

Supplementary Information for the Chemical Communications

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

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Preparation of the catalysts

All the solvents and reagents were used as received without any further purification. Propylene oxide (PO), adamantane, tetra-*n*-butylphosphonium chloride and tetra-*n*-butylphosphonium bromide were all reagent grade and purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). *N,N*-dimethylformamide (DMF) and toluene were from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), while P(*n*-Bu)₃ (tri-*n*-butylphosphine), PEt₃ (triethylphosphine), P(*n*-Oct)₃ (tri-*n*-octylphosphine), PPh₃ (triphenylphosphine) and SilicaGel60 (neutral, 100-200 mesh) were from Kanto Chemical Co., Inc. (Tokyo, Japan). P(*n*-Bu)₄I (tetra-*n*-butylphosphoniumiodide) was purchased from Alfa Aesar Co. (Ward Hill, USA). All the functionalized SiO₂'s were purchased from Aldrich Chemical Co., Ltd. (Milwaukee, USA). These materials contained covalently bound terminal chloro- or bromo-propylene groups on Si's, which were denoted as SiO₂-C₃H₆-Cl and SiO₂-C₃H₆-Br, respectively.

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The amount of the loaded functional groups was 0.71 mmol/g and 1.4 mmol/g, respectively. The loading amount of the functionalized SiO₂ with a phenyl methylene linker was 0.63 mmol/g. Chloro-functionalized porous polystyrene-divinylbenzene resin, ArgoPore-ClTM, was purchased from Argonaut Technologies Inc. (Redwood City, USA). The loading of the functional groups on this solid was 0.98 mmol/g.

Phosphonium immobilized SiO₂ was prepared by reacting the terminal monohalogenated alkyl functionalized SiO₂'s and trialkylphosphines. The reaction was performed in a round bottomed three necked flask equipped with a TeflonTM coated magnetic stirrer bar or a stirring blades driven by a pulse motor and a condenser, which was connected to an Ar line. Five gram of SiO₂-C₃H₆-Cl was placed in the flask under a slow stream of Ar. Ninety ml of toluene was added and the slurry gently stirred. Then 500 mg of P(*n*-Bu)₃ was added and the flask was heated to 110°C in an oil bath for seven days with continuous stirring under a slow stream of Ar. The slurry was vacuum filtrated using a membrane filter (ADVANTEC Toyo Kaisha Ltd., Tokyo, Japan). The filtered functionalized silica was washed with 150 ml of acetone, followed by 150 ml of methanol and 150 ml of ethyl ether. Then, it was dried in air for several minutes. The resulting powder was introduced to a Schlenk tube and dried under vacuum at room temperature for 60 min. Afterwards, the tube was heated in an oil bath at 50°C and dried for 30 min under a continuous vacuum. Next, the bath temperature was raised to 100°C and the solid was dried for an additional 60 min under vacuum. The resulting solid was stored in a desiccator. All the other functionalized solids were prepared by a similar method. PS-PhCH₂-P(*n*-Bu)₃Br, SiO₂-C₃H₆-P(*n*-Bu)₃I, and SiO₂-PhCH₂-P(*n*-Bu)₃Br were prepared from their corresponding chlorides by ion exchange techniques. NaBr or KI saturated methanol was used for the ion exchange reaction of the solid catalysts. Finally, the filtered solids were washed with methanol, acetone, and diethylether. Then the solids

were dried using the procedure described above. Analyses of the functionalized silica gels were performed at Mitsubishi Chemical Group, Science and Research Center Inc. The flask combustion method was used to analyze the P content. The residual ashes were trapped by buffered water and then the concentration of the ortho-phosphate was determined by colorimetric titration using molybdate. The halogen concentrations were determined by ion chromatography. The analysis data of PS-P(*n*-Bu)₃Cl (%): C, 82.4; H, 8.54; N, <0.3; P, 2.2; Cl, 3.6. PS-P(*n*-Bu)₃Br (%): C, 81.0; H, 8.17; N, <0.3; P, 2.2; Cl, 0.9; Br, 5.4. SiO₂-C₃H₆-P(*n*-Bu)₃Cl (%): P, 0.98; Cl, 2.9. SiO₂-C₃H₆-P(*n*-Bu)₃Br(%): P, 1.3; Cl, <0.15; Br, 6.9. SiO₂-C₃H₆-P(*n*-Bu)₃I (%): P, 0.82; Cl, 1.7; I, 4.1. SiO₂-C₃H₆-PEt₃Cl (%): P, 1.7; Cl, 3.1. SiO₂-C₃H₆-P(*n*-Oct)₃Cl (%): P, 0.57; Cl, 3.0. SiO₂-PhCH₂-P(*n*-Bu)₃Cl (%): P, 1.4; Cl, 3.5. SiO₂-PhCH₂-P(*n*-Bu)₃Br (%): P, 1.2; Cl, 1.5; Br, 3.8.

We have estimated the amount of silanol by TG (Bruker axs, TG-DTA2000SA), for SiO₂-C₃H₆-P(*n*-Bu)₃Br, the catalyst used in entry 7, Table 1. The weight loss from 150 to 1000 °C was 20.5 %, among which 18.1 % is attributed to the loss of organic groups from the silica surface (calculated from the elemental analysis data). The 2.4 % difference of the weight loss can be attributed to silanol groups. Simple calculation says that the content of silanol group is 2.7 mmol/g.

Propylene carbonate synthesis reaction from propylene oxide and CO₂

Propylene carbonate (PC) synthesis tests were conducted in an autoclave (SUS316, inner volume was 20 ml) connected with a screw cap bind to a straight tube. A magnetic stirrer bar (1 cm), 50 mg of adamantane (inner standard), and the catalyst (400 to 800 mg, see Note #) were added to the autoclave. Then, a stream of Ar gas gently flowed inside the vessel. Afterwards the screw cap was sealed and 4 ml (57.2 mmol) of PO was introduced

from the top of the tube using a syringe. After being equipped with a pressure gauge and a needle valve, liquid CO₂ was introduced through a valve at room temperature. The autoclave was heated in an oil bath at the reaction temperature. Additional CO₂ was slowly introduced using a high-pressure liquid chromatography pump (HITACHI, L6000) until the pressure reached 10 MPa. During the reaction, CO₂ was added through the valve, if needed, to keep the pressure inside constant. **Caution:** Reactions are conducted under high pressure. Extreme care must be used.

Upon completion of the reaction, the autoclave was cooled in an ice bath. Then, the inner gas was slowly released by carefully opening the needle valve through a sintered glass filter tube set in a DMF filled trap. The product was determined by gas chromatography (GC) (Shimadzu GC17A) with a 0.2 mm x 20 m DB-WAX capillary column (J&W scientific) using a FID detector. The column temperature was initially set at 40°C for 10 min, then it was increased by 10 degrees per 1 min for 21 min, and maintained at 250°C for additional 10 min.

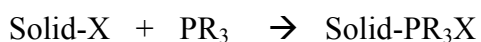
Note #: The exact weight catalyst charged was shown in Table S1.

Table S1. Summary of the phosphorous loading on the immobilized catalysts used in the

catalytic reactions and their analysis data; the entry numbers are according to those in Table 1.

Entry No.	Catalyst	Linker loading (mmol/g)	Catalyst Weight (mg)	P (mmol) ^{a)} Theoretical	P (mmol/g)	
					loading based on analysis	P (mmol) Actually used
4	PS-(4-C ₆ H ₄)CH ₂ -P(<i>n</i> -Bu) ₄ Cl	0.98	584	0.57	0.72	0.42
5	PS-(4-C ₆ H ₄)CH ₂ -P(<i>n</i> -Bu) ₄ Br	0.98	584	0.57	0.7	0.41
6	SiO ₂ -C ₃ H ₆ -P(<i>n</i> -Bu) ₃ Cl	0.7	806	0.57	0.32	0.26
7	SiO ₂ -C ₃ H ₆ -P(<i>n</i> -Bu) ₃ Br	1.41	400	0.57	0.46	0.18
8	SiO ₂ -C ₃ H ₆ -P(<i>n</i> -Bu) ₃ I	0.7	806	0.57	0.26	0.21
9	SiO ₂ -C ₃ H ₆ -PEt ₃ Cl	0.7	806	0.57	0.55	0.44
10	SiO ₂ -C ₃ H ₆ -P(<i>n</i> -Oct) ₃ Cl	0.7	806	0.57	0.18	0.15
11	SiO ₂ -(4-C ₆ H ₄)CH ₂ -P(<i>n</i> -Bu) ₃ Cl	1.3	441	0.57	0.46	0.20
12	SiO ₂ -(4-C ₆ H ₄)CH ₂ -P(<i>n</i> -Bu) ₃ Br	1.3	441	0.57	0.4	0.18

a) Assuming the 100% conversion of the following reaction.



Flow reactor experiment

A PC synthesis test was also performed in a high-pressure fixed-bed continuous-flow reactor, which was operated in the up-flow mode. The reactor consisted of 316 stainless steel tubes (10 mm inner diameter and 250 mm long), which were loaded with the SiO₂-C₃H₆-P(*n*-Bu)₃Br catalyst. The reactor was encased in an electric furnace, which was thermostatically controlled by a thermocouple that read the temperature of the catalyst bed. The bottom part of the catalyst bed was filled with glass beads (1 mm outer diameter), which acted as a preheating zone. The pressure in the reactor was controlled by a backpressure regulator (JASCO, 880-81). A mixture of propylene oxide and

supercritical CO₂, which was continuously introduced into the reactor with an HPLC pump (JASCO, SCF-201), passed through the catalyst bed and the backpressure regulator, which expanded to separate the liquid products from the CO₂. The liquid products were periodically collected using a bubbler (200 ml) containing DMF (25 ml) and analyzed by GC using adamantane (50 mg) as the internal standard. The reaction conditions were 10 g of catalyst and a total pressure of 10 MPa. The temperature was gradually increased from 90 to 160°C to maintain a PO conversion above 80%. The flow rate of propylene oxide was 0.1 cm³·min⁻¹, while the liquid CO₂ had a flow rate of 0.2 cm³·min⁻¹. The weight hourly space velocity (WHSV) was 0.5 h⁻¹. **Caution:** The heat from the reaction may cause the temperature to spontaneously rise. Extreme care must be used to prevent the reactor from overheating.

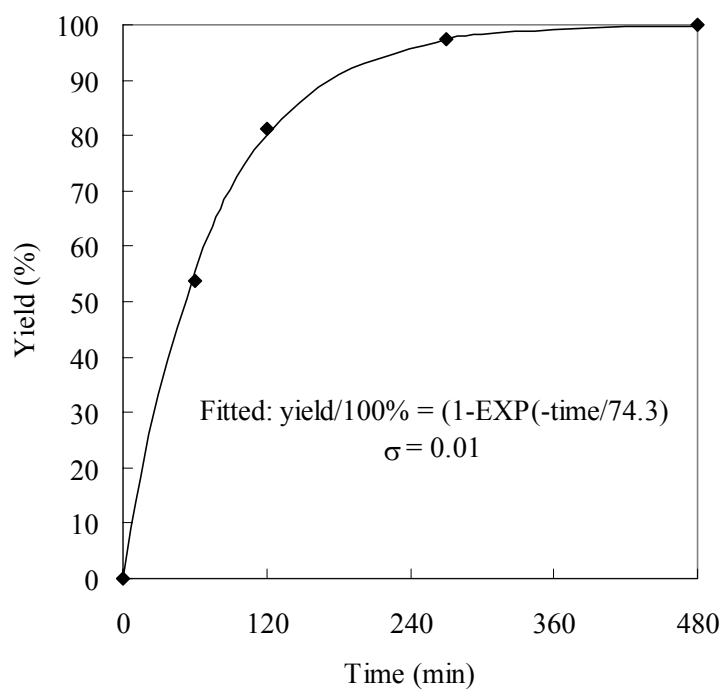


Fig. S-1 Time course of the PC yield change fitted with an exponential curve. Conditions: PO, 57.2 mmol; SiO₂-P(*n*-Bu)₃Br, 402 mg; supercritical CO₂, 10 MPa; 100°C.

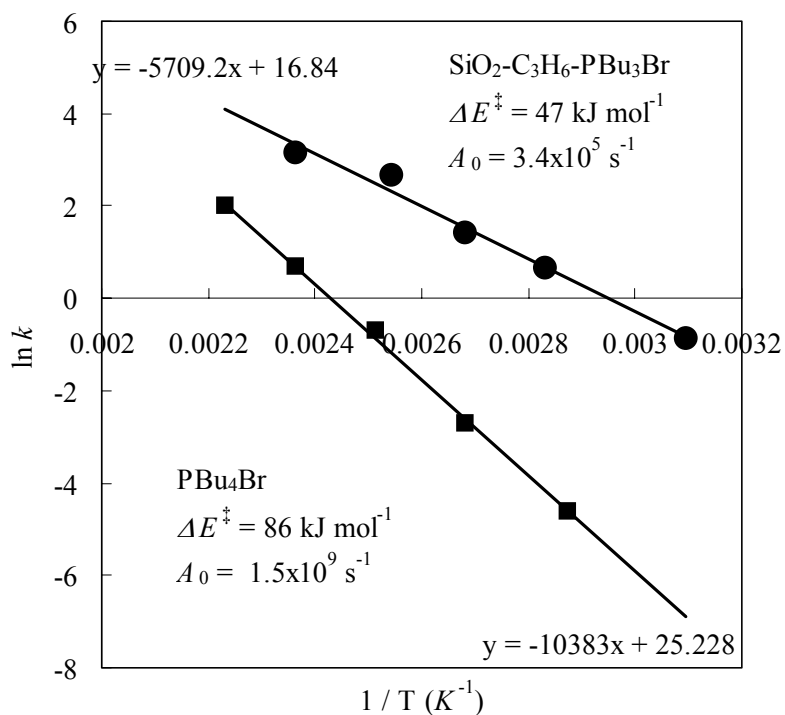


Fig. S-2 Arrhenius plot of the PC synthesis reaction. Comparison of k for SiO₂-C₃H₆-P(*n*-Bu)₃Br (—●—) and P(*n*-Bu)₄Br (---■---). Conditions: PO, 57.2 mmol; catalyst, 0.1 mol%; supercritical CO₂, 10 MPa; 1 h.