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An aluminum(III) picket fence phthalocyanine-based heterogeneous catalyst for ring-expansion carbonylation of epoxides

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An effective heterogeneous catalyst for ring-expansion carbonylation of epoxides may have additional advantages over the homogeneous counterpart in terms of facile product separation and recyclability. A new Al(III) picket fence phthalocyanine complex was synthesized and directly knitted using the Friedel-Crafts reaction to prepare solid porous network, which was untimatly used to immobilize $[Co(CO)_4]^-$ ions. The resulting heterogeneous catalyst, [Lewis acid]* $[Co(CO)_4]^-$, efficiently catalyzes the conversion of various expoxides into corresponding β -lactones with high selectivity (99%) and stoichiometric conversion under mild reaction conditions, along with good functional group tolerance.

Introduction

 β -lactones are valuable intermediates and precursors in organic and polymer chemistry.¹⁻³ Especially, β -butyrolactone is high demand as a monomer for the production of the thermoplastic biopolymer poly(3-hydroxybutyrate).⁴⁻⁶ A simple one step ringexpansion carbonylation of epoxides to β -lactones has proved to be industrially viable because the epoxide and carbon monoxide starting materials are typically inexpensive.⁷⁻¹²

A series of well-defined [Lewis acid]⁺[Co(CO)₄]⁻ catalysts, including [(salph)M]⁺[Co(CO)₄]⁻ and [(porphyrin)M]⁺[Co(CO)₄]⁻ (M=Al³⁺ or Cr³⁺), have been developed by Coates' group for epoxide carbonylation.¹¹⁻¹⁸ A mechanism for [Lewis acid]⁺[Co(CO)₄]⁻-catalyzed carbonylation involving (1) epoxide activation by the [Lewis acid]⁺ species; (2) ring opening by Co(CO)₄⁻; (3) CO insertion; and (4) ring-closure was proposed (Scheme 1, pathway A).¹⁸ Although these catalysts are highly efficient, their industrial application may be problematic owing to limitations in their separation and reuse.

Accordingly, our group previously reported two heterogeneous catalysts for epoxide carbonylation to lactones as a means of addressing these drawbacks.^{19,20} However, the high pressure of CO necessary for efficient and selective carbonylation (60 bar) hinders the study of these catalysts in typical nonspecialized laboratories and their application in industry. Recently, although Román-Leshkov *et al.* reported the metal-organic framework-based heterogeneous catalyst



Scheme 1. (a) Mechanism of epoxide carbonylation (pathway A) and ketone formation (Pathway B).

Co(CO)₄--incorporated Cr-MIL-101 for the continuous gas-phase production of β -lactones from epoxides under CO at 20 bar, its carbonylation activity (site time yield: 176 h⁻¹) was far lower than that of the optimized homogeneous catalyst (740 h⁻¹).⁸ Therefore, the development of heterogeneous catalysts that are efficient under mild reaction conditions is of great importance.

Recently, we demonstrated that phthalocyanine (Pc) species are an excellent alternative to porphyrins in epoxide carbonylation catalysts.²¹ In that study, commercial aluminum phthalocyanine chloride (AIPcCI) was reacted with $Co_2(CO)_8$ to generate the epoxide carbonylation catalyst [AIPc]⁺[Co(CO)₄]⁻ in *situ*. This catalyst shows efficient catalytic activity in single and double carbonylations depending on the reaction temperature conditions. It was envisioned that if a Pc-based heterogeneous catalyst was used for the epoxide carbonylation, it may show an excellent carbonylation activity, as well as an advantage on the product separation.

In the current study, an AIPc-based heterogenized catalyst was rationally designed and used for epoxide carbonylation under a CO pressure of just 10 bar and at room temperature. The catalyst showed not only highly efficient catalytic activity and selectivity (99%), but also functional group tolerance.

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Experimental sections

Materials and methods. Propylene oxide (PO) was distilled in a mixture of KOH/CaH₂ under N₂ atmosphere. Dimethoxyethane (DME) and tetrahydrofuran (THF) were distilled using sodium/benzophenone. Allyl glycidyl ether (>99%), benzyl glycidy ether (99%), and epichlorohydrin (>99%) were purchased from Sigma-Aldrich Co. without purification prior to use. Oxetane (>98%) was supplied by TCI without further purification.

Synthesis of 4,5-bis(2-di-*iso*-propylphenoxy)phthalonitrile ligand. The ligand was synthesized according to a previously reported procedure with a little modification.²² Specifically, 4,5-dichlorophthalonitrile (1.97 g, 0.01 mol), 2-isopropylphenol (3.41 g, 0.025 mol), K₂CO₃ (11.04 g, 0.08 mol) were stirred in anhydrous *N*,*N*-dimethylformamide (12 mL) at 70 °C for 36 h under N₂ atmosphere. On cooling, the reaction mixture was poured into water (100 mL). The resulting precipitate was filtered and washed with water, then dry in vacuum at 60 °C for overnight. Recrystallization from methanol gave a light-blue solid (2.51 g, 63%).

Synthesis of AlPc'Cl monomer (1). 4,5-bis(2-isopropylphenoxy)phthalonitrile (2.38 g, 6.0 mmol) was added to a solvent-mixture of quinoline (0.75 mL) and nitrobenzene (1.2 mL) in a 25 mL round-bottom flask. The solution was cooled in an ice-bath and AlCl_3 (0.21 g, 1.6 mmol) was added to the mixture. The reaction was run at 210 $^\circ C$ for 4 h under $N_2.$ The resulting blue-greenish solution was cooled to room temperature and dissolved in CH2Cl2. The organic layer was washed with HCl aqueous solution (1.0 M) and water. The crude product was purified by column chromatography on SiO₂ eluting with CH₂Cl₂/CH₃OH (20:1) and dried at 80 °C under vacuum for 24 h to give a dark-green solid (1.63 g, 66%).

Synthesis of the AlPc'-based porous polymer network (2). The AlPc'Cl monomer (0.82 g, 0.5 mmol) was dissolved in CH_2Cl_2 (10 mL). After the solution was cooled using ice-water, the catalyst AlCl₃ (1.06 g, 8.0 mmol) was added under N₂ atmosphere. The reaction was run at 0 °C for 4 h, 26 °C for 8 h, 40 °C for 12 h, 60 °C for 12 h, and 80 °C for 24 h. The resulted precipitate was filtered and washed with water, methanol, acetone, and THF, respectively. Next, the resulted polymer was further purified using Soxhlet extraction for 48 h with THF as solvent. After drying at 120 °C in a vacuum for overnight, the product was obtained as a deep blue powder (0.82 g, 100%).

Synthesis of catalyst (3). In a glove box, the network 2 (0.60 g), $KCo(CO)_4$ (1.61 g), and THF (15 mL) were mixed in a vial of 20 mL. The suspension was filtered and washed several times with THF after stirring for 48 h at room temperature. The obtained catalyst was purified two times using the process of dispersion several hours/filtration/washing. The product was given after drying under vacuum (0.59 g, 98%).

Epoxide carbonylation. In a typical procedure, the catalyst (20 mg, 1.75 wt% of cobalt determined from an inductively coupled plasma atomic emission spectroscopy (ICP-AES)) was added into a 100-mL stainless steel reactor in a glove box. After the reactor was flushed with CO, the prepared PO solution in DME (0.1 M, 1.54 g) was injected into the reactor under CO flow. The reaction was run at room temperature for 1 h under 10-bar CO. The reaction solution was transferred to a vial after cooling the reactor and releasing excess CO. The crude product was analyzed by ¹H NMR spectrum with naphthalene as an internal standard.

Results and Discussion

DOI: 10.1039/C8TA11877A Unsubstituted metal Pcs exhibit very poor solubilities that typically fall in the range 10^{-5} – 10^{-7} M in organic solvents owing to aggregation of the macrocyclic Pc units by π - π stacking.^{23,24} The introduction of bulky phenoxy substituents on peripheral Pc positions is one of the most effective strategies for disrupting this stacking and thus improving the solubility of metal Pcs.^{25,26} Therefore, a phenoxy-substituted AIPc was chosen for the construction of a heterogeneous catalyst.

Journal of Materials Chemistry A

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Scheme 2. Procedure for the synthesis of catalyst 3.

The synthetic process is shown in Scheme 2. First, the monomer **1** is synthesized according to a slight modification of a previously reported method.^{27,28} The solubility of the bulky phenoxy-substituted AIPc'Cl is significantly improved compared to that of commercial AIPcCl, enabling purification by column chromatography. The structure of AIPc'Cl was confirmed by ¹H NMR (Fig. S1), elemental analysis (Fig. S2), and Fourier-transform infrared (FT-IR) spectroscopy. All analytical data are consistent with the predicted structure.

Then, the polymer network **2** are prepared from **1** and a CH_2CI_2 cross-linker via an AlCI₃-catalyzed Friedel-Crafts reaction (Scheme 2). The Friedel-Crafts reaction has been recently demonstrated to be a valuable route to porous polymer network that avoids the need for monomers with specific polymerizable functionalities.²⁹⁻³² This strategy has the advantages of high yield, low cost, and easy handling. It is worthy of note that this is the first report of the use of the Friedel-Crafts reaction for the construction of Pc-based porous network in the literature.³³⁻³⁹

The prepared **2** is insoluble in nearly all organic solvents. The scanning electron microscopy (SEM) image of **2** (Fig. 1a) reveals that it has a morphology comprising aggregated spherical nanoparticles. The transmission electron microscope (TEM) image of **2** clearly showed the presence of hierarchical nanosized pores on the network surface (Fig. 1b and Fig. S3). IR measurement was performed to confirm the formation and chemical structure of **2** (Fig. 1c). For the monomer **1**, the IR absorption peak at 3070 cm⁻¹ is characteristic of the C-H bonds on the aromatic ring and the peaks at 1450 cm⁻¹ and 1340 cm⁻¹ correspond to the C=N and C-N stretching vibrations,

Journal of Materials Chemistry A



Fig. 1 Characterization of the network **2** and catalyst **3** using SEM (a), TEM (b), FT-IR (c), solid-state ¹³C NMR (d), XPS (e) and BET (f).

respectively.40-42 After the Friedel-Crafts reaction, the characteristic C=N and C-N bond vibrations remain, indicating that the Pc' ring is sufficiently stable during the reaction, and the intensity of the peak at 3070 cm⁻¹ is reduced significantly, suggesting that the aromatic ring is alkylated and confirming the formation of methylene linkages. This result is consistent with those of previous studies in which the intensity of the aromatic group signal is decreased upon Friedel-Crafts reaction.43 Elemental analysis is a very useful tool for the composition characterization of the network 2. Elemental analysis of the network 2 indicated that the actual C/N molar ratio (14.9) is higher than the predicated value (14.0), as illustrated in Scheme 1b, further indicating multiple alkylation of the aromatic ring (Fig. S4). Compared to monomer 1, the solid-state ¹³C NMR spectrum of the network 2 showed additional signals at 43 ppm and 49 ppm, which may be attributed to the carbon atoms in the methylene linker (Fig. 1d and Fig. S5). This result is in agreement with those previously reported for crosslinked aromatic rings using similar methods.^{29,31} The signals at δ = 153, 132, and 111 ppm corresponded to the carbon atoms of the phthalocyanine and aromatic groups. Based on the above analyses, the alkylation of the aromatic ring is confirmed and the chemical structure of the Pc' ring remains intact without decomposition during the Friedel-Crafts reaction.

In comparison, if commercial AIPcCI is employed under the same reaction conditions, no insoluble product (e.g., in CH_3OH) is afforded. This result indicates that the commercial AIPcCI monomer exhibits a lower Friedel-Crafts reactivity than that of 1 and therefore the knitting together of aromatic rings in the monomer does not proceed. Powder X-ray diffraction analysis

of **2** revealed an amorphous peak at $2\theta = 21^\circ$, indicating that the bulky phenoxy substituents prevent the close packing of the Pc' units (Fig. S6). Therefore, the introduction of bulky phenoxy substituents to the peripheral Pc positions is crucial for the prevention of Pc unit aggregation and thus for knitting the monomers together to form a network.

The Al content of **2** was evaluated using energy-dispersive Xray (EDX) spectroscopy and ICP-AES. EDX analysis revealed that 84.2% of the Pc' rings was coordinated to Al atoms in **2** (Al: 1.29 wt%) based on the calculation of the Al/N atomic ratio (Fig. S7). ICP-AES revealed that the Al content in **2** is 1.26 wt%, which is close to the value from the EDX analysis. This high metal content is attributed to the fact that the network **2** is prepared by direct polymerization of metalated Pc' monomers rather than postmetalation of a porous organic polymer.^{19,20,44}

To replace Cl^{-} in **2** with $Co(CO)_{4^{-}}$, the network **2** were treated with excess KCo(CO)₄ to provide a green catalyst in stoichiometric yield. The SEM image of the catalyst 3 demonstrates that the morphology of the network is not changed during the KCo(CO)₄ reaction (Fig. S8). An IR peak at 1883 cm⁻¹, which is attributed to absorption by the CO in $Co(CO)_4$, is presented by the product (Fig. 1c). The Co anion in the catalyst 3 was investigated using X-ray photoelectron spectroscopy (XPS), revealing a Co⁻ (2p_{1/2}) peak at 797.8 eV and a Co⁻ (2p_{3/2}) peak at 782.3 eV, similar to those observed in our previous studies (Fig. 1e).^{19,20} XPS also revealed that the AI (2p) electron binding energy (74.3 eV) is 0.5 eV lower than that of the network 2 (Fig. S9), further demonstrating the success of the anion exchange reaction. ICP-AES revealed that the AI/Co atomic ratio of the catalyst 3 is 1:0.65, which is close to that revealed by the EDX data (Al/Co = 1:0.61, Fig. S10). These results indicate that approximately 65% of the Al sites are paired with $Co(CO)_{4}$. The other 35% of the Al sites may exist as ion pairs with Cl⁻ as a counter ion. The reason for the partial replacement may be the high degree of cross-linking in the network, resulting in not all the Cl⁻ sites being available for ion-exchange.

To evaluate the porosities of the network **2** and catalyst **3**, Brunauer-Emmet-Teller (BET) analysis at 77 K was performed. The shapes of the sorption isotherms (Fig. 1f) indicate wide pore-size distributions. The rapid uptake of nitrogen gas in the low-relative-pressure regions (P/P₀ <0.001) is due to the filling of micropores, while the obvious hysteresis and sharp rise in the high-relative-pressure regions (P/P₀ >0.9) indicates the presence of mesopores and macropores in the network according to the Barrett-Joyner-Halenda model (Fig. S11). The BET surface areas of **2** and **3** are 660 and 470 m² g⁻¹ with pore volumes of 0.6 and 0.4 cm³ g⁻¹, respectively. These results indicate that the network-bound Cl⁻ (approximately 65%) is substituted by Co(CO)₄⁻, resulting in the inclusion of Co(CO)₄⁻ in the network.

Considering that the catalyst generated *in situ* by the commercially available AIPcCl and $Co_2(CO)_8$ has been shown to have efficient carbonylation activity at room temperature,²¹ the carbonylation reactions used to evaluate the catalytic activity of catalyst **3** in the present study were conducted at room temperature. First, PO carbonylation was performed in DME using the heterogeneous catalyst at room temperature (23 °C) for 1 h under a CO pressure of 40 bar in a 100-mL stainless steel tube reactor. Full conversion of PO was confirmed using ¹H NMR spectroscopy, resulting in a 95% yield of β -butyrolactone and a molar ratio of β -butyrolactone to acetone of >99:1, which is

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similar to our reported result for the *in situ* homogeneous catalyst (Table 1, entry 1, Fig. S12).

Significantly, if low-pressure CO (10 bar) is used for the carbonylation under otherwise identical reaction condition, very similar results to that using a CO pressure of 40 bar are achieved (Table 1, entry 2, Fig. S13). In other words, the product selectivity is not affected by using different CO pressures in the range 10–40 bar. In contrast, our previously reported heterogeneous catalysts and different Coates' homogeneous catalysts show much higher selectivities for the ketone side products under relatively low CO pressures (<15 bar).^{16,17,19,45} One possible explanation for this difference is that the AIPc'-based catalyst promotes faster ring-closing than ketone generation. The generation of ketone products occurs via β -elimination by the intermediate I followed by enolate protonation and rearrangement in two stages and consistent with Coates' work (Scheme 1, pathway B).¹⁸

Subsequently, the activity and selectivity of the heterogeneous catalyst was evaluated using other substrates

under 10-bar CO at room temperature. In the case of glycidyl ethers with functional groups (e.g., allyl or benzyl), full conversion of the starting material is achieved and the selectivity for lactones is >99% (Table 1, entries 3 and 4, Figs. S14 and S15). Epichlorohydrin, a traditionally challenging substrate for carbonylation, shows similar selectivity and activity to those of the glycidyl ethers (Table 1, entry 5, Fig. S16). Only one catalyst reported in the literature effects quantitative carbonylation of epichlorohydrin.^{8,10,13,14,17} Oxetane has a lower ring-strain energy than three-membered epoxides and consequently few catalysts have been reported for its carbonylation.^{11,46-49} However, our AlPc'-based heterogeneous catalyst exhibits oxetane-carbonylation activity, even at room temperature and under 10-bar CO (Table 1, entry 6, Fig. S17). These results reveal that the AIPc'-based heterogeneous catalyst not only exhibits functional group tolerance but also efficient activity and high selectivity in the carbonylation of oxygen-containing rings.

Table 1. Carbonylation of different substrates using the catalyst**3**.^a

No	substrate	CO (bar)	Tim e (h)	Yield (%) ^b	Lacto keto	one: one ^b
1	0	40	1	95	>99	<1
2	<u>م</u>	10	1	94	>99	<1
3		10	22	98	>99	<1
4		10	22	97	>99	<1
5	CI	10	22	97	>99	<1
6		10	22	96	>99	

^aThe feed molar substrate/Co ratio was 30. ^bYields and lactone/ketone ratios determined by ¹H NMR with naphthalene as an internal standard. A substrate solution prepared with DME (0.1 M, 1.54 g) was injected into the reactor with the catalyst (20 mg) under CO flow.

The solvent dependence of the carbonylation activity in the heterogeneous catalyst is consistent with 1that9061Coates' homogeneous systems.¹⁸ Weakly coordinating solvents (e.g., DME) show higher activity than more strongly coordinating solvents (e.g., THF) (Fig. S18).

To demonstrate the catalytic synergy between the network Al sites and $Co(CO)_4$, the network 2 and $KCo(CO)_4$ were used separately for oxetane carbonylation. As expected, no ybutyrolactone formation was observed, probably due to the lack of $Co(CO)_4^-$ for CO insertion and an appropriate [Lewis acid]⁺ species for oxetane activation (Fig. S19). Notably, an equimolar mixture of the network 2 and KCo(CO)₄ promotes γbutyrolactone formation to some extent. This may be attributed to partial in situ formation of Al/Co sites resulting in fractional carbonylation activity for the mixture. However, the yield is much lower than that achieved using the network 2 containing post-synthetically introduced Co(CO)₄- (Fig. S20). Notably, Román-Leshkov's group reported a similar carbonylation activity using an in situ generated catalyst derived from Cr-MIL-101 and Na[Co(CO)₄].⁸ It is believed that the co-existence of both a Lewis acid with appropriate acidity and $Co(CO)_{4}$ is necessary for efficient carbonylation.

The heterogeneous nature of the catalyst **3** was confirmed using a filtration test. Specifically, the catalyst **3** in a PO carbonylation mixture was filtered after reaction for 1 h, and the PO carbonylation in the resulting colorless filtrate was assessed. Even when the reaction time was extended to 24 h, the β -butyrolactone concentration did not increase and unreacted PO was detected in the mixture (Fig. S21), confirming that the catalyst is heterogeneous in nature.

Table 2	Recyclability o ⁻	f catalyst for PO	carbonylation. ^a
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Cycle	e Yield (%)	β-butyrolactone:Acetone ^b
1	94	> 99:1
2	92	> 99:1
3	75 ^c	> 99:1
4 ^d	95	> 99:1

^aReaction conditions: catalyst 50 mg; DME; feed molar PO/cobalt ratio 30; CO 10 bar; 23 °C, 1 h. ^bDetermined by ¹H NMR spectroscopy. ^cUnreacted PO. ^dRegenerated catalyst used for PO carbonylation.

To evaluate the recyclability of the heterogeneous catalyst, the green solid was recovered after the initial run using simple filtration, washed with DME, and used directly for the next run. The catalytic performance of the recovered catalyst is shown in Table 2. In the second cycle, the ratio of β -butyrolactone to acetone is maintained at >99:1. However, the yield of β butyrolactone in the third run is decreased from 94% to 75%, a 19% reduction. After three catalytic cycles, the SEM images showed no morphological change of the catalyst 3 (Fig. S22). The BET surface area and pore volume of the catalyst 3 after three cycles is 390 m² g⁻¹ and 0.3 cm³ g⁻¹, respectively, which is slightly lower than that of fresh catalyst **3** (470 m² g⁻¹, 0.4 cm³ g⁻ ¹), demonstrating the porous structure is still existed (Fig S23). ICP showed that there were no Al species in the filtrate after each cycle, but that some Co was present, indicating that the reduction in activity of the catalyst **3** can be attributed to the leaching of $Co(CO)_4$. Notably, the catalytic performance of the Journal of Materials Chemistry A

catalyst after successive runs is restored by treating it with $KCo(CO)_4$ (Table 2, entry 4).

Conclusions

novel heterogeneous catalyst, [AlPc'-based porous network]⁺[Co(CO)₄]⁻, was rationally designed and prepared for epoxide carbonylation. The synthesis of the catalyst involves a facile Friedel-Crafts alkylation of AIPc'Cl monomers and subsequent replacement of Cl⁻ with Co(CO)₄⁻. The heterogeneous catalyst showed efficient activity and high selectivity for epoxide carbonylation under a lower CO pressure and reaction temperature than those previously reported for similar catalysts, as well as excellent functional group tolerance. Considering the favorable catalytic performance of AIPc'-based heterogeneous catalyst under mild reaction condition, the application of this catalyst for epoxide carbonylation in gas-phase reactors is currently in progress.

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