Supporting Information

Ruthenium Complex Immobilized on Supported Ionic-Liquid-

Phase (SILP) for Alkoxycarbonylation of Olefins with CO₂

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Section 1. Materials and Synthetic procedures

General Information. All reagents were used without further purification. Imidazole (99%), dodecyl bromide (99%), 1-methylimidazole (99%), potassium carbonate (K₂CO₃, 99%), (3-chloropropyl) trimethoxysilane (98%), thionyl chloride (99%), triethylene glycol monomethyl ether (98%), pyridine (99%), chloroform (CHCl₃ 98%), triruthenium dodecacarbonyl (Ru₃(CO)₁₂, 99%), tetrahydrofuran (THF, 99.9%), methanol (MeOH, GC), toluene (99%), acetonitrile (MeCN, 99%), and anhydrous lithium chloride (LiCl, 99%) were abtained from Innochem Scientific Co., Ltd. Cyclohexene (99%), anhydrous magnesium sulfate (MgSO₄ 99.5%), anhydrous sodium sulfate (Na₂SO₄ 99.5%), sodium hydroxide (NaOH, 96%) and isooctane (99.8%) were purchased from Aladdin Reagent, Ltd. Silica gel 60 was received from Alfa Reagent, Ltd. The N₂ sorption isotherms were measured on an automatic volumetric adsorption equipment (Micromeritics ASAP 2020) at 77 K. The Brunauer-Emmett-Teller (BET) method was applied for the specific surface areas and pore volume. Pore size distribution was obtained through the nonlocal density functional theory (NLDFT) method. The morphologies and structures were investigated by the Hitachi SU8020 Field emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 5 kV and all the samples were mounted on a carbon tape and coated with gold prior to measurement. During the SEM observations, the elemental distribution was analyzed by energy-dispersive X-ray spectroscopy (EDS) in the highvacuum operating mode. Transmission electron microscopy (TEM) images were obtained with JEM-2100F at 200 kV. The Fourier transform infrared (FT-IR) spectra

were collected on a Thermo Nicolet 380 with KBr tabletting method in a range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. The ¹H and ¹³C NMR data were detected via a Bruker Avance III 600 MHz spectrometer. The CP-MAS ²⁹Si NMR and ¹³C NMR measurements were carried out with a Bruker AVANCE III HD 500 MHz spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi spectrometer by get the sample on the aluminized sheet. Elemental analysis (CHNS mode) was operated on a Vario EL Cube elemental analyzer. CO2 adsorption measurements were recorded using a Quantachrome Nova 4000e. Thermogravimetric analysis (TGA) was performed on the Shimadzu TA-60WS Thermal analyzer in a range of 30~800 °C with a heating rate of 10 °C min⁻¹ under nitrogen. GC-MS was performed using Shimadzu GCMSQP2020, column Rtx-5MS30m×0.25µm. GC analysis was performed using Aglient GC-7890B equipped with a capillary column (DB-FFAP, $30 \text{ m} \times 0.32 \text{ mm}$) using a flame ionization detector. The temperatures of injector and FID were both controlled at 250 °C. The components were separated according to the following program: an initial temperature of 100 °C held for 2 min, heated to 200 °C at a rate of 25 °C min⁻¹ and then held for 5 min. Gas-phase GC were performed on Agilent 8890 equipped with a HP-PLOT Al₂O₃ column leading to a thermal conductivity detector (TCD).

1. Synthesis of 1-methyl-3- (trimethoxysilyl propyl) imidazolium chloride (IL-A)





IL-A was synthesized according to the method reported by other authors.¹ In the

experiment, 1-methylimidazole (2.05 g, 25 mmol) and (3-chloropropyl) trimethoxysilane (5.12 g, 25 mmol) were mixed in a dry round-bottomed flask (100 ml) with reflux condenser tube at 95 °C for 24 h under argon atmosphere. After the reaction, the mixture was washed with anhydrous diethyl ether (3 × 20 ml), and then dried under vacuum at 80 °C for 24 h to afford light yellow viscous liquid (yield = 94%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 10.18 (s, 1H), 7.59 (t, 1H), 7.28 (t, 1H), 4.07 (t, 2H), 3.87 (s, 3H), 3.29 (s, 9H), 1.74 (t, 2H), 0.36 (t, 2H), ¹³C NMR (151 MHz, CDCl₃, 298 K): δ = 137.2, 123.8, 121.9, 51.4, 50.4, 36.2, 23.9, 5.7.

2. Synthesis of 1-dodecyl-3- (trimethoxysilyl propyl) imidazolium chloride (IL-B)



Scheme S2. Synthesis of IL-B

Synthesis of N-dodecylimidazole²

Imidazole (2.724 g, 40 mmol), K₂CO₃ (8.29 g, 60 mmol), dodecyl bromide (5.12 g, 36 mmol) and acetonitrile (80 ml) was mixed in a three necked round-bottomed flask (250 ml) with reflux condenser tube at 80 °C for 12 h. After the reaction, solvent was removed by evaporation under reduced pressure. Water (200 ml) was added to the reaction mixture and then extracted three times with dichloromethane (3×200 ml). Organic phases were combined and dried over sodium sulfate. The crude product was purified under reduced distillation (110 °C /5.4 Pa) to give N-dodecylimidazole as a colorless liquid (yield = 75%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.39 (s, 1H), 6.97 (s, 1H), 6.83 (s, 1H), 3.84 (t, 2H), 1.69 (m, 2H), 1.19 (m, 18H), 0.81 (t, 3H), ¹³C NMR (151 MHz, CDCl₃, 298 K): δ = 137.0, 129.2, 118.7, 47.0, 31.9, 31.0, 29.5, 29.4, 29.4, 29.3, 29.0, 26.5, 22.6, 14.1.

Synthesis of IL-B

IL-B was synthesized according to the method reported by other authors.² In the glove-box, N-dodecylimidazole (2.36 g, 10 mmol) and (3-chloropropyl)

trimethoxysilane (1.99 g, 10 mmol) were mixed in a pressure flask (38 ml). The reaction mixture was heated at 110 °C for 48 h under stirring. After the reaction, the mixture was washed with anhydrous diethyl ether (3 × 20 ml), and then dried under vacuum at 80 °C for 24 h to afford light yellow viscous liquid IL-B (yield = 89%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 10.50 (s, 1H), 7.41 (s, 1H), 7.38 (s, 1H), 4.30 (m, 4H), 3.49 (m, 6H), 3.35 (m, 2H), 1.17 (m, 27H), 0.80 (t, 3H), 0.57 (t, 2H), ¹³C NMR (151 MHz, CDCl₃, 298 K): δ = 137.7, 122.0, 121.9, 51.7, 50.7, 31.9, 30.4, 29.6, 29.5, 29.4, 29.3, 29.1, 26.3, 24.2, 22.7, 14.1, 5.9.

3. Synthesis of 1-(2-(2-(2-Methoxyethoxy) ethoxy) ethyl)-3-

(3(trimethoxysilyl)propyl)-1H-imidazol-3-ium chloride (IL-C)



Scheme S3. Synthesis of IL-C

Synthesis of sodium imidazolide (ImNa)

Sodium imidazolate (ImNa) was synthesized according to the reference.³ Imidazole (13.62 g, 0.2 mol) and NaOH (8.2 g, 0.205 mol) were introduced in a 50 ml round-bottom flask equipped with a condenser. The mixture was heated at 110 °C under stirring. After 4 h, a homogeneous liquid-phase was obtained and the product was placed in a vacuum oven for 48 h at 80 °C in order to remove all water produced in the course of the reaction. Then the faint yellow solid was obtained and stored in the glove box (yield = 80%). ¹H NMR (600 MHz, D₂O, 298 K): δ = 7.52 (s, 1H), 6.91 (m, 2H). Synthesis of triethylene glycol monomethyl chloride (TGMCl)⁴

Triethylene glycol monomethyl ether (12.0 g, 72 mmol), pyridine (5.7 g, 72 mmol) and CHCl₃ (60 ml) was mixed in a three necked round-bottomed flask (250 ml) with reflux condenser tube. The mixture was heated at 110 °C for 48 h under stirring,

followed by adding thionyl chloride (11.0 g, 92 mmol) slowly into the solution. Then a brown liquid mixture was obtained, which was washed with water (3 × 100 ml), dried with MgSO₄. CHCl₃ was removed by evaporation under reduced pressure. The crude product was purified under reduced distillation (60 °C /5.4 Pa) to give TGMCl as faint yellow liquid (yield = 52%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 3.75 (t, 2H), 3.65 (m, 8H), 3.54 (m, 2H), 3.37 (s, 3H), ¹³C NMR (151 MHz, CDCl₃, 298 K): δ = 71.9, 71.3, 70.6, 70.5, 58.9, 42.7.

Synthesis of 1-(2-(2-(2-Methoxyethoxy) ethoxy) ethyl) imidazole (MEETMi)

A mixture of ImNa (4.50 g, 0.05 mol), TGMCl (8.94 g, 0.045 mol) and THF (30 ml) were added in a three necked round-bottomed flask (250 ml). The mixture was stirred at reflux for 10 h and filtered; the filtrate was concentrated under reduced pressure to removed THF. Then CH₂Cl₂ (30 ml) was added to the residue, which was filtered again to remove the precipitation. The filtrate was concentrated under reduced pressure to remove CH₂Cl₂. The crude product was purified under reduced distillation (120 °C /5.4 Pa) to give MEETMi as colorless liquid (yield = 65%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.42 (s, 1H), 6.89 (s, 1H), 6.88 (s, 1H), 3.98 (t, 2H), 3.66 (t, 2H), 3.48 (m, 6H), 3.41 (m, 2H), 3.24 (s, 3H), ¹³C NMR (151 MHz, CDCl₃, 298 K): δ = 137.3, 128.8, 119.3, 71.7, 70.4, 70.3, 70.3, 58.8, 46.8.

Synthesis of IL-C

IL-C was synthesized according to IL-B. (yield = 56%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 10.08 (s, 1H), 7.65 (m, 2H), 4.45 (m, 2H), 4.18 (m, 2H), 3.69 (m, 2H), 3.37 (m, 17H), 3.17 (s, 3H), 1.82 (m, 2H), 0.43 (m, 2H), ¹³C NMR (151 MHz, CDCl₃, 298 K): δ = 137.1, 123.6, 121.3, 71.7, 70.1, 69.6, 68.9, 58.8, 51.5, 50.6, 50.3, 49.6, 49.4, 48.3, 24.0, 7.2, 5.8.

Section 2. Tables S1-S3

Sample	BET surface area	pore volume (cm ³ /g)	
Silica gel	514	0.832	
SILP[C1]-A	353	0.453	
[Ru]@SILP-B-2	384	0.404	
[Ru]@SILP-C-2	113	0.128	
[Ru]@SILP-A-1	354	0.454	
[Ru]@SILP-A-2	324	0.443	
[Ru]@SILP-A-3	307	0.436	

Table S1. Physical Properties of the Supported ILs hybrids

Table S2. Ruthenium content of the [Ru]@SILP-X*

Catalyst	Ru ₃ (CO) ₁₂ loading(wt.%)	Ru ₃ (CO) ₁₂ (mmol/g)	
[Ru]@SILP-A-2	1.1839	0.0185	
[Ru]@SILP-B-2	1.7671	0.0276	
[Ru]@SILP-C-2	0.7152	0.0112	
[Ru]@SILP-A-1	0.5941	0.0093	
[Ru]@SILP-A-3	2.2206	0.0347	
*. D-44-11ICD			

*: Detected by ICP

Entry	Sample	C (wt%)	H (wt%)	N (wt%)	IL loading (mmol/g)	IL loading (wt%)
1	[Ru]@SILP-A-1	10.18	1.82	2.97	1.06	29.7
2	[Ru]@SILP-A-2	10.26	1.84	2.95	1.05	29.4
3	[Ru]@SILP-B-2	12.97	2.36	1.57	0.56	24.3
4	[Ru]@SILP-C-2	16.32	2.80	2.82	1.01	41.7
5	[Ru]@SILP-A-3	10.37	1.76	2.91	1.04	29.2
6*	[Ru]@SILP-A-2	10.20	1.86	2.40	0.86	24.1

Table S3. Summary of elemental analysis results

*: After using for four runs.

Calculation method:

Since silica gel has no nitrogen element, so the amount of ionic liquid within [Ru]@SILP-X-m calculated based on the nitrogen content, taking [Ru]@SILP-A-2 as an example:

IL loading (mmol/g) = 2.95*10/(14*2) = 1.05 mmol/g.

IL loading (wt%) = 1.05*280.5/10 = 29.4 wt%.

The corresponding percentage of IL decorated into the surface and channel of silica gel:

The quality of ruthenium in [Ru]@SILP-X-m is negligible.

Under ideal condition, IL-X loading $(mmol/g) = n_{IL-X} / (m_{SiO2} + m_{IL-X})$

For [Ru]@SILP-A-2: IL-A loading (mmol/g) = 8.9/ (5.0+2.50)

=1.19 mmol/g

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For [Ru]@SILP-B-2: IL-B loading (mmol/g) = 8.9/ (5.0+3.87)
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=1.00 mmol/g
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For [Ru]@SILP-C-2: IL-C loading (mmol/g) = 8.9/ (5.0+3.67)
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=1.03 mmol/g

The real IL impregnation percentage:

For [Ru]@SILP-A-2: 1.05/1.19=88.2% For [Ru]@SILP-B-2: 0.56/1.00=56.0% For [Ru]@SILP-C-2: 1.01/1.03=98.1%





Fig. S1 N₂ adsorption isotherms (a) and BJH pore size distribution (b) of the [Ru]@SILP-A catalysts with different ratios of ruthenium



Fig. S2 FT-IR spectra of (a) SILP[Cl]-B and [Ru]@SILP-B-2; (b) SILP[Cl]-C and



Fig. S3 EDS analysis of N, Cl elements in [Ru]@SILP-A-2, [Ru]@SILP-B-2 and [Ru]@SILP-C-



Fig. S4 XPS spectra of Cl 2p in [Ru]@SILP-X-2 (X = A, B and C).



Fig. S5 Influences of (a) ruthenium content (160 °C, 20 h, $CO_2 4$ MPa, MeOH 4 ml, LiCl 2 equiv.); (b) LiCl dosage (other conditions remain unchanged); (c) CO_2 pressure (other conditions remain unchanged) and (d) MeOH dosage (other conditions remain unchanged) on the performance of [Ru]@SILP-A hybrids.





Fig. S7 Recyclability examination of [Ru]@SILP-B-2. Reaction conditions: **1a** (2 mmol), [Ru]@SILP-B-2 (2.8 mol% Ru), MeOH (4 ml), CO₂ (4 MPa), 160 °C, 20 h; Yield was determined by GC-FID analysis using isooctane as an internal standard.



Fig. S8 FT-IR spectra of the [Ru]@SILP-A-2 catalyst before use (fresh) and after using for four



Fig. S9 The SEM image of the [Ru]@SILP-A-2 catalyst after using for four runs.

Section 4. NMR spectra



NMR Spectrum 1 ¹H NMR (600 MHz, CDCl₃, 298K) and ¹³C NMR (151 MHz) of IL-A



NMR Spectrum 2 ¹H NMR (600 MHz, CDCl₃, 298K) and ¹³C NMR (151 MHz) of Ndodecylimidazole



NMR Spectrum 3 ¹H NMR (600 MHz, CDCl₃, 298K) and ¹³C NMR (151 MHz) of IL-B



NMR Spectrum 4 ¹H NMR (600 MHz, CDCl₃, 298K) and ¹³C NMR (151 MHz) of TGMCl



NMR Spectrum 5 ¹H NMR (600 MHz, CDCl₃, 298K) and ¹³C NMR (151 MHz) of MEETMi



NMR Spectrum 6 $^1\mathrm{H}$ NMR (600 MHz, CDCl_3, 298K) and $^{13}\mathrm{C}$ NMR (151 MHz) of IL-C

Section 5. References

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