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Functionalized Periodic Mesoporous Organosilica: A Highly Enantioselective Catalyst for the Michael Addition of 1,3-Dicarbonyl Compounds to Nitroalkenes

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Abstract: A functionalized periodic mesoporous organosilica with incorporated chiral bis(cyclohexyldiamine)-based Ni^{II} complexes within the silica framework was developed by the co-condensation of (1*R*,2*R*)-cyclohexyldiamine-derived silane and ethylene-bridge silane, followed by the complexation of $NiBr_2$ in the presence of (1*R*,2*R*)-*N*,*N*′-dibenzylcyclohexyldiamine. Structural characterization by XRD, nitrogen sorption, and TEM disclosed its orderly mesostructure, and FTIR and solid-state NMR spectroscopy demonstrated the incorporation of well-defined single-site bis(cyclohexyldiamine)-based Ni^{II} active centers within periodic mesoporous organosilica. As a chiral heterogeneous catalyst, this functionalized periodic mesoporous organosilica showed high catalytic activity and excellent enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes, comparable to those with homogeneous catalysts. In particular, this heterogeneous catalyst could be recovered easily and reused repeatedly up to nine times without obviously affecting its enantioselectivity, thus showing good potential for industrial applications.

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

Introduction

Great success has been achieved in the immobilization of homogeneous catalysts within silica-based mesoporous materials for asymmetric catalysis.[1] Various self-assemblies of functionalized inorganosilanes and organosilanes through postsynthesis and co-condensation methods have dominated the preparation of heterogeneous catalysts. Some of these inorganosilane-based mesoporous materials, such as MCM-41,[2] SBA–15,[3] and SBA-16,[4] have been successfully used to immobilize homogeneous chiral catalysts and have exhibited excellent enantioselectivities in various asymmetric reactions. In particular, as a typical organosilane-based mesoporous material, periodic mesoporous organosilicas (PMOs) with a bridging chiral moiety within the silica framework have shown some salient features in asymmetric catalysis.[5] Besides the general advantages of inorganosilane-based mesoporous materials, such as relatively large surface area, tunable pore volume, and well-defined pore arrangement, periodic mesoporous organosilicas have obvious hydrophobicity, owing to their intrinsic organic functionality on their inner surface, which can promote catalytic activity. More importantly, functionalized periodic mesoporous organosilicas with chiral ligands embedded within the silica framework possess special rigidity, which is beneficial for the construction of suitable chiral microenvironments to enhance enantioselectivity. Moreover, they also exhibit superior thermal and mechanical stability relative to polymer-supported catalysts, which makes them easy to separate and convenient to recycle. Although lots of periodic mesoporous organosilicas with achiral-functionalized alkyl and aryl groups embedded within silica frameworks have been reported,[6] only a few examples have successfully incorporated chiral functionality within the silica framework.[5,7] Moreover, most of these still frameworks suffer from lower catalytic activities and enantioselectivities than their corresponding homogeneous catalysts. Thus, exploiting suitable chiral-functionalized periodic mesoporous organosilicas for highly efficient asymmetric catalysis remains a scientific and technological challenge.

As one type of important carbon–carbon bond-formation reactions, chiral bis(cyclohexyldiamine)-based Ni^{II} com-

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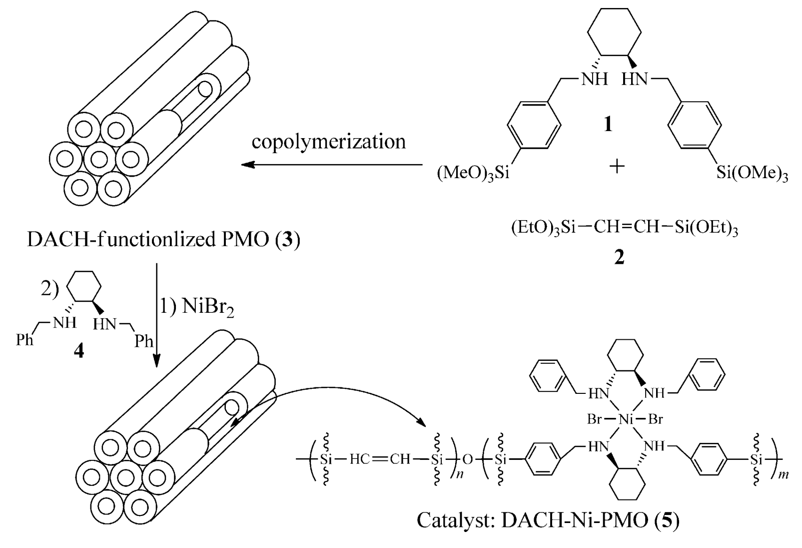


Scheme 1. Synthesis of heterogeneous catalyst **5**.

plexes exhibit high catalytic activity and excellent enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes.[8] In particular, their chiral products are used extensively as useful chiral building blocks to generate chiral amino acids and five-membered nitrogen heterocycles.[9] More importantly, the investigation of its catalytic mechanism has disclosed that single-site bis(cyclohexyldiamine)-based Ni^{II} active species play an exclusive role in this asymmetric addition reaction.[8a] Thus, the immobilization of chiral bis(cyclohexyldiamine)-based Ni^{II} complexes within periodic mesoporous organosilicas could not only eliminate unexpected disturbances to solve the complicated compatibility of functionalities in a heterogeneous catalysis system but it could also further elucidate the catalytic mechanism from the viewpoint of solid-state chemistry.

We are interested in mesoporous-silica-supported heterogeneous catalysts;[10] in particular, their use in the development of silica-based heterogeneous catalysts. Recently, we have reported a series of chiral, heterogeneous, inorganosilica-based ruthenium, rhodium, and iridium catalysts and some of these have showed highly catalytic activity and excellent enantioselectivity in the asymmetric transfer hydrogenation of ketones.[11] Herein, we report the successful incorporation of chiral bis(cyclohexyldiamine)-based Ni^{II} complexes within ethylene-bridged periodic mesoporous organosilica to afford an organosilane-based chiral heterogeneous Ni^{II} catalyst that has shown high catalytic activity and excellent enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes. Moreover, an exploration of the heterogeneous mono(cyclohexyldiamine)-based Ni^{II} catalyst and an investigation of the recyclability of the heterogeneous bis(cyclohexyldiamine)-based Ni^{II} catalyst were also performed.

Results and Discussion

Synthesis and structural characterization of the heterogeneous catalyst: The chiral heterogeneous bis(cyclohexyldiamine)-based ethylene-bridged Ni^{II} catalyst, abbreviated as DACH-Ni-PMO (**5**, DACH = (1*R*,2*R*)-1,2-diaminocyclohexane), was prepared as outlined in Scheme 1. First, (1*R*,2*R*)-*N*,*N*′-dibenzylcyclohexyldiamine-derived silane, with trimethlysilyl groups at the 4-positon of the aromatic ring, was synthesized according to a literature procedure.[3a] Then, the co-condensation of (1*R*,2*R*)-DACH-derived silane **1** and ethylene-bridged silane **2** afforded (1*R*,2*R*)-DACH-functionalized periodic mesoporous organosilica DACH-functionalized PMO **3** as a white powder.[10b] Finally, the heterogeneous catalyst (**5**) was successfully obtained by the direct complexation of $NiBr_2$ with compound **3** in the presence of (1*R*,2*R*)-*N*,*N*′-dibenzylcyclohexyldiamine (**4**). To eliminate any unreacted starting materials, the heterogeneous catalyst was purified by Soxlet extraction under reflux conditions in toluene, thus affording pure DACH-Ni-PMO (**5**) as a pale powder. Inductively coupled plasma (ICP) optical-emission spectrometry analysis showed that the loading of Ni in catalyst **5** was 19.68 mg (0.34 mmol), which was approximately consistent with the thermogravimetric (TG) analysis (see the Supporting Information, Figure S2). In addition, the molar ratio of Ni atoms to N atoms (almost 25 %), as calculated from 1.91 % N, suggested the generation of well-defined single-site active centers within the periodic mesoporous organosilica.

As shown in Figure 1, FTIR spectroscopy of the (1*R*,2*R*)-DACH-functionalized PMO (**3**) and of heterogeneous catalyst **5** showed the characteristic bands of PMO-type materi-

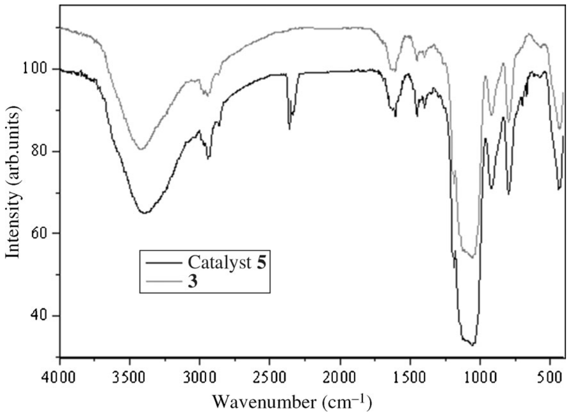


Figure 1. FTIR spectra of compounds **3** and **5**.

als at around 3421, 1189, 1609, and 440 cm^{-1} for ν(O–H), ν(Si–C), ν(Si–O) and ω(C–H), respectively.[12] The relatively weak bands between 3100–2800 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of the C–H bonds, whilst the bands between 1610–1400 cm^{-1} were attributed to stretching vibrations of the C=C bonds both in the ethylene groups and in the aromatic rings. In comparison with compound **3**, the bands at 1609, 1453, and 1403 cm^{-1} in compound **5** were consistently more intense, thus implying that (1*R*,2*R*)-*N*,*N'*-dibenzylcyclohexyldiamine (**4**) participated in the coordination of Ni centers to form bis(cyclohexyldiamine)-based Ni^{II} complexes within the periodic mesoporous organosilica.

The incorporation of bis(cyclohexyldiamine)-based Ni^{II} complexes within periodic mesoporous organosilica was further confirmed by solid-state NMR spectroscopy. As shown in Figure 2, the ^{13}C cross-polarization magic angle spinning (CP MAS) NMR spectrum of compound **5** clearly showed the characteristic peaks of bis(cyclohexyldiamine)-based Ni^{II} complexes. Notably, the protons of the aromatic rings inside and outside the silica framework gave obviously different chemical-shift values. In sharp contrast to those of (1*R*,2*R*)-DACH-functionalized PMO **3** (see the Supporting Information, Figure S1), the chemical shifts of the Ph groups outside the silica framework (denoted by asterisks, Figure 2) were at their normal values, whilst those inside the silica framework were obviously shifted down-field, owing to the deshielding effect of the ethylene groups within the silica framework. Similarly, a difference between the protons on the methylene moiety of the benzyl groups inside and outside the silica framework was also observed. To further confirm these structural arrangements, the ^{13}C CP MAS NMR spectrum of a mono(cyclohexyldiamine)-based Ni^{II}–acetylacetone intermediate,[8a] which was obtained by the treatment of heterogeneous catalyst **5** with acetylacetone, was also investigated. As shown in Figure 3, we found that the mono(cyclohexyldiamine)-based Ni^{II}–acetylacetone intermediate showed the same typical peaks as the bis(cyclohexyldiamine)-based Ni^{II} complexes and only the intensity of the peaks varied. The obviously less-intense peaks (denoted by asterisks, Figure 3) should be ascribed the protons of the Ph groups outside the silica framework, thus indicating that parts of the bis(cyclohexyldiamine)-based Ni^{II} complexes were displaced by acetylacetone molecules. This behavior suggested that the potential ligand displacement between (1*R*,2*R*)-*N*,*N'*-dibenzylcyclohexyldiamine and the substrates would play an important role in the catalytic performance (see below). In addition, the undisplaced peaks of the protons on the aromatic rings remained at their original values, thus demonstrating that these protons in the aromatic rings were inside the silica framework. In particular, two new peaks at $\delta = 193$ and 102 ppm corresponded to the C atoms of the C=O group and the enolized position, respectively, which was evidence for the formation of the mono(cyclohexyldiamine)-based Ni^{II}–acetylacetone intermediate. All of these observations demonstrated the successful incorporation of bis(cyclohexyldiamine)-based Ni^{II} complexes within periodic mesoporous organosilica.

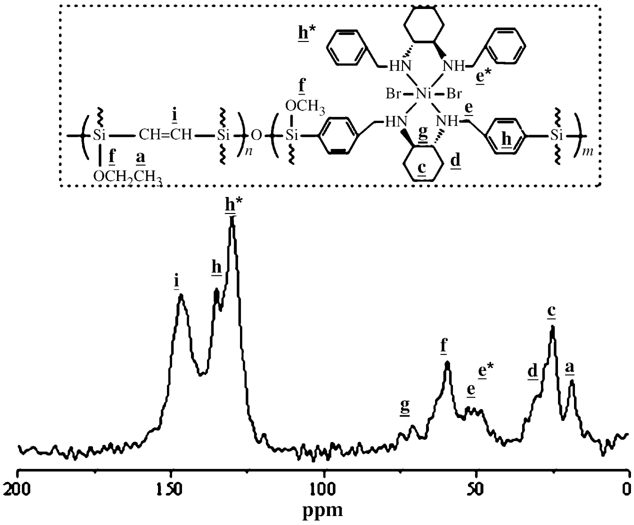


Figure 2. Solid-state ^{13}C CP MAS NMR spectrum of compound **5**.

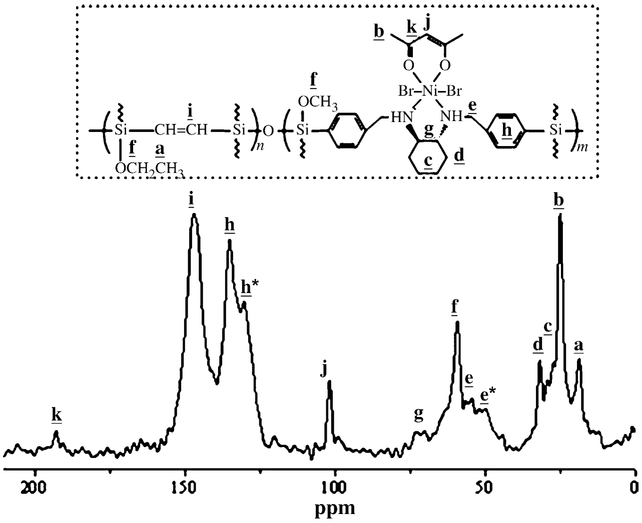


Figure 3. Solid-state ^{13}C CP MAS NMR spectrum of compound **5** after treatment with acetylacetone.

The ^{29}Si CP MAS NMR spectra (Figure 4) clearly showed that DACH-functionalized PMO (**3**) and heterogeneous cat-

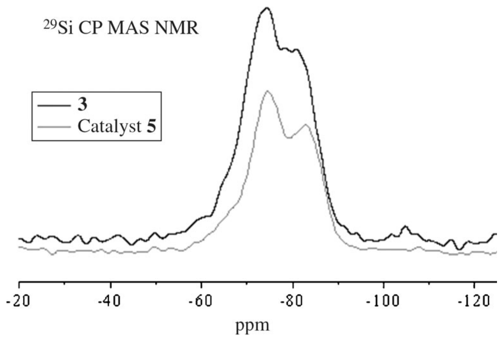


Figure 4. Solid-state ^{29}Si MAS NMR spectra of compounds **3** and **5**.

alyst **5** possessed the organosilicate framework.[5,10a,b] In the case of the heterogeneous catalyst (**5**), the characteristic signals of the T series at $\delta = -74.5$ and -82.9 ppm, which corresponded to T^2 (R−Si(OAr)$_2$(OH)) and T^3 (R−Si(OAr)$_3$), suggested that all of the Si species were covalently attached to carbon atoms,[10a–b] whereas the most intense T^2 signal revealed that the R−Si(OAr)$_2$(OH) species were predominantly inside the silica framework. Furthermore, the absence of signals for the Q series from $\delta = -90$ to -120 ppm indicated that no cleavage of the carbon−silicon bond occurred during the hydrolysis/condensation process.

The (1*R*,2*R*)-DACH-functionalized PMO material (**3**) and the heterogeneous catalyst (**5**) showed the same intense d_{100} diffraction peak as those of typical PMO materials in their small-angle XRD patterns (Figure 5), thus suggesting that the hexagonal pore structure (*p*6*mm*) could be preserved after the co-condensation and complexation.[10b] TEM analysis further confirmed that both the (1*R*,2*R*)-DACH-functionalized PMO material (**3**) and the heterogeneous catalyst (**5**) formed highly ordered mesostructures with hexagonal arrangements (Figure 6). In addition, nitrogen-adsorption/-desorption isotherms of both the (1*R*,2*R*)-DACH-functionalized PMO material (**3**) and the heterogeneous catalyst (**5**) exhibited typical type-IV isotherms with a H_1 hysteresis loop and a visible step at $P/P_0 = 0.30$–0.70, which corresponded to the capillary condensation of nitrogen in the mesopores (Figure 7). As shown by the structural parameters (Figure 5), the complexation of NiBr$_2$ within the periodic mesoporous organosilicas caused a decrease in mesopore size, surface area, and pore volume, presumably owing to the coverage of the pore surface with bis(cyclohexyldiamine)-based Ni^{II} complexes, thereby leading to an increase in the wall-thickness.[13] Based on these above studies, a chiral heterogeneous PMO-based Ni^{II} catalyst with a highly ordered mesostructure could be readily obtained in this case.

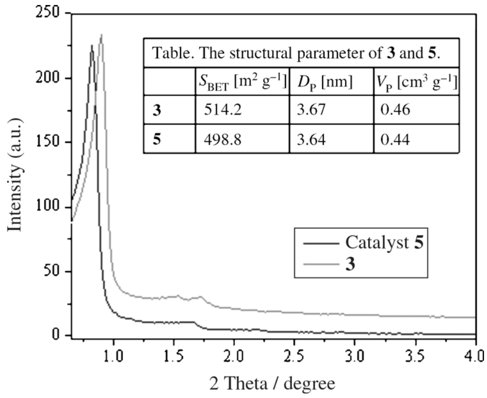


Table. The structural parameter of **3** and **5**.

	S_{BET} [m^2 g^{-1}]	D_P [nm]	V_P [cm^3 g^{-1}]
3	514.2	3.67	0.46
5	498.8	3.64	0.44

Figure 5. Powder XRD patterns of compounds **3** and **5**.

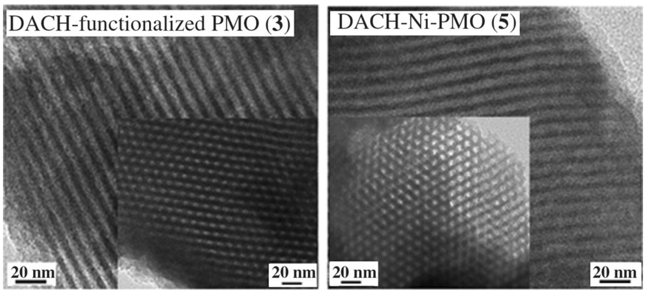


Figure 6. TEM images of compounds **3** and **5**, viewed along the [100] and [001] directions.

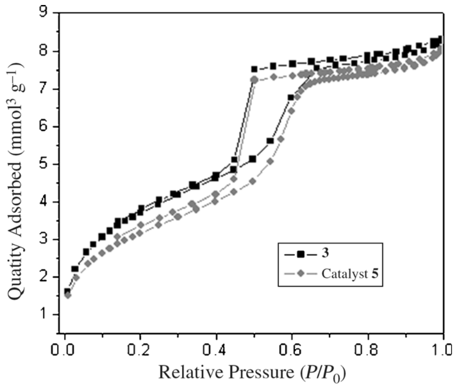
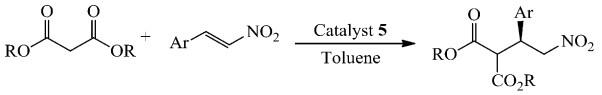


Figure 7. Nitrogen adsorption–desorption isotherms of compounds **3** and **5**.

Catalytic properties of the heterogeneous catalysts: The asymmetric Michael addition of malonate to nitroalkenes has been investigated extensively as one type of important carbon−carbon bond-formation reactions.[8,14] With heterogeneous catalyst **5** in hand, we first examined its catalytic activity and enantioselectivity in the asymmetric Michael addition of diethylmalonate to nitrostyrene. As shown in Table 1, entry 1, the catalytic addition of diethylmalonate to nitrostyrene gave chiral products with more than 99 % conversion and 94 % *ee*, which were comparable to the values with the parent homogeneous catalyst (Table 1, entry 1, in parentheses[8a]). In this case, the high enantioselectivity might be due to the fact that the bis(cyclohexyldiamine)-based Ni^{II} active centers that were incorporated within the periodic mesoporous organosilicas remained in the same chiral microenvironment as the parent homogeneous catalyst. To confirm this conclusion, X-ray photoelectron spectroscopy (XPS) of the heterogeneous catalyst (**5**) and the homogeneous bis(cyclohexyldiamine)-based Ni^{II} complex, abbreviated as DACHNiDACH, was performed. As shown in Figure 8, the XPS spectra of the heterogeneous catalyst (**5**) showed almost the same Ni 2p$_{3/2}$ electron-binding energy as the parent DACHNiDACH complex (855.53 versus 855.51 eV),[15] thus confirming that the high enantioselectivity originated from the unchanged chiral-coordination microenvironment.

Based on this excellent result, heterogeneous catalyst **5** was further investigated systemically in this asymmetric addition reaction. We found that most of the tested substrates

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



Entry	R	Ar	Run	t [h]	Conv. [%][b]	*ee* [%][b]	TOF
1	Et	Ph	1	8	>99(99)	94(94)[c]	6.3
2	Et	Ph	1	12	89	94[d]	3.7
3	Et	Ph	1	48	45	89[e]	0.5
4	Et	Ph	1	48	29	1[f]	0.3
5	Me	Ph	1	8	>99	95	6.3
6	Bn	Ph	1	12	>99	94	4.2
7	*i*Pr	Ph	1	16	>99	95	3.1
8	*t*Bu	Ph	1	120	76	95	0.3
9	Et	4-MePh	1	12	99	95	4.1
10	Et	4-OMePh	1	12	98	95	4.1
11	Et	4-BrPh	1	12	>99	93	4.2
12	Et,	2-ClPh	1	12	>99	95	4.2
13	Me	Ph	2	12	>99	95[g]	4.2
14	Me	Ph	3	12	>99	95[g]	4.2
15	Me	Ph	4	12	>99	95[g]	4.2
16	Me	Ph	5	12	>99	94[g]	4.2
17	Me	Ph	6	12	>99	94[g]	4.2
18	Me	Ph	7	12	>99	93[g]	4.2
19	Me	Ph	8	12	>99	94[g]	4.2
20	Me	Ph	9	12	98	94[g]	4.1

[a] Reaction conditions: catalyst (58.8 mg, 0.02 mmol of Ni, based on ICP analysis), nitroalkene (1.0 mmol), malonate (1.0 mmol), toluene (4.0 mL), 40 °C, 12–120 h; turnover frequency (TOF = mole of substrate converted per mole of Ni complex per hour). [b] Determined by chiral HPLC analysis (Chiralcel AD-H column; see the Supporting Information, Figures S3 and S4); conversion was calculated by using an external standard. [c] Data are taken from reference [8a]. [d] Data were obtained by using a physical mixture of (1*R*,2*R*)-DACH-functionalized PMO (**3**) and $NiBr_2$ in the presence of (1*R*,2*R*)-*N*,*N'*-dibenzylcyclohexyldiamine as a catalyst. [e] Data were obtained by using a physical mixture of (1*R*,2*R*)-DACH-functionalized PMO (**3**) and $NiBr_2$ in the absence of (1*R*,2*R*)-*N*,*N'*-dibenzylcyclohexyldiamine. [f] Data were obtained by using 20% mol of (1*R*,2*R*)-DACH-functionalized PMO (**3**) as a catalyst. [g] Data were obtained by using the reused DACH-Ni-PMO (**5**) as a catalyst.

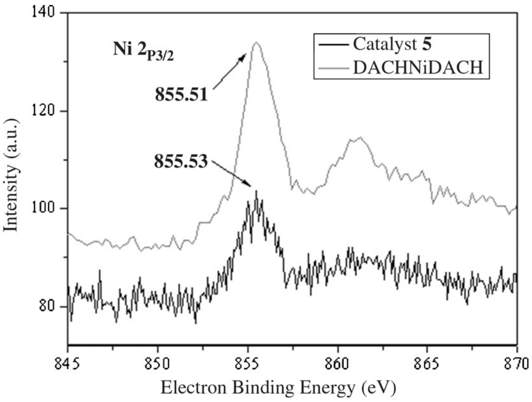


Figure 8. XPS spectra of DACHNiDACH and compound **5**.

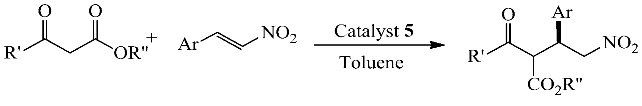
afforded their corresponding products with high conversions and excellent enantioselectivities under similar conditions. More interestingly, the steric properties of substituted malonates significantly affected their catalytic activities. As shown in Table 1, entries 1 and 4–7, as the alkyl ester group (R) became enlarged, their asymmetric reactions needed longer reaction times to reach completion. Indeed, in the case where the R group was a *tert*-butyl group (Table 1, entry 7), the reaction was not complete within three days. A reasonable explanation for this result was that the steric bulk of the mesopores was responsible for this trend, in which the large, sterically substituted malonates found it difficulty to enter the nanopores, thereby leading to prolonged reaction times. Evidence to support this view came from two comparable experiments, in which physical mixtures of the (1*R*,2*R*)-DACH-functionalized PMO (**3**) and an equimolar amount of the malonate (diethylmalonate or di-*tert*-butylmalonate) were suspended in the solution under the same conditions. After stirring for 4 h and filtering, the molar ratio of the two reactants in solution was 1:11.5, as detected by GC analysis, thus confirming that di-*tert*-butylmalonate found it more difficult to penetrated the mesopores, owing to the steric bulk of the mesopores. Furthermore, the electronic properties of the substituents on the nitroalkenes did not affect its catalytic activity and enantioselectivity. The reactions of diethyl malonate with electron-rich and electron-poor substituents on the nitroalkenes were equally efficient in the asymmetric Michael addition of diethylmalonate to nitroalkenes (Table 1, entries 8–11).

To gain better insight into the nature of this heterogeneous catalysis and to eliminate the disturbance that originates from mono(cyclohexyldiamine)-based Ni^{II} complexes within PMO materials, two control experiments were also carried out in which the asymmetric addition of diethylmalonate to nitrostyrene was performed with (1*R*,2*R*)-DACH-functionalized PMO (**3**) and $NiBr_2$ in the presence or absence of (1*R*,2*R*)-*N*,*N'*-dibenzylcyclohexyldiamine as the heterogeneous catalysts. We found that the former reaction afforded the corresponding products with 89% conversion and 94% *ee* (Table 1, entry 2), whilst the latter reaction gave the corresponding products with 45% conversion and 89% *ee* (Table 1, entry 3). The former result suggested that the catalyst that was synthesized by an in situ postmodification method also showed moderate catalytic performance. Its lower catalytic activity than that of catalyst **5** should be due to the fact that a small amount of $NiBr_2$ had not coordinated during the catalytic process, in which the loss of Ni was detected by ICP analysis in solution. The latter reaction indicated that the presence of mono(cyclohexyldiamine)-based Ni^{II} complexes was a key factor in determining chiral performance. Obviously, its lower catalytic efficiency than that of the heterogeneous catalyst (**5**) should be ascribed to the nature of the mono(cyclohexyldiamine)-based Ni^{II} complexes,[8a] in which the absence of additional (1*R*,2*R*)-*N*,*N'*-dibenzylcyclohexyldiamine group as a Brönsted base could not activate diethylmalonate to form deprotonated metal-bound acetylacetone, thereby resulting in decreased catalytic performance. In other words, bis(cyclohexyldiamine)-based Ni^{II} active centers within periodic mesoporous organosilicas played a dual role as the homogeneous catalyst:[8a] 1) the displaced ligands could activate diethylmalonate to enhance the catalytic activity, as shown by the ^{13}C CP MAS NMR spectrum of the mono(cyclohexyldiamine)-based Ni^{II}-acetylacetone intermediate (see above), and 2) mono(cyclohexyldiamine)-based Ni^{II} complexes could control the chiral microenvironment to improve the enantioselectivity.

An important feature of the design of heterogeneous catalyst **5** is its easy and reliable separation by simple filtration and that the reused catalyst could still retain its catalytic activity and enantioselectivity over multiple cycles. As shown in Table 1, entries 12–19, heterogeneous catalyst **5** clearly showed good reusability for the addition of dimethylmalonate to nitrostyrene, in which the *ee* values, as well as the conversions, did not drop notably after its continuous nine runs. To elucidate that the recycling efficiency was derived from the heterogeneous catalyst itself, rather than form noncovalent adsorption, a hot-filtration experiment was carried out. In this case, the heterogeneous catalyst (**5**) was filtered from the reaction mixture after 8 h and the reaction was continued for a further 12 h. We found that there was no appreciable change in either the conversion or *ee* values of the chiral products. This result ruled out the role of noncovalent physical adsorption, thereby confirming that the high recyclability was derived from the heterogeneous catalyst itself.

Importantly, this heterogeneous catalyst (**5**) could also be applied to the asymmetric Michael addition of β-ketoesters to nitroalkenes. As shown in Table 2, their corresponding products were formed with high conversions and excellent enantioselectivities under similar conditions. Taking dimethylacetoacetate as an example, the catalytic reaction afforded chiral products with more than 99 % conversion and 95 % *ee*, which was comparable to that with a homogeneous catalyst (Table 2, entry 1, in parentheses[8a]). Furthermore, this catalytic reaction could be completed within the same reaction time as that with the homogeneous catalyst, thus demonstrating that the ethylene moiety worked as the hydrophobic inner wall to rapidly draw reactants into the nanopore, thereby accelerating the reaction rate relative to other heterogeneous catalysts, which needed prolonged reaction times owing to the general features of heterogeneous catalysis.[11b] To confirm this conclusion, a similar heterogeneous inorganosilica-supported Ni^{II} catalyst was prepared by the similar co-condensation of (1*R*,2*R*)-DACH-derived silane (**1**) with tetraethylorthosilicate, in which O−Si−O groups acted as the inner wall rather than the phenyl moieties. With this catalyst, a reaction time of 18 h was needed to complete this reaction, thus confirming that the enhanced reaction rate in the case of heterogeneous catalyst **5** should be ascribed the high hydrophobicity of the nanopores.

Table 2. Asymmetric Michael addition of β-ketoesters to a nitroalkene.[a]



Entry	R′	R″	Ar	*t* [h]	Conv. [%][b]	d.r. (a/b)[b]	*ee* [%] (a/b)
1	Me	Me	Ph	6	>99	1.2:1 (1:1)	95 (93) (94 (94))
2	Me	Et	Ph	6	>99	1.3:1	94 (93)
3	Me	*i*Pr	Ph	8	>99	1.5:1	95 (95)
4	Me	*t*Bu	Ph	8	>99	1.7:1	95 (92)
5	*i*Pr	Et	Ph	8	96	1:1	97 (97)

[a] Reaction conditions: catalyst (58.8 mg, 0.02 mmol of Ni, based on ICP analysis), nitroalkene (1.0 mmol), β-ketoester (1.0 mmol), toluene (4.0 mL), 40 °C, 6–8 h. [b] Determined by chiral HPLC analysis (Chiralcel AD-H column; see the Supporting Information, Figure S5); conversion was calculated by using an external standard. [c] Data refer to those in Ref. [8a].

Conclusion

In conclusion, we have successfully immobilized chiral bis(cyclohexyldiamine)-based Ni^{II} complexes within periodic mesoporous organosilica to afford a chiral, heterogeneous, PMO-supported Ni^{II} catalyst (**5**). This catalyst exhibited high catalytic activity and excellent enantioselectivity in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes, comparable to those with homogeneous catalysts. In particular, this research also disclosed that chiral bis(cyclohexyldiamine)-based Ni^{II} complexes within the periodic mesoporous organosilica played a crucial role in determining both the catalytic and enantioselective performance. More importantly, heterogeneous catalyst **5** could be recovered and reused up to nine times without obviously affecting its enantioselectivity, thus showing good potential for industrial applications.

Experimental Section

Preparation of (1*R*,2*R*)-DACH-functionalized PMO (3): In a typical synthesis, the structure-directing agent (pluronic P123, 2.0 g) was fully dissolved in a mixture of 0.2 M hydrochloric acid (80 mL) and KCl (6.0 g). Then, bis(triethyoxysilyl)ethylene (3.46 g, 9.00 mmol) was added as the silica precursor at 40 °C. After a pre-hydrolysis period of 40 min, (1*R*,2*R*)-DACH-$[(CH_2PhSi(OMe)_3]_2$ (**1**, 0.53 g, 1.00 mmol) was added, in which the initial molar ratio of Si/P123/KCl/HCl/water in the mother solution was 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 EtOH before being dried overnight on a filter funnel. The surfactant template was removed by heating at reflux in acidic EtOH (400 mL per gram) for 24 h. The solid was filtered, rinsed again with EtOH, and dried at 60 °C under reduced pressure overnight to afford (1*R*,2*R*)-DACH-functionalized PMO (**3**, 1.26 g) as a white powder. ^{13}C CP MAS NMR (100.6 MHz): $\delta = 145.4$ (*C*H=*C*H), 133.5 (*C*H of the Ph rings inside the framework), 73.9, 69.3 (*C* atoms of the cyclohexyl group that are connected to the N atom), 57.3 ($O-CH_3$ and $O-CH_2CH_3$), 51.2–49.0 ($N-CH_2Ph$), 35.2–20.5 (*C* atoms in the cyclohexyl group that are not connected to the N atom), 16.6 ppm ($O-CH_2CH_3$); ^{29}Si MAS NMR (79.5 MHz): $\delta = -74.3$ (T^2), −81.0 ppm (T^3); IR (KBr): $\tilde{\nu} = 3420.1$ (s), 2984.5 (w), 2942.9 (w), 2869.4 (w), 1609.9 (m), 1452.9 (w), 1403.0 (w), 1189.4 (s), 1049.3 (s), 925.8 (m), 802.3 (m), 440.2 cm^{-1} (m); $S_{BET} = 514.2\ m^2g^{-1}$; $d_{pore} = 3.67$ nm; $V_{pore} = 0.46\ cm^3g^{-1}$; elemental analysis found (%) found: C 32.60, H 4.52, N 0.81.

Preparation of heterogeneous catalyst 5: To a stirring suspension of (1*R*,2*R*)-DACH-functionalized PMO (**3**, 1.0 g) in dry MeCN (50 mL) was added $NiBr_2$ (51.84 mg, 0.24 mmol) and *N*,*N*′-dibenzyl diamine (70.56 mg, 0.24 mmol) at room temperature. The resulting mixture was heated at reflux for 12 h. After cooling to room temperature, the mixture was filtered through filter paper and rinsed with excess CH_2Cl_2. After Soxlet extraction (toluene) for 24 h to remove any homogeneous and unreacted starting materials, the solid was dried overnight at 60°C under vacuum to afford heterogeneous catalyst **5** (1.04 g) as a pale powder. ICP analysis showed that the Ni loading was 19.68 mg (0.34 mmol) per gram of catalyst. ^{13}C CP MAS NMR (161.9 MHz): $\delta = 146.9$ (*C*H=*C*H), 135.3 (*C*H of the Ph rings inside the framework), 130.4 (*C*H of the Ph rings outside the framework), 74.9, 70.9 (*C* of the cyclohexyl group that are connected to the N atom), 59.7 (O$-$*C*H_3 and O$-$*C*H_2CH_3), 53.1, 50.6, 48.5 (N$-$*C*H_2Ph), 33.7, 30.4, 25.4 (*C* atoms in the cyclohexyl group that are not connected to the N atom), 18.8 ppm (O$-CH_2$*C*H_3); ^{29}Si MAS NMR (300 MHz): $\delta = -74.5$ (T^2), -82.9 ppm (T^3); IR (KBr): $\tilde{\nu} = 3413.2$ (s), 3083.0 (w), 2976.2 (w), 2942.8 (w), 2869.3 (w), 1609.7 (m), 1452.9 (w), 1403.0 (w), 1189.4 (s), 1049.3 (s), 925.8 (m), 802.3 (m), 695.5 (w), 662.2 (w), 440.2 cm^{-1} (m); $S_{BET} = 498.8\ m^2g^{-1}$; $d_{pore} = 3.64$ nm; $V_{pore} = 0.44\ cm^3g^{-1}$; elemental analysis found (%): C 38.50, H 5.38, N 1.91.

Treatment of heterogeneous catalyst 5 with acetylacetone: To heterogeneous catalyst **5** (300 mg) was added acetylacetone (2.0 mL) and the mixture was stirred for 12 h at room temperature. The mixture was then filtered through filter paper and rinsed with excess CH_2Cl_2. After Soxlet extraction (toluene) for 24 h to remove any homogeneous and unreacted start materials, the solid was dried overnight at 60°C under vacuum to afford the mono(cyclohexyldiamine)-based Ni^{II}–acetylacetone intermediate as a pale powder. ^{13}C CP MAS NMR (161.9 MHz): $\delta = 192.7$ (*C* of the C=O group), 146.8 (*C*H=*C*H), 134.9 (*C*H of the Ph rings inside the framework), 130.1 (*C*H of the Ph rings outside the framework), 101.8 (*C*H atom at the enolized position), 73.1, 70.3 (*C* atoms of the cyclohexyl group that are connected to the N atom), 59.2 (O$-$*C*H_3 and O$-$*C*H_2CH_3), 56.4, 52.4, 52.0, 50.0 (N$-$*C*H_2Ph substituted by acetylacetone and N$-$*C*H_2Ph unsubstituted by acetylacetone), 27.3 (*C*H_3 of acetylacetone), 32.1, 29.7, 24.9 (*C* atoms in the cyclohexyl group that are not connected to the N atom), 18.5 ppm (O$-CH_2$*C*H_3).

General procedure for asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes: In a typical procedure, heterogeneous catalyst **5** (58.8 mg, 0.02 mmol of Ni, based on ICP analysis), nitrostyrene (0.15 g, 1.0 mmol), dimethylmalonate (1.0 mmol), and toluene (4.0 mL) were added into a 10 mL round-bottomed flask and the mixture was heated at 40°C for 8–28 h. During that time, the reaction was monitored constantly by TLC. After the completion of the reaction, the heterogeneous catalyst was filtered through filter paper for the recycling experiments. The aqueous solution was extracted with Et_2O (3×3.0 mL) and the combined Et_2O extracts were washed twice with brine and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by column chromatography on silica gel to afford the desired product. Conversion was calculated by using an external standard and the *ee* value was determined by chiral HPLC analysis with a UV/Vis detector and a Daicel AD-H chiralcel column ($\Phi = 0.46$ cm × 25 cm). The absolute configurations of the compounds were assigned by comparison of their optical rotations to literature values.[8a]

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