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SUPPLEMENTARY INFORMATION

Ionic Liquid/Metal-Organic Framework Hybrid Generated by Ion-Exchange Reaction: Synthesis and Unique Catalytic Activity

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Experimental

General methods

All chemicals and solvents used in this research were of reagent grade and used without further purification. X-ray powder diffraction data were collected on a Rigaku RINT-2200 Right System (Ultima IV) diffractometer with CuKα radiation. XPS spectra were collected by X-ray photoelectron spectrometer (JEOL JPS-9010MC) with Mg Kα radiation. MOF powders were placed on Indium substrate, and Cr 2P, C 1S, S 2P, N 1S and Cl 2P peaks were observed. Thermogravimetric analyses were recorded on a Rigaku Thermo plus TG-8120 apparatus in the temperature range between 298 and 773 K at a heating rate of 5 $Kmin^{-1}$. SEM measurements were executed by JSM-7001FA, JEOL. Elemental analysis of the obtained sample was performed using SEM equipped with an energy-dispersive X-ray (EDX) microanalyzer operating at 15 kV. ^{1}H NMR spectra were recorded on a JEOL JNM-A500 spectrometer. The ^{1}HNMR chemical shifts are referenced to the residual internal $CDCl_3$. FT-IR spectra were obtained using a FT/IR-6300 spectrometer (JASCO) using ATR technique. Sorption isotherm measurements were recorded using an automatic volumetric adsorption apparatus (BELSORP-max; BEL Japan). The as-synthesized samples were evacuated under high vacuum ($<10^{-2}$ Pa) at 393 K for 2 hrs to remove guest molecules.

Synthesis of MIL-101(SO_3H)

Monosodium 2-sulfoterephthalic acid (3.35 g, 12.5 mmol), CrO_3 (1.25 g, 12.5 mmol) and concentrated aqueous hydrochloric acid (0.91 g (12 N), 25 mmol) were dissolved in water (50 ml), then transferred to Teflon-lined stainless steel autoclave. The resulting solution was heated at 453 K for 6 days under hydrothermal conditions. The reaction product was finally obtained after washing three times with DMF under sonication.

Syntheses of ILs@MIL-101(SO_3H)

In a typical procedure, 50 mg of MIL-101(SO_3H) was added in 1ml of BMimCl and the resulting suspension was heated at 120 ^oC under vacuum for 12 hrs. After filtration, thorough washing by methanol overnight with soxhlet apparatus and drying in vacuo, green powder of BMimCl@MIL-101(SO_3H) was obtained.

Reaction of alkene substrates with CO_2 gas

In a typical procedure, BMimCl@MIL-101(SO_3H)(10 mg, 0.15 mol% [$BMim^+$]) and propylene oxide (0.25 ml, 3.4 mmol) were put into pressurized vessel and then started the reaction at 120 ^oC after introducing CO_2 gas. After the reaction, the reaction was checked by ^{1}HNMR

measurement.

Supporting data

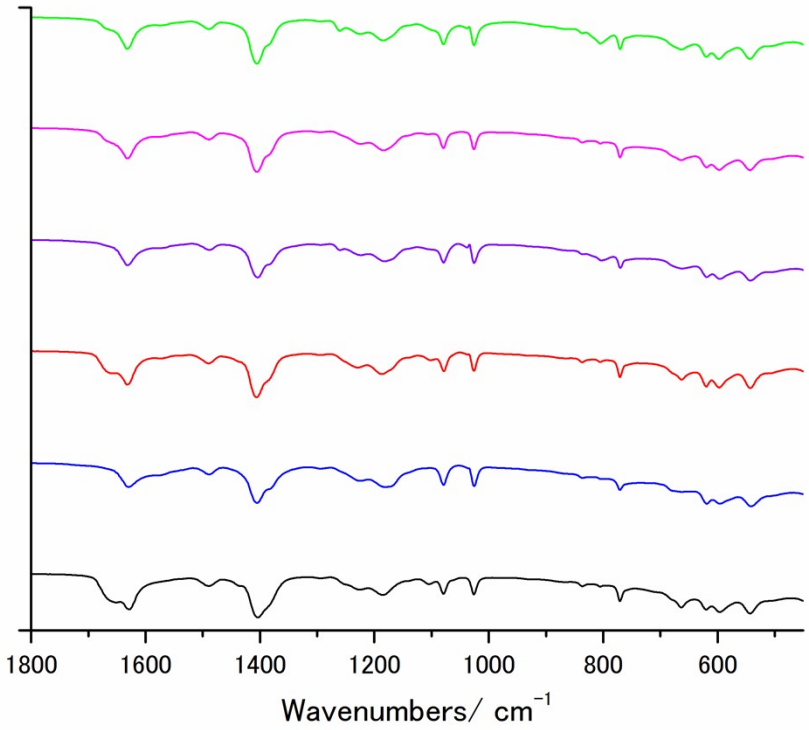

Fig. S1. IR spectra of MIL-101(SO_3H) and ILs@MIL-101(SO_3H). black line: MIL-101(SO_3H); blue line: EMimCl@MIL-101(SO_3H); red line: BMimCl@MIL-101(SO_3H); purple line: MOimCl@MIL-101(SO_3H); pink line: $BMimBF_4$@MIL-101(SO_3H); light green line: BMimBr@MIL-101(SO_3H).

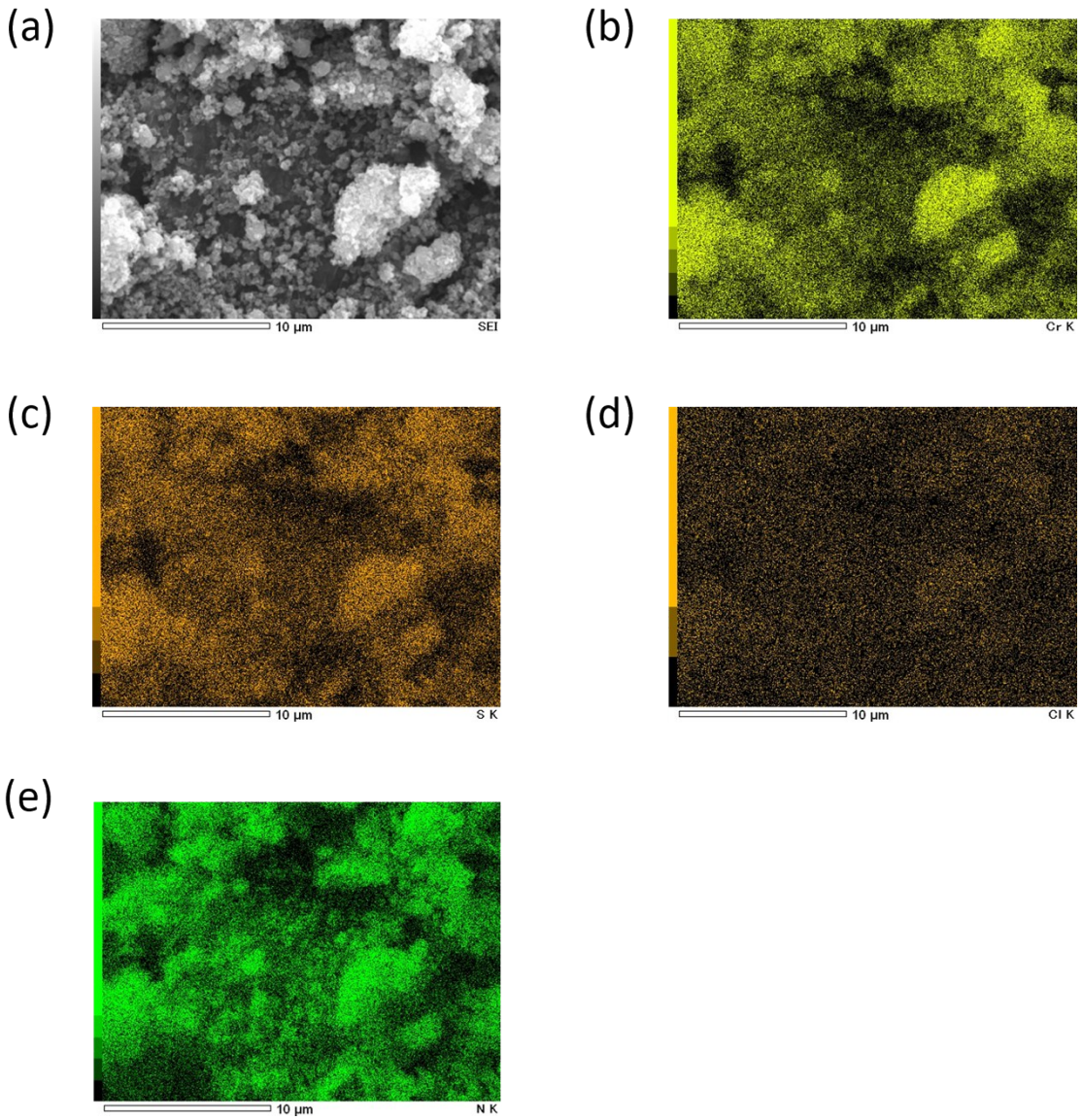

Fig. S2. (a) SEM image of BMimCl@MIL-101(SO_3H), EDX mapping of (b) Cr, (c) S and (d) Cl elements of BMimCl@MIL-101(SO_3H).

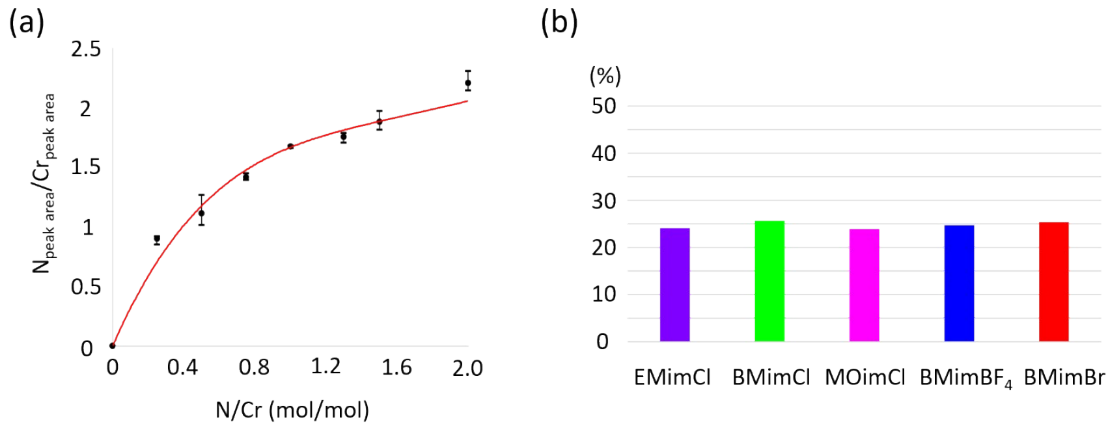

Fig. S3. (a) The calibration curve generated from XPS measurements with the standard samples obtained by controlled mixing of MIL-101 and BMimCl. The y axis corresponds to the peak area ratios (N/Cr) obtained from XPS measurements. The x axis corresponds to the actual molar ratios in the samples. (b) Percentage of SO_3H groups in MIL-101(SO_3H) showing the ion-exchange reactions with corresponding ILs.

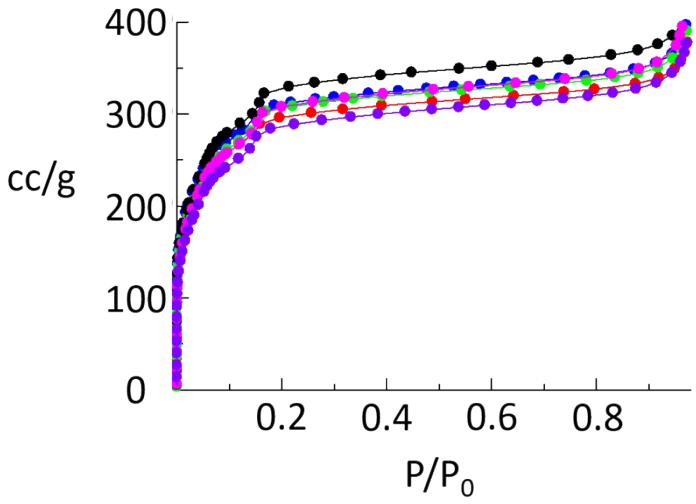

Fig. S4. N_2 adsorption isotherms at 77 K of ILs@MIL-101(SO_3H). black line: MIL-101(SO_3H); blue line: EMimCl@MIL-101(SO_3H); red line: BMimCl@MIL-101(SO_3H); purple line: MOimCl@MIL-101(SO_3H); pink line: $BMimBF_4$@MIL-101(SO_3H); light green line: BMimBr@MIL-101(SO_3H).

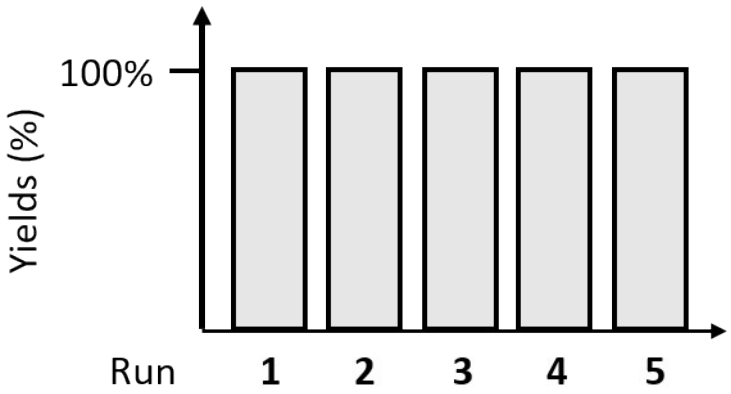

Fig. S5. The progress of the reaction yields of poly(propylene oxide) along with the repeated usages of BMimCl@MIL-101(SO_3H) as catalyst.

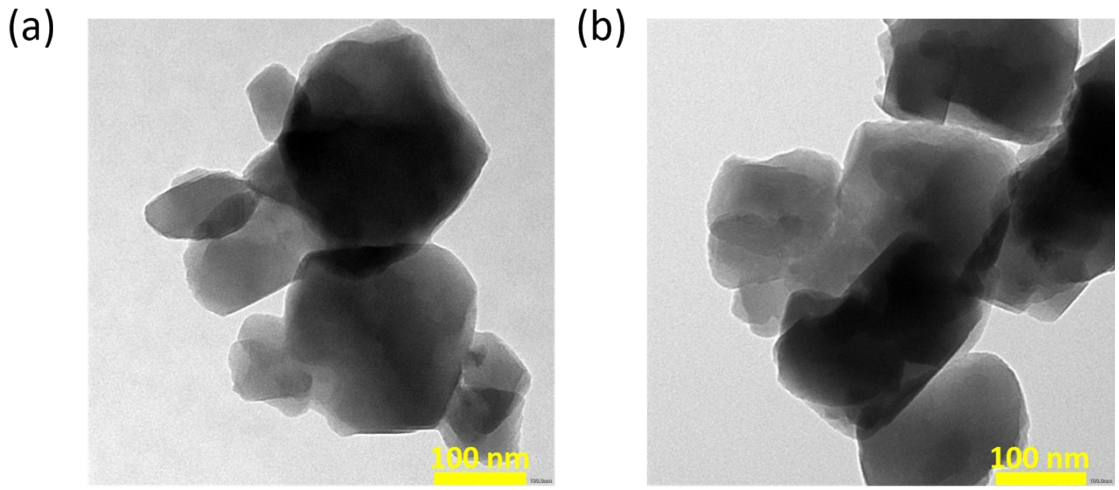

Fig. S6. TEM pictures of (a) MIL-101(SO_3H) and (b) BMimCl@MIL-101(SO_3H).

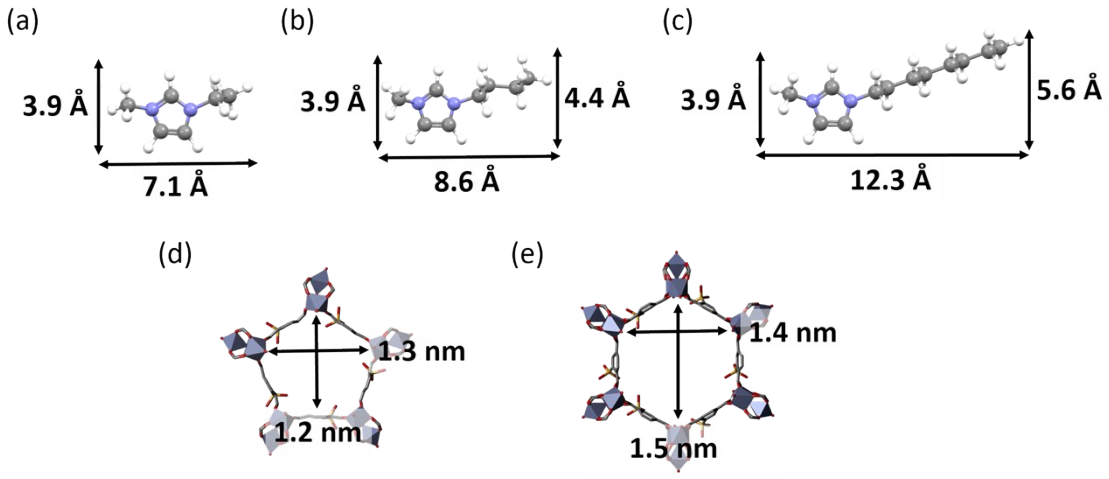

Fig. S7. Molecular sizes of (a) EMimCl, (b) BMimCl and (c) MOimCl. (d)(e) Pore window sizes of MIL-101(SO_3H).

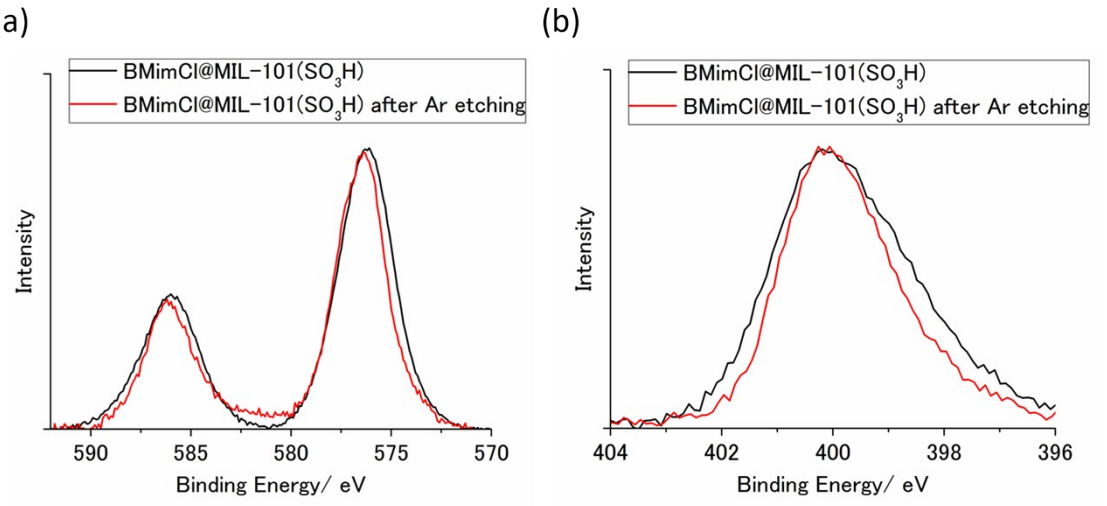

Fig. S8. XPS spectra of BMimCl@MIL-101(SO_3H) before and after Ar ion-beam etching. Close-up peaks of (a) Cr 2p and (b) N 1s.