

MCM-41 Grafted Quaternary Ammonium Salts as Recyclable Catalysts for the Sequential Synthesis of Dimethyl Carbonate from Epoxides, CO₂, and Methanol

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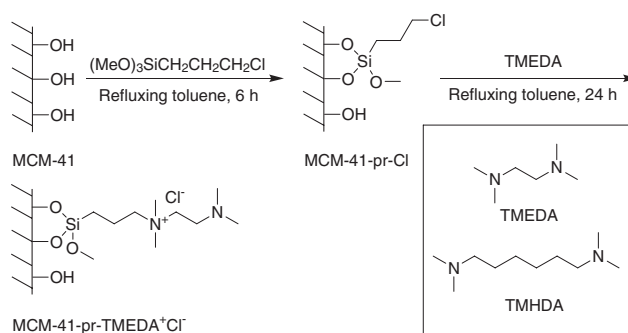
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One kind of novel heterogenous bifunctional catalyst, MCM-41 grafted quaternary ammonium salts with terminal amino group, was prepared. These catalysts exhibited excellent catalytic performance and good reusability in the sequential synthesis of dimethyl carbonate from epoxides, CO₂, and methanol.

With the development of industrial production, environmental problems caused by CO₂ such as the greenhouse effect have attracted wide attention. Meanwhile, CO₂ is an abundant, renewable, and economic carbon resource. Therefore, transformation of CO₂ to other useful compounds has important significance.¹ However, CO₂ is the most oxidized state of carbon and acts as a relatively inert molecule. Therefore, the activation of CO₂ is a challenging topic in catalysis and high-energy starting materials such as epoxides are generally needed for the high-efficient conversion of CO₂.

Dimethyl carbonate (DMC) is considered to be a safe, non-corrosive, and environmentally benign chemical and energy source. It can be used as carbonyl source and alkylating reagent in pharmaceuticals and agricultural chemicals. Additionally, DMC also can be used as solvent, fuel oil additive, and electrolyte.² Up to now, several routes have been developed for DMC synthesis. Among them, transesterification is a commercialized and environmentally friendly route for massive production of DMC, and this method is also considered to be one of the most valuable and promising routes for large-scale CO₂ utilization.³ The transesterification process can be divided into a one-step and a two-step methods. The two-step method has the advantages of mild reaction conditions, high selectivity, and low investment, while the complicated operation process is one of the main drawbacks for this route due to the separation of cyclic carbonate intermediates. As for the one-step method, although it eliminates the drawback of separations, most of catalysts are difficult to recover owing to the solubility of the active component and the occurrence of side reactions is unavoidable. Moreover, rigorous reaction conditions are usually required. To solve all these problems, a sequential transesterification process is reported, in which the cycloaddition of epoxide with CO₂ and the transesterification of cyclic carbonate with methanol proceeds step by step catalyzed by the same catalyst without the separation of intermediates.⁴ However, for reported catalyst K₂CO₃/BrBu₃PEG₆₀₀₀PBu₃Br, the only defect is that the loss of K₂CO₃ is inevitable due to its solubility in methanol. Hence, efficient and recyclable catalysts are highly desired for this process.

As mentioned in the literature,^{3d} quaternary ammonium salts are active for the cycloaddition of epoxide and CO₂, and tertiary amines can promote the transesterification reaction. Inspired by this work, herein, we synthesized MCM-41 grafted quaternary



Scheme 1. Preparation route of MCM-41 grafted quaternary ammonium salts with terminal amino groups.

ammonium salts with terminal amino groups. These novel bifunctional catalysts exhibited excellent catalytic performance and good reusability in the sequential synthesis of dimethyl carbonate from epoxides, CO₂, and methanol. To the best of our knowledge, no MCM-41 grafted quaternary ammonium salts with terminal amino groups as catalysts for the sequential synthesis of DMC has been reported. In a typical organo-functionalization, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was grafted onto MCM-41 in two steps as shown in Scheme 1. 10 g of MCM-41 was reacted with 6 mL of 3-(chloropropyl)trimethoxysilane in 100 mL of dry toluene for 6 h under refluxing. The anchored moiety MCM-41-pr-Cl was filtered and washed with dichloromethane (30 mL × 3). 14 g of MCM-41-pr-Cl was obtained after drying at 110 °C (elemental analysis %: C, 7.505; H, 1.463; Cl, 6.890%). Then 2.5 g of MCM-41-pr-Cl was treated with 2.5 mL of TMEDA in 60 mL of toluene for 24 h also under refluxing. After being filtered, washed with dichloromethane (15 mL × 3) and dried at 100 °C, 2.8 g of MCM-41-pr-TMEDA⁺Cl⁻ was obtained (elemental analysis %: C, 14.122; H, 3.284; N, 3.230; Cl, 6.295%). MCM-41-pr-TMHDA⁺Cl⁻, MCM-41-pr-*n*-Bu₃N, and silica gel anchored TMEDA (SG-pr-TMEDA⁺Cl⁻) were obtained in the same manner.

To gain insight into the elemental chemical states of catalyst, MCM-41-pr-TMEDA⁺Cl⁻ was characterized by X-ray photoelectron spectroscopy. C, O, Si elements for MCM-41 and C, N, O, Si, Cl elements for MCM-41-pr-TMEDA⁺Cl⁻ were observed in XP full spectra analysis, indicating the obvious changes in elemental composition (Figure S3⁶). The N 1s spectrum can be divided into two peaks at 399.8 and 402.6 eV as shown in Figure 1, which could be assigned to nitrogen in the tertiary amino moiety and quaternary ammonium group, respectively.⁵ Therefore, MCM-41 grafted TMEDA with bifunctional groups was successfully prepared. The peak area ratio of quaternary ammonium to tertiary amino moiety was 1.45, this suggesting

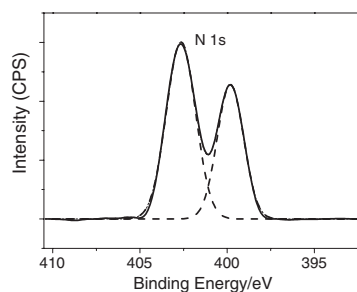


Figure 1. N 1s XP spectrum of MCM-41-pr-TMEDA⁺Cl⁻.

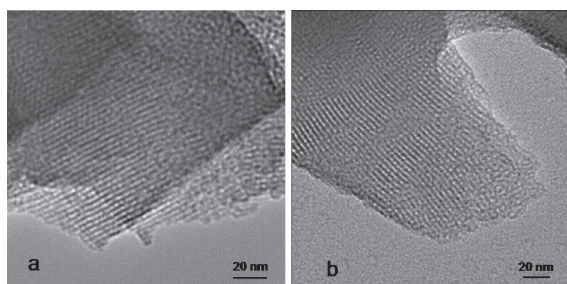


Figure 2. TEM images of (a) MCM-41 and (b) MCM-41-pr-TMEDA⁺Cl⁻.

that a fraction of bis(quaternary ammonium salt) was also formed during the reaction of MCM-41-pr-Cl with TMEDA.

TEM images of MCM-41 and MCM-41-pr-TMEDA⁺Cl⁻ confirmed the mesoporous structure even after grafting of the organic functionality as shown in Figure 2, indicating the long-range ordering and mesostructural arrangement of MCM-41 are not significantly disturbed after organo-functionalization.

The catalytic performance of MCM-41 grafted catalyst was investigated for the sequential synthesis of DMC. As shown in Table 1, MCM-41-pr-TMEDA⁺Cl⁻ and MCM-41-pr-TMHDA⁺Cl⁻ exhibited better catalytic activity than MCM-41-pr-*n*-Bu₂N and SG-pr-TMEDA⁺Cl⁻ using ethylene oxide as the substrate (Entries 1–4), which may be due to the special organic groups and mesoporous structure of the designed catalyst. Meanwhile, for most substrates, MCM-41-pr-TMEDA⁺Cl⁻ exhibited excellent catalytic activity for cycloaddition and very good catalytic effect for transesterification with 36–79% DMC yields observed (Entries 5–11). DMC yields were influenced by the substituent of oxide with different electron-supplying capacity and a sequence of alkoxy > phenyl > alkyl was obtained. However, only 36% yield for glycidyl phenyl ether was observed because of the poor solubility of corresponding cyclic carbonate in methanol. A low DMC yield was also predicted for cyclohexene oxide, the reason for which may be that its special cyclic molecular structure hampered the nucleophilic attack from the chloride and therefore decreased the rate of ring opening. Experiments were also carried out to examine the recyclability of the catalyst using ethylene oxide as the substrate (Entry 12). A slight decrease in the yield of DMC was observed, indicating that catalyst was not only insoluble in the reaction mixture but also can be reused.

In conclusion, one kind of novel bifunctional catalyst, MCM-41 grafted quaternary ammonium salts with terminal amino groups, was prepared for the sequential synthesis of

Table 1. Synthesis of DMC catalyzed by MCM-41 grafted quaternary ammonium salts with terminal amino groups^a

| Entry | Substrate | Con./% | Cyclic carbonate | | DMC yield/% |
|-----------------|-----------|--------|------------------|---------|-----------------|
| | | | Sel./% | Yield/% | |
| 1 ^b | | 61 | 99 | 60 | 52 |
| 2 ^c | | 73 | 99 | 72 | 58 |
| 3 | | >99 | 99 | 99 | 85 |
| 4 ^d | | >99 | 99 | 99 | 72 |
| 5 | | >99 | 99 | 99 | 68 |
| 6 | | 90 | 99 | 90 | 55 |
| 7 | | 98 | 98 | 97 | 70 |
| 8 | | >99 | 99 | 99 | 36 ^e |
| 9 | | 99 | 98 | 98 | 74 |
| 10 | | >99 | 99 | 99 | 79 |
| 11 | | 35 | 96 | 34 | — ^f |
| 12 ^g | | 98 | 99 | 97 | 75 |

^aReaction procedure: epoxide, 30 mmol; methanol, 750 mmol; MCM-41-pr-TMEDA⁺Cl⁻, 10 wt % epoxide. Operation procedures: synthesis of carbonates at 120 °C, 2 MPa, and 6 h. After cooling and depressurization, methanol was added and then the mixture was refluxed for 4 h at 120 °C. ^bMCM-41-pr-*n*-Bu₂N was used as catalyst. ^cSG-pr-TMEDA⁺Cl⁻ as catalyst. ^dMCM-41-pr-TMHDA⁺Cl⁻ as catalyst. ^e12 h. ^fNot detected. ^gMCM-41-pr-TMEDA⁺Cl⁻ was used for the sixth time.

dimethyl carbonate. Compared with amine-grafted catalysts, these catalysts exhibited excellent catalytic performance and good reusability. We believe that these bifunctional catalysts will lead to further applications in carbon dioxide fixation reactions, and additional studies are underway.

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