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
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 catalytic 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 diaminonium-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 diaminium 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)₂O)₃₀(CH₃CH₂O)₃₀H) as the mesopore SDA by following the procedure reported elsewhere [45]. The nominal molar composition used for the synthesis was 15SiO₂/0.017P123/1.83HCl/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-APTS). 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 15SiO₂/0.017P123/1.83HCl/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-APTS was added to the toluene solution and reacted on a hot plate under reflux conditions for 1 h. The samples functionalized with 3-APTS were collected by filtration, washed thoroughly with ethanol,

and dried in an oven at 100 °C. The NH$_3$ groups in the 3-APTM-functionalized solid powders were further protonated with a dilute aqueous solution of HX (X = F, Cl, Br). In a typical protonation process, 1 g of solid powder functionalized with 3-APTM was dispersed in 30 ml of distilled water in a polypropylene bottle, and 10 ml of 0.2 M HX solution was added to this mixture. The mixture was stirred for 1 h, collected by filtration, washed thoroughly with distilled water, and dried in an oven at 100 °C.

2.2. Characterization

X-ray diffraction (XRD) patterns were acquired with a Bruker D8 Venture D8 diffractometer equipped with a Cu-K$_\alpha$ radiation source operated at 40 W (40 kV, 1 mA). Transmission electron microscope (TEM) images were acquired with a JEOL JEM-2100 F field-emission microscope operated at 200 kV. Elemental analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using a PerkinElmer optical emission spectrometer (Optima 7000 DV). N$_2$ physisorption analysis for determination of the surface area and mesopore size was carried out using a Micromeritics ASAP2020 volumetric analyzer at liquid nitrogen temperature (77 K). The surface area was calculated from the adsorption data obtained at $P/P_0$ values between 0.05 and 0.2 by applying the Brunauer-Emmett-Teller (BET) equation. The average mesopore size was determined from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. For micropore analysis, $A$ sorption data was carried out using a QuantaChrome Autosorb IQ volumetric analyzer at liquid argon temperature (87 K). The surface area was calculated from the adsorption data obtained at $P/P_0$ values between 0.05 and 0.2 by applying the Brunauer-Emmett-Teller (BET) equation. The average micropore size and micropore volume were determined from the adsorption branch of the isotherm using the non-localized density functional theory (NDLFT) that is considered as the reasonable model for the analysis of hierarchically microporous and mesoporous materials [46]. For Fourier-transform infrared (FT-IR) measurement, all samples were pressed into a self-supporting wafer without a binding agent (ca. 8–12 mg cm$^{-2}$). Before the IR measurements, each sample was degassed at 550 °C for 2 h under vacuum and cooled to room temperature in a lab-made IR cell. Pyridine was used as a base probe molecule for measurement of the acidity. Pyridine was adsorbed on the degassed sample wafer for 1 h at room temperature, and the weakly bound species were desorbed for 1 h under vacuum at 150 °C. After cooling to room temperature, the IR spectrum was collected using an FT-IR spectrometer (PerkinElmer Spectrum Two) with 40 scans and 2 cm$^{-1}$ resolution in the range of 4000–400 cm$^{-1}$. IR spectra were also collected after desorption of pyridine at different temperatures from 150 °C to 400 °C. For quantification of the total Brønsted and Lewis acid sites, the molar extinction coefficient of the pyridine IR bands at 1545 cm$^{-1}$ ($\varepsilon = 1.67$ cm mmol$^{-1}$) and 1450 cm$^{-1}$ ($\varepsilon = 2.22$ cm mmol$^{-1}$) were used, respectively [47].

2.3. Catalytic reaction

The catalytic reaction was performed using a Teflon-lined stainless-steel autoclave containing the reactant solution dissolved in an organic solvent. In a typical reaction process, 10 mmol (700 μl) of PO (Daegu Chemical, 99.5%) was dissolved in 14 ml of organic solvent containing 0.1 g of catalyst. The organic solvent was varied as hexane, toluene, ethanol, acetonitrile, and dimethylformamide (DMF). Prior to the catalytic test, the reactor was purged with CO$_2$ and subsequently pressurized with CO$_2$ to the designated pressure (1–20 bar) while the temperature of the reactor was increased to the designated temperature (60–160 °C). After the catalytic reaction, the reactor was cooled to below room temperature in an ice bath, and the reaction solution was separated from the solid catalyst by using a syringe filter. The collected solution was analyzed with a gas chromatograph (GC, Younglin YL-6500) equipped with a flame-ionization detector (FID) by using a capillary column (DB-5, length: 30 m; diameter: 0.32 mm; thickness: 1.5 μm) in the presence of dodecane as an internal standard. Helium was used as carrier gas with flow rate of 3.0 cm$^3$ min$^{-1}$. For recyclability test, the spent catalyst was collected from the reaction solution by filtration and washed thoroughly with DMF, ethanol and acetone in a successive manner. After drying the spent catalyst in an oven at 80 °C, the spent catalyst was reused in a fresh reaction solution.

3. Results and discussion

3.1. Synthesis and characterization of the catalysts

Fig. 1 shows the characterization data for the catalysts prepared in this work. Fig. 1A shows the low-angle XRD patterns of the ordered mesoporous materials based on SBA-15. The XRD pattern of SBA-15 (bottom in Fig. 1A) shows the most intense reflection at 2θ = 0.94°, with less intense reflections at 2θ values of 1.65° and 1.87°. These XRD reflections correspond to the (100), (110), and (200) lattice planes, indicating the hexagonally ordered framework with $p6mm$ symmetry. When Al or Zn was incorporated into SBA-15 via the post-metalation functionalization and subsequent treatment with the acid halide (HX, where $X = $ F, Cl, and Br), it was still possible to distinguish the XRD
reflections of the pristine SBA-15 structure. It is noteworthy that HF treatment should be detrimental to the framework of silica-based materials. However, HF treatment of SBA-15 functionalized with 3-APTMS did not destroy the pristine framework structure, which might be due to the protective effect of the functionalized organic groups on the silica surface.

Fig. 1B shows the high-angle XRD patterns of the zeolites, where the XRD peaks of the zeolite catalyst synthesized in this work are located at positions similar to those of the conventional BEA zeolite with a solely microporous framework as the reference. The broader peaks in the profile of the developed catalyst relative to that of the conventional BEA zeolite suggest that the mesoporous BEA zeolite was synthesized with nanocrystalline morphology. Similar to SBA-15, no change was observed upon functionalization and acid treatment of the mesoporous BEA zeolite. This is also due to the organic groups covering the zeolite framework. Fig. 1C shows the FT-IR spectra of NH₃Br/Al-SBA-15, NH₃Br/Meso-BEA(Na⁺), and NH₃Br/Meso-BEA(H⁺) for analysis of the functionalized group. The FT-IR spectra of NH₃Br/Al-SBA-15, NH₃Br/Meso-BEA(Na⁺), and NH₃Br/Meso-BEA(H⁺) show strong IR absorption bands at 1617 cm⁻¹ which are characteristic of the N–H stretching in the quaternized NH₃⁺ group [48]. This suggests that the ammonium (NH₃⁺) group was successfully tethered on the catalyst supports. Further, as the counter anion, the halide anions should interact with the ammonium group.

To evaluate the elemental composition of the hybrid catalyst, NH₃Br/Meso-BEA(H⁺), as the representative catalyst, was further characterized via TEM and elemental mapping (Fig. 2). As proposed from the XRD analysis above, the TEM image clearly confirms that the nanocrystalline zeolite particles with an average diameter of 10 nm were aggregated, leading to intercrystalline mesoporosity (Fig. 2A and inset). Based on the N₂ sorption data, the Meso-BEA(H⁺) sample possessed a very high BET surface area of 581 m² g⁻¹ and a total pore volume of 0.95 cm³ g⁻¹ (see Fig. S2 and Table S1 in the Supporting information). The average mesopore size was 12.2 nm. Due to the high mesoporosity, the catalyst could be functionalized with a large amount of organic groups (0.65 mmol g⁻¹). Indeed, after functionalization with the organic groups, the BET surface area and total pore volume were reduced to 369 m² g⁻¹ and 0.67 cm³ g⁻¹, respectively. In addition, according to the Ar sorption data, there was slight decrease in micropore volume and average micropore diameter from 0.65 to 0.56 nm upon functionalization of organic groups (Fig. S3 and Table S2 in the Supporting information). This indicated that the organic functionalization could occur not only on the mesopore surface, but also inside the micropore space. The functionalized organic groups were clearly observed by elemental mapping. Fig. 2B–E indicate that all the elements (Si, Al, N, and Br) were evenly localized over the catalyst. In particular, from the elemental mapping of the catalyst prepared herein, it was confirmed that the organic-inorganic hybrid architecture was successfully constructed on the mesoporous BEA zeolite without any observable damage to the framework.

3.2. Catalytic reaction results

Table 1 shows a summary of the reaction results for evaluation of the catalyst performance. Except for the evaluation of the halide effect (Entries 3–5), the reactions in Table 1 were carried out using DMF as the organic solvent. Entry 1 is the blank test without the addition of a catalyst, which confirmed that PO conversion to PC was impossible in the absence of a catalyst. Entry 2 shows the catalytic ability of SBA-15, demonstrating that the purely siliceous SBA-15 was not active for the current reaction. Entries 3–5 show the catalytic performance of SBA-15 tethered with different ammonium halides (-NH₃X, where X = F, Cl, and Br). In order to exclude the effect of the solvent, these catalysts were tested under neat conditions without addition of the organic solvent. As summarized in Table 1, the variation of the halide in the SBA-15 catalyst changed the catalytic activity, which was calculated by assuming that the active catalytic site is the ammonium halide group (see Table S3 in the Supporting information for the ammonium halide content). The turnover frequency (TOF) increased dramatically in the order: NH₃F/SBA-15 (trace), NH₃Cl/SBA-15 (1.47 h⁻¹), and NH₃Br/SBA-15 (9.15 h⁻¹). This indicates that the Br⁻ acted as the strongest nucleophile and plausibly accelerated the ring-opening step of PO prior
showed no activity herein. It is thus proposed that the catalytic con-
milder in terms of temperature and pressure, and the catalyst
produced a PC yield of 55.7% with a TOF of 26.0 h
Zhong et al. reported that the Zn-SBA-15 catalyst
the catalytic contribution of electrophilic Al or Zn in SBA-15 is negli-
This negligible catalytic activity of the Al-SBA-15 and Zn-SBA-15 catalysts and the lack of synergy in their counterpart catalysts func-
insufficient electropolarity of Al or Zn in the amorphous framework of
This deduction is reasonable because the acidic strength on Al-
and Zn-SBA-15 is much lower or almost negligible compared to
which means that the binding strength of acidic sites on Al-SBA-15 and
SBA-15 possesses plenty of Lewis acid sites (0.424 mmol g
an active catalyst for the same reaction [50]. Zhong et al. reported that the Zn-SBA-15 catalyst
produced a PC yield of 55.7% with a TOF of 26.0 h
Compared with the results obtained under neat conditions, the TOF
value decreased to 3.33 h
In the usual catalytic reactions showing synergistic interplay of
When the mesoporous zeolites were functionalized with NH3Br to
These TOF values were achieved for both the NH3Br/Meso-
leads to the proposal that the role of the Lewis acid sites should be much more important
and the strong acidity of the zeolite framework in the hybrid catalyst
support that the role of the Lewis acid sites in the absence of the NH3Br functional
to construct the organic-inorganic hybrid catalysts, a dramatic enhance-
ment in the TOF values was achieved for both the NH3Br/Meso-
continuous. Consequently, the higher TOF achieved with Meso-BEA(Na+)(H+) having fewer total acid sites but having a larger amount
of Lewis acid sites in both NH3Br/SBA-15 and Al-SBA-15, respectively. Compared to
amount of Lewis acid sites than Meso-BEA(H+). Of the two zeolite catalysts, Meso-BEA(Na+) produced PC
higher than that achieved with the Meso-BEA(H+) catalyst
The present reaction conditions (100 °C with 10 bar CO2) produces a PC yield of 55.7% with a TOF of 26.0 h

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<th>Time (h)</th>
<th>P (bar)</th>
<th>Temp (°C)</th>
<th>Solvent</th>
<th>Yield (mmol)</th>
<th>TOF (h⁻¹)</th>
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* Moles of propylene carbonate produced per mole of ammonium halide per hour.

** Moles of propylene carbonate produced per mole of aluminum per hour.

Table 1

Results of cycloaddition of CO₂ to propylene oxide using various catalysts under various reaction conditions.

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This negligible catalytic activity of the Al-SBA-15 and Zn-SBA-15 catalysts and the lack of synergy in their counterpart catalysts func-
tialized with NH3Br was attributed to the very weak and insuffi-
cient electropolarity of Al or Zn in the amorphous framework of
SBA-15. This deduction is reasonable because the acidic strength on Al-
SBA-15 and Zn-SBA-15 is much lower or almost negligible compared to
to those of crystalline aluminosilicate materials such as zeolites [51],
which means that the binding strength of acidic sites on Al-SBA-15 and
Zn-SBA-15 to the reactant PO is very weak. Indeed, when we tried to
quantify and qualify the acid sites of Al-SBA-15 and Zn-SBA-15 with FT-
IR spectroscopy measured after the adsorption of pyridine molecule as the
base probe and followed with desorption at 150 °C, FT-IR peaks corresponding to Brønsted and Lewis acid sites were inappreciable (Fig.
S4 and Table S4 in the Supporting Information). This means that both
Al-SBA-15 and Zn-SBA-15 have no acidity or very weak acidity that is
not strong enough to be detected by pyridine adsorption followed with
desorption at 150 °C (Fig. S4 and Table S4 in the Supporting informa-
on the contrary, mesoporous BEA zeolites having a crystalline
aluminosilicate framework exhibited strong acidity as confirmed by FT-
IR spectroscopy (Fig. S4 and Table S4 in the Supporting Information).
From the FT-IR spectra acquired after the adsorption of pyridine as the
basic probe molecule, it is deduced that the Meso-BEA(Na+)(H+) catalyst
possessed plenty of Lewis acid sites (0.424 mmol g⁻¹) without a
quantifiable number of Brønsted acid sites (Fig. S4 and Table S4 in the
Supporting Information). In the case of the Meso-BEA(H+) catalyst,
most of the acid sites were Brønsted acid sites (0.658 mmol g⁻¹),
whereas the density of Lewis acid sites was 0.177 mmol g⁻¹. In addi-
tion, after the desorption of pyridine at 200 °C, the number of Lewis
acid sites on the Meso-BEA(Na+)(H+) sample was still much larger than that
on Meso-BEA(H+). This suggests that the Lewis acid sites on Meso-
BEA(Na+) are much stronger and plentiful than those on Meso-
BEA(H+). Of the two zeolite catalysts, Meso-BEA(Na+) produced PC
with a TOF value of 1.65 h⁻¹ (Entry 11), which is more than 10 times
higher than that achieved with the Meso-BEA(H+) catalyst
(TOF = 0.13 h⁻¹; Entry 12). Consequently, the higher TOF achieved with Meso-BEA(Na+)(H+) having fewer total acid sites but having a larger amount
of Lewis acid sites than Meso-BEA(H+) leads to the proposal that
the role of the Lewis acid sites should be much more important
than that of the Brønsted acid sites in the absence of the NH3Br func-
tional group.

When the mesoporous zeolites were functionalized with NH3Br to
construct the organic-inorganic hybrid catalysts, a dramatic enhance-
ment in the TOF values was achieved for both the NH3Br/Meso-
BEA(Na+) and NH3Br/Meso-BEA(H+) catalysts. Based on the number of
NH3Br groups introduced onto the hybrid catalyst, NH3Br/Meso-
BEA(Na+) and NH3Br/Meso-BEA(H+) exhibited TOF values of
4.50 h⁻¹ (Entry 13) and 6.69 h⁻¹ (Entry 14), respectively. In particular,
the TOF value of NH3Br/Meso-BEA(H+) was more than twice that of
the NH3Br functionalized SBA-15-based catalysts (Entries 6, 9, 10).
From this comparison, it is clear that the synergistic interplay of NH3Br
and the strong acidity of the zeolite framework in the hybrid catalyst
produces higher catalytic activity.

In the usual catalytic reactions showing synergistic interplay of
dual- or multi-catalytic sites, the distance between the different catalytic sites is considered as an important factor for achieving synergy [52,53]. Controlled reactions were carried out to elucidate the role of the distance between the NH2Br and acid sites to produce catalytic synergy. Entries 15–16 show the results for the catalytic reaction in the physical catalyst mixture, wherein the NH2Br functional group and acid sites on the zeolite were intentionally positioned far from each other. In order to position the NH2Br group far away from the acid sites on the zeolite surface, NH2Br was introduced onto SBA-15 and the resultant NH2Br/SBA-15 catalyst was physically mixed with the Meso-BEA(Na+) or Meso-BEA(H+ ) catalyst. In this manner, the distance between the NH2Br functional group and the acid sites on the zeolite should be much farther than that in the hybrid catalyst, where the distance between the two catalytic sites of the former is not on the molecular scale. As proved in Entries 15–16, the physical mixture of catalysts gave TOF values of 3.59 h−1 and 3.01 h−1, respectively. These TOF values are in a similar range to those obtained over the NH2Br functionalized SBA-15-based catalysts (Entries 6, 9, 10), meaning that no catalytic synergy could be induced by simple addition of a zeolite catalyst having strong acidity. In other words, this result suggests that making close proximity in a small molecular scale between the NH2Br group and the acid sites on the zeolite surface is crucial for achieving catalytic synergy.

It is also remarkable that the NH2Br/Meso-BEA(H+) hybrid catalyst can exhibit very high catalytic activity under neat conditions in the absence of an organic solvent. For this catalytic run, an excess of PO was used not only as the reactant, but also as the solvent (Entry 17). In response to the increased amount of PO, the reactor was pressurized with 20 bar of CO2 in the expectation that the production of PC could be enhanced. Indeed, the hybrid catalyst produced 21.2 mmol of PC after 10 h of reaction, corresponding to about 60% conversion of PO to PC within 10 h. This high yield of PC in the absence of an additional organic solvent including DMF, ethanol and acetone. Subsequently, the spent catalyst was tested in the fresh reaction solution. The result proved that the hybrid catalyst exhibited very good recyclability without significant loss of initial activity during five catalytic runs (Table S5 in the Supporting Information). In addition, the solvent-free reaction condition is very meaningful in view of green chemistry, because very little or almost negligible amounts of pollutant chemicals are produced during the reaction.

The recyclability of the NH2Br/Meso-BEA(H+) hybrid catalyst was examined by testing the spent catalyst after the catalytic run. For this purpose, the spent catalyst was washed thoroughly with organic solvent including DMF, ethanol and acetone. Subsequently, the spent catalyst was tested in the fresh reaction solution. The result proved that the hybrid catalyst exhibited very good recyclability without significant loss of initial activity during five catalytic runs (Table S5 in the Supporting Information). In addition, the crystallinity of NH2Br/Meso-BEA(H+) hybrid catalyst is retained during the recyclability test. Slight decrease of XRD peaks is attributed to the reactant and product species adsorbed during the catalytic reaction, which contributed destructive interference of X-ray light and hence decrease of intensity (Fig. S5 in the Supporting Information).

3.3. Effect of reaction parameters and kinetic studies

The effects of the other reaction parameters were investigated using the NH2Br/Meso-BEA(H+) hybrid catalyst, for which the PC yield was correlated with the reaction parameters and the resultant correlations are graphically represented in Fig. 3. Fig. 3A shows the effect of the solvent on the PC yield. Although the hybrid catalyst exhibited sufficiently high catalytic activity in the absence of a solvent, an organic solvent is sometimes required in various industrial processes. The efficient high catalytic activity in the absence of a solvent, an organic solvent on the PC yield. Although the hybrid catalyst exhibited sufficiently high catalytic activity in the absence of a solvent, an organic solvent on the PC yield. Additionally, the activation energy is much larger than that of NH2Br/Al-SBA-15, indicating the catalytic power of the former is much stronger than the latter. In addition, the hybrid catalyst gave the smallest Ea value (37.3 kJ mol−1) compared to other catalysts published elsewhere.

The pre-exponential factor (A), a mathematical constant that could also be physically defined as the collision frequency factor, was 1.34 × 104 h−1 for the NH2Br/Al-SBA-15 catalyst, which is about 2 orders of magnitude larger than that of the NH2Br/Meso-BEA(H+)
This could be explained by the higher mesoporosity of the SBA-15 catalyst than the zeolite catalyst. The highly mesoporous structure would allow the reactant molecules to diffuse into the catalytic sites more efficiently than in the zeolite catalyst, thereby enhancing the collision frequency. Nonetheless, due to the higher activation energy of the NH3Br/Al-SBA-15 catalyst, the resultant catalytic activity was lower than that of the NH3Br/Meso-BEA(H+) catalyst.

3.4. Proposed reaction mechanism

Based on the synergistic effects of the NH3Br/Meso-BEA(H+) hybrid catalyst demonstrated by the reaction results, a reaction mechanism for the cooperative cycloaddition of CO2 to PO to produce PC was proposed as shown in Fig. 5. First, oxygen in PO was coordinated to the Lewis acid sites (i.e., empty p-orbital of Al) or protonic Brønsted acid sites on the zeolite surface. During the efficient binding of oxygen atom in PO by electrophilic acid sites on the zeolite surface, the adjacent bromide in the NH3Br group on the same surface attacks the carbon atom bonded to oxygen atom in PO and subsequently triggers the ring-opening of PO (step I→II). CO2 was then inserted into the ring-opened oxyanion species via nucleophilic attack of the oxyanion (step III); the resultant carboxylate anion then attacked the carbon atom bonded to the bromine via intramolecular nucleophilic attack (step IV). Finally, the re-cyclized PC product was formed and desorbed from the catalyst surface (step V). This proposed reaction mechanism reminds us that the electrophilic function (i.e., strong acid sites of zeolite) and the nucleophilic function (i.e., bromide in NH3Br) should be constructed in a molecular scale on the same surface, in order to activate the PO molecule by the two functions simultaneously.

4. Conclusions

An organic-inorganic hybrid catalyst based on the crystalline BEA zeolite having a hierarchically microporous and mesoporous structure was constructed by tethering the NH3Br group on the mesopore wall via Si-O-Si covalent linkages. This organic-inorganic hybrid material exhibited much better catalytic activity than the catalysts having single functionalities (i.e., acidic BEA zeolite without the NH3Br group and NH3Br-tethered SBA-15 without acid sites) in the cycloaddition of CO2.
to PO for the production of PC. Through controlled catalytic studies, it was clearly evidenced that the main catalytic component having high nucleophilicity (i.e., bromide in NH$_3$Br group) should be located near the co-catalytic component having electrophilic strong acid sites on the surface of a single catalyst. It was also revealed that the close proximity of the NH$_3$Br and the zeolite acid sites contributed on the decrease of activation energy, which is the ultimate reason for acceleration of the catalytic reaction rates compared to that achieved with the NH$_3$Br/Al-SBA-15 catalyst. The strength of acid sites is also prominent for making catalytic enhancement, as proved by that the NH$_3$Br/Al-SBA-15 and NH$_3$Br/Zn-SBA-15 showed no appreciable catalytic synergetic effects due to the very weak acidity. The mesoporous zeolite-based hybrid catalyst is a very stable and powerful heterogeneous catalyst that exhibits high catalytic activity under neat conditions without any organic solvent and good recyclability without significant loss of the initial activity and crystallinity for up to five runs. The research scope described in this work would be further extended to various epoxide molecules having bulkier geometry than PO and to gas-phase reaction system with continuous bed reactor, which are under progress in our laboratory. In particular, the current research may provide great opportunity and research inspirations not only for the green-chemical processes involving CO$_2$ utilization reported in this work, but also for other catalytic conversions requiring two or multiple catalytic functions.

Conflicts of interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcou.2018.07.009.

References