



Organic-inorganic multifunctional hybrid catalyst giving catalytic synergies in cooperative coupling between CO₂ and propylene oxide to propylene carbonate



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ABSTRACT

An organic-inorganic hybrid catalyst was synthesized by silylation of silanol (Si–OH) groups with ammonium bromide group on the mesopore wall of mesoporous zeolite having a hierarchically nanoporous architecture, conferring both electrophilic and nucleophilic functions due to the acid sites of the zeolite and bromide in the functional group, respectively. In the coupling of carbon dioxide and propylene oxide for production of propylene carbonate, the hybrid catalyst exhibited a synergistic enhancement in activity leading to a two-fold higher product yield than the catalysts having a single catalytic function. Comprehensive reaction studies revealed that the catalytic synergy could only be obtained by achieving close proximity between the ammonium bromide group and acid sites on the zeolite surface. The acidity was also crucial, where no synergy was observed for a similarly designed organic-inorganic hybrid catalyst constructed on weakly acidic ordered mesoporous silica SBA-15. Comparison of the activation energy of the catalysts supported the observation that the zeolite-based hybrid catalyst with stronger acidity gave rise to a lower activation energy (37.3 kJ mol⁻¹) than the SBA-15-based hybrid catalyst with weaker acidity (51.3 kJ mol⁻¹). The mesoporous zeolite-based hybrid catalyst was very active under neat conditions without additional organic solvent, and showed good recyclability without significant loss of the initial activity for up to five runs.

1. Introduction

Carbon dioxide is one of the most prominent greenhouse gases and is associated with increased global temperature and climate change [1–9]. Accordingly, control of CO₂ emission is of prime importance in the current society, where three general strategies are employed for this purpose, namely, carbon capture, utilization, and sequestration (CCUS) [2–4]. The ultimate solution for reducing CO₂ emission is to consume the generated CO₂. This may be accomplished by using CO₂ as an environmentally benign, cheap, and abundant sustainable C1 building block for the production of organic chemicals, hydrocarbon fuels, and valuable materials. Various technologies for CO₂ utilization have been developed, as exemplified by thermochemical hydrogenation, electrochemical reduction, and photochemical conversion [5,6]. However, most of the known technologies require a large energy input to make the process feasible, and thus encounter a big thermodynamic constraint [7,2–9]. One of the energy-efficient technologies for CO₂ utilization is the coupling of CO₂ with epoxide rings to form five-membered cyclic carbonate [10–19]. Such a cycloaddition reaction requires a low

energy supply and milder reaction conditions than other CO₂ utilization processes because the epoxide ring is a very reactive reagent due to the strained three-membered molecular geometry. This process is also very attractive and atom-economical in terms of green chemistry because CO₂ can be incorporated into the epoxide ring without the formation of byproducts [12]. As a specific example, propylene oxide (PO) can be coupled with CO₂ to produce propylene carbonate (PC, C₄H₆O₃) having a five-membered heterocyclic geometry [12,11–19]. PC is a very important chemical in current industry that can be widely used as a polar aprotic solvent due to its high dipole moment (4.9 D), an electrolyte in Li batteries due to its high dielectric constant (64), a monomer for synthesis of polycarbonates and polyurethanes via ring-opening polymerization, and an intermediate chemical for pharmaceuticals and agricultural compounds [12–16]. In particular, the cycloaddition of CO₂ to PO produce PC has become central to the polycarbonate industry since the Asahi chemical company developed a new and green-chemical non-phosgene process for the production of polycarbonate [10].

Since the invention of the non-phosgene process, various types of

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catalysts have been developed for the conversion of PO to PC in the presence of CO₂ [20–38]. For example, PC can be produced via the cycloaddition of CO₂ in the presence of a quaternary ammonium halide, phosphonium halide, or alkali metal halide as the typical homogeneous catalysts under high temperature and pressure conditions (40 – 80 bar CO₂ at > 120 °C) [20–22]. In the organometallic compound-based homogeneous catalyst system, transition metal complexes are generally used as the catalyst in conjunction with ammonium salt or alkali metal salt [23]. The homogeneous catalyst shows remarkably high catalytic activity with almost 100% PC yield, but in this case, metal leaching and catalyst separation problems are encountered [24–26]. As an example of a heterogeneous-type catalyst, Mg–Al amphoteric mixed metal oxide was used as a bifunctional catalyst for the simultaneous activation of CO₂ and epoxide over the basic oxide sites and acidic Al sites on the catalyst surface, respectively [12]. Metal-organic frameworks (MOFs) have also been used as heterogeneous catalysts in the presence of a quaternary ammonium halide (e.g., *n*-Bu₄N⁺X⁻), wherein the open metal sites in the MOFs could activate the oxygen atom in the epoxide ring, and the halide anion (X⁻) triggered the ring-opening and subsequent addition of CO₂ [27]. Previous studies on the cycloaddition of PO to CO₂ commonly indicated that two different catalytic functions are necessary for giving better catalytic performance [28–30]. An electrophilic activator (oxophilic in most cases) such as Lewis or Brønsted acid sites is necessary for activation of oxygen atom in the epoxide ring. As the main catalyst, a nucleophile such as a halide anion is necessary to induce the opening of the epoxide-ring. The halide anion attacks the carbon bonded to the oxygen in the epoxide-ring while the oxygen is coordinated to the electrophilic activator as the co-catalyst. In other words, it can be recommended to construct both nucleophilic and electrophilic catalytic functions in a catalyst for good catalytic performance.

Accordingly, this work was undertaken in order to design a new heterogeneous catalyst having both nucleophilic and electrophilic catalytic functions in a single catalyst architecture. For this purpose, zeolite is one of the promising candidates not only as the catalyst having an electrophilic function originated from the acid sites (i.e., Brønsted and Lewis acid), but also as the catalyst platform for introduction of a desirable function. In addition, zeolites are well known as solid, strong acid catalysts having uniform microporous structures in a crystalline aluminosilicate framework, where the micropore diameter can be defined between 0 and 2 nm. Zeolites possess good stability and high porosity compared to other nanoporous materials [39–44]. However, though the zeolites intrinsically possess the electrophilic acid sites due to the aluminosilicate framework, the acid sites are not considered as the main catalyst for the cycloaddition of CO₂ to epoxide ring according to the published works. As the main catalytic component, a halide anion known as a strong nucleophile would be necessary for triggering the catalytic reaction [29–32].

For the design of a new heterogeneous catalyst having both acidic sites and halide anions, mesoporous zeolites having intrinsic micropores and secondary mesopores are good candidates. They possess large mesoporosity with high external surface area and large pore volume due to the presence of mesopores [39–44]. The surface of mesopore wall is terminated with silanol (Si–OH) groups in a large density that can be utilized for organic functionalization [44]. In the present work, an organic-inorganic hybrid structure is designed by functionalization of ammonium bromide group via two-step post-synthetic treatments on the surface of mesoporous zeolite having BEA framework structure (see Fig. S1 in the Supporting information for the framework structure of BEA and its lattice parameters). In order to incorporate large density of organic functional group on the zeolite surface, the large volume and size of mesopores is prerequisite. There are various synthesis routes for the mesoporous zeolites reported so far [39–44], among which the synthesis of BEA zeolite with cyclic diammonium-type molecule as the mesopore directing agent is reported to produce mesoporous zeolites with high degree of mesoporosity with large mesopore size around

10 nm [41,42]. In addition, among the high-silica zeolites having strong acidity, the BEA zeolite can be synthesized to possess high aluminum content with Si/Al ratio of around 10. Such highly aluminous BEA zeolite is useful for having large density of strong acid sites. In particular, BEA zeolite is classified as large-pore zeolites due to the 12-membered-ring micropore aperture, and hence it has higher efficiency for molecular diffusion than the zeolites having smaller micropores. On this ground, the mesoporous BEA zeolite is selected for the synthesis of organic-inorganic hybrid catalyst. The resultant hybrid material can possess the electrophilic acid sites due to the aluminosilicate framework of zeolite and the nucleophilic halide groups due to the functionalized ammonium bromide. The hybrid material is investigated for the first time as a heterogeneous catalyst in the conversion of PO to PC in the presence of CO₂ under liquid-phase batch reaction conditions. The catalytic results show that the hybrid catalyst having bifunctionality (i.e., zeolite acid site and ammonium halide) exhibited very high catalytic activity than other catalysts having a single function. Through the comprehensive characterization of the hybrid catalyst and the catalytic reaction studies, the origin of the catalytic enhancement in the hybrid catalyst is elucidated with proposing the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

The mesoporous BEA zeolite was synthesized by the addition of an organic structure-directing agent (SDA) to a cyclic diammonium salt by following the literature procedure [41]. The nominal molar composition used for the synthesis was 30Na₂O/2.5Al₂O₃/100SiO₂/10SDA/15H₂SO₄/6000H₂O, where water-glass (Daejung Chemical, 29%SiO₂ and 9%Na₂O in H₂O) and Al₂(SO₄)₃·16H₂O (Aldrich, > 95%) were used as the silica and alumina source, respectively. The synthesis solution was hydrothermally treated at 150 °C for 5 d under agitation. The as-synthesized form of BEA zeolite was calcined at 550 °C for 4 h and further ion-exchanged to the Na⁺ or H⁺-form with 1 M NaCl or NH₄NO₃ aqueous solution, respectively, three separate times (NH₄NO₃/Al = 10). Hereafter, the mesoporous BEA zeolites in the Na⁺ and H⁺-forms are denoted as Meso-BEA(Na⁺) and Meso-BEA(H⁺), respectively. Inductively coupled plasma-atomic emission spectroscopic (ICP-AES) analysis indicated that the Si/Al ratio of the resultant Meso-BEA zeolite series was 12.5.

Ordered mesoporous silica SBA-15 was synthesized with P123 triblock-co-polymer (Aldrich, HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H) as the mesopore SDA by following the procedure reported elsewhere [45]. The nominal molar composition used for the synthesis was 1SiO₂/0.017P123/1.83HCl/195H₂O, where tetraethylorthosilicate (Aldrich, 98%) was used as the silica source. The as-synthesized form of SBA-15 was calcined at 550 °C for 4 h and further used for the functionalization of (3-aminopropyl)trimethoxysilane (Aldrich, 3-APTMS). For preparation of Al and Zn-incorporated SBA-15 (Al-SBA-15 and Zn-SBA-15), Al or Zn precursors were added to the synthesis mixture with the adequate molar composition of SBA-15 for the direct incorporation of Al or Zn into the framework of SBA-15. The nominal molar composition used for the synthesis was 1SiO₂/0.017P123/1.83HCl/195H₂O/0.025Al₂O₃ or 0.05ZnO. Aluminum nitrate nonahydrate (Aldrich, 98%) and zinc nitrate hexahydrate (Daejung, 98%) were used as the Al and Zn precursors, respectively. After the synthesis, the as-synthesized forms of Al-SBA-15 and Zn-SBA-15 were further calcined at 550 °C for 4 h by following the same process described above.

For functionalization of the mesoporous BEA zeolite and SBA-15 with organic species, 1 g of sample was degassed at 300 °C for 3 h and mixed with toluene as a solvent. Subsequently, 5 mmol (ca. 877 μL) of 3-APTMS was added to the toluene solution and reacted on a hot plate under reflux conditions for 1 h. The samples functionalized with 3-APTMS were collected by filtration, washed thoroughly with ethanol,

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