonoPhos/FDU-12 demonstrates high activity and enantioselectivity in the asymmetric hydrogenation of itaconic acid dimethyl ester.
MonoPhos/FSU-12 exhibits the highest activity and enantioselectivity with >99% conversion within only 10 min (entry 5). In comparison, only 50% conversion is obtained on Rh-MonoPhos under identical conditions (entry 2). The TOF of the supported Rh-MonoPhos varies in the range of 2400 to 4800 h⁻¹, and the TOF of Rh-MonoPhos is only 936 and 1260 h⁻¹ respectively in hexane and CH₂Cl₂. The high catalytic activity of the supported solid catalysts might be related to their high surface area and pore volume which is beneficial for the dispersing of the catalyst and the transportation of the substrate.

The porous structure of the silica supports has significant influence on the activity of supported Rh-MonoPhos. The TOF of the solid catalysts decreases in the order of Rh-MonoPhos/FSU-12 > Rh-MonoPhos/SBA-15 > Rh-MonoPhos/silica gel. The low activity of Rh-MonoPhos/silica gel is due to the low surface area and disordered pore structure of silica gel. Notably, Rh-MonoPhos/FSU-12 shows higher activity than Rh-MonoPhos/SBA-15 in spite that the latter possesses higher BET surface area (440 m²/g vs 266 m²/g) and larger pore volume (0.69 cm³/g vs 0.40 cm³/g). This suggests that the interconnected cage-like pore structure of FSU-12 should be more favorable for the catalyst dispersing and mass transport in comparison to SBA-15 with channel-like porous structure. The above results indicate that ordered mesoporous structure and interconnected cage-like pores will benefit the high catalytic performance of immobilized Rh-MonoPhos.

The influence of Rh loading on the catalytic performance of Rh-MonoPhos/FSU-12 is also investigated (entries 5-8). Increasing the catalyst loading from 0.05 to 0.20 mmol/g, the activity of Rh-MonoPhos/FSU-12 decreases significantly (TOF from 4800 h⁻¹ to 2830 h⁻¹) while the enantioselectivity increases slightly (from 94% ee and 96% ee). The low activity at high catalyst loading might be due to the low surface area and pore volume which would cause a decreased diffusion rate of reactants and products during the catalytic process.

**Fig. 5** Kinetic plots of asymmetric hydrogenation of itaconic acid dimethyl ester on the solid catalyst Rh-MonoPhos/FSU-12 (0.05 mmol/g).

Rh-MonoPhos/FSU-12 (Rh content of 0.05 mmol/g) could smoothly catalyze the reaction and the reaction kinetic is shown in Fig. 5. As the reaction time increases, the conversion of itaconic acid dimethyl ester greatly increases. To exclude the conversion contribution from the leached Rhodium in the solution, the reaction is stopped after 40% consumption of the reactant and the filtrate is immediately isolated through a rapid centrifugation. The filtrate is continuously stirred under the same reaction conditions, and no increasing of the conversion is found. These results confirm that the catalytic activity is truly contributed by the solid catalyst instead of the leached Rh complex in the filtrate.

**Fig. 6** Recycling results of Rh-MonoPhos/FSU-12 (Rh content of 0.05 mmol/g) in asymmetric hydrogenation of itaconic acid dimethyl ester. Reaction time for the cycle 1, 2, 3 and 4 is 15, 15, 30 and 30 min, respectively.

The stability of the solid catalyst is investigated using Rh-MonoPhos/FSU-12 as a model catalyst in the asymmetric hydrogenation of itaconic acid dimethyl ester. The solid catalyst can be easily recovered via simple centrifugation and no obvious loss of catalytic activity is found for the first three cycles of reaction. For the fourth cycle, the conversion on Rh-MonoPhos/FSU-12 decreases to 82% while the enantioselectivity remains almost unchanged.

**Conclusions**

Via a simple adsorption procedure, the metal complex catalyst Rh-MonoPhos is successfully immobilized on several silica materials, leading to efficient solid catalysts of asymmetric hydrogenation. The activity of the solid catalysts can be enhanced significantly via mesopore introduction. It was found that mesoporous silicas with cage-like pores benefit the high activity of the immobilized Rh-MonoPhos. The obtained solid catalyst can be recycled for several times and maintains almost the same activity and enantioselectivity. This immobilization strategy for metal complex catalysts may be applicable to other catalytic systems too.

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**Notes and references**

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Via a facile adsorption strategy, highly efficient solid catalysts for asymmetric hydrogenation of itaconic acid dimethyl ester were fabricated.

\[ \text{Rh-MonoPhos/FDU-12} \quad \text{TOF} \ 4800 \ h^{-1}, \ 96.0 \ % \ ee. \]