[CoCl(TPPyP)], a novel bifunctional catalyst for the coupling reaction of carbon dioxide and propylene oxide

Tiegang Ren[a], Weijie Li[a], Zhanwei Bu[a,b]*, Lirong Yang[a] and Zhiqiang Wang[a]

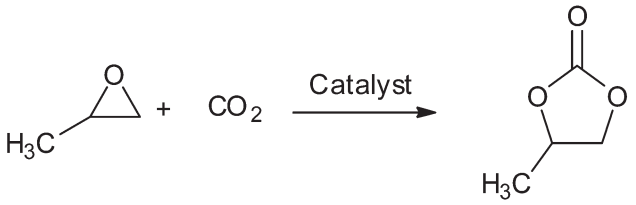
[a]*Fine Chemistry and Engineering Research Institute, Henan University, Kaifeng 475004, Henan, P. R. China*
[b]*Henan Tianguan Enterprise Group Co., Ltd., Nanyang 473000, Henan, P. R. China*

A novel bifunctional catalyst chloro[*meso*-tetrakis(1-phenylpyrazol-4-yl)porphyrin] cobalt(III), [CoCl(TPPyP)], has been prepared and used to catalyse the synthesis of propylene carbonate from carbon dioxide and propylene oxide under mild conditions. Propylene carbonate was obtained with a yield of 25.2% at 100 °C in the absence of co-catalyst. A reaction mechanism is proposed.

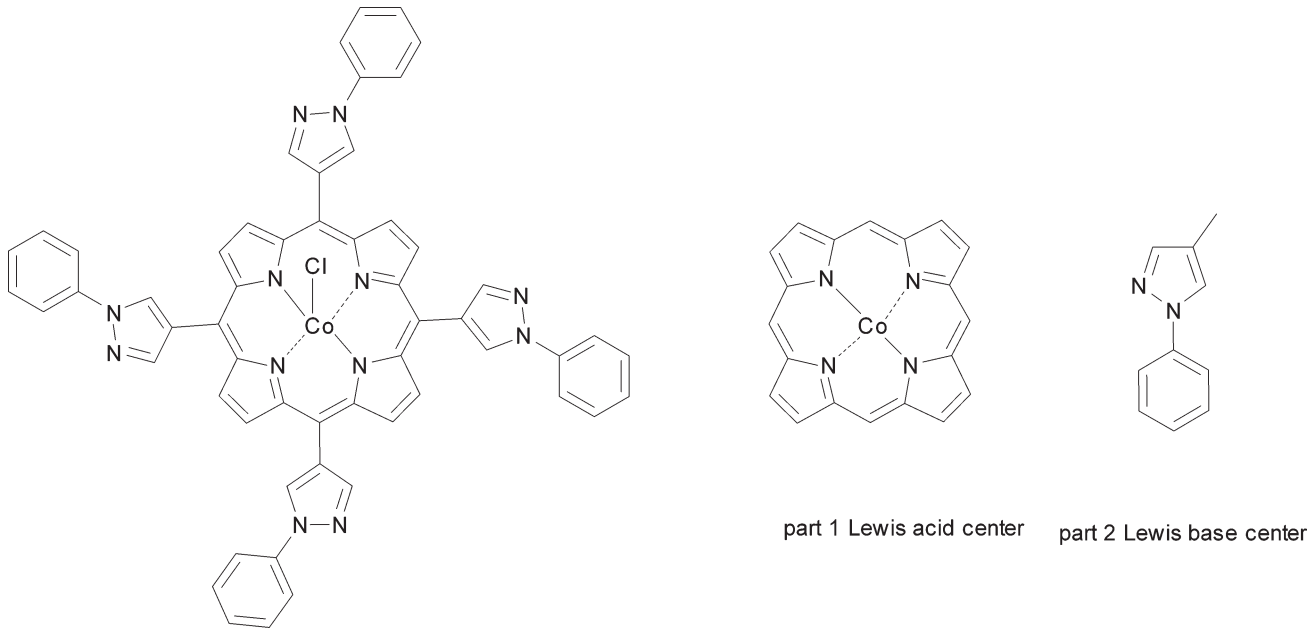
Keywords: chloro[*meso*-tetrakis(1-phenylpyrazol-4-yl)porphyrin]cobalt(III), carbon dioxide, propylene oxide, propylene carbonate, bifunctional catalyst

The chemical fixation of carbon dioxide has been extensively studied recently, due to the demand for a low-cost carbon source and the urgent need to reduce the levels of greenhouse gases.[1–3] One of the most promising reactions applicable to the chemical fixation of carbon dioxide is the synthesis of propylene carbonate from CO_2 and propylene oxide (Scheme 1). Since commercialisation in the mid-1950s, propylene carbonate has found numerous applications as an attractive solvent, a reactive intermediate, a fine chemical, *etc*.[4,5]

Various catalysts including metal oxides, zeolites, organic bases, alkali metal halides, ionic liquids, quaternary ammonium salts, salen complexes, phthalocyanine complexes and metalloporphyrin complexes have been successively developed for the coupling reaction of CO_2 and propylene oxide.[6–16] In particular, metalloporphyrinates, as a novel class of catalysts for preparing polycarbonates or carbonates from carbon dioxide and epoxides, have been found to exhibit high activity towards the coupling reaction. Inoue *et al.*[17,18] found that the copolymerised product of carbon dioxide and epoxides in the presence of aluminum porphyrin as the catalyst had a narrow distribution of molecular weight which could be well controlled by adjusting reaction conditions. Kruper and Deller[19] reported the catalyst system [CrCl(TPP)] /DMAP (dimethyl aminopyridine) for preparing propylene carbonate from CO_2 and propylene. Since then, various similar catalyst systems such as [Co(TPP)X]/DMAP,[20] Cu(II) porphyrin/DMAP,[16] [M(TPP)X]/PTAT(M = Co, Mn, Fe, Ru; X = Cl, Br, OAc, OTs)[21] have been reported. Unfortunately, the above-mentioned catalysts exhibited very low or even zero catalytic reactivity for the coupling reaction of CO_2 and propylene oxide in the absence of co-catalysts (*e.g.*, 1-methylimidazale, DMAP, quaternary ammonium, phosphonium salts *etc*.). For example, Inoue *et al.* [17] found that 1-methylimidazale as a co-catalyst played a key role in the coupling reaction of CO_2 with propylene oxide generating propylene carbonate, which prompted us to consider that *N*-phenylpyrazole might play the same role as 1-methylimidazale in the reaction of CO_2 and epoxides, similar to that reported by Inoue *et al.* Therefore, we synthesised the complex [CoCl(TPPyP)] (Scheme 2), in which one



Scheme 1 The synthesis of propylene carbonate (PC) from CO_2 and propylene oxide.



Scheme 2 Structure of chloro-[*meso*-tetrakis(1-phenylpyrazole-4-yl) porphyrin] cobalt (III).

* Correspondent. E-mail: buzhanwei@henu.edu.cn

N-phenylpyrazole ring is linked to the *meso*-position of porphyrin ring and the Co-porphyrin is the Lewis acidic centre and phenylpyrazole is the Lewis base segment. This means that [CoCl(TPPyP)] should have bifunctional catalytic activity for the coupling reaction of CO_2 with propylene oxide.

Experimental

Melting points were measured on Netzsch STA449C Simultaneous Thermal Analysis spectrometer. Mass spectra were determined on an Agilent 1100LC-MS mass spectrometer; ^{1}H NMR spectra were recorded on an INOVA-400 spectrometer in $CDCl_3$ using TMS as an internal standard. Elemental analyses were performed with a PE2400 elemental analysis apparatus. Tetramethoxypropane and phenylhydrazine were commercially available and used without further purification. Pyrrole was distilled under reduced pressure before use. Commercial CO_2 (99.99%) was used without further purification. Propylene oxide (PO) was distilled from CaH_2 under nitrogen before use. CH_2Cl_2 was washed successively with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and brine, dried over $CaCl_2$, and distilled over CaH_2 under dinitrogen. DMAP were purchased from Aldrich and used without further purification.

Synthesis of the catalyst

Meso-*tetrakis(1-phenylpyrazol-4-yl)porphyrin (TPPyPH$_2$)*

Meso-tetrakis(1-phenylpyrazol-4-yl)porphyrin ($TPPyPH_2$) was synthesised according to the literature.[22] A three-necked round-bottomed flask fitted with a reflux condenser was charged with propionic acid (70 mL) and nitrobenzene (30 mL). 1-Phenyl-4-formylpyrazole (1.72 g, 10 mmol) and pyrrole (0.67 g, 10 mmol) were added at near reflux, then the reaction was refluxed for 1 h. After the removal of the solvent, the residue was purified by column chromatography on neutral alumina eluting with CH_2Cl_2/Et_2O. The first red fraction was collected and further purified by column chromatography on silica gel eluting with CH_2Cl_2/Et_2O to offer the final product: 0.21 g, 13.6%. Mp. 305.9 °C; MS (*m/z*) 879 and 880; UV($CHCl_3$): λ_{max}(nm)/logε: 425(5.62), 523(4.33), 564(4.36), 660(4.41). ^{1}H NMR ($CDCl_3$) δ: –2.591 (s, 2H, NH), 7.430–7.466 (t, 4H, Ph-H, J = 7.2 Hz), 7.617–7.657 (t, 8H, Ph-H, J = 8.0 Hz), 8.089 (d, 8H, Ph-H, J = 8.0 Hz), 8.618 (s, 4H, pyrazole-H_5), 8.80 (s, 4H, pyrazole-H_3), 9.235 (s, 8H, pyrrole-H_β). Anal. Calcd for $C_{56}H_{38}N_{12}$: C:76.52; H:4.36; N:19.12. Found: C, 76.31; H, 4.62; N, 19.05%.

Meso-*tetrakis(1-phenylpyrazol-4-yl)porphyrincobalt(II), [Co(TPPyP)]*

$TPPyPH_2$ (2.86 g, 3.25 mmol) was refluxed for 1 h in acetic acid with cobalt chloride hexahydrate (1.5 equiv of $TPPyPH_2$) and sodium acetate.[23–25] The crystalline product was collected by filtration and washed with water, aqueous sodium bicarbonate, water, and methanol and was dried *in vacuo* to give a red solid of [Co(TPPyP)]. Yield: 3.04 g, 91%. UV (CH_2Cl_2), λ_{max}/nm: 423, 534, 605. IR(cm^{-1}): 1001.37 (Co-N).

*Chloro[*meso-*tetrakis(1-phenylpyrazol-4-yl)porphyrin]cobalt(III), [CoCl(TPPyP)]*[24,25] To a suspension of [Co(TPPyP)] (1.0 g, 1 mmol) in MeOH (500 mL) was added 3 mL of aqueous 37% HCl solution. The mixture was stirred at room temperature in an open flask for 5 h and then filtered to give a purple solid. Recrystallisation from $CHCl_3$-EtOH to gave the final product. Yield: 0.83 g, 85%. UV (CH_2Cl_2), λ_{max}/nm: 429, 550, 656. ESI-MS (*m/z*) Calcd (M-Cl)$^+$ 935.9, found: 935.3. Anal. Calcd for $C_{56}H_{36}N_{12}ClCo$: C, 69.24; H, 3.74; N, 17.30. Found: C, 69.46; H, 3.87; N, 17.00%.

Coupling reactions of CO_2 and propylene oxide(PO); general procedures

The reactions were carried out in a 100 mL stainless steel autoclave equiped with a magnetic stirring device. In a typical procedure, the autoclave reactor (dried *in vacuo*) was charged with [CoCl(TPPyP)] (0.024 g, 0.025 mmol) and DMAP (0.006 g, 0.05 mmol) then purged with nitrogen gas. Then propylene oxide (8.3 g, 0.143 mol) and CH_2Cl_2 (1 mL) were added into the reactor with a hypodermic syringe, followed by pressurising with CO_2 to 4.5 MPa and stirring at the desired temperature (80–120 °C). Upon completion of the reaction, the reactor was cooled, and the product was transferred to a round-bottom flask after discharging excessive CO_2. Residual reactants and solvent were removed *in vacuo* and product propylene carbonate was isolated as a colourless liquid via Kugelrohl distillation. Characterisation of the product was by ^{1}H NMR ($CDCl_3$) δ: 1.50 (d, J = 6.24 Hz, 3H, CH_3), 4.05 (t, J = 7.82 Hz, 1H, CH_2CH), 4.59 (t, J = 8.02 Hz, 1H, CH_2CH), 4.82–4.92 (m, CH).

Results and discussion

Synthesis of the catalyst

Two established methods for porphyrin synthesis via the tetracyclisation of aldehydes and pyrrole developed by Adler and Lindsey, respectively, had been reported to yield pyrazole substituted porphyrins.[22,26,27] With slight variations of the reaction conditions, we found that it was possible to obtain *meso*-tetrakis(1-phenylpyrazol-4-yl)porphyrin in improved yields compared to the Lindsey method. For an abundant electron five-membered aromatic heterocycle, it is more difficult for the tetra-cyclisation of 1-phenyl-4-formylpyrazole with pyrrole than with benzaldehyde. The existence of nitrobenzene can increase the reaction temperature, and as an oxidant it was also advantageous to improve the yield. Furthermore, the workup procedure was simplified allowing the synthesis and purification of porphyrin in a scale of up to 40–50 mmol of starting material in two days.

Coupling reaction of CO_2 and propylene oxide(PO)

The presence of both a Lewis acid centre and a Lewis base centre is essential for the high efficiency and selectivity of the catalyst. So we designed a catalyst which owns both centres and its structure is shown in Scheme 2. The cobalt-porphyrin acts as a Lewis acid centre and the phenylpyrazole as another.

It is imperative to incorporate a Co–Cl bond into the synthesised catalyst, otherwise no propylene carbonate is obtained from the coupling reaction of CO_2 with propylene oxide. Thus when [Co(TPPyP)] untreated with concentrated hydrochloric acid was used as the catalyst in the coupling reaction of CO_2 with propylene oxide, no target product was harvested (Table 1, entry 1). Similarly, even in the presence of co-catalyst DMAP, [Co(TPPyP)] untreated with concentrated HCl still had no catalytic activity for the coupling reaction of CO_2 with propylene oxide (Table 1, entry 2). However, after being treated with concentrated HCl, the resulting [CoCl(TPPyP)] exhibited significantly increased catalytic activity for the same coupling reaction (Table 1, Entries 4–7). In a first attempt to catalyse the coupling reaction of CO_2 and propylene oxide, [CoCl(TPPyP)] was used as the catalyst without co-catalyst. When the reaction was carried out at 100 °C for 24 h, a moderate PC yield of 25.2% with a TON of 1391 and a TOF for 58 h^{-1} were obtained (Table 1, entry 3). To the best of our knowledge, all of the [M(TPP)X] catalysts suffer from no catalytic reactivity or very low catalyst reactivity in absence of the

Table 1 Reaction of CO_2 and propylene oxide catalyzed by [CoCl(TPPyP)][a]

Entry	Catalyst/co-catalyst	Time/h	Temperature/°C	Yield/%[b]	TON[c]	TOF[d]
1	[Co(TPPyP)]	24	100	No	–	–
2	[Co(TPPyP)]/DMAP	24	100	No	–	–
3	[CoCl(TPPyP)]	24	100	25.2	1391	58
4	[CoCl(TPPyP)]/DMAP	24	100	23.7	1304	54.4

[a] Reaction conditions: [CoCl(TPPyP)] (0.025 mmol), DMAP (2 equiv), propylene oxide (10 mL, 5716 equiv), CO_2(4.5MPa), CH_2Cl_2 (1mL).
[b] Isolated yield.
[c] Moles of propylene oxide produced per mole of cobalt complex.
[d] Moles of propylene oxide produced per mole of cobalt complex per hour.

Table 2 The coupling reaction of CO_2 and propylene oxide by the cobalt porphyrin system[a]

Entry	Catalyst/co-catalyst	Time/h	Temperature/°C	Yield/%[b]	TON[c]	TOF[d]
1	[CoCl(TPPyP)]	24	80	Trace	–	–
2	[CoCl(TPPyP)]	24	90	25	1379	57.5
3	[CoCl(TPPyP)]	24	100	25.2	1391	58
4	[CoCl(TPPyP)]	24	110	16.7	921	38.4
5	[CoCl(TPPyP)]	24	120	13.9	766	31.9
6	[CoCl(TPPyP)]/DMAP	24	80	21.3	1172	48.8
7	[CoCl(TPPyP)]/DMAP	24	100	23.7	1304	54.4
8	[CoCl(TPPyP)]/DMAP	24	120	69.7	3844	160.1
9	[CoCl(TPPyP)]/DMAP	18	90	18.3	1012	56.2
10	[CoCl(TPPyP)]/DMAP	6	120	21.5	1164	193.9

[a]Reaction conditions: [CoCl(TPPyP)] (0.025 mmol), DMAP (2 equiv.), propylene oxide (10 mL, 5716 equiv.), CO_2 (4.5 MPa), CH_2Cl_2 (1mL).
[b]Isolated yield.
[c]Moles of propylene oxide produced per mole of cobalt complex.
[d]Moles of propylene oxide produced per mole of cobalt complex per hour.

co-catalysts. The results proved our assumption that the phenylpyrazole worked as a Lewis base centre for this reaction.

Preliminary tuning of reaction conditions

The reaction conditions of the coupling reaction of CO_2 and propylene oxide have been studied tentatively. The results are listed in Table 2. When propylene oxide (5716 equiv. to [CoCl(TPPyP)]) was added in a stainlesss steel autoclave and pressurised by CO_2 at 4.5 MPa and 90 °C in the presence of [CoCl(TPPyP)], the reaction of CO_2 and propylene oxide proceeded smoothly, generating propylene carbonate at a yield of 25% in 24 h (Table 2, entry 2). While the other conditions were kept unchanged but temperature was increased to 100 °C, 110 °C and 120 °C, propylene carbonate was obtained at a yield of 25.2%, 16.7%, and 13.9%, respectively (Table 2, entries 3, 4 and 5). As an exception, trace propylene carbonate was obtained and 0.0589 g of poly(propylene carbonate) were collected in the presence of [CoCl(TPPyP)] at a lowered temperature of 80 °C (Table 2, Entry 1). This indicates that temperature has a significant effect on the coupling reaction.

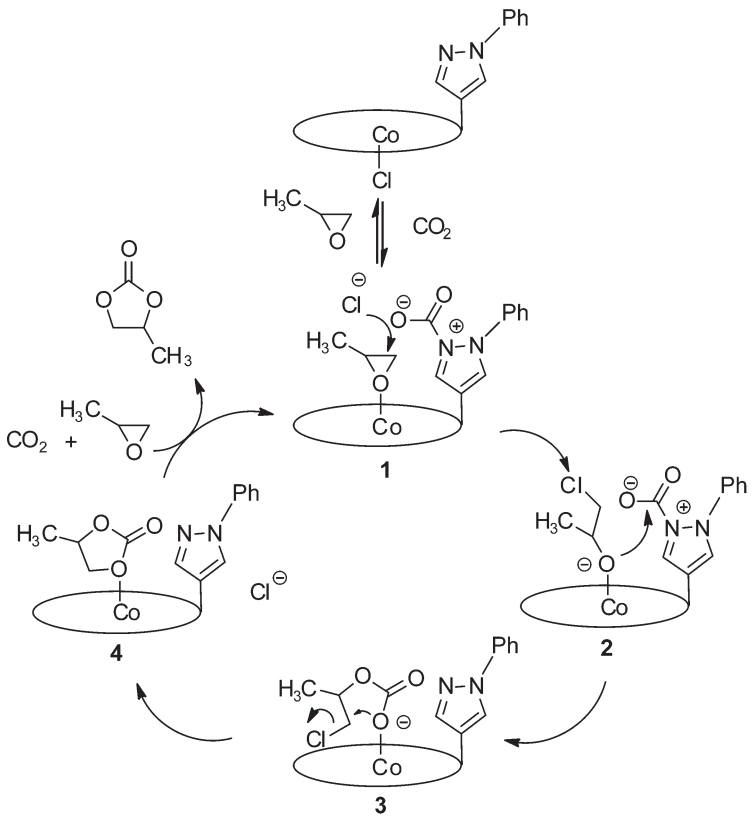
Moreover, when co-catalyst DMAP was introduced into the coupling reaction system of CO_2 and propylene oxide, increased reactivity was generally obtained (Table 2, entries 6–8). In particular, propylene carbonate was obtained in a high yield of 69.7% after 24 h reaction at a relatively higher temperature of 120 °C (Table 2, entry 8).

It is to be noted that at a reaction temperature of 100 °C, [CoCl(TPPyP)] showed a higher reactivity for the coupling reaction than [CoCl(TPPyP)]/DMAP (Table 2, entries 3 and 7). This implies that the co-catalyst DMAP is sensitive to reaction temperature in terms of its catalytic efficiency for the coupling reaction of CO_2 with propylene oxide.

Possible mechanism

It has been proposed that the coupling of carbon dioxide with epoxides to yield cyclic carbonates probably requires activation through both a Lewis acid and a Lewis base: the former activates the epoxide and the latter attacks the less sterically hindered carbon atom to open the epoxide ring. The generated oxy-anion species then reacts with CO_2 to give the corresponding cyclic carbonate.[28,29]

Based on the molecular structure of [CoCl(TPPyP)] and coupling reaction results, we propose a possible mechanism for the coupling reaction of propylene oxide and carbon dioxide (Scheme 3) that is similar to that reported by others.[17,20] In this mechanism, as illustrated in Scheme 3, the Lewis acid centre of [CoCl(TPPyP)] first coordinates



Scheme 3 Proposed mechanism for the coupling reaction of CO_2 with propylene oxide catalyzed by [CoCl(TPPyP)].

to PO and activates it for ring-opening. At the same time, CO_2 is activated by the Lewis base centre to produce intermediate **1**. The chloride ion act as a nucleophilic reagent, attacking the less-hindered carbon atom of the coordinated PO to produce the requisite metal alkoxide intermediate **2**.[30] When both the PO and CO_2 have been activated, PC is transformed by an intramolecular cyclic elimination reaction. The bulky peripheral substituents in the tetrapyrazolyl porphyrins could block the binding sites of the metal, thereby inhibiting the metal centres from activating and opening the epoxide at too high or too low a temperature. This might be cited to explain why propylene carbonate was obtained at a relatively lower yield above 100 °C or below 100 °C. In addition, the pyrazole ring with a lower alkalinity might account for the lowered catalytic activity of [CoCl(TPPyP)] as compared with DMAP at a reaction temperature of above 100 °C.

This mechanism can explain why [Co(TPPyP)] has no catalyst activity even in presence of DMAP, because there is no chloride ion to open the PO ring to generate intermediate **2**. This mechanism might also be cited to explain the gradual loss in activity of [CoCl(TPPyP)] when the reaction temperature is above 100 °C, as the molar equivalents of CO_2 in solution are gradually diminished with the rise of reaction temperature, and this would lead to reduced formation of intermediate **3**, thereby reducing the reaction rate.

Conclusions

An attempt has been made to synthesise a bifuctional metalloporphyrin catalyst which is applicable to preparing propylene carbonate by the coupling reaction of CO_2 with propylene oxide. The synthesised bifunctional catalyst [CoCl(TPPyP)] can be used to prepare propylene carbonate from carbon dioxide and propylene oxide under mild conditions. Provided that the reaction temperature and duration are properly adjusted, it will be feasible to synthesise propylene carbonate from CO_2 and propylene oxide with improved catalytic efficiency even in the absence of co-catalyst like DMAP. This may help to open a new door to more efficient chemical fixation of carbon dioxide.

The authors gratefully thank the Natural Science Foundation of the Education Department of Henan Province, China (No 2009B150005) and the Natural Science Foundation of the Science and Technology Department of Henan Province, China, (No 092102210172), for financial support.

Received 10 February 2010; accepted 19 May 2010
Paper 101001 doi: 10.3184/030823410X12762744367622
Published online: 28 July 2010

References

1 D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps and D.R. Billodeaux, *Acc. Chem. Res.*, 2004, **37**, 836.
2 G.W. Coates and D.R. Moore, *Angew. Chem. Int. Ed*., 2004, **43**, 6618.
3 T. Takata, Y. Furusho, K. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo and M. Sisido, *J. Am. Chem. Soc*., 1998, **120**, 4530.
4 A-A.G. Shaikh. *Chem Rev*., 1996, **96**, 951.
5 J.H. Clements, *Ind. Eng. Chem. Res*., 2003, **42**, 663.
6 H. Yasuda, L.N. He, T. Sakakura and C. Hu, *J. Catal*., 2005, **233**, 119.
7 J.W. Huang and M. Shi, *J. Org. Chem*., 2003, **68**, 6705.
8 B.M. Bhanage, S. Fujita, Y. Ikushina and M. Arai, *Appl. Catal. A:General*, 2001, **219**, 259.
9 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc*., 1999, **121**, 4526.
10 M. Aresta, A. Dibenedetto, L. Gianfrate and C. Pastore, *J. Mol. Catal. A*, 2003, **204**, 245.
11 M. Tu and R.J. Davis, *J. Catal*., 2001, **199**, 85.
12 L.F. Xiao, F.W. Li, and C.G. Xia, *Appl. Catal. A: General*, 2005, **279**, 125.
13 H. Kawanami, A. Sasaki, K. Matsuia and Y. Ikushima, *Chem. Commun*., 2003, 896.
14 H.S. Kim, J.J. Kim, H. Kim and H.G. Jang, *J. Catal*., 2003, **220**, 44.
15 J. Sun, S. Fujita and M. Arai, *J. Organomet. Chem*., 2005, **690**, 3490.
16 R. Srivastava, T.H. Bennur and D. Srinivas, *J. Mol. Catal. A*, 2005, **226**, 199.
17 T. Aida and S. Inoue, *J. Am. Chem. Soc*., 1983, **105**, 1304.
18 T. Aida, M. Ishikawa and S. Inoue, *Macromolecules*, 1986, **19**, 8.
19 W.J. Kruper and D.D. Dellar, *J. Org. Chem*., 1995, **60**, 725.
20 R.L. Paddock, Y. Hiyama, J.M. McKay and T.N. SonBinh, *Tetrahedron Lett*., 2004, **45**, 2023.
21 L.L. Jin, H.W. Jing, T. Chang, X.L. Bu, L.Wang and Z.L. Liu, *J. Mol. Catal. A*, 2007, **261**, 262.
22 C.C. Guo, T.G. Ren, J. Wang, C.Y. Li and J.X. Song, *J. Porphy. Phthal*., 2005, **9**, 430.
23 A.D. Adler, F.R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem*., 1970, **32**, 2443.
24 Y.S. Qin, X.H. Wang, S.B. Zhang, X.J. Zhao and F.S. Wang, *J. Polym. Sci. Part. A: Polym. Chem*., 2008, **46**, 5959.
25 H. Sugimoto and K. Kuroda, *Macromolecules*, 2008, **41**, 312.
26 A. Werner, S.M. Ana, F. Alain, E. Jose, F.C. Cristina and F.F. Concepcion, *Tetrahedron*, 1995, **51**, 4779.
27 S.M. Ana, D.L.H. Antoni, B. Mikael, F.C. Cristina, F.F. Concepcion and E. Jose, *Tetrahedron*, 1996, **52**, 10811.
28 H. Xie, S. Li and S. Zhang, *J. Mol. Catal. A*, 2006, **250**, 30.
29 X.B. Lu, B. Liang, Y.J. Zhang, Y.Z. Tian, Y.M. Wang, C.X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc*., 2004, **126**, 3732.
30 M. North and R. Pasquale, *Angew. Chem. Int. Ed*., 2009, **48**, 2946.