Enantioselective Addition of Malonates and β-Keto Esters to Nitroalkenes over an Organonickel-Functionalized Periodic Mesoporous Organosilica

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periodic Abstract: A mesoporous organosilica (PMO) with chiral cyclohexyldiamine-based nickel(II) complexes incorporated within the silica framework was prepared through a co-condensation of (1R,2R)-cyclohexyldiamine-derived silane and Phbridged silane followed by complexation of nickel(II) bromide in the presence of (1R, 2R)-N, N'-dibenzylcyclohexyldiamine. Structural analyses by X-ray powder diffraction, nitrogen sorption and transmission electron microscopy disclosed its orderly mesostructure while characterization by solid-state NMR and X-ray photoelectron spectroscopy demonstrated the well-defined single-site chiral bis(cyclohexyldiamine)-based nickel(II) active centers incorporated

Introduction

Periodic mesoporous organosilicas (PMOs) with a chiral moiety bridged within the silica framework for asymmetric catalysis have attracted a great deal of interest due to their relatively large surface area and pore volume, orderly pore arrangement and salient surface chemistry.^[1] Large surface area and pore volume can enhance effectively the loadings and the dispersibility of chiral metal complexes while tuneable pore dimensions and well-defined pore arrangement are beneficial to control the chiral microenvironment of catalytic active centers, exhibiting a superiority in stereocontrol performance. More importantly, relative to inorganosilica-supported catalysts, periodic mesoporous organosilicas with organic functionality embedded within the silica framework possess an obvious hydrophobicity that can promote significantly the reaction rate of organic reactions, presenting a high efficiency in catalytic performance. In addition, they

within the PMO material. In particular, as a heterogeneous chiral catalyst, this periodic mesoporous organosilica showed high catalytic activity and excellent enantioselectivity in asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes (more than 92% conversions and up to 99% *ee* values). More importantly, this heterogeneous catalyst could be recovered easily and reused repeatedly nine times without obviously affecting its *ee* value, showing good potential for industrial applications.

Keywords: asymmetric catalysis; heterogeneous catalysis; immobilization; mesoporous materials; Michael addition

also exhibit superior thermal and mechanical stability relative to polymer-supported catalysts, showing a potential application in industry. Up to now, although lots of periodic mesoporous organosilicas containing alkyl and aryl groups have been reported^[2] and some periodic mesoporous organometalsilicas with incorporated chiral functionality within silica framework have been explored,^[1,3] however, to the best of our knowledge, most of them still suffer from lower catalytic activities and enantioselectivities than the respective homogeneous catalysts. Main problems are attributed to mismatched hydrophobicity/hydrophilicity of the heterogeneous catalyst, complicated compatibility of functionalities and an undesired chiral microenvironment of active centers, which will inevitably decrease catalytic activity and enantioselectivity. Thus, exploiting a suitable periodic mesoporous organosilica to adjust its hydrophobicity, to optimize its compatibility and to control its chiral microenvironment plays an

important role in the design of PMO-supported chiral catalysts.

Chiral bis(cyclohexyldiamine)-based Ni(II) complexes are one type of highly effective catalysts for asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes,^[4] in which chiral products as useful chiral building blocks are used extensively to generate chiral amino acids and five-membered nitrogen heterocycles.^[5] More importantly, the investigation of the catalytic mechanism discloses that singlesite bis(cyclohexyldiamine)-based Ni(II) active species play an exclusive role in this asymmetric addition reaction, which is beneficial to eliminate unexpected disturbance in a heterogeneous catalysis system. Based on the high catalytic efficiency and exclusive function of bis(cyclohexyldiamine)-based Ni(II) active species, making use of the hydrophobicity of PMO materials, it is reasonable to expect that immobilization of chiral bis(cyclohexyldiamine)-based Ni(II) complexes within periodic mesoporous organosilicas will exhibit high catalytic efficiency and desired enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes.

We are interested in mesoporous silica-supported heterogeneous catalysts,^[6] especially, a series of mesoporous inorganosilica-supported chiral Ru, Rh and Ir catalysts have shown high catalytic activity and enantioselectivity in asymmetric transfer hydrogenation of ketones.^[7] As an extension of our previous studies, we herein immobilized successfully chiral bis(cyclohexyldiamine)-based Ni(II) complexes within the phenylbridged periodic mesoporous organosilica and prepared a PMO-supported chiral Ni(II) catalyst, which showed high catalytic activity and excellent enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes. Meanwhile, a comparison of mono(cyclohexyldiamine)-based Ni(II) heterogeneous catalysts and an investigation of reusability of bis(cyclohexyldiamine)-based Ni(II) heterogeneous catalyst are also discussed in detail.

Results and Discussion

Synthesis and Characterization of the Catalyst

chiral bis(cyclohexyldiamine)-based phenyl-The bridged heterogeneous Ni(II) catalyst, abbreviated as DACH-Ni-PMO (5) [DACH = (1R, 2R) - 1, 2-diaminocyclohexane], was prepared as outlined in Scheme 1. Firstly, the (1R,2R)-DACH-functionalized PMO (3) was synthesized by the co-condensation of (1R, 2R)-DACH-derived silane $(1)^{[3c]}$ and Ph-bridged silane (2)P123 $\{(CH_2-CH_2O)_{20}[CH_2]$ using pluronic $(CH_3)CH_2O_{70}(CH_2CH_2O_{20})$ as a structure-directing agent according to our previous reports (see Experimental Section).^[6c] The raw catalyst was then obtained by direct complexation of 3 with 0.93 equivalents of NiBr₂ in the presence of 0.93 equivalents of (1R,2R)-N,N'-dibenzylcyclohexyldiamine (4). Finally, Soxhlet extraction of the raw catalyst under reflux conditions in toluene afforded pure catalyst DACH-Ni-PMO (5) in the form of a pale powder. The inductively coupled plasma (ICP) optical emission spectrometer analysis showed that the loading of Ni in the catalyst 5 was 20.51 mg (0.35 mmol) per gram of catalyst while the elemental analysis disclosed that the mole amount of N was 1.414 mmol per gram of catalyst calculated from the mass% of N (1.98%). The 1:4 mole ratio of Ni to N atoms suggested generation of



Scheme 1. Preparation of 3 and 5.

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Figure 1. The FT-IR spectra of 3 and 5.

the well-defined single-site active centers within the periodic mesoporous organosilica.

Figure 1 shows the FT-IR spectra of the (1R,2R)-DACH-functionalized PMO (3) and the heterogeneous catalyst 5. Generally, both 3 and 5 exhibited the characteristic bands of the PMO-type materials around 3423, 1648, 1080 and 522 cm⁻¹ for ν (O–H), δ (O-H), ν (Si-O) and ω (C-H), respectively.^[8] The relatively weak bands between 3100-2800 cm⁻¹ were assigned to asymmetric and symmetric stretching vibrations of C-H bonds while the bands between 1610–1450 cm⁻¹ were attributed to breathing vibrations of C=C bonds in the aromatic ring.^[9] The peaks indicative of $\nu(Si-C)$ should appear at 1100 cm⁻¹, however, they were difficult to be distinguished because of the overlapping by the absorbance from ν -(Si–O).^[10] In comparison with **3**, the intensity of absorbance at 1602, 1561 and 1451 cm^{-1} in the 5 (assigned to the vibration of C=C bonds in aromatic ring) increased consistently, implying that (1R,2R)-N,N'-dibenzylcyclohexyldiamine (4) participated in the coordination of Ni centers. All these observations demonstrated the successful incorporation of bis(cyclohexyldiamine)-based Ni(II) complexes within the periodic mesoporous organosilica.

The incorporation of bis(cyclohexyldiamine)-based Ni(II) complexes within the periodic mesoporous organosilica could be further confirmed by the solidstate NMR spectra. Although there were the relatively broad peaks in ¹³C cross polarization (CP) MAS NMR spectrum of **5** due to the paramagnetic character of bis(cyclohexyldiamine)-based Ni(II) complexes, it was still clear that each characteristic peak could be observed, in which the typical chemical shift values were strongly similar to those of (1*R*,2*R*)-DACHfunctionalized PMO (**3**) (see Figure S1 in the Supporting Information). A further evidence to support the presence of bis(cyclohexyldiamine)-based Ni(II) complexes within the periodic mesoporous organosili-



Figure 2. The ¹³C CP MAS NMR spectrum of **5** treated with acetylacetone.



Scheme 2. The catalyst 5 treated with acetylacetone.

ca was the ¹³C CP MAS NMR spectrum of the mono(cyclohexyldiamine)-based Ni(II)-acetylacetone intermediate^[4a] obtained by treatment of the heterogeneous catalyst 5 with acetylacetone. As shown in Figure 2, it was found that the mono(cyclohexyldiamine)-based Ni(II)-acetylacetone intermediate (Scheme 2) showed the typical peaks around 18-25 ppm corresponding to the C atoms in the cyclohexyl group and the peaks at 60 ppm corresponding to the C atoms in the cyclohexyl group connected to nitrogen atom. Meanwhile, the peak around 31 ppm derived from the C atoms in the CH2 group connected to the aromatic rings and the peak around 134 ppm corresponding to the C atoms in the aromatic rings were also observed. More importantly, there were two new peaks at 193 and 101 ppm, which were assigned to the C atoms of C=O and the C atoms of the enolization. These structural assignments confirmed the formation of mono(cyclohexyldiamine)-based Ni(II)acetylacetone intermediate^[4a,b] due to a ligand dis-

placement between (1R,2R)-N,N'-dibenzylcyclohexyldiamine and acetylacetone, proving indirectly the presence of bis(cyclohexyldiamine)-based Ni(II) complexes within this periodic mesoporous organosilica. In addition, the ²⁹Si CP MAS NMR spectrum of the heterogeneous catalyst 5 (see Figure S1 in the Supporting Information) demonstrated that the heterogeneous catalyst 5 possessed an organosilicate framework^[1a,3b,6c]</sup> with R-Si(OAr)₂(OH) (R=chiral organo-</sup>metallic functionality) as the main part of silica framework. The characteristic signals of the T-series at -62.2, -71.0 and -79.9 ppm corresponding to T^1 $[R-Si(OAr)(OH)_2]$, T² $[R-Si(OAr)_2(OH)]$ and T³ [R-Si(OAr)₃] suggested that all Si species were covalently attached to carbon atoms^[3b,6c] while the most intense T^2 signal revealed that $R-Si(OAr)_2(OH)$ species were predominant in the silica framework. Furthermore, the absence of signals for the Q-series from -90 to -120 ppm indicated that no cleavage of the carbon-silicon bond occurred during the hydrolysiscondensation process.

The TG/DTA curves of the heterogeneous catalyst 5 are presented in Figure 3. An endothermic peak around 361 K with a weight loss of 8% could be attributed to the release of physically adsorbed water. In addition, an exothermic peak around 545 K with a weight loss of 4% could be assigned to the oxidation of chiral diamine ligands embedded in the pore wall while another exothermic peak at 782 K with the weight loss of 41% resulted from the oxidation of the phenyl fragments embedded in the pore wall.^[1a] All the peaks observed here were strongly similar to those of the parent (1R,2R)-DACH-functionalized PMO materials (3) (see Figure S2 in the Supporting Information). It was worth mentioning that a new exothermic peak around 626 K with a weight loss of 9% could be assigned to the oxidation of bis(cyclohexyldiamine)-based Ni(II) complexes in the pore channel when compared to the TG/DTA curve of 3. These observations further demonstrated the successful incorporation of bis(cyclohexyldiamine)-based Ni(II) complexes within the periodic mesoporous organosilica.

In order to investigate the electronic state of the nickel center within the periodic mesoporous organosilica, the heterogenous catalyst 5 and the corresponding homogeneous bis(cyclohexyldiamine)-based Ni(II) complex (DACHNiDACH) were examined by X-ray photoelectron spectroscopy (XPS). As shown in Figure 4, the XPS spectra of the heterogeneous catalyst 5 gave the Ni $2p_{3/2}$ binding energy around 855.54 eV, indicating that the nickel center presented in the divalent state.^[11] Meanwhile, it was easily found that the heterogeneous catalyst 5 had the nearly same Ni $2p_{3/2}$ electron binding energy as the parent DACH-NiDACH complex, suggesting that the nickel center within the periodic mesoporous organosilica retained its original chiral coordination microenvironment that would dominate the chiral performance discussed later.

The mesostructural morphology and the pore arrangements of (1R,2R)-DACH-functionalized PMO (3) and the heterogeneous catalyst 5 were further characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and nitrogen adsorption-desorption techniques. The small-angle XRD patterns (Figure 5) revealed that the heterogeneous



Figure 4. The XPS spectra of DACHNiDACH and 5.

SETT (m2/g)

396.7

357.8

2

2 Theta/degree

Dp (nm)

5.95

5.56

3

 V_P (cm³/g)

0.71

0.65



Figure 3. The TG/DTA curves of 5.

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400

100

Mass Loss(%) $^{\circ}$

40

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Catalyst 5



Figure 6. The TEM images of 3 and 5 viewed along the [100] and [001] directions.



Figure 7. The nitrogen adsorption-desorption isotherms of 3 and 5.

catalyst 5 presented the same d_{100} diffraction peak as (1R,2R)-DACH-functionalized PMO materials (3), suggesting that the dimensional-hexagonal pore structure (p6mm) observed in PMO-type materials could be preserved after the complexation.[3b] The TEM morphologies further confirmed that 5 had a highly ordered mesostructure with the dimensional-hexagonal arrangement as shown in Figure 6. Nitrogen adsorption-desorption isotherms of both 3 and 5 (Figure 7) exhibited typical IV type isotherms with H_1 hysteresis loop and a visible step at $P/P_0 = 0.40-0.90$, corresponding to capillary condensation of nitrogen in mesopores. As shown by the structural parameters listed in the table inserted in Figure 5, the complexation of NiBr₂ within the periodic mesoporous organosilicas caused a decrease in mesopore size, surface area, and pore volume, obviously due to coverage of pore surface with bis(cyclohexyldiamine)-based Ni(II) complexes, leading to an increase of the wall thickness.^[12] Based on the above studies, we can safely conclude that the PMO-supported chiral Ni(II) catalyst with ordered mesostructure could be readily obtained in this case.

Catalytic Properties of the Heterogeneous Catalyst

The asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes is one kind of important carbon-carbon bond formation reactions.^[4,13] With the heteogeneous catalyst 5 in hand, we examined its catalytic activity and enantioselectivity in the asymmetric Michael addition of malonates to nitroalkenes at first. As shown in Table 1, when the mole amount of the heterogeneous catalyst 5 was decreased down to 2.0 mol%, the catalytic reaction of diethyl malonate addition to nitrostyrene gave a chiral product with more than 99% conversion and 94% ee value (entry 1). Such an enantioselectivity was comparable to that of the homogeneous catalyst (entry 1 versus the value in brackets^[4a]). It is worth mentioning that the catalytic reaction could be completed wihtin 8 h, suggesting that the phenyl moiety working as a hydrophobic inner wall could accelerate reaction rate. In order to prove this assumption the condensation of (1R,2R)-DACH-derived silane (1) and tetraethylorthosilicate was compared, in which O-Si-O groups worked as the inner wall rather than the phenyl moiety. The experiment showed that 18 h of reaction time were needed to complete this catalytic reaction, confirming that the enhanced reation rate in the case of the heterogeneous catalyst 5 should be ascribed the good hydrophobicity of the nanopores. Of particular note is that the reaction could also be run at a high substrate/catalyst ratio without affecting obviously the ee value, as exemplified by the asymmetric Michael addition with 0.5 mol% of catalyst (entry 2). The high enantioselectivity in these cases should be due to the fact that bis(cyclohexyldiamine)-based Ni(II) active centers incorporated within the periodic mesoporous organosilicas retained the same chiral microenviron-

catalyst 5 NO₂ toluene ĊO₂R Entry Time [h] Conv. [%]^[b] ee [%]^[b] R, Ar 1 Et, Ph 8 (5) >99(99)94 (94) 92^[c] 2 Et. Ph 24 83 88^[d] 3 Et, Ph 36 76 91^[e] 4 Et, Ph 36 89 1^[f] 36 5 Et, Ph 38 89^[g] Et, Ph 36 61 6 7 Me. Ph 8 >99 94 >99 8 Bn, Ph 12 94 95 9 i-Pr, Ph 16 >99 95 10 t-Bu, Ph 120 63 Et, 4-MeC₆H₄ 99 95 12 11 12 Et, 4-MeOC₆H₄ 12 98 95 13 Et, 4-BrC₆H₄ 12 >99 93 95 14 Et, 2-ClC₆H₄ 12 >99

Table 1. Asymmetric Michael addition of malonates to nitroalkenes.^[a]

- ^[a] Reaction conditions: catalysts (57.0 mg, 0.02 mmol of Ni, based on the ICP analysis), nitroalkenes (1.0 mmol), malonate (1.20 mmol) and 4.0 mL toluene, reaction temperature (40°C), reaction time (8–120 h).
- ^[b] Determined by chiral HPLC analysis using Chiralcel AD-H columns (see Figure S4 in the Supporting Information) and the conversions were calculated by the internal standard method.
- ^[c] Data were obtained with 0.5 mol% of catalyst.
- ^[d] Data were obtained using a physical mixture of (1*R*,2*R*)-DACH-functionalized PMO (3) plus NiBr₂ in the presence of (1*R*,2*R*)-*N*,*N*'-dibenzylcyclohexyldiamine as a catalyst.
- Data were obtained using a physical mixture of (1*R*,2*R*)-DACH-functionalized PMO (3) plus the homogeneous bis(cyclohexyldiamine)-based Ni(II) complexes as a catalyst.
- ^[f] Data were obtained using 20 mol% of (1*R*,2*R*)-DACH-functionalized PMO (**3**) as a catalyst.
- ^[g] Data were obtained using mono(cyclohexyldiamine)based Ni(II) complex as a catalyst.

ment as in the homogeneous catalyst as was proven by the XPS studies mentioned above.

On the basis of the above excellent results, the heterogeneous catalyst **5** was further investigated systemically in the asymmetric addition of malonates to nitroalkenes (Table 1). In general, high conversions and no side products, and excellent enantioselectivities were obtained under similar conditions for all tested substrates. Also it was found that the steric properties of substituted malonates did significantly affect the catalytic activity. From entries 1 and 7–10, it is seen that the reaction time must be prolonged as the alkyl ester group (R) is enlarged. In particular, the reaction could not be completed when R was *tert*-butyl (entry 10), even on prolongation to 3 days. A possible explanation is that the size of mesopores delayed the entrance of the substrate, leading to a prolonged reaction time. Evidence to support the view was provided by three comparable experiments, in which each mixture of (1R,2R)-DACH-functionalized PMO (3) material and the equivalent mole reactant (diethyl malonate or di-isopropyl malonate or di-tert-butyl malonate) was suspended in the solution under the same conditions, respectively. It was found that, after stirring for 4 h and filtering, the mole ratio of the three reactants in the solution was 1:1.5:9.6 as detected by the GC analyses, demonstrating that the large steric substituted malonates were more difficult to penetrate into the mesopores due to the size effect of the mesopores. However, the electronic properties of substituents at the nitroalkenes did not affect catalytic activity and enantioselectivity, in which the reactions of diethyl malonate with electron-rich and electron-poor substituted nitroalkenes were equally efficient (entries 11–14).

As shown in Table 2, this heterogeneous catalyst 5 could also be applied to the asymmetric Michael addition of β -keto esters to nitroalkenes, in which high conversions and the excellent enantioselectivities were obtained. Taking dimethyl acetoacetate as an example, the catalytic reaction afforded chiral products with more than 99% conversion and more than 99% ee values (entry 1), in which both enantioselectivities were higher than those of the homogeneous catalyst (both 99% ees in entry 1 versus 94% ees in the literature^[4a]). This behaviour suggested that there was a positive confinement effect with bis(cyclohexyldiamine)-based Ni(II) active centers within PMO-type mesoporous materials, in which a similar positive confinement effect of an enhanced enantioselectivity had also been observed in the inorganosilicas-type mesoporous materials.^[14] More importantly, the catalytic reaction could be completed within the same reaction time as that of the homogeneous catalyst, further confirming that the phenyl moiety worked as a hydrophobic inner wall that could draw rapidly reactants into the nanopore, thereby greatly accelerating the reaction rate. Similarly, the steric properties of two substituents at the β -keto ester did affect significantly the catalytic activity due to the size effect of the nanopores discussed above (entries 1-6). For example, ethyl isobutyrylacetate was more difficult to convert even in a prolonged reaction time due to the relatively large steric substituents (entry 6).

To gain better insight into the nature of the heterogeneous catalysis and to eliminate the non-covalent adsorption during the catalytic process, two control experiments for the asymmetric addition of diethyl malonate to nitrostyrene were also carried out using (1R,2R)-DACH-functionalized PMO (3) plus NiBr₂ in the presence of (1R,2R)-N,N'-dibenzylcyclohexyldiamine and (1R,2R)-DACH-functionalized PMO (3)

Entry	$R' \xrightarrow{I} OR'' Ar \xrightarrow{I} NO_2 \xrightarrow{Catalyst 5} R' \xrightarrow{I} OO_2 OO_2R''$										
	R′	R″	Ar	Time(h)	Conv. [%]	dr (a:b)	ee [%] (a:b)				
1	Me	Me	Ph	6 (6)	98 (94)	1.3:1 (1:1)	>99 (99) [94 (94)] ^[4a]				
2	Me	Me	$4-BrC_6H_4$	4	> 99	2.7:1	>99 (>99)				
3	Me	Et	Ph	5	>99	1.2:1	93 (94)				
4	Me	<i>t</i> -Bu	Ph	10	>99	1.8:1	94 (96)				
5	Me	<i>t</i> -Bu	$4-BrC_6H_4$	10	>99	2:1	93 (96)				
6	<i>i</i> -Pr	Et	Ph	12	92	1:1	91 (92)				

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Table 2. Asymmetric Michael addition of β -ketoester to nitroalkenes.^[a]

^[a] *Reaction conditions:* catalysts (57.0 mg, 0.02 mmol of Ni, based on the ICP analysis), nitroalkenes (1.0 mmol), β -keto ester (1.20 mmol) and 4.0 mL toluene, reaction temperature (40 °C), reaction time (4–12 h).

^[b] Determined by chiral HPLC analysis using Chiralcel AD-H columns (see Figure S4 in the Supporting Information) and the conversion was calculated by the internal standard method

plus the homogeneous bis(cyclohexyldiamine)-based Ni(II) complexes as heterogeneous catalysts. It was found that the former afforded the corresponding products with 76% conversion and 88% ee value (entry 3 in table 1) while the latter gave the corresponding products with 89% conversion and 91% ee value (entry 4 in Table 1). The former result suggested that the catalyst synthesized by an in situ post-modification method could result in a medium catalytic performance. Lower catalytic activity and enantioselectivity than those of the catalyst 5 should be due to the fact that the small part of NiBr₂ had not been coordinated during the catalytic process, in which the loss of Ni was detected by ICP analysis in solution. The latter indicated that the chiral microenvironment had not been changed as derived from non-covalent adsorption. Lower conversion than that of the catalyst 5 suggested that part of the homogeneous catalyst did not participate in the catalytic reaction due to jamming from physical absorption.^[7a,b] However, when both heterogeneous catalysts of the above control experiments were allowed to undergo a process of Soxhlet extraction, it was found that the catalytic reactions using the treated heterogeneous catalysts only gave traces of products. This fact ruled out the role of the non-covalent physical adsorption, explaining that the nature of this heterogeneous catalysis was derived from the heterogeneous catalyst 5 itself.

To further consolidate the role of bis(cyclohexyldiamine)-based Ni(II) active centers within periodic mesoporous organosilicas, we also investigated the asymmetric addition of diethyl malonate to nitrostyrene using (1R,2R)-DACH-functionalized PMO (3) itself and (1R,2R)-DACH-functionalized PMO (3) plus NiBr₂ in the absence of (1R,2R)-N,N'-dibenzylcyclohexyldiamine as heterogeneous catalysts. In the case of (1R,2R)-DACH-functionalized PMO (3) itself as a heterogeneous catalyst, when the mole amount of **3** was enhanced greatly to 20 mol%, it was found that the catalytic reaction could afford 38% of product although without any enantioselective background (entry 5 in Table 1), which was strongly similar to that of (1R,2R)-N,N'-dibenzylcyclohexyldiamine itself as a Brønsted base in a homogeneous catalysis system.^[4a] This behaviour demonstrated that (1R,2R)-DACHfunctionalized PMO (3) itself acts as a Brønsted base that could deprotonate diethyl malonate and accordingly anticipate the addition of nitrostyrene. In the case of (1R,2R)-DACH-functionalized PMO (3) plus NiBr₂ in the absence of (1R,2R)-N,N'-dibenzylcyclohexyldiamine as a heterogeneous catalyst, we treated this heterogeneous catalyst via a Soxhlet extraction process to keep a pure mono(cyclohexyldiamine)based Ni(II) complex within the PMO material. The result showed that the chiral product with 61% conversion and 89% ee value (entry 6 in Table 1) was observed, however, the reaction needed 36 h. Obviously the lower catalytic efficiency than that of the heterogeneous catalyst 5 should be ascribed to the nature of mono(cyclohexyldiamine)-based Ni(II) complexes in the absence of one equivalent (1R,2R)-N,N'-dibenzylcyclohexyldiamine as a Brønsted base. All these observations confirmed that bis(cyclohexyldiamine)based Ni(II) active centers within periodic mesoporous organosilicas played a crucial role in both catalytic and enantioselective performances.

An important feature of the design of the heterogeneous catalyst **5** was its easy and reliable separation *via* simple filtration and the reused catalyst could still retain its catalytic activity and enantioselectivity through multiple cycles. As shown in Table 3, the heterogeneous catalyst **5** had an obvious high reusability for the dimethyl malonate addition to nitrostyrene, in which the *ee* values as well as the conversions did not drop obviously after a continuous nine times recycling. In order to demonstrate that the recycle efficiency was derived from the heterogeneous catalyst itself, a filtration experiment was carried out. In this Table 3. Reusability of the catalyst 5 for dimethylmalonate addition to nitrostyrene.^[a]

Run time		MeO OMe + Ph NO2			catalyst 5 toluene	→ MeC	O Ph CO ₂ Me				
	1	2	3	4	5	6	7	8	9	10	
Conv. [%] ee [%] ^[b]	>99.9 94.4	>99.9 94.0	>99.9 93.7	>99.9 93.5	>99.9 93.3	99.8 93.2	>99.9 93.1	>99.9 92.7	99.1 92.6	89.9 92.4	

^[a] *Reaction conditions:* catalysts (57.0 mg, 0.02 mmol of Ni, based on the ICP analysis), nitrostyrene (0.15 g, 1.0 mmol), dimethyl malonate (0.16 g, 1.20 mmol) and 4.0 mL toluene, reaction temperature (40 °C), reaction time (8 h).

^[b] Determined by chiral HPLC analysis using Chiralcel AD-H columns (see Figure S5 in Supporting Information) and the conversions were calculated by the internal standard method.

case, the heterogeneous catalyst 5 was filtered from the reaction mixture after 4 h and the reaction was continued for further 12 h. It was found that there was no appreciable change either in conversion or *ee* value of the chiral products. This fact eliminated the role of homogeneous mono(cyclohexyldiamine)-based Ni(II) complexes or the homogeneous bis(cyclohexyldiamine)-based Ni(II) complexes, confirming that the recycle efficiency was derived from heterogeneous catalyst itself. In order to analysis the reasons for the decreased reactivity at the tenth recycle, an ICP analvsis was undertaken. The result showed that the Ni amount of the catalyst 5 in the solid state at the tenth recycle was 16.73 mg Ni per gram catalyst, meaning that the leached amount at the tenth reuse was 18.4% relative to the starting amount. This behaviour indicated that the leaching of Ni metal might be responsible for the decreased reactivity at the tenth recycle. In order to further consolidate this judgment, the Ni amount at the ninth recycle was also investigated. It was found that the leaching amount at ninth recycle was 8.27 mg Ni per gram catalyst, suggesting that the leached amounts at the ninth recycle was 9.1%. This value was nearly consistent with the 9.6% loss of (1R,2R)-N,N'-dibenzylcyclohexyldiamine detected by elemental analysis (1.79% of N at the ninth recycle means 9.5% of the lost amounts relative to 1.98% of N in the starting amount). These observations confirmed that the decreased reactivity originated from the leaching of Ni metal.

Conclusions

In conclusion, we have immobilized successfully the chiral bis(cyclohexyldiamine)-based Ni(II) complexes within the periodic mesoporous organosilica and obtained a PMO-supported chiral Ni(II) catalyst (5). This heterogeneous catalyst exhibited highly catalytic activity and excellent enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes, which were comparable to those of

the homogeneous catalyst. In particular, this research did also disclose that the nature of this heterogeneous catalysis was derived from the heterogeneous catalyst itself, demonstrating that chiral bis(cyclohexyldiamine)-based Ni(II) complexes within the periodic mesoporous organosilica played a crucial role in both catalytic and enantioselective performance. More importantly, the heterogeneous catalyst **5** could be recovered and reused nine times without affecting obviously its *ee* value, showing good potential in industrial application.

Experimental Section

General Remarks

All experiments, which were sensitive to moisture or air, were carried out under an argon atmosphere using standard Schlenk techniques. 1,4-Bis(triethyoxysilyl)benzene, surfactant P123 { $(CH_2-CH_2O)_{20}[CH_2(CH_3)CH_2O]_{70}(CH_2CH_2O)_{20}$ }, (1*R*,2*R*)-1,2-cyclohexyldiamine and NiBr₂ were purchased from Sigma–Aldrich Company Ltd. and used as received. Compound 1 {(1R,2R)-DACH-[$(CH_2PhSi(OMe)_3]_2$ } was synthesized according to the reported literature.^[3c] The products were analyzed by using HPLC with a UV-Vis detector using a Daicel AD-H or OD-H chiralcel columns(Φ 0.46×25 cm).

Characterization

The Ni loading amount in the catalyst was analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using the KBr method. X-ray powder diffraction (XRD) was carried out on a Rigaku D/Max-RB diffractometer with CuK α radiation. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin–Elmer PHI 5000C ESCA system. All the binding energies were calibrated by using the contaminant carbon (C_{1s}=284.6 eV) as a reference. Thermal gravimetric analysis (TGA) was performed with a Perkin–Elmer Pyris Diamond TG analyzer under an air atmosphere with

a heating ramp of 5 K min⁻¹. Solid-state ${}^{13}C$ (100.5 MHz) and ${}^{29}Si$ (79.4 MHz) CP-MAS NMR were obtained on a Bruker DRX-400 spectrometer.

Preparation of (1*R***,2***R***)-DACH-Functionalized Organosilicas (3)**

In a typical synthesis, 2.0 g of structure-directing agent (pluronic P123) were fully dissolved in a mixture of 80 mL hydrochloric acid (0.2 N) and 6.0 g KCl. Then, 3.62 g (9.00 mmol) of 1,4-bis(triethyoxysilyl)benzene were added as the silica precursor at 40 °C. After a pre-hydrolysis period of 40 min, 0.53 g (1.00 mmol) of (1R,2R)-DACH-[(CH₂PhSi(OMe)₃]₂ (1) were added, in which the initial molar ratio is Si:P123:KCl:HCl:H₂O in the mother solution is 1.0:0.017:4.0:0.80:218 (Si refers to the total silica source). The reaction mixture was stirred at 40 °C for 24 h and aged at 100 °C for 24 h. The resulting solid was filtered and rinsed with excess ethanol before being dried overnight on a filter. The surfactant template was removed by refluxing in acidic ethanol (400 mL per gram) for 24 h. The solid was filtered and rinsed with ethanol again, and dried at 60 °C under reduced pressure overnight to afford (1R,2R)-DACH-functionalized organosilicas (3) in the form of a white powder; yield: 1.38 g. IR (KBr): v = 3423.5 (s), 3062.1 (w), 2933.7 (w), 2851.1 (w), 1648.7 (m), 1602.3(w), 1561.5 (w), 1451.3 (w), 1383.3 (w), 1155.6 (s), 1079.2 (s), 949.7 (m), 861.3 (w),810.3 (w), 698.9 (w), 620.4 (w), 536.5 (w), 520.1 cm⁻¹ (m); elemental analysis (%): C 50.62, H 4.41, N 1.05; S_{BET}: 396.7 m²g⁻¹; d_{pore}: 5.95 nm; V_{pore}: 0.71 cm³g⁻¹; ²⁹Si MAS NMR (79.5 MHz): T¹ (δ = -64.3 ppm), T² (δ = -72.3 ppm), T^{3} ($\delta = -79.7 \text{ ppm}$); ¹³C CP MAS NMR (100.6 MHz): $\delta =$ 132.7, 69.8, 57.3, 51.2, 33.5, 23.1, 16.1 ppm.

Preparation of the Heterogeneous Catalyst 5

To a stirred suspension of (1R, 2R)-DACH-functionalized organosilicas (3) (1.0 g) in 50 mL dry acetonitrile were added NiBr₂ (81.70 mg, 0.38 mmol) and (1R,2R)-N,N'-dibenzylcyclohexyldiamine (111.72 mg, 0.38 mmol) at room temperature. The resulting mixture was refluxed for 12 h. After cooling down to room temperature, the mixture was then filtered through filter paper and rinsed with excess CH₂Cl₂. After Soxhlet extraction in toluene solvent to remove homogeneous and unreacted starting materials for 24 h, the solid was dried at 60°C under vacuum overnight to afford the heterogeneous catalyst 5 as a pale powder; yield: 1.05 g. ICP analysis showed that the Ni loading-amount was 20.51 mg (0.35 mmol) per gram catalyst. IR (KBr): v =3420.1 (s), 3052.9 (w), 2978.4 (w), 2933.6 (w), 2860.3 (w), 1648.7 (m), 1602.3(w), 1561.4 (w), 1451.2 (w), 1387.2 (w), 1155.6 (s), 1081.2 (s), 932.1 (m), 863.8 (w), 810.7 (w), 647.9 (w), 522.7 cm⁻¹ (m); elemental analysis (%): C 56.18, H 4.89, N 1.98; S_{BET} : 357.8 m²g⁻¹; d_{pore}: 5.56 nm; V_{pore}: 0.65 cm³g.⁻¹; ²⁹Si MAS NMR (300 MHz): T¹ ($\delta =$ -62.2 ppm), T² ($\delta = -71.0$ ppm), T³ ($\delta = -79.9$ ppm); ¹³C CP MAS NMR (100.6 MHz): $\delta = 134.0$, 130.0, 75.8, 72.4, 69.3, 60.3, 53.7, 50.0, 31.6, 25.3, 18.7 ppm.

General Procedure for Asymmetric Michael Addition of 1,3-Dicarbonyl Compounds to Nitroalkenes

A typical procedure was as follows: the heterogeneous catalyst 5 (57.0 mg, 0.02 mmol based on Ni from ICP), nitrostyrene (0.15 g, 1.0 mmol), dimethyl malonate (1.20 mmol) and 4.0 mL toluene were added in a 10-mL round-bottom flask in turn. The mixture was allowed to react at 40 °C for 8-28 h. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the heterogeneous catalyst was filtered through filter paper for the recycle experiment. The aqueous solution was extracted by Et₂O $(3 \times 3.0 \text{ mL})$. The combined Et₂O layer was washed with brine twice and dehydrated with Na₂SO₄. After the evaporation of Et₂O, the residue was purified by silica gel flash column chromatography to afford the desired product. The conversion was calculated by the internal standard method and the ee value could be determined by chiral HPLC analysis with a UV-Vis detector using a Daicel OD-H chiralcel column (Φ 0.46×25 cm).

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