

# Synergistic hybrid catalyst for cyclic carbonate synthesis: Remarkable acceleration caused by immobilization of homogeneous catalyst on silica†

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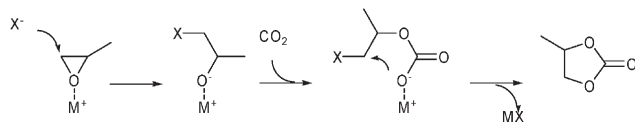
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The catalytic activity of phosphonium salts towards cyclic carbonate synthesis from propylene oxide and CO<sub>2</sub> has been enormously enhanced by their immobilization onto silica that itself has no catalytic activity.

Immobilization of molecular catalysts onto a solid support is a promising strategy to facilitate the separation of the catalyst from the products. However, this approach generally decreases the catalytic performance, including the activity and/or selectivity.<sup>1</sup> Herein, we introduce an example of a synergistic organic–inorganic hybrid catalyst where the inorganic support facilitates catalyst separation and synergistically promotes the catalytic activity of the organic part.<sup>2</sup>

The CO<sub>2</sub> fixation reaction with alkylene oxides to produce cyclic carbonates, raw materials for polycarbonate,<sup>3</sup> has received increasing attention.<sup>4,5</sup> This reaction is industrially operated using halide-containing organic or inorganic salts, including tetraethylammonium bromide or potassium iodide, as homogeneous catalysts. A typical reaction mechanism includes a ring opening by the halogen ion followed by CO<sub>2</sub> insertion (Scheme 1).<sup>6</sup> We have been developing an efficient solid catalyst for carrying out this reaction in a fixed-bed flow reactor.



**Scheme 1** Proposed reaction mechanism.

Previously, we reported that solid catalysts such as SmOCl and Cs-P-Si oxide, which have both acidic and basic characteristics, are effective for cycloaddition.<sup>7</sup> Hence, we expected a basic molecular part immobilized on an acidic solid support to result in an efficacious acid–base catalyst for the carbonate synthesis. One candidate is phosphonium salt immobilized on silica. Table 1 summarizes the catalytic activities of phosphonium halides, including those immobilized on polystyrene (PS) and silica (SiO<sub>2</sub>). The catalytic activities were evaluated by batch reactions

at 10 MPa and 100 °C for 1 h (see electronic supplementary information for experimental details†).

When polystyrene based immobilized phosphonium salts such as PS-(4-C<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>-P(*n*-Bu)<sub>3</sub>X (X = Cl, Br) (in this notation, the solid support, linker, and onium parts are connected by hyphens) were used, the catalytic activity normalized to each onium unit was nearly identical to the corresponding molecular catalysts used in a homogeneous fashion (Table 1, entries 1 and 2 vs entries 4 and 5). However, the immobilization of phosphonium halides on silica (*e.g.* SiO<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-P(*n*-Bu)<sub>3</sub>X, X = Cl, Br, I) dramatically increased the catalytic activities compared to the corresponding homogeneously used onium salts (entries 1 to 3 vs entries 6 to 8). It was noteworthy that the pseudo-first order rate constant of SiO<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-P(*n*-Bu)<sub>3</sub>I normalized to a phosphorus atom was about 300 times larger than that of P(*n*-Bu)<sub>4</sub>I. Since silica itself did not display catalytic activity for the cycloaddition even at 200 °C, the promotion effect by silica was strikingly synergistic.<sup>8</sup> Although Tundo *et al.* previously used these phosphonium salts supported on silica as a solid phase-transfer catalyst for S<sub>N</sub>2 reactions in sc-CO<sub>2</sub>, such a tremendous effect as shown in this paper was not reported.<sup>9</sup>

An almost quantitative amount of propylene carbonate was produced (propylene carbonate yield of 99.7% and propylene oxide recovery of 0.2%) using SiO<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-P(*n*-Bu)<sub>3</sub>I, the best catalyst, and only trace amounts of 1-iodo-2-propanol and

**Table 1** Catalytic activity for propylene carbonate synthesis<sup>a</sup>

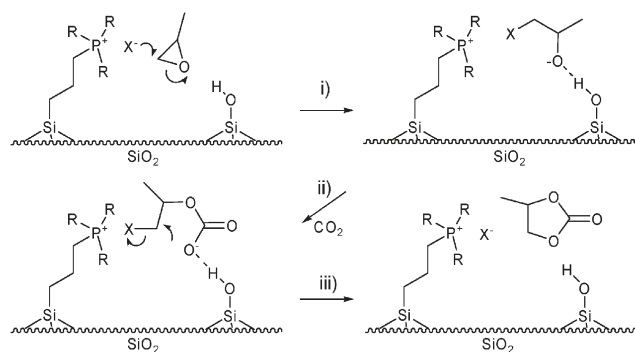
Entry	Catalyst	Phosphorus <sup>b</sup> (mmol)	Yield (%)	k <sup>c</sup> (min <sup>-1</sup> )
1	P( <i>n</i> -Bu) <sub>4</sub> Cl	0.57	10	0.18
2	P( <i>n</i> -Bu) <sub>4</sub> Br	0.57	4	0.07
3	P( <i>n</i> -Bu) <sub>4</sub> I	0.57	5	0.09
4	PS-(4-C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> -P( <i>n</i> -Bu) <sub>3</sub> Cl <sup>d</sup>	0.42	8	0.19
5	PS-(4-C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> -P( <i>n</i> -Bu) <sub>3</sub> Br <sup>d</sup>	0.41	9	0.22
6	SiO <sub>2</sub> -C <sub>3</sub> H <sub>6</sub> -P( <i>n</i> -Bu) <sub>3</sub> Cl	0.26	29	1.3
7	SiO <sub>2</sub> -C <sub>3</sub> H <sub>6</sub> -P( <i>n</i> -Bu) <sub>3</sub> Br	0.18	53	4.1
8	SiO <sub>2</sub> -C <sub>3</sub> H <sub>6</sub> -P( <i>n</i> -Bu) <sub>3</sub> I	0.21	100	26
9	SiO <sub>2</sub> -C <sub>3</sub> H <sub>6</sub> -PEt <sub>3</sub> Cl	0.44	44	1.3
10	SiO <sub>2</sub> -C <sub>3</sub> H <sub>6</sub> -P( <i>n</i> -Oct) <sub>3</sub> Cl	0.14	12	0.85
11	SiO <sub>2</sub> -(4-C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> -P( <i>n</i> -Bu) <sub>3</sub> Cl	0.20	9	0.44
12	SiO <sub>2</sub> -(4-C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> -P( <i>n</i> -Bu) <sub>3</sub> Br	0.18	37	2.5

<sup>a</sup> 100 °C, 1 h, 10 MPa of CO<sub>2</sub>, 4 ml (57.2 mmol) of propylene oxide, 0.57 mmol of homogeneous catalyst or 400–800 mg of immobilized catalyst (0.57 mmol halogen based on the initial halogen content before quaternization). <sup>b</sup> Absolute amount of phosphorus determined by elemental analyses. <sup>c</sup> Pseudo-first order rate constant normalized to phosphorus. <sup>d</sup> The polystyrene portion was ArgoPore<sup>®</sup> resins.

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† Electronic supplementary information (ESI) available: catalyst preparation and characterization, and the other experimental details. See DOI: 10.1039/b517140g

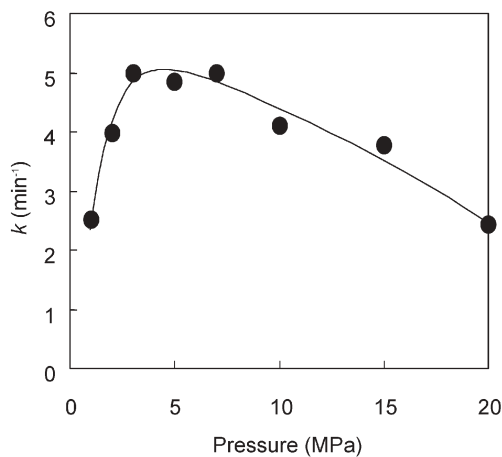


**Scheme 2** Possible acceleration mechanism on the synergistic hybrid catalyst.

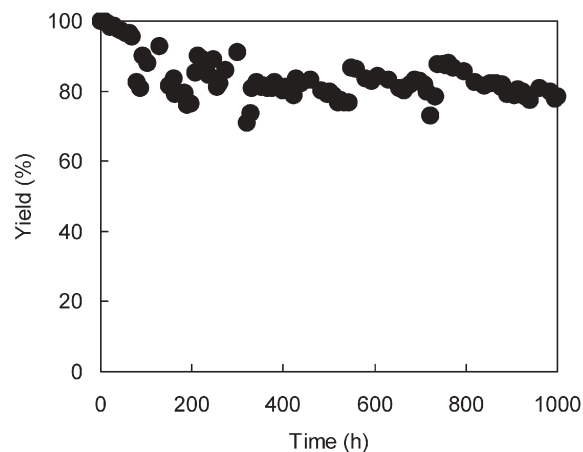
1-iodo-3-propanol (total 0.1%) were detected as by-products by GCMS (Table 1, entry 8). In the cationic part, shorter alkyl chains on the phosphonium ion tended to display better catalytic activity. The tendency was  $-\text{PEt}_3(\text{R})^+ \sim -\text{P}(n\text{-Bu})_3(\text{R})^+ > -\text{P}(n\text{-Oct})_3(\text{R})^+$  (entries 6, 9, and 10), which, interestingly, was the opposite tendency of the phase transfer ability of onium salts.<sup>10</sup>

The phosphonium group covalently bound to the silica surface through a relatively rigid 4-phenylenemethylene-linker gave much lower reaction rates compared to those with a flexible trimethylene-linker (Table 1, entries 11 and 12 vs 6 and 7), but the rates were still higher than those observed for  $\text{P}(n\text{-Bu})_4\text{Cl}$  and  $\text{P}(n\text{-Bu})_4\text{Br}$ .

This effect of linker structure indicated that cooperative catalysis by the silica surface and the onium part results in the enhanced activity. Scheme 2 shows a plausible acceleration mechanism, in which the acidic surface silanol groups interact and activate propylene oxide, which is subsequently attacked by a nucleophile to open the ring.<sup>11</sup> The apparent activation energy in the temperature range of 50–175 °C for  $\text{SiO}_2\text{-C}_3\text{H}_6\text{-P}(n\text{-Bu})_3\text{Br}$  was 47 kJ·mol<sup>-1</sup>, which was much smaller than the value estimated for  $\text{P}(n\text{-Bu})_4\text{Br}$  (86 kJ·mol<sup>-1</sup>). On the other hand, the frequency factor of  $\text{SiO}_2\text{-C}_3\text{H}_6\text{-P}(n\text{-Bu})_3\text{Br}$  ( $3 \times 10^5 \text{ s}^{-1}$ ) was much smaller than that of  $\text{P}(n\text{-Bu})_4\text{Br}$  ( $2 \times 10^9 \text{ s}^{-1}$ ). The mechanism illustrated in Scheme 2 is consistent with the large decrease in the activation energy and the frequency factor upon immobilization.



**Fig. 1** Pressure effect on the reaction rate constants. All reaction conditions, except pressure, are the same as given in the footnote to Table 1.



**Fig. 2** Propylene carbonate yield during a continuous flow reaction with a fixed-bed reactor. Conditions:  $\text{SiO}_2\text{-C}_3\text{H}_6\text{-P}(n\text{-Bu})_3\text{Br}$  10 g (8.5 mmol phosphorus), propylene oxide flow = 0.1 ml min<sup>-1</sup> (WHSV = 0.5 h<sup>-1</sup>), CO<sub>2</sub> flow = 0.2 ml min<sup>-1</sup>, under 10 MPa, temperature gradually raised from 90 °C to 160 °C.

Fig. 1 shows the pressure effect of the  $\text{SiO}_2\text{-C}_3\text{H}_6\text{-P}(n\text{-Bu})_3\text{Br}$  system. Since the rate increased as the pressure (CO<sub>2</sub> concentration) increased in the range of 1–3 MPa, the rate-determining step should be CO<sub>2</sub> insertion (step ii), Scheme 2). However, above 5 MPa the rate negatively depended on the pressure. Since the reactions in Table 1 were conducted in the latter pressure range (10 MPa), the remarkable acceleration effect by immobilization should be attributed to the ring opening (step i), Scheme 2) rather than the promotion of CO<sub>2</sub> insertion (step ii).

Finally, a fixed-bed flow reactor experiment using  $\text{SiO}_2\text{-C}_3\text{H}_6\text{-P}(n\text{-Bu})_3\text{Br}$  as a catalyst clearly demonstrated the merit of immobilization. The conversion of propylene oxide was greater than 80% with a selectivity over 99.9% for more than 1000 h (Fig. 2). A single phosphonium group produced over 11,500 molecules of propylene carbonate, which was transparent and colorless, during this period. The total productivity of the experiment was equivalent to 580 ton per month per ton-catalyst.

In conclusion, we have demonstrated that phosphonium halides covalently bound to SiO<sub>2</sub> exhibit excellent catalytic activities for synthesizing propylene carbonate from propylene oxide and CO<sub>2</sub>. The pseudo-first order rate constant of the catalyst normalized to phosphorus atom is about 300 times larger than that of the corresponding homogeneous catalyst. Generalizations and applications of these new synergistic hybrid catalysts are currently underway.

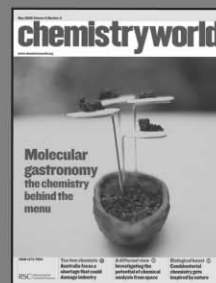
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