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Preparation of polystyrene-supported Lewis acidic Fe(III) ionic liquid and its application in catalytic conversion of carbon dioxide

Jian Gao, Qing-Wen Song, Liang-Nian He *, Chang Liu, Zhen-Zhen Yang, Xu Han, Xue-Dong Li, Qing-Chuan Song

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

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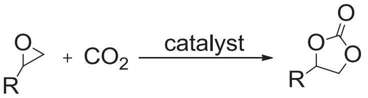
ABSTRACT

A polystyrene-supported Lewis acidic iron-containing ionic liquid was proved to be recyclable and efficient heterogeneous catalyst for converting CO_2 into cyclic carbonate without utilization of any organic solvent or additive. Excellent yields and selectivity were obtained under mild reaction conditions. Notably, the catalyst could be readily recovered and reused over five times without appreciable loss of catalytic activity. A possible catalytic cycle was proposed. The present protocol has successfully been applied to reactions of aziridines/propargyl amines with CO_2. This kind of the catalyst presented herein would have great potential in industrial application thanks to its featured advantages.

1. Introduction

Great efforts have been directed towards the fixation and utilization of CO_2 in the past two decades. In view of organic synthesis, CO_2 can be regarded as an easily available renewable carbon resource and an attractive C1 building block in organic synthesis, which has the advantages of being non-toxic, abundant, and economical.[1–4] Therefore, the chemical fixation of CO_2 is of great significance from the viewpoint of better utilization of carbon resources and environment concern. One of the most promising methodologies in this area is the atom efficient insertion of CO_2 into epoxides to afford five-membered cyclic carbonates as shown in Scheme 1, which can serve as electrolytes in secondary batteries, valuable monomers of polycarbonates, and polyurethanes, aprotic polar solvents, and raw materials in chemical reactions.[5–9]



Scheme 1. Cycloaddition of CO_2 to epoxides.

In this respect, numerous homogeneous catalysts have been developed for the synthesis of cyclic carbonates, including amines and phosphines,[10] alkali metal halides and onium salts,[11] organometallic compounds,[12] CO_2 adducts of *N*-heterocyclic carbenes[13] and especially ionic liquids (ILs)[4,9,14] firstly reported by Deng and co-workers,[14a] which have been attracting rising interest in the last decades with a diversified range of applications because of their potential advantages including negligible vapor pressure, good thermal stabilities, wide liquid temperature ranges and diversiform structure/property modulation.[15] Particularly, Kawanami and co-workers found that 1-alkyl-3-methylimidazolium salts exhibited high rate and effective activity for the synthesis of cyclic carbonate under supercritical CO_2 and BF_4^- was the most effective among the counter anions (NO_3^-, $CF_3SO_3^-$, BF_4^-, and PF_6^-) of imidazolium salts.[14c] Nevertheless, homogeneous catalysts are usually undesirably dissolved in the products making some procedures inevitably required to separate the products with catalyst recovery. Such separation procedure like distillation under reduced pressure would be cumbersome and high energy-consumed. To address this issue, heterogeneous catalysts have been also developed for the cycloaddtion reaction, such as metal oxides,[16] oxychlorides,[17] Cs-loaded zeolite, and alumina,[18] active species including supported ILs through polymers,[19] silica,[12e,20] which could have a synergistic effect discovered by Sakakura,[20d] zeolite,[21] and other materials.[22] Notably, in this regard, an imidazolium chloride IL grafted onto a highly cross-linked polymer matrix developed by Han and co-workers[19g] could be a representative example. Although significant advances have been made, most of the above heterogeneous catalysts cannot meet the current industrial demands because of some drawbacks, such as

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* Corresponding author. Tel./fax: +86 22 2350 3878; e-mail address: heln@nankai.edu.cn (L.-N. He).

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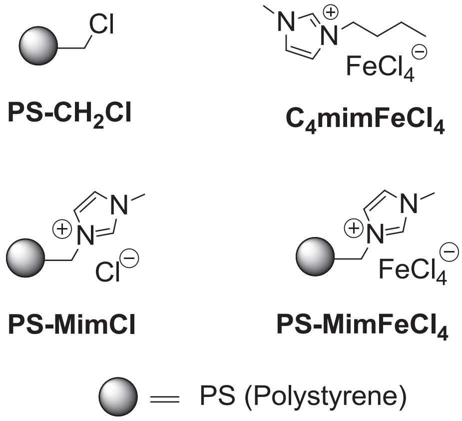
the need for a cosolvent[16d,20l] or cocatalyst,[19d,20c,22c] low catalyst activity,[19b] long reaction time,[12e,20l] or the requirement for high CO_2 pressure.[20d] Therefore, there is continuing motivation for developing low cost, highly efficient, and practical catalysts for the chemical fixation of CO_2 to cyclic carbonates.

Recently, the synthesis and application of task-specific ILs containing transition metals have drawn much attention in this thriving research field. The functionalized ILs are regarded as novel and promising materials, which would favorably combine spectroscopic, and/or magnetic properties with high catalytic activity, presumably originating from incorporated metals. In particular, the Fe(III) based IL, e.g., $[C_4mim][FeCl_4]$ (Scheme 2) possessing attractive properties of both IL and the Lewis acidic $FeCl_3$, was found to have great application in catalysis.[23] As one of the most inexpensive and non-pollutant metals, iron catalysis would be of great interest and is constantly growing from a standpoint of sustainable catalysis.[24] And various iron salts and its complexes, which possess unique properties, such as distinct Lewis acid character have been proved to be efficacious, alternative and promising transition-metal catalysts in a broad range of synthetic transformations.[24]



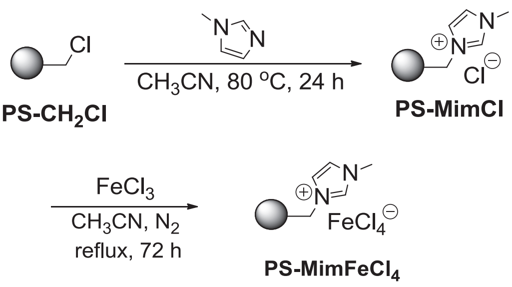
Scheme 2. Ionic liquids used in this study.

Cross-linked polystyrene is one of the most useful polymers owing to its compatibility with a wide range of reaction conditions.[25] Furthermore, because of its easy preparation, recyclability, low cost, and non-solubility in any commonly used organic solvent and water, cross-linked polystyrene has attracted considerable attention as an efficient support for homogeneous catalyst immobilization.[19g,26] In this context, we envisioned that a type of Lewis acidic iron-containing IL being covalently grafted onto polystyrene ($PS\text{-}MimFeCl_4$, Scheme 2), could be utilized as a recyclable heterogeneous catalyst for the cycloaddition reaction of CO_2 with epoxides. More importantly, the presence of the Lewis acidic iron center in the anionic part could activate an epoxide, thus facilitate its ring-opening. As a result, we designed and prepared a new kind of polystyrene-supported iron-containing ionic liquid, e.g., $PS\text{-}MimFeCl_4$, which displayed high catalytic activity for the cycloaddition reaction of CO_2 with epoxides together in the absence of any additional organic solvent or additive.

2. Results and discussion

2.1. Synthesis of polystyrene-supported iron-containing ionic liquid $PS\text{-}MimFeCl_4$

A cross-linked polystyrene was functionalized with iron-containing IL ($MimFeCl_4$) using a modified procedure based on literature.[19h,27] The preparative procedure of the polystyrene-supported Lewis acidic Fe(III) based ionic liquid, i.e., $PS\text{-}MimFeCl_4$ is depicted in Scheme 3, whose structure was characterized by using FT-IR, SEM (Scanning Electron Microscopy), TGA (Thermogravimetric Analysis)/DTA (Differential Thermal Analysis) and AAS (Atomic Absorption Spectroscopy).



Scheme 3. Synthetic route of polystyrene-supported iron-containing IL catalyst.

2.2. Characterization of polystyrene-supported iron-containing ionic liquid $PS\text{-}MimFeCl_4$

FT-IR spectroscopy provided unequivocal evidence for the graft of iron-containing IL onto polystyrene via a covalent bond manner. Four typical peaks[19h] centered at 1606, 1566, 1154, and 1085 cm^{-1}, respectively, could correspond to the feature band absorption of the imidazolium ring (Fig. 1). On the other hand, those peaks are absent in non-functionalized polystyrene resin. Furthermore, the bands at 1263 and 671 cm^{-1} of CH_2Cl group absorption[19i] disappears in the FT-IR spectra of $PS\text{-}MimFeCl_4$, indicating full functionalization of $PS\text{-}CH_2Cl$. The above result is a clear indication of the chemical immobilization of imidazolium $FeCl_4^-$ on polystyrene. In addition, the IL loading was determined to be 2.62 mmol/g by using AAS technique.

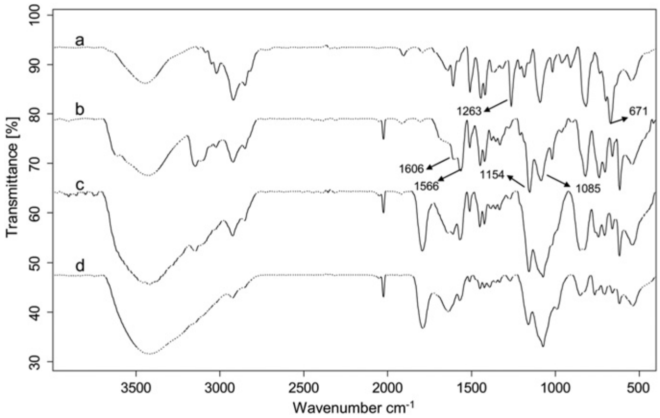


Fig. 1. FT-IR spectra comparison of: (a) $PS\text{-}CH_2Cl$, (b) fresh $PS\text{-}MimFeCl_4$, (c) the first recycled $PS\text{-}MimFeCl_4$, (d) the fifth recycled $PS\text{-}MimFeCl_4$.

The morphology of $PS\text{-}MimFeCl_4$ was further observed using SEM as shown in Fig. 2, showing that microscopic appearance of the polymer changed obviously after it has been functionalized with $MimFeCl_4$. The surface of the $MimFeCl_4$ functionalized polymer became rough in comparison with that of the support ($PS\text{-}CH_2Cl$). However, the particle agglomeration is irregular. Thermal stability would also be important for practical application of the polymer-supported IL since vigorous shaking, filtration, or drastic acid–base treatment may be encountered. In this aspect, the thermal stability of $PS\text{-}MimFeCl_4$ was measured using TGA and DTA, as depicted in Fig. 3. It is observed that the weight loss of the catalyst