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Aluminum phthalocyanine complex covalently bonded to MCM-41 silica as heterogeneous catalyst for the synthesis of cyclic carbonates

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Abstract

Aluminum phthalocyanine complex was covalently bonded to the silica surface of mesoporous MCM-41 molecular sieve via two different routes. The resulting anchored complex was characterized by X-ray powder diffraction (XRD), nitrogen adsorption and UV–VIS spectroscopy, and used as catalyst for the cycloaddition of CO_2 and epoxides to produce cyclic carbonates. Its catalytic activity can be markedly enhanced in the presence of a quaternary ammonium salt, such as n-Bu_4NBr. The catalyst exhibits good stability as well as high catalytic activity in reaction conditions, and was subjected to utilization for 10 recycles without obvious loss of activity. The catalytic mechanism of the anchored aluminum phthalocyanine complex, combined with n-Bu_4NBr as co-catalyst, for ring-opening of epoxides and activation of CO_2 are also discussed in detail.

Keywords: Aluminum phthalocyanine; MCM-41; Carbon dioxide; Epoxide; Cyclic carbonate; Synergistic effect

1. Introduction

Metallophthalocyanines (MPc) are particularly attractive as potential catalysts for organic reaction such as oxidation because of their rather inexpensive and simple preparation on a large scale and their chemical and thermal stability [1]. By adequate substitution on the aromatic rings, a variety of phthalocyanine derivatives have been prepared in an attempt to improve their catalytic performance and their solubility in various reaction media [2]. However, these phthalocyanine macromolecules usually show strong tendency for aggregation in solution, which probably makes remarkable influence on the catalytic performance [3]. It has been reported that upon self-association in solution the photocatalytic activity of the phthalocyanine complexes has been decreased by 5–10 times [4–6]. Obviously, a monomolecular distribution of the active catalytic centers is favorable for obtaining maximum catalytic activity. In addition, the soluble phthalocyanine catalysts are not easily separated from the organic constituents of the reaction mixture. These have stimulated the study of the heterogenization of these catalysts by a variety of routes. One route (ship-in-a-bottle synthesis) for immobilization of phthalocyanines inside molecular sieves such as NaY, NaEMT or VPI-5 has been widely used [7–9]. The catalyst preparation is remarkably simple, with adsorption of dicyanobenzene and tetramerization by heating. The transition metal ions are introduced

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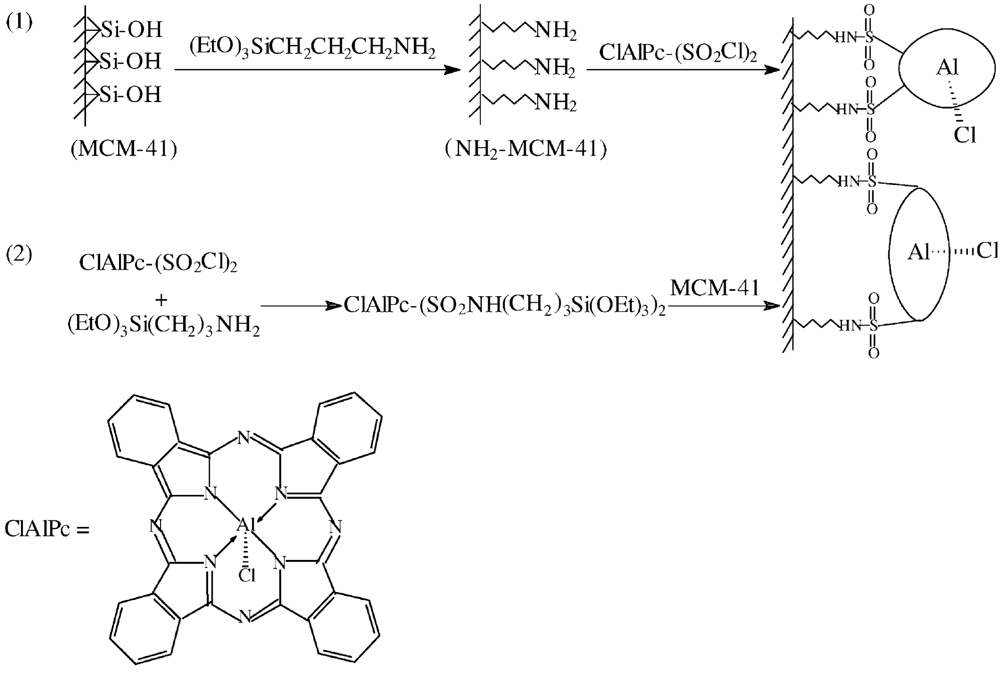
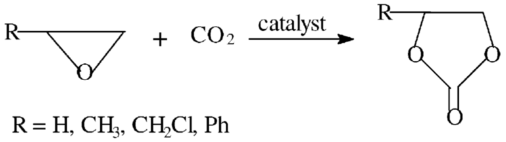


Scheme 1. Synthetic routes of monomeric ClAlPc catalyst supported on MCM-41 silica.

in the zeolite by ion exchange. It has been found that the encapsulation of MPc inside the zeolite Y supercages increases their turnover numbers as oxidation catalysts with respect to that of the unsupported complexes [10,11]. Unfortunately, this method also causes several problems: uncomplexed metal, intermediates and metal-free phthalocyanine may block the diffusion pathways of reactants and/or products. Some papers reported metallic porphyrins or phthalocyanines coordinately bonded to pyridine-, imidazole- or amino-modified silica [12,13]. The main drawback was catalyst leaching and/or deactivation after prolonged or repeated usage, which resulted in the loss of activity [14]. In fact, the covalent anchoring of phthalocyanine complexes onto silica by the reaction between reactive groups present in the siliceous surfaces and aromatic ring of phthalocyanines is a promising strategy to solve catalyst leaching and/or deactivation. It has been reported [15,16] that immobilization of phthalocyanines was performed by covalently bonding to modified silica surfaces to obtain heterogeneous catalysts with non-aggregated complexes. These covalently bonded phthalocyanine catalysts exhibited similar reaction kinetics as the homogeneously dissolved low molecular weight analogue.

Recently, mesoporous materials, such as MCM-41 possessing regularly hexagonal arrays of uniform cylindrical mesopores, has been more extensively studied as host materials for spacious molecules like porphyrins or other transition metal complexes [17–19]. In the present paper, aluminum phthalocyanine complex was covalently bonded to the silica surface of mesoporous MCM-41 molecular sieve via two different routes (Scheme 1) and was used as a heterogeneous catalyst for synthesis of cyclic carbonates from carbon dioxide and epoxides (Scheme 2). The immobilized phthalocyanine complex exhibits



Scheme 2.

excellent stability as well as good catalytic activity under reaction conditions.

2. Experimental

2.1. Materials

All chemicals used were of reagent grade. Aluminum phthalocyanine (ClAlPc) was kindly supplied by Shenyang Research Institute of Chemical Engineering. The aluminum complex of disulfophthalocyanine [ClAlPc$(SO_3H)_2$] was prepared according to the method of the literature [20] by the reaction of ClAlPc with fuming sulfuric acid of 30% (a mixture of 70% H_2SO_4 and 30% SO_3) at 73–75 °C, and ClAlPc$(SO_3H)_2$ was converted to dichlorosulfonylphthalocyanine [ClAlPc$(SO_2Cl)_2$] by treatment with $SOCl_2$. In a typical preparation, 5 g of ClAlPc was stirred in 60 ml fuming sulfuric acid of 30% for 8 h at 73–75 °C, and after cooling to room temperature, the resulting solution was poured onto ice pieces. The resulting suspension was filtered and the residue was washed with 1% hydrochloric acid and ice/water mixture. After dried in vacuo at 100 °C, 5.5 g of dark-blue solid was obtained. An amount of 3 g of this aluminum complex of phthalocyanine was refluxed for 10 h with 10 ml of thionyl chloride and a few drops of pyridine in 30 ml of benzene. The product was filtrated off, washed with dry benzene and dried at 100 °C in vacuo. Analysis of sulfur in the product was carried out by high temperature combustion—iodimetry method.

2.2. Preparation of amino-modified MCM-41 silica

The parent MCM-41 was synthesized according to a previously described method [21] with cetyltrimethylammonium bromide (CTAB) as the template. The obtained white solid was washed with adequate deionized water at ambient temperature and dried for 24 h at 100 °C in vacuo. The as-synthesized MCM-41 was extracted with supercritical carbon dioxide modified with CH_2Cl_2/MeOH mixture at 30 MPa and 95 °C for removing the template molecules. Thermogravimetric analysis indicated that the template molecules in mesoporous channels of MCM-41 had been nearly quantitatively removed by this method.

Amino-modified MCM-41 silica was prepared by addition of 3-aminopropyltriethoxysilane (APTES, 2 g) to a suspension of freshly activated MCM-41 silica (3 g) in refluxing toluene (50 ml) and then stirred for 10 h. After distillation of a toluene fraction containing ethanol, the heating and distillation sequences were repeated twice. The modified solid was filtered, washed in a Soxhlet apparatus with dichloromethane, and then dried at 100 °C in vacuo. Elemental analysis (%): C, 5.14; H, 1.36; N, 1.74. Thermogravimetric loss (in air): 8.4% (organic weight/sample weight). The number of aminopropyl groups was estimated at 1.24 mmol g^{-1} of the modified MCM-41.

2.3. Grafting of ClAlPc$(SO_2Cl)_2$ onto amino-modified MCM-41 silica

An amount of 3 g of the amino-modified MCM-41 silica was suspended in a DMF solution of 1 g ClAlPc$(SO_2Cl)_2$, and further stirred at 50–60 °C for 24 h. A green/blue solid was obtained by filtration, washed in a Soxhlet apparatus with DMF under reduced pressure and dichloromethane, respectively, and then dried at 100 °C in vacuo. The product was designated as ClAlPc-MCM-41a. Elemental analysis (%): C, 17.91; H, 2.15; N, 5.23, Al, 0.79. Thermogravimetric loss (in air): 28.1%.

2.4. Grafting of ClAlPc-$(SO_2NHCH_2CH_2CH_2Si(OEt)_3)_2$ onto MCM-41 silica

For a comparison, the grafting of ClAlPc-$(SO_2NHCH_2CH_2CH_2Si(OEt)_3)_2$, obtained by treatment of ClAlPc$(SO_2Cl)_2$ with APTES, onto MCM-41 silica was also performed. In a typical preparation, 2 mmol of ClAlPc$(SO_2Cl)_2$ was dissolved in 100 ml DMF, followed by the dropwise addition of a mixture of 4 mmol $NH_2CH_2CH_2CH_2Si(OEt)_3$ and pyridine at 80 °C under continuous stirring. After 12 h of stirring, 5 g of MCM-41 silica was suspended in the mixture solution and further stirred at 110 °C for 24 h. A green/blue solid was obtained by filtration, Soxhlet extraction successively with DMF and CH_2Cl_2, and then dried at 100 °C in vacuum. The product was designated as ClAlPc-MCM-41b. Elemental analysis (%): C, 11.1; H, 0.86; N, 3.27; Al, 0.62. Thermogravimetric loss (in air): 19.7%.

2.5. Characterization

The as-synthesized MCM-41 and functionalized MCM-41 silica were characterized by XRD (XRD, RIGAKU D/Max 3400, Cu Kα radiation). The pore diameter, pore volume and BET surface areas were calculated from nitrogen adsorption isotherms at 77 K according to the Barrett–Joyner–Halenda (BJH) method using a micromeritics instrument from Quantachrome Corporation. Infrared spectra were recorded under ambient conditions with a Nicolet 50X FT-IR spectrophotometer using the Nujol mull method (MCM-41 samples were dispersed in liquid paraffin under a nitrogen atmosphere, and then put on KBr-disk for FT-IR analysis). TGA measurements were performed (Mettler-Toledo TGA/SDTA851^{e}) in N_2 with a heating rate of 10 °C min^{-1}, from 25 to 1000 °C. The ClAlPc-MCM-41 samples were further characterized by UV–VIS spectroscopy (Shimadzu, UV–VIS-NIR UV3100). Elemental analyses were performed on a Perkin-Elmer 2400 analyzer. The ClAlPc contents of the functionalized MCM-41 were determined by Al^{3+} analyses using spectrophotometric method with chrome azurol S as a chromogenic agent, after calcination followed by complete digestion of the aluminosilicate using HF/HNO_3 mixture.

2.6. Catalytic test

The cycloaddition of CO_2 with epoxides was carried out in a 75-ml stainless steel autoclave, in which 0.1 mmol of ClAlPc-MCM-41 (based on ClAlPc), and then 250 mmol of epoxide were sealed. After the autoclave was heated to the desired temperature, CO_2 was discharged into it. The reaction was run for 2 h under 4.0 MPa CO_2 constant pressure and continuously stirring. Then the autoclave was half-submerged in a bath of ice/water mixture and the excess gases were vented. The remainder mixture was degassed and dissolved in methanol for the measurement of cyclic carbonates by means of gas chromatography with butyl acetate as an internal standard. The ClAlPc-MCM-41 catalysts were recovered by filtration, and then washed with methanol. Pure cyclic carbonates were obtained via distillation under reduced pressure. The spectral data are as follows: ethylene carbonate [IR: 1775, 1805, 1163, 1072, 973 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS): δ 4.51 (s, 4H); T_m: 36.5 °C]; propylene carbonate [IR: 1793, 1183, 1120, 1075, 1052 cm^{-1}; ^{1}H-NMR: δ 1.4 (d, 3H), 3.9–4.1 (q, 1H), 4.4–4.6 (t, 1H), 4.7–4.9 (m, 1H)]; chloropropylene carbonate [IR: 1798, 1166, 1072, 1045 cm^{-1}; ^{1}H-NMR: δ 3.7–3.8 (m, 1H), 4.3–4.5 (q, 1H), 4.5–4.7 (q, 1H), 4.9–5.1 (m, 1H)]; phenyl ethylene carbonate [IR: 1813, 1168, 1069, 770, 669 cm^{-1}; ^{1}H-NMR: δ 4.2–4.3 (t, 1H), 4.6–4.8 (t, 1H), 5.5–5.7 (t, 1H), 7.3–7.4 (q, 5H)].

3. Results and discussion

3.1. Preparation and characterization of ClAlPc-MCM-41

ClAlPc was covalently anchored onto MCM-41 silica by two routes, as shown in Scheme 1. ClAlPc-MCM-41a was obtained by the grafting of $ClAlPc(SO_2Cl)_2$ onto mesoporous MCM-41 silica after functionalization of the surface with APTES. The ethoxy group of the silane chain can react with the silanol groups of MCM-41 to give ethanol and an aminopropyl chain at the silica surface that is able to react with $ClAlPc(SO_2Cl)_2$. ClAlPc-MCM-41b was prepared by the grafting of $ClAlPc\text{-}(SO_2NHCH_2CH_2CH_2Si(OEt)_3)_2$, obtained by treatment of $ClAlPc(SO_2Cl)_2$ with APTES, onto MCM-41 silica.

The small-angle XRD (SAXRD) patterns of the samples obtained in the present study are depicted in Fig. 1. All of the samples display three or four reflection peaks that are assigned to the (1 0 0), (1 1 0), (2 0 0) and (2 1 0) reflection of hexagonally ordered MCM-type structures. The d_{100} values and the positions of all reflection peaks for the functionalized samples (ClAlPc-MCM-41) are similar to the unfunctionalized MCM-41. On the other hand, the marked loss of peak intensity at the low-angle reflections for ClAlPc-MCM-41 indicates that ClAlPc should be anchored onto the internal surface of the mesopores of MCM-41. The adsorption isotherms of N_2 (Fig. 2) at 77 K also confirm that ClAlPc is indeed loaded into the mesoporous channels of MCM-41. The parameters calculated from nitrogen adsorption data using the BJH method are listed in the Table 1. The adsorption curve for pure MCM-41 with a type IV isotherm and distinct capillary condensation characteristic of MCM-41 shows a pore

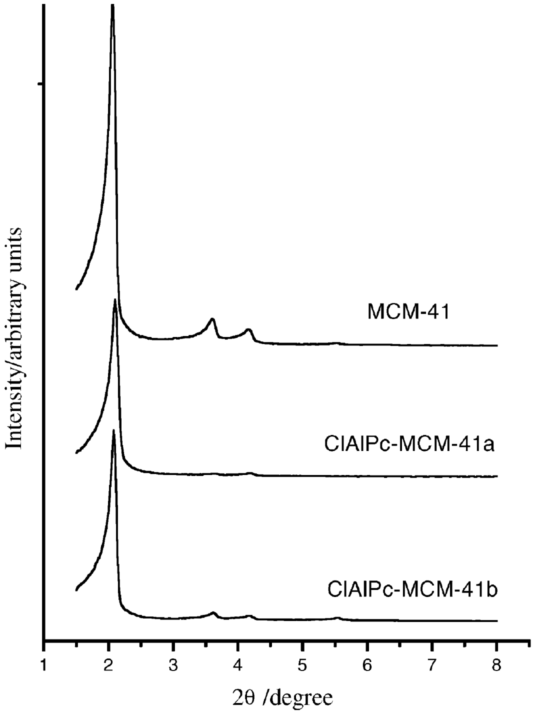


Fig. 1. Powder XRD patterns of the series of MCM-41 samples.

volume of 0.902 $cm^3\,g^{-1}$. The pore volume decreases to 0.298 $cm^3\,g^{-1}$ for ClAlPc-MCM-41a and 0.445 $cm^3\,g^{-1}$ for ClAlPc-MCM-41b. No significant lattice contraction was indicated by SAXRD and thus we conclude that this decrease in pore volume is a result of loaded ClAlPc. The inflection point of the functionalized samples becomes less sharp and shifts to lower relative pressure. This shift indicates the presence of smaller mesopores due to the immobilization of the phthalocyanine complex. However, the mesoporous structure is maintained as indicated by the overall shape of the isotherms and from SAXRD results. Furthermore, the success in immobilizing the phthalocyanine complex onto MCM-41 can be confirmed by FT-IR (Fig. 3). The functionalization with ClAlPc-$(SO_2NHCH_2CH_2CH_2Si(OEt)_3)_2$ resulted in a significant decrease in the peak intensity at about 3700 cm^{-1} ascribed to silanol (SiOH) groups, indicating the replacement of H atom of surface SiOH groups with the functional groups via covalent linkage. Thermal gravimetric analysis was made to determine the decomposition temperature of the phthalocyanine complex in the silica matrix (Table 1). ClAlPc-$(SO_2NH_2)_2$ has a decomposition temperature between 380 and 670 °C, and the phthalocyanine

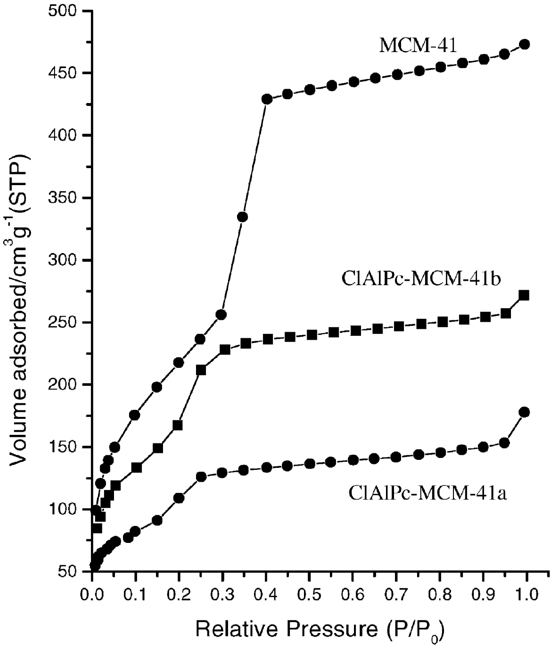


Fig. 2. Nitrogen adsorption curves of the series of MCM-41 samples at 77 K.

Table 1
Properties of the series of MCM-41 samples

Sample	Al^{3+} content (wt.%)	d_{100} (nm)	Pore diameter (BJH) (nm)	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Decomposition temperature (°C)[a]
MCM-41	–	4.25	3.05	892	0.902	–
NH_2-MCM-41	–	4.25	2.68	705	0.617	–
ClAlPc-MCM-41a	0.79	4.26	1.94	449	0.298	325–757
ClAlPc-MCM-41b	0.62	4.26	2.13	652	0.446	340–750

[a] Decomposition temperature of ClAlPc-$(SO_2NH_2)_2$ is 380–670 °C.

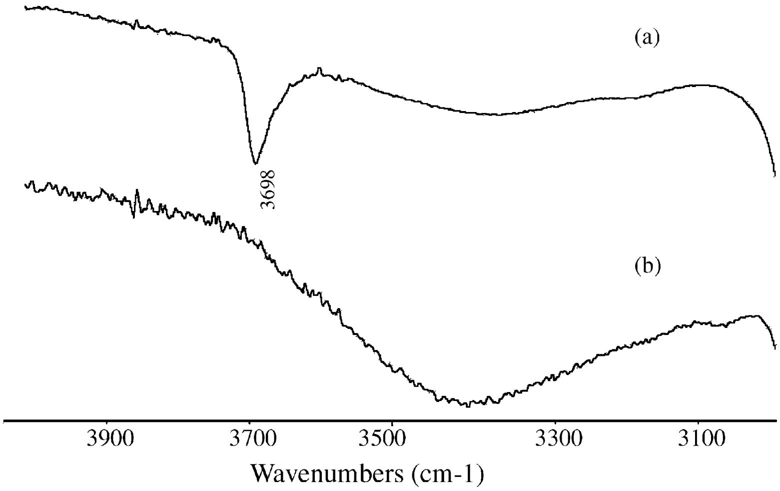


Fig. 3. FT-IR spectra of the hydroxy groups of (a) MCM-41; and (b) ClAlPc-MCM-41b.

complex in ClAlPc-MCM-41b decomposes between 340 and 750 °C. These data indicate that the thermal stability of the phthalocyanine complex remained after covalently bonded to MCM-41.

The nature of the immobilized ClAlPc in MCM-41 was further characterized by UV–VIS spectroscopy (Fig. 4). The grafting of the phthalocyanine complex is clearly evidenced by the two characteristic absorption bands of the macrocycle at 300–400 nm (soret band) and 600–700 nm (Q-band). It is generally known that monomers of phthalocyanine in solution show a very strong absorption around 650–700 nm with a weaker satellite band around 600 nm [22]. Blue shifts of the Q-band for the dimer occur. The peaks at 601 and

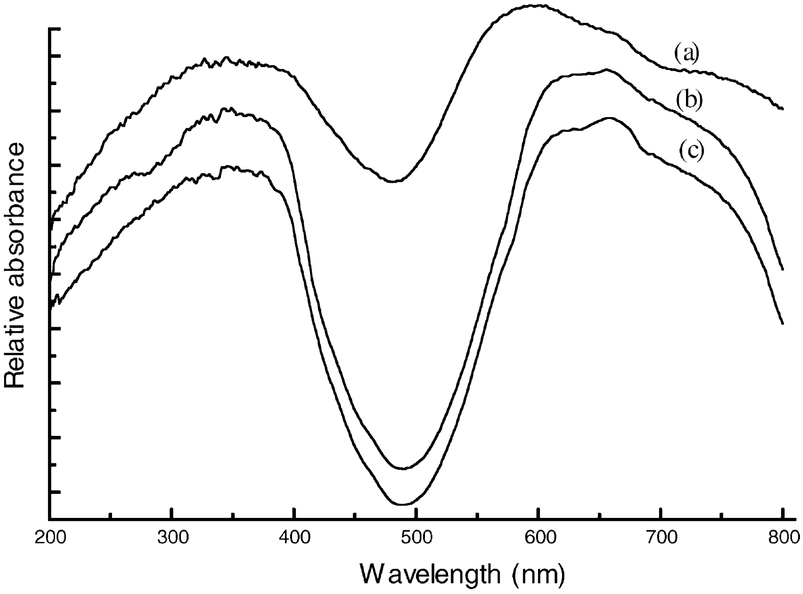


Fig. 4. UV–VIS absorption spectra of (a) ClAlPc-$(SO_2NH_2)_2$; (b) ClAlPc-MCM-41a; (c) ClAlPc-MCM-41b.

660 nm in ClAlPc-MCM-41 samples are consistent with those of dimeric and monomeric species, respectively. It can be seen from Fig. 4 that the majority of the phthalocyanine complex immobilized in MCM-41 is in a monomeric form, while that of ClAlPc-$(SO_2NH_2)_2$ (Fig. 4a) is in a dimer form. The broading of the characteristic absorption bands of the macrocycle probably results from interactions between neighboring macrocycles [23,24]. If the phthalocyanines are disordered, differences in the local environments of the molecules result in a “spreading” of the transition energies and a “broadening” of the spectra.

3.2. Catalytic properties of ClAlPc-MCM-41 silica

In previous papers [25,26], we reported that ClAlPc (or combined with a Lewis base as co-catalyst) was effective catalyst for cycloaddition of CO_2 with epoxides to form corresponding cyclic carbonates. In the present case, ClAlPc was covalently anchored onto MCM-41 and used as heterogeneous catalyst for synthesis of cyclic carbonates from CO_2 and epoxides. The experimental results are shown in Table 2. In a similar manner to ClAlPc or soluble substituted aluminum phthalocyanine complexes, ClAlPc-MCM-41 itself can effectively catalyze the reaction of CO_2 and ethylene oxide to produce ethylene carbonate at elevated temperature. Furthermore, existence of tetraalkyl ammonium halides, such as n-Bu_4NBr, can remarkably promote the conversion of the epoxide to cyclic carbonate at the same temperature. It is interesting that in the presence of n-Bu_4NBr, the catalytic activity of ClAlPc-MCM-41a is only a half of that of ClAlPc-MCM-41b at the same conditions. Possible reasons for this unexpectedly low catalytic activity of ClAlPc-MCM-41a could be the fact that part of ClAlPc was grafted to the surface by Al–N bond, or excess $-NH_2$ groups is coordinated to Al^{3+} of ClAlPc anchored onto MCM-41, which all drastically changes the coordination of the active sites. Based on elemental analyses of NH_2-MCM-41 and ClAlPc-MCM-41a, it is concluded that free $-NH_2$ groups up to 60% did not take part in the reaction for covalent immobilization of ClAlPc on the silica.

The immobilized catalyst is easily recovered by filtration, and was subjected to utilization for 10 recycles without obvious loss of activity (Fig. 5). Furthermore, the binary catalyst, comprising ClAlPc-MCM-41 and n-Bu_4NBr, also shows very high catalytic activity towards the reaction of CO_2 and other epoxides to produce corresponding cyclic carbonates. The results are listed in Table 2. The formation rate of cyclic carbonates from various epoxides and CO_2 is in the order: $CH_2Cl > H > Ph > CH_3$, which is reverse to the order observed when pentavalent organoantimony compounds were used as catalysts [27].

Table 2
The formation rates of cyclic carbonates from CO_2 and epoxides with various catalytic systems[a]

Entry	Catalyst	Temperature (°C)	Epoxide (R)	TOF[b] (turnovers per hour)
1	ClAlPc[c] -MCM-41a	110	H	43
2	ClAlPc-MCM-41b	110	H	30
3	ClAlPc	110	H	19
4	ClAlPc-MCM-41b	125	H	84
5	ClAlPc-MCM-41b	140	H	205
6	ClAlPc-MCM-41a	140	H	326
7	ClAlPc	140	H	188
8	n-Bu_4NBr	110	H	70
9	ClAlPc-MCM-41a/n-Bu_4NBr	110	H	247
10	ClAlPc-MCM-41b/n-Bu_4NBr	110	H	415
11	ClAlPc-MCM-41b/n-Bu_4NI	110	H	428
12	ClAlPc-MCM-41b/n-Bu_4NBr	110	CH_3	280
13	ClAlPc-MCM-41b/n-Bu_4NBr	110	CH_2Cl	452
14	ClAlPc-MCM-41b/n-Bu_4NBr	110	Ph	384

[a] Reaction conditions: ClAlPc-MCM-41/n-Bu_4NBr/epoxide (1/1/2500 (molar ratio)); reaction time: 2 h.
[b] TOF: mole of product (cyclic carbonate)/mol of catalyst per hour.
[c] Based on Al^{3+} content of ClAlPc-MCM-41.

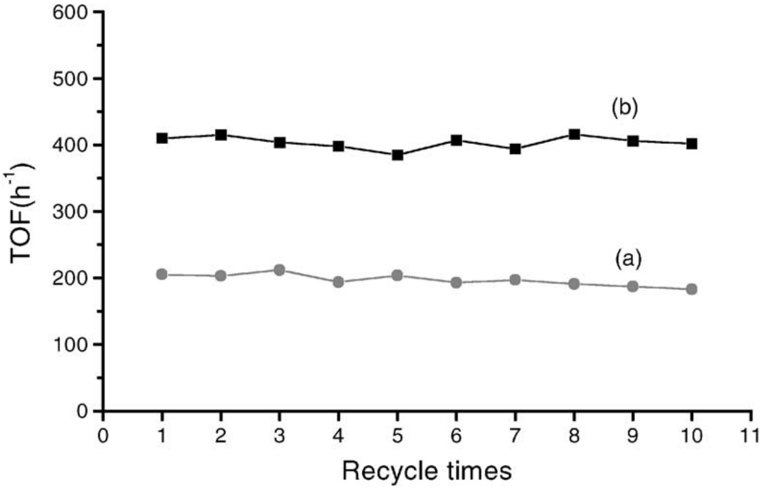
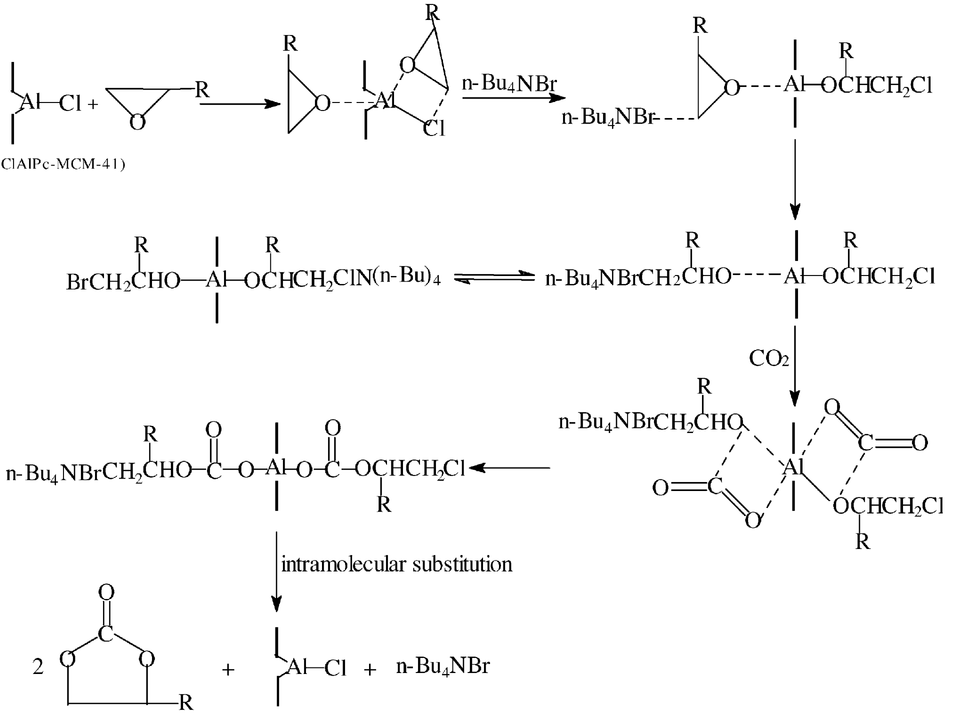


Fig. 5. A plot of catalytic activity vs. recycle times of ClAlPc-MCM-41b. The reaction conditions are the same as Table 2. (a) ClAlPc-MCM-41b alone as catalyst, reaction temperature: 140 °C; (b) ClAlPc-MCM-41b/*n*-Bu_4NBr as catalyst at 110 °C, fresh *n*-Bu_4NBr was added the autoclave after every recycle of ClAlPc-MCM-41b.

The formation of cyclic carbonates from CO_2 and epoxides can proceed via various reaction pathways: direct insertion of CO_2 into the C–O bond of epoxides, cyclic elimination of linear carbonate formed, polymerization/depolymerization process, etc. These pathways may not operate exclusively, but one of them might be expected to predominate for a given catalytic system, or under certain experimental conditions [28]. It is well known that ring-opening of epoxides is generally described in terms of two pathways: an acid-catalyzed cleavage and a base-catalyzed cleavage. In the present cases, epoxides are ring-opened according to base-catalyzed cleavage, identically to the cases of propylene oxide with Al(L)TPP [29,30] or Al(L)Pc(*t*-Bu)$_4$ [31,32]. Smaller binding constants of epoxides or thiiranes to cadmium, zinc, or magnesium α,β,γ,δ-mesotetraphenylporphyrins have been observed spectrophotometrically [33], and the crystal structure of a metal epoxide complex has been reported for a ruthenium porphyrin derivative of styrene oxide [34]. When compared to these Cd(II), Zn(II), or Mg(II) complexes, analogous Al(III) complexes have higher electrophilicity and thus trendency to form complexes with electron-donor ligands. In this case, ClAlPc, which was monomolecularly dispersed onto the external and the internal surface of MCM-41, probably interacts with epoxides by two types: the coordination of epoxides to Al^{3+} of ClAlPc, and nucleophilic attack resulting from Cl^- ion of ClAlPc towards epoxides, as shown in Scheme 3. These interactions have synergistic effect on each other. The formation of hexacoordinated complex could cause electronic transfer from oxygen atom of epoxides to central metal ion of ClAlPc, thus reducing the Al–Cl bond strength. This might be beneficial for the insertion of epoxides into the Al–Cl bond of ClAlPc. On the other hand, the coorindated epoxides are readily ring-opened in view of nucleophilic attack of even poorly nucleophilic reagents. Therefore, the synergistic effect of the binary catalyst, consisted of ClAlPc-MCM-41 and *n*-Bu_4NBr, for ring-opening of epoxides results from nucleophilicity of highly reactive anions of quaternary salt and the electrophilic interaction of ClAlPc with epoxides. The activation of CO_2 may be generally initiated by nucleophilic attack of the alcoholate (–OCH_2CH_2Br) at the carbon atom of CO_2, and weak interaction between the central metal ion of ClAlPc and the lone pairs of one oxygen of CO_2. The synergistic effect is sufficient to promote the insertion of CO_2 to Al–O bond of Pc(Cl)Al–OCH_2CH_2Br or PcAl–OCH_2CH_2Cl to form linear carbonates, which are transformed into cyclic carbonates by intramolecular substitution of halides.



Scheme 3. The possible formation mechanism of cyclic carbonates from CO_2 and epoxides in the presence of binary catalyst.

4. Conclusion

Aluminum phthalocyanine complex has been covalently anchored onto the surface of mesoporous MCM-41 silica via two routes. (1) Anchoring was performed by modifying MCM-41 material with APTES followed by reaction with dichlorosulfonylphthalocyanine complexes. (2) Anchoring was also realized by the grafting of ClAlPc-$(SO_2NHCH_2CH_2CH_2Si(OEt)_3)_2$, obtained by treatment of ClAlPc$(SO_2Cl)_2$ with APTES, onto MCM-41 silica. The anchoring resulted in a decrease of surface area, average pore diameter as well as pore volume, indicating phthalocyanine complexes indeed loaded into the mesoporous channels of MCM-41. However, no significant lattice contraction was observed by SAXRD and the mesoporous structure was still maintained as revealed by the adsorption isotherms of N_2 at 77 K. UV–VIS spectra show that the majority of the phthalocyanine complex immobilized in MCM-41 is in a monomeric form, while the thermal stability of the phthalocyanine remained in the silica matrix.

In a similar manner to soluble substituted aluminum phthalocyanine complexes, ClAlPc-MCM-41, or together with *n*-Bu_4NBr, exhibited very high catalytic activity towards the reaction of CO_2 and epoxides to produce corresponding cyclic carbonates. The formation rate of cyclic carbonates from various epoxides and CO_2 was in the order: $CH_2Cl > H > Ph > CH_3$, which was reverse to the order observed when pentavalent organoantimony compounds were used as catalysts. The immobilized aluminum complex exhibited enhanced stability in the reaction conditions, and was subjected to utilization for 10 recycles without obvious loss of activity. Depending on the synthetic route, the supported catalysts differed strongly in the their catalytic activities.

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