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PAPER

N-Heterocyclic carbene functionalized MCM-41 as an efficient catalyst for chemical fixation of carbon dioxide†

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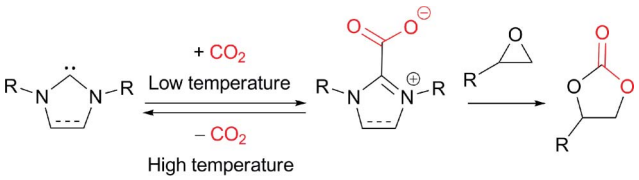
N-Heterocyclic carbene (NHC) functionalized MCM-41 was synthesized by reacting 1,3-bis-(4-allyl-2,6-diisopropylphenyl) imidazolium chloride with MCM-41 using 3-mercaptopropyltrimethoxysilane as silane coupling agent, and its CO_2 adduct (designated as MCM-41-IPr-CO_2) was further synthesized by the reaction with CO_2. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to investigate the reversible CO_2 capture-release ability of MCM-41-NHC. MCM-41-IPr-CO_2 adduct proved to be an efficient heterogeneous catalyst for the cycloaddition of CO_2 to epoxides or aziridines with excellent regioselectivity under mild conditions. Moreover, the catalyst could be recovered easily through a simple filtration process and reused multiple times without obvious loss in activity, owing to CO_2 as protective group for effectively stabilizing the NHC anchored on MCM-41.

Introduction

Chemical fixation of carbon dioxide into desirable, economically competitive products has attracted much attention in the last few decades due to economic and environmental benefits arising from the utilization of renewable sources and the growing concern of the greenhouse effect.[1–5] One of the most promising ways that effectively utilizes CO_2 is the synthesis of cyclic carbonates through the coupling reaction with epoxides.[6,7] This 100% atom economical reaction has been a commercial process for producing cyclic propylene and ethylene carbonates for over fifty years.[8] Numerous homogeneous and heterogeneous catalyst systems associated with metal complexes,[9–24] organic bases or ammonium salts,[25–28] metal oxides,[29–31] have been developed for this transformation.

Although nucleophilic organic bases or quaternary organic ammonium salts show activity for catalyzing the coupling of CO_2 with epoxides, the activation of CO_2 during the reaction is not clear. On the contrary, it is generally known that NHC as a nucleophile can activate CO_2 to form imidazolium carboxylates (designated as NHC–CO_2 adduct),[32,33] in which the angle of the O–C–O bond is close to 130°, indicating a strong activation of CO_2. However, the application of such carboxylates has been limited to the preparation of precursors to NHC-metal complexes,[34,35] halogen-free ionic liquids[36] and some stoichiometric transcarboxylation reactions.[37,38] CO_2 chemical transformation catalyzed by NHC is rare.[39–41] According to recent research on the thermal stability of NHC–CO_2, we found that NHC could effectively activate CO_2 and catalyze the coupling reaction of CO_2 with epoxides to give the corresponding cyclic carbonates in excellent yields (Scheme 1).[42]



Scheme 1 Activation of CO_2 and chemical conversion by the coupling with epoxides catalyzed by *N*-heterocyclic carbene.

Homogeneous catalysts regarding NHC often pose a serious threat to the practical utility due to difficulties in catalyst separation from the mixture of product and solvents. Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[43] MCM-41 has a regular pore diameter and a specific surface area more than 700 m^2g^{-1}.[44] Its large pore size allows passage of large molecules through the pores to reach to the surface of the channel.[45–47] It is generally believed that high surface area of heterogeneous catalysts results in high catalytic activity.

Based on the understanding described above, herein, we report the synthesis of novel heterogeneous catalyst containing NHC anchored in MCM-41, as well as its application for CO_2 activation and further chemical transformation.

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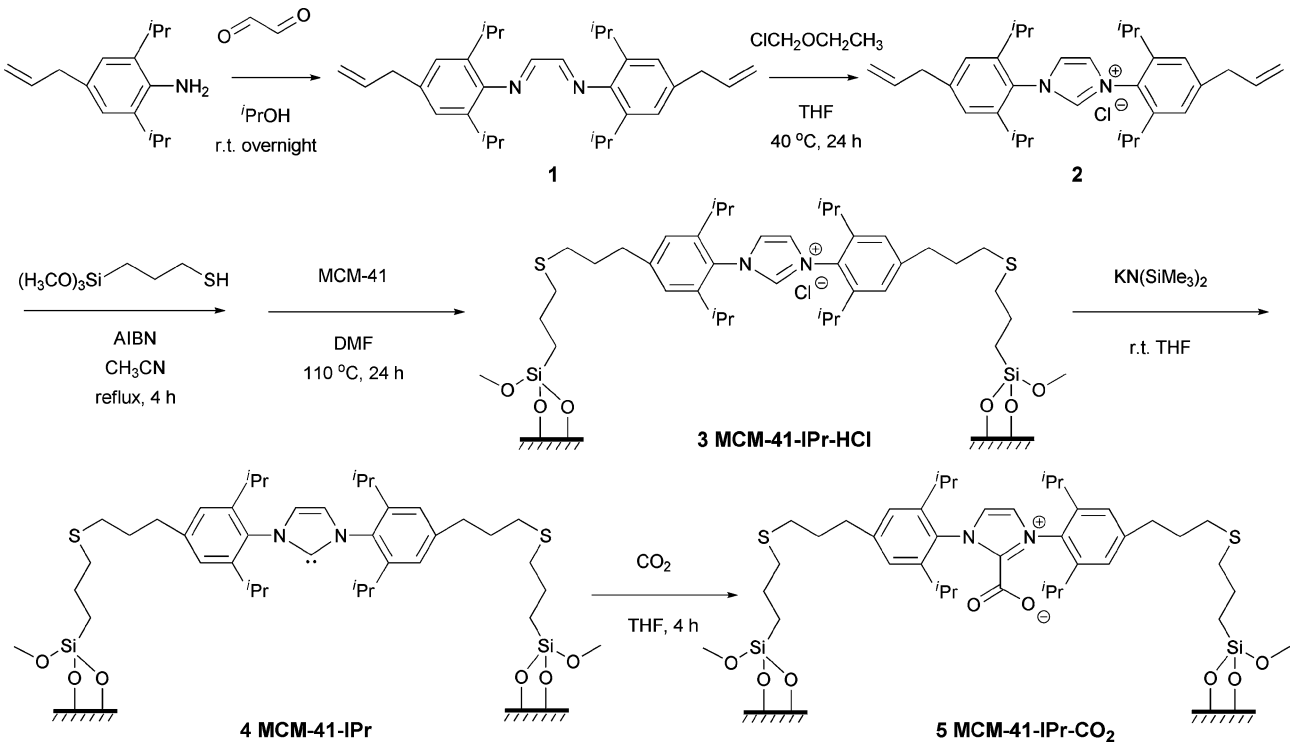


Scheme 2 Synthesis of MCM-41-supported *N*-heterocyclic carbene.

Results and discussion

As shown in Scheme 2, 1,3-bis-(2,6-diisopropylphenyl) imidazol-2-ylidene (IPr) functionalized MCM-41 (designated as MCM-41-IPr) was prepared by reacting 1,3-bis-(4-allyl-2,6-diisopropylphenyl) imidazolium chloride with MCM-41 using 3-mercaptopropyltrimethoxysilane as silane coupling agent, and its CO_2 adduct was further synthesized by the reaction with CO_2. The successful incorporation of *N*-heterocyclic carbene moiety was confirmed by elemental analysis (0.46 mmol g^{-1}).

Reversible CO_2 fixation by NHC was observed both in solution and solid state. Usually, CO_2 is captured by NHC at relatively low temperatures less than 100 °C, and the activated CO_2 is easily released by heating. We have recently demonstrated that a reversible system for efficient trap and release of CO_2 by 1-benzyl-3-(2,6-diisopropylphenyl)imidazol -2-ylidene (IBnPr) attached to polymer side chains, which exhibited higher CO_2 fixing efficiency (57% CO_2 fixing efficiency with a CO_2 flow 40 mL min^{-1} at 40 °C for 60 min) than the previously reported amine-functionalized polymers.[48]

CO_2 capture ability of IPr was evaluated by thermogravimetric analysis (TGA) under the same experimental conditions. Fig. 1 shows that 72.5% fixing efficiency could be found within 100 min. This result indicates that IPr could be more efficient in CO_2 capture than IBnPr. The reversible CO_2 fixation-release behavior of MCM-41-IPr was evaluated as a highly-efficient CO_2 adsorbent.

Fig. 2 displays *in situ* DRIFTS difference spectra that record the reversible trap and release of CO_2 by MCM-41-IPr. Initial MCM-41-IPr-CO_2 spectrum was recorded at 120 °C as background (curve **a**). 1662 cm^{-1} is attributable to asymmetric $\nu(CO_2)$ vibration of MCM-41-IPr-CO_2. When increasing the

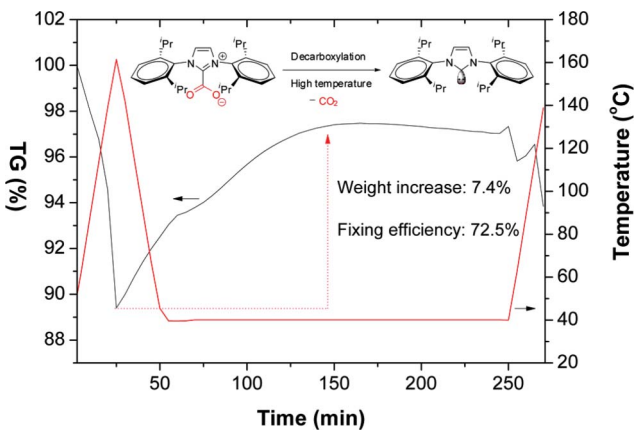


Fig. 1 CO_2 fixing efficiency of IPr monitored by TGA.

temperature to 180 °C, a band at 1662 cm^{-1} was observed and grew rapidly (curves **b** and **d**) which indicated that MCM-41-IPr-CO_2 decarboxylated upon heating. When the temperature was reduced to 40 °C and CO_2 was introduced, the intensity of the band at 1662 cm^{-1} was obviously weakened, almost recovering its initial position (curves **c** and **e**). The experimental process was repeated twice under the same conditions. This demonstrated that MCM-41-IPr could effectively trap CO_2 at relatively low temperatures and release the activated CO_2 at enhanced temperatures reversibly.

During our previous investigations, we found that the five-membered cyclic carbonates could be obtained in excellent yield from IPr-CO_2 adduct (0.5 mol%) catalyzed coupling reaction of epoxides with CO_2 under mild conditions (2.0 MPa CO_2, 120 °C, 24 h).[42] Therefore, this coupling was also used as model reaction

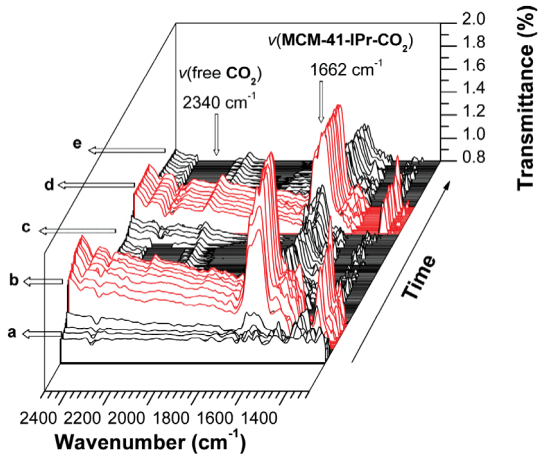
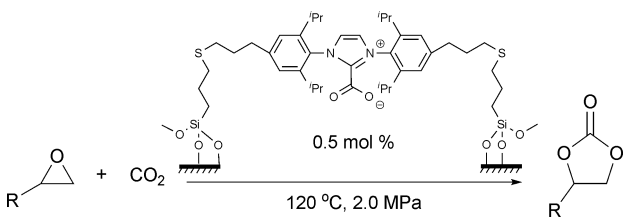


Fig. 2 DRIFTS difference spectra recorded the reversible binding CO_2 behavior of MCM-41-IPr. (a) 120 °C, N_2: 200 mL min^{-1}, background; (b) (d) 180 °C, N_2: 200 mL min^{-1}, CO_2 release of MCM-41-IPr-CO_2; (c) (e) 40 °C, CO_2: 200 mL min^{-1}, CO_2 activation of MCM-41-IPr.

to evaluate the activity of MCM-41-IPr-CO_2, as heterogeneous NHC catalyst, in CO_2 chemical fixation.

To our delight, MCM-41-IPr-CO_2 proved to be an effective catalyst for the coupling reaction of CO_2 with propylene oxide (Table 1 entries 1 and 2). Complete conversion of propylene oxide was achieved in 48 h at 120 °C with a low catalyst loading of 0.5 mol% MCM-41-IPr-CO_2, and no by-product was observed in the resulting product by means of ^{1}H NMR analysis. As expected, the rate is less than that in the reaction carried out with the homogeneous IPr-CO_2 as catalyst, suggesting that the MCM-41-supported catalyst suffered from diffusion resistance. For comparison purposes, we also tested the catalytic activity of free IPr for this reaction. A similar activity in comparison with its CO_2 adduct (IPR-CO_2) was observed at the same conditions. Indeed, when the system temperature is less than 120 °C, in the presence of free CO_2, MCM-41-IPr rapidly reacts with CO_2 to form the corresponding CO_2 adduct (MCM-41-IPr-CO_2).

Table 1 Coupling of epoxides with CO_2 catalyzed by MCM-41-IPr-CO_2[a]



Entry	–R	Time (h)	Yield (%)[b]
1	–Me	24	72
2	–Me	48	100
3	–Et	48	95
4	–^{n}Bu	48	90
5	–Ph	48	87
6	–Me[c]	48	100

[a] Typical reaction conditions: 50 mmol epoxides, 0.5 mol% MCM-41-IPr-CO_2, 4 mL CH_2Cl_2, 2.0 MPa CO_2. [b] Yield determined by ^{1}H NMR spectroscopy. [c] (*R*)-Propylene oxide.

Table 2 MCM-41-IPr-CO_2 recycling studies in the coupling of CO_2 with 1,2-butylene oxide[a]

Entry	Catalyst cycle[b]	Yield (%)[c]
1	Fresh	95
2	1	94
3	2	92
4	3	91

[a] Reaction conditions: 50 mmol 1,2-butylene oxide, 0.5 mol% MCM-41-IPr-CO_2, 4 mL CH_2Cl_2, 2.0 MPa CO_2 at 120 °C for 48 h. [b] No additional MCM-41-IPr-CO_2 was added in the recycling experiments. [c] Yield (%) of product determined using ^{1}H-NMR.

We further investigated the reactions using a variety of monosubstituted terminal epoxides as the substrates under the same conditions, and the results are outlined in Table 1 (entries 3–5). The coupling reaction of CO_2 with epoxides proceeded smoothly to give the corresponding cyclic carbonates in good to excellent yields with 100% selectivity. Recently, Barbarini and coworkers reported 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) functionalized MCM-41 as catalyst for the coupling of styrene oxide with CO_2,[25] and 90% yield was obtained at 140 °C within 70 h.

To test the regiochemistry regarding epoxide ring-opening in this reaction, we also performed the coupling reaction of (*R*)-propylene oxide with CO_2 under the same conditions (entry 6), and found that the corresponding (*R*)-propylene carbonate was obtained in 100% yield with retention of stereochemistry. This indicates that the nucleophilic attack of the carboxylate anion exclusively occurs at the less sterically hindered carbon atom of the terminal epoxide.

Furthermore, the more important investigation on the recyclability of MCM-41-IPr-CO_2 was also performed using 1,2-butylene oxide as the substrate at the optimized reaction conditions (Table 2). In each cycle, the catalyst MCM-41-IPr-CO_2 could be easily recovered by simple filtration and rinse with THF, respectively. After drying, the recovered catalyst was reused for the next run. It is generally known that free NHC shows air and moisture sensitivity. We were delighted to find that MCM-41-IPr-CO_2 was very stable, retaining high activity and selectivity even after three recycles without any addition of fresh catalyst. The stability of IPr-CO_2 adduct anchored in MCM-41 was also confirmed by FT-IR analysis. As shown in Fig. 3, the recyclable catalyst showed obvious vibration at 1662 cm^{-1} similar to the fresh MCM-41-IPr-CO_2. It should ascribe to the bound CO_2 as a protective group of NHC, which avoids the decomposition of NHC during filtration and washing with THF.

Encouraged by the successful results of CO_2-fixation using epoxides, we next extended the scope of this catalytic system. Very recently, Ikariya and co-wokers reported the carboxylative cyclization of propargylic alcohols with CO_2 catalyzed by NHC–CO_2 (5 mol%) to form cyclic carbonates under mild reaction conditions (2.5–10 MPa CO_2, 40–100 °C, 15 h).[41] Among NHC, IPr showed lower catalytic activity due to the negative effect of the electron-withdrawing aryl substituents on the NHC nitrogen atoms. In contrast, MCM-41-IPr (5 mol%) exhibited higher catalytic activity and 15% yield could be obtained with a temperature increase to 120 °C (2.0 MPa CO_2, 24 h).

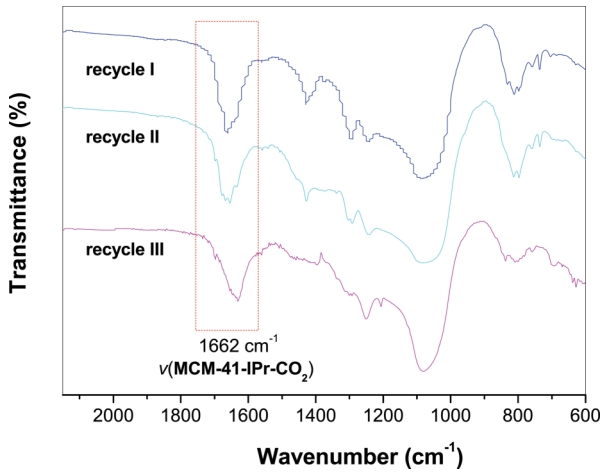
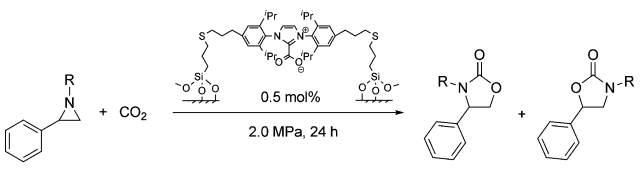


Fig. 3 FT-IR spectra of catalyst after recycle.

Further investigations on substitutes find that *N*-substituted aziridines could be effectively transformed to oxazolidinones with CO_2 catalyzed by MCM-41-IPr. In contrast with the analogous epoxides/CO_2 coupling, the carboxylation of aziridines with CO_2 could proceed in the more mild conditions and the results were summarized in Table 3. It is worth mentioning that 5-aryl-2-oxazolidinones were preferentially formed under the identical reaction conditions. Variation of temperature (80–120 °C) had no influence on the regioselectivity of oxazolidinones (Table 3, entries 1–3). While the regioselectivity can be significantly enhanced from 65 : 35 to an exclusive generation of 5-substituted oxazolidinones (entries 1 and 4–6) as the alkyl substituent at the nitrogen atom is augmented. 1-*c*Hex-2-phenylaziridine afforded lower yield (80%) under same experimental conditions which may result from the high steric hindrance of nitrogen atom.[49]

As for the cycloaddition mechanism of CO_2 with epoxides or aziridines catalyzed by MCM-41-IPr-CO_2, we speculated a mechanism shown in Scheme 3. The zwitterionic moiety IPr-CO_2 on MCM-41 firstly attacks the strained three-membered heterocyclic rings to generate the new zwitterion. Then the nucleophilic attacks of the formed oxy or nitrogen anions toward the carbon atom of carbonyl group produced cyclic carbonates or oxazolidinones by intramolecular cyclic elimination. Finally, the produced MCM-41-IPr quickly reacted with CO_2 to regenerate MCM-41-IPr-CO_2 adduct.

Table 3 Coupling of *N*-substituted aziridines with CO_2 catalyzed by MCM-41-IPr-CO_2[a]



Entry	–R	*T*/°C	Conv. (%)[b]	Isolated yield (%)[c]	Regioselectivity (%)[d]
1	–Me	80	>99	95	65 : 35
2	–Me	100	>99	94	64 : 36
3	–Me	120	>99	94	64 : 36
4	–Et	80	>99	92	92 : 8
5	–Bn	100	>99	94	100
6	–*c*Hex	100	83	80	100

[a] Reaction conditions: aziridines (2 mmol), MCM-41-IPr-CO_2 (20 mg), CH_2Cl_2 1.5 mL. [b] Determined by GC using biphenyl as an internal standard. [c] The total yield of 4-substituted oxazolidinones and 5-substituted oxazolidinones. [d] Molar ratio of 5-substituted oxazolidinones to 4-substituted oxazolidinones, determined by ^{1}H NMR.

Conclusions

In summary, MCM-41-IPr is endowed with multi-ability for CO_2 activation and chemical conversion. *In situ* DRIFTS demonstrated its reversible binding with CO_2. MCM-41-IPr-CO_2 adduct was found to be an efficient heterogeneous catalyst for the cycloaddition of CO_2 to epoxides or aziridines with excellent regioselectivity. Moreover, it could be recovered easily through a simple filtration process and reused multiple times without significant loss in catalytic activity owing to CO_2 as a protective group.

Experimental

All air or water sensitive reactions were carried out under nitrogen using standard Schlenk-line techniques. Epoxides were dried over calcium hydride and fractionally distilled under a nitrogen atmosphere prior to use. Carbon dioxide (99.999%) was purchased from Dalian Institute of Special Gases and used as received. Tetrahydrofuran was distilled under N_2 atmosphere from sodium/benzophenone. Methylene chloride and acetonitrile were distilled from calcium hydride under N_2 atmosphere. *N*,*N*-Dimethylformamide was distilled under N_2 atmosphere from powdered BaO.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^{1}H, 400 MHz) spectrometer. Their peak frequencies were referenced *versus* an internal standard (TMS) shifts at 0 ppm for ^{1}H NMR and against the solvent, chloroform-*d* at 77.0 ppm for ^{13}C NMR, respectively.

LC-MS were performed on a Thermo Finnigan LCQ Advantage spectrometer in ESI model-I (ESI-MS) with spray voltage 4.8 KV and atmospheric pressure chemical ionization (APCI-MS). High resolution mass spectrometry (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with *Z*-spray ionization source.

Thermo-gravimetric analyses were measured on Mettler-Toledo TGA/SDTA851e.

Stereoconfiguration of propylene carbonate, which was synthesized by the coupling reaction of (*R*)-propylene oxide with CO_2 catalyzed by MCM-41-IPr-CO_2, was determined by chiral capillary GC analysis (GC column, 2,6-dibutyl-3-butyryl-β-Cyclodex, 30 m × 0.25 mm id × 0.25 μ m film; injection *T* = 250 °C; detection *T* = 250 °C) using a Hewlett Packard 5890 Gas Chromatograph with N_2 as a carry gas.

Preparation of 4-Allyl-2,6-diisopropylaniline

4-Allyl-2,6-diisopropylaniline was prepared according to the literature.[50] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.85 (s, 2H, Ar*H*), 5.96–5.98 (m, 1H, C*H*=CH_2), 5.03–5.10 (m, 2H, CH=CH_2), 3.65 (s, 2H, NH_2), 3.32 (d, 2H, *J* = 7.2 Hz, Ph–CH_2), 2.89–2.94 (m, 2H, C*H*(CH_3)$_2$), 1.27 (d, 12H, *J* = 6.8 Hz, CH(CH_3)$_2$).

Preparation of *N*,*N*′-bis-(4-allyl-2,6-diisopropyl-phenyl) ethanediimine (1)

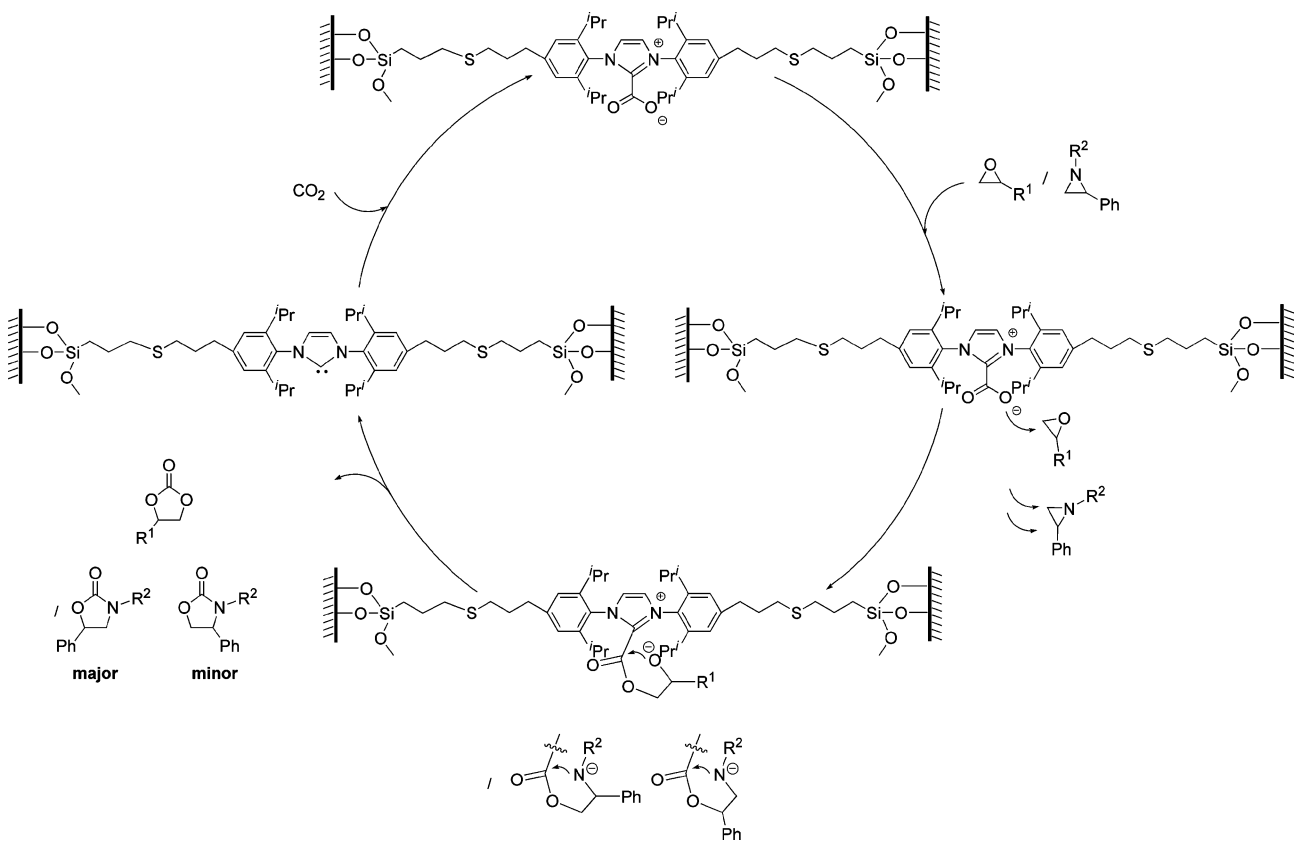
A 50 mL round-bottom flask was charged with 4-allyl-2,6-diisopropylaniline(1.8 g, 8.2 mmol), 40% aqueous solution of glyoxal (0.6 g, 4.1 mmol) and 30 mL of absolute isopropyl alcohol. A few drops of formic acid were added as catalyst. The color of the reaction mixture turned from colorless to yellow gradually, and a yellow precipitate appeared after a few hours. The reaction mixture was stirred over night and the yellow solid was collected by filtration and purified by silica gel column chromatography (eluent : petroleum ether/EtOAc = 20 : 1) to give the corresponding **1** as a yellow solid (1.77 g, 94% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.08 (s, 2H, N=C*H*), 6.99 (s, 4H, Ar*H*), 5.96–6.04 (m, 2H, C*H*=CH_2), 5.08–5.15 (m, 4H, CH=CH_2), 3.40 (d, 4H, J = 6.8 Hz, ArCH_2), 2.89–2.96 (m, 4H, C*H*(CH_3)$_2$), 1.18 (d, 24H, J = 6.8 Hz, CH(CH_3)$_2$).

Preparation of 1,3-bis-(4-allyl-2,6-diisopropyl-phenyl) imidazolium chloride (2)

Under N_2, a 100 mL three-neck round-bottomed flask was charged with chloromethylethyl ether (0.96 mL, 10.4 mmol) in 20 mL THF. To this solution was added a solution of *N*,*N*′-bis-(4-allyl-2,6-diisopropylphenyl)ethanediimine (2.4 g, 5.2 mmol) in 20 mL THF and 2 drops of water. The reaction mixture was stirred at 40 °C for 16 h during which time the color of the reaction mixture turned brown and a white precipitate appeared. The precipitate was collected by filtration and purified by silica gel column chromatography (eluent: CH_2Cl_2–EtOH = 10 : 1) to give the corresponding **2** as a white solid (1.04 g, 40% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.94 (s, 1H, NC(*H*Cl)N), 8.12 (s, 2H, N=C*H*), 7.14 (s, 4H, Ar*H*), 5.92–6.03 (m, 2H, C*H*=CH_2), 5.14–5.19 (m, 4H, CH=CH_2), 3.47 (d, 4H, J = 6.4 Hz, ArCH_2), 2.40–2.44 (m, 4H, C*H*(CH_3)$_2$), 1.25 (d, 24H, J = 6.8 Hz, CH(CH_3)$_2$). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.95, 138.71, 129.28, 128.04, 125.45, 117.31, 40.20, 39.95, 29.03, 24.45, 23.78. **HRMS** (*m*/*z*) Calcd. for $C_{33}H_{45}ClN_2$: 504.3271, found: 469.3838 $(M–Cl)^+$.

Preparation of MCM-41-IPr-HCl (3)

Under N_2, a solution of 1,3-bis-(4-allyl-2,6-diisopropyl-phenyl)imidazolium chloride (0.78 g, 1.50 mmol) and 3-mercaptopropyltrimethoxysilane (0.9 mL, 3.0 mmol) in previously deaerated anhydrous MeCN (10 mL) was stirred at 70 °C for 4 h in the presence of 2,2′-azobisisobutyronitrile (AIBN, 120 mg, 0.75 mmol) as radical initiator. Then the solvent was removed under reduced pressure and previously dehydrated MCM-41 (1.5 g) and DMF (30 mL) were added to reactor. The suspension stirred at 110 °C for 24 h. The solid was filtered and soxhlet extracted with $CHCl_3$ for 6 h. **Anal**. **Calcd**. for loading amount of IPr-HCl groups (based on N analysis): 0.46 mmol g^{-1}.



Scheme 3 Possible mechanism for the reaction of CO_2 with epoxides or aziridines catalyzed by MCM-41-IPr-CO_2.

Preparation of MCM-41-IPr-CO_2 (5)

Under N_2, 100 mL three-neck round-bottomed flask was charged with MCM-41-IPr-HCl (1.0 g), THF (30 mL) and potassium bis (trimethylsilyl)amide (1.25 mL, 0.91 M in THF). High purity CO_2 gas (99.999%) was bubbled into the solution. The suspension was stirred 4 h at room temperature, filtered and washed with THF (3 × 10 mL). Then the product was dried under high vacuum. **FT-IR** ν(C═O): 1662 cm^{-1} (KBr disc).

Preparation of aziridines

All of the aziridines were synthesized according to the following literature procedures.[49,51]

1-Methyl-2-phenylaziridine. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19–7.30 (m, 5H, Ph–*H*), 2.47 (s, 3H, -CH_3), 2.25 (dd, 1H, J = 3.2 Hz, J = 3.2 Hz, Ph–C*H*), 1.89 (d, 1H, J = 3.2 Hz, N–CH_2), 1.61 (d, 1H, J = 3.2 Hz, N–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.20, 128.27, 125.94, 47.92, 42.30, 39.35.

1-Ethyl-2-phenylaziridine. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18–7.31 (m, 5H, Ph–*H*), 2.44 (q, 2H, J = 8.0 Hz, -CH_2CH$_3$), 2.30 (dd, 1H, J = 4.0 Hz, J = 4.0 Hz, Ph–C*H*), 1.89 (d, 1H, J = 4.0 Hz, CH–N–CH_2), 1.64 (d, 1H, J = 8.0 Hz, CH–N–CH_2), 1.19 (t, 3H, J = 8.0 Hz, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.23, 127.96, 126.75, 126.13, 55.86, 41.12, 37.56, 14.46.

1-Benzyl-2-phenylaziridine. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18–7.33 (m, 10H, Ph–*H*), 3.68 (ABq, 2H, J_{AB} = 16.0 Hz, Ph–CH_2), 2.50 (q, J = 4.0 Hz, Ph–C*H*), 1.99 (d, 1H, J = 4.0 Hz, CH–N–CH_2), 1.86 (d, 1H, J = 8.0 Hz, CH–N–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.09, 139.08, 128.49, 128.34, 127.82, 126.96, 126.87, 126.23, 64.73, 41.50, 37.94.

1-Cyclohexyl-2-phenylaziridine. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18–7.30 (m, 5H, Ph–*H*), 2.35 (dd, 1H, J = 4.0 Hz, J = 4.0 Hz, Ph–C*H*), 1.19–1.85 (m, 13H, *c*Hex-*H*). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.65, 128.18, 126.65, 126.42, 69.72, 40.11, 35.90, 32.96, 32.28, 26.12, 24.87, 24.84.

DRIFTS experiment of MCM-41-IPr-CO_2

The DRIFTS spectra were carried out using a Bruker Equinox 55 FT-IR spectrometer. Temperature was controlled with a thermocouple. MCM-41-IPr-CO_2 was loaded into the DRIFTS cell and flushed with N_2 (200 mL min^{-1}) for 30 min and the temperature of the system was raised at a rate of 20 °C min^{-1} to 120 °C. The background spectra were recorded and then temperature was increased to 180 °C. After 1 h, the temperature was reduced to 40 °C. Then CO_2 was introduced with a flow rate of 200 mL min^{-1} for 30 min. The process was repeated twice under the same conditions. The spectra were recorded every minute.

General procedure of MCM-41-IPr-CO_2 catalyzed coupling reaction

In a typical procedure, MCM-41-IPr-CO_2 firstly was placed in a pre-dried 40 mL autoclave. After the autoclave was sealed, it was degassed and purged with high purity N_2 three times. Then substrates (epoxides or aziridines) and CH_2Cl_2 were added to autoclave under N_2 and the autoclave was closed and pressurized with 2.0 MPa CO_2. The reaction was carried out at a desired temperature for some time with continuous stirring. Then, the autoclave was cooled, and the excess CO_2 was slowly vented. The yields of target products were determined by ^{1}H NMR analysis and GC.

Recycling experiment of MCM-41-IPr-CO_2

MCM-41-IPr-CO_2 (0.5 g, 0.25 mmol IPr-CO_2 moiety) was placed in a pre-dried 40 mL autoclave. After the autoclave was sealed, it was degassed and purged with high purity N_2 three times. Then 50 mmol of 1,2-butylene oxide and 4 mL of CH_2Cl_2 were added to autoclave under N_2 and the autoclave was closed and pressurized with 2.0 MPa CO_2. The reaction was carried out at 120 °C for 48 h with continuous stirring. Then, the autoclave was cooled, and the excess CO_2 was slowly vented. The yield of 1,2-butylene carbonate was determined by ^{1}H NMR analysis. The reaction mixture was filtered and washed with THF (50 mL) under N_2. The recovered MCM-41-IPr-CO_2 was dried under vacuum and directly used for the next run.

Characterization of carbonates and oxazolidinones

Propylene carbonate. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.82–4.87 (m, 1H, C*H*), 4.55 (t, 1H, J = 8.0 Hz), 4.03 (t, 1H, J = 8.0 Hz, C*H*), 1.51 (d, 3H, J = 6.4 Hz, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.34, 73.84, 70.85, 19.34. **FT-IR** ν(C═O): 1801 cm^{-1} (Film).

1,2-Butene carbonate. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.54 (t, 1H, J = 8.1 Hz, C*H*), 4.13 (dd, 1H, J = 8.1 Hz), 1.74–1.95 (m, 2H, CH_2), 1.0 (t, 3H, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.91, 78.82, 69.84, 27.65, 9.22. FT-IR ν(C═O): 1795 cm^{-1} (Film).

1,2-Hexene carbonate. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.67–4.74 (m, 1H, C*H*), 4.53 (t, 1H, J = 8.2 Hz, C*H*), 4.07 (dd, 1H, J = 8.2 Hz, C*H*), 1.60–2.0 (m, 6H, CH_2), 0.91 (t, 3H, J = 7.1 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.53, 77.45, 69.72, 33.75, 26.63, 22.55, 14.02. **FT-IR** ν(C═O): 1802 cm^{-1} (Film).

Phenyl ethylene carbonate. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26–7.47 (m, 5H, Ar*H*), 5.67 (t, 1H, J = 8.0 Hz, ArC*H*), 4.79 (t, 1H, J = 8.0 Hz, C*H*), 4.34 (t, 1H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.83, 135.74, 129.64, 129.12, 125.85, 71.12. FT-IR ν(C═O): 1755 cm^{-1} (KBr disc).

3-Methyl-5-phenyloxazolidin-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35–7.42 (m, 5H, Ph–*H*), 5.48 (t, 1H, J = 8.0 Hz, Ph–C*H*), 3.92 (t, J = 8.0 Hz, -CHCH_2-), 3.45 (t, J = 8.0 Hz, -CHCH_2-), 2.93 (s, 3H, -CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.33, 138.81, 129.01, 128.92, 125.65, 74.29, 54.58, 31.11. **ESI-MS** calcd. for $C_{10}H_{11}NO_2$, 177.1, found 178.1 $(M+H)^+$, 200.1 $(M+Na)^+$, 377.0 $(2\,M + Na)^+$. **FT-IR** ν(C═O): 1754 cm^{-1} (Film).

3-Methyl-4-phenyloxazolidin-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30–7.69 (m, 5H, Ph–*H*), 4.52–4.78 (m, 2H, Ph–C*H* and -CHCH_2-), 4.05–4.12 (dd, 1H, J = 8.0 Hz, -CHCH_2-), 2.71 (s, 3H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.80, 137.79, 129.49, 129.25, 127.00, 69.89, 62.31, 29.42. ESI-MS calcd. for $C_{10}H_{11}NO_2$, 177.1, found 200.1 $(M+Na)^+$, 377.2 $(2\,M + Na)^+$. FT-IR ν(C═O): 1764 cm^{-1} (Film).

3-Ethyl-5-phenyloxazolidin-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27–7.43 (m, 5H, Ph–*H*), 5.49 (t, 1H, J = 8.0 Hz, Ph–C*H*), 3.93 (t, 1H, J = 8.0 Hz, CH–CH_2), 3.29–3.46 (m, 3H, CH–CH_2 and -CH_2CH$_3$), 1.18 (t, 3H, J = 8.0 Hz, -CH$_2$CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.80, 138.97, 128.90, 125.64, 74.43, 51.73, 39.04, 12.72. ESI-MS calcd. for $C_{11}H_{13}NO_2$, 191.1, found 192.1 $(M+H)^+$, 214.1 $(M+Na)^+$, 405.2 (2 M + Na)$^+$. FT-IR ν(C═O): 1747 cm^{-1} (Film).

3-Ethyl-4-phenyloxazolidin-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30–7.44 (m, 5H, Ph–*H*), 4.81 (t, 1H, J = 8.0 Hz, Ph–C*H*), 4.62 (t, 1H, J = 8.0 Hz, CH–CH_2), 4.10 (t, 1H, J = 8.0 Hz, CH–CH_2), 3.48–3.57 (m, 1H, -CH_2CH$_3$), 2.80–2.89 (m, 1H, -CH_2CH$_3$), 1.05 (t, 3H, J = 8.0 Hz, -CH$_2$CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.42, 137.89, 129.45, 129.24, 127.36, 70.01, 59.53, 37.04, 12.19. ESI-MS calcd. for $C_{11}H_{13}NO_2$, 191.1, found 192.1 $(M+H)^+$, 214.1 $(M+Na)^+$. FT-IR ν(C═O): 1757 cm^{-1} (Film).

3-Benzyl-5-phenyloxazolidin-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27–7.35 (m, 10H, Ph–*H*), 5.43 (t, 1H, J = 8.0 HZ, Ph–C*H*), 4.45 (ABq, 2H, J_{AB} = 20.0 Hz, Ph–CH_2), 3.74 (t, 1H, J = 8.0 Hz, CH–N–CH_2), 3.28 (t, 1H, J = 8.0 Hz, CH–N–CH_2). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.96, 138.56, 135.61, 128.85, 128.13, 128.02, 125.53, 74.51, 51.48, 48.31. **ESI-MS** calcd. for $C_{16}H_{15}NO_2$, 253.1, found 254.1 $(M+H)^+$, 276.0 $(M+Na)^+$, 292.0 $(M+K)^+$. **FT-IR** ν(C═O): 1736 cm^{-1} (KBr disc).

3-Cyclohexyl-5-phenyloxazolidin-2-one. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33–7.39 (m, 5H, Ph–*H*), 5.46 (t, 1H, J = 8.0 Hz, Ph–C*H*), 3.88 (t, 1H, J = 8.0 Hz, CH–N–CH_2), 3.74 (m, 1H, C*H*–N–CH$_2$), 3.39 (t, 1H, J = 8.0 Hz, CH–N–CH_2), 1.0–1.9 (m, 10 H, cHex-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.27, 139.14, 128.92, 128.76, 125.53, 74.63, 52.63, 48.38, 32.36, 30.14, 25.43, 25.36, 25.34. ESI-MS calcd. for $C_{15}H_{19}NO_2$, 245.1, found 246.1 $(M+H)^+$, 268.1 $(M+Na)^+$, 284.0 $(M+K)^+$, 491.2 (2 M + H)$^+$, 513.3 (2 M + Na)$^+$, 529.3 (2 M + K)$^+$. FT-IR ν(C═O): 1746 cm^{-1} (KBr disc).

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Notes and references

1 M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975.
2 W. Leitner, *Coord. Chem. Rev.*, 1996, **153**, 257.
3 A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951.
4 T. Sakakura, J. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
5 X. L. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
6 D. J. Darensbourg and M. W. Holtcamp, *Coord. Chem. Rev.*, 1996, **153**, 155.
7 D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388.
8 J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663.
9 T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1983, **105**, 1304.
10 W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725.
11 R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498.
12 X.-B. Lu, X.-J. Feng and R. He, *Appl. Catal., A*, 2002, **234**, 25.
13 Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 6705.
14 X.-B. Lu, Y.-J. Zhang, B. Liang, X. Li and H. Wang, *J. Mol. Catal. A: Chem.*, 2004, **210**, 31.
15 X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537.
16 T. R. J. Achard, L. A. Clutterbuck and M. North, *Synlett.*, 2005, 1828.
17 W. Clegg, R. M. Harrington, M. North and R. Pasquale, *Chem.–Eur. J.*, 2010, **16**, 6828.
18 L.-N. He, H. Yasuda and T. Sakakura, *Green Chem.*, 2003, **5**, 92.
19 C. X. Miao, J. Q. Wang, Y. Wu, Y. Du and L. N. He, *ChemSusChem*, 2008, **1**, 236.
20 X. Zhang, Y.-B. Jia, X.-B. Lu, B. Li, H. Wang and L.-C. Sun, *Tetrahedron Lett.*, 2008, **49**, 6589.
21 T. Chang, L. Jin and H. Jing, *ChemCatChem*, 2009, **1**, 379.
22 X.-B. Lu, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 3732.
23 S. Zhang, Y. Huang, H. Jing, W. Yao and P. Yan, *Green Chem.*, 2009, **11**, 935.
24 P. Yang and H. Jing, *Adv. Synth. Catal.*, 2009, **351**, 1325.
25 A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartrio, *Tetrahedron Lett.*, 2003, **44**, 2931.
26 Y. M. Shen, W. L. Duan and M. Shi, *Eur. J. Org. Chem.*, 2004, 3080.
27 W. Calo, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561.
28 J. M. Sun, S. Fujita, F. Y. Zhao and M. Arai, *Green Chem.*, 2004, **6**, 613.
29 T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 1997, 1129.
30 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526.
31 H. Yasuda, L. N. He and T. Sakakura, *J. Catal.*, 2002, **209**, 547.
32 N. Kuhn, M. Steimann and G. Weyers, *Z. Naturforsch. Teil B*, 1999, **54**, 427.
33 H. A. Duong, T. N. Tekavec, A. M. Arif and J. Louie, *Chem. Commun.*, 2004, 112.
34 A. M. Voutchkova, A. R. Chianese and R. H. Crabtree, *J. Am. Chem. Soc.*, 2005, **127**, 17624.
35 A. M. Voutchkova, M. Feliz, E. Clot and R. H. Crabtree, *J. Am. Chem. Soc.*, 2007, **129**, 12834.
36 M. Smiglak, J. D. Holbrey and R. D. Rogers, *Green Chem.*, 2007, **9**, 90.
37 I. Tommasi and F. Sorrentino, *Tetrahedron Lett.*, 2005, **46**, 2141.
38 I. Tommasi and F. Sorrentino, *Tetrahedron Lett.*, 2009, **50**, 104.
39 L. Q. Gu and Y. G. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 914.
40 S. N. Riduan, Y. G. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322.
41 Y. Kayaki, M. Yamamoto and T. Ikariya, *Angew. Chem., Int. Ed.*, 2009, **48**, 4194.
42 H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu and X.-B. Lu, *J. Org. Chem.*, 2008, **73**, 8039.
43 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
44 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
45 W. Zhou, J. M. Thomas, D. S. Shephard, B. F. G. Johnson, D. Ozkaya, T. Maschmeyer, R. G. Bell and Q. Ge, *Science*, 1998, **280**, 705.
46 H. Li and X. Lu, *Chin. J. Catal.*, 2009, **30**, 587.
47 C. J. Liu, S. G. Li, W. Q. Pang and C. M. Che, *Chem. Commun.*, 1997, 65.
48 H. Zhou, W.-Z. Zhang, Y.-M. Wang, J.-P. Qu and X.-B. Lu, *Macromolecules*, 2009, **42**, 5419.
49 Y. Du, Y. Wu, A.-H. Liu and L.-N. He, *J. Org. Chem.*, 2008, **73**, 4709.
50 M. Elliott and N. F. Janes, *J. Chem. Soc. C*, 1967, 1780.
51 V. Capriati, S. Florio, R. Luisi and B. Musio, *Org. Lett.*, 2005, **7**, 3749.

