Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Get Rid of the Shackle from Supports: Construct Recoverable Semi-Homogeneous Catalysts with Attapulgite

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Contents

1. Methods

General information

Carbon dioxide (CO_2, 99%) was purchased from commercial sources and used without further purification. ATP were purchased from Jiangsu jiuchuan nanomaterials technology co. Ltd. The following structural formula is proposed for our ATP: $(Mg_{2.86}Fe_{0.22}Al_{0.92})(Si_{7.69}Al_{0.31})O_{20}(OH)_2(OH_2)_4E^+_{1.17}(H_2O)_4$ (E represents exchangeable cation). The reagents used in the experiment are all commercially available analytical reagents. The infrared spectra were recorded on a Burker VERTEX 70 FTIR spectrometer using KBr pellets in the 400-4000cm^{-1} region. In situ di□use reflectance infrared FT-IR spectra were performed on a BRUKER TENSOR27 FT-IR instrument. The ^1H NMR data were collected on a JNM-ECS 400M NMR spectrometer. Scanning electronic microscopy (SEM) images were recorded on an Apreo S electron microscope operating at 30kV. The contents of C, H and N were tested and recorded by Eelementar Vario EL elemental analyzer.

Preparation of CTA/ATP Catalyst

The mixture of attapulgite (5.0 g), cetyltrimethylammonium bromide (0.5 g) was vigorous stirred under ultrasonic dispersion in ultrapure water (50 mL) for 2 hours. The product was centrifuged and dried (100 °C; 12 h). After drying, the white powder was collected for use.

Verification of Catalytic Performance

The mixture of epichlorohydrin (0.925 mg), CTA/ATP catalyst (40.0 mg) and was added to the high pressure steel kettle with PTFE liner. Carbon dioxide gas (1.8 MPa) was filled into the kettle and reacted at a certain temperature for a specific time. After the reaction, the mixture in the reactor was taken out with dichloromethane and the conversion rate was calculated by ^1H NMR.

Through centrifuging, washing (ultrapure water 10 mL*2 and dichloromethane 10 mL*2) and drying (100 °C; 12 h), catalyst was reused in reaction cycles. The catalytic performance test process of reaction cycles is the same as before.

2. Catalyst characterization

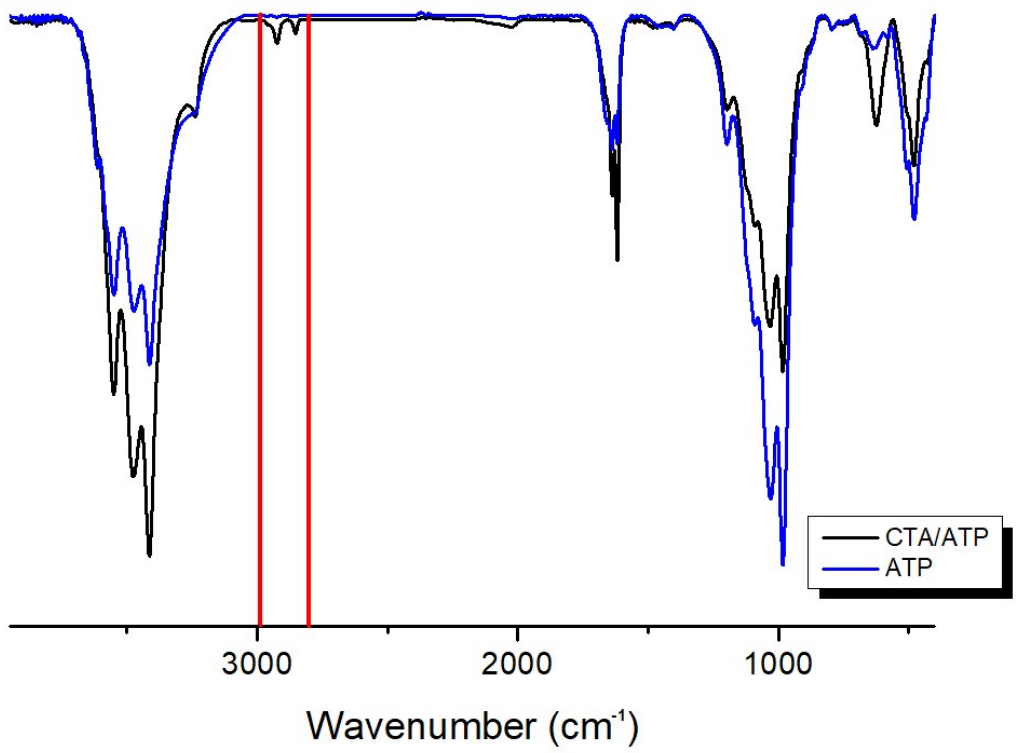

Figure S1 Infrared Spectroscopy spectrum of ATP and CTA/ATP.

Table S1. The major element of ATP analyzed by EDX.[1]

Element	O	Si	Mg	Al	Fe
Atomic (%)	68.1	20.4	7.6	3.1	0.7
Weight (%)	55.3	29.0	9.3	4.3	2.1

3. Catalysis details

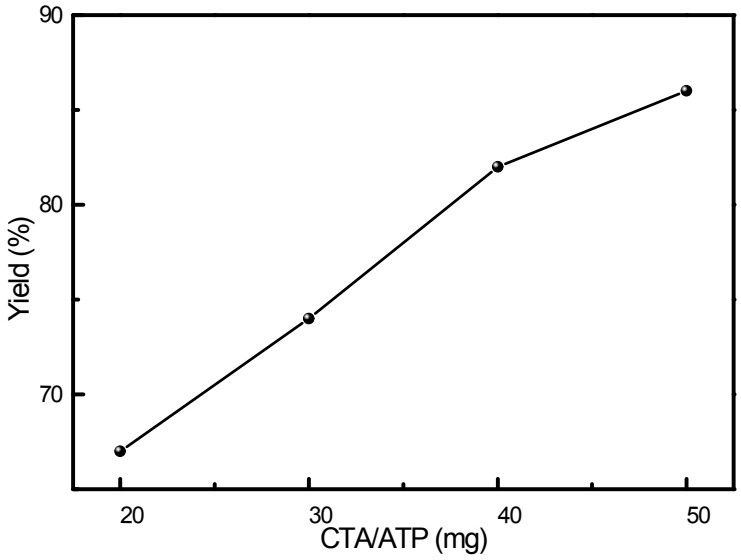

Figure S2. Effect of catalyst content on the yield. Reaction conditions: 10 mmol epichlorohydrin, 4 h, 120 °C, 1.8 MPa CO_2.

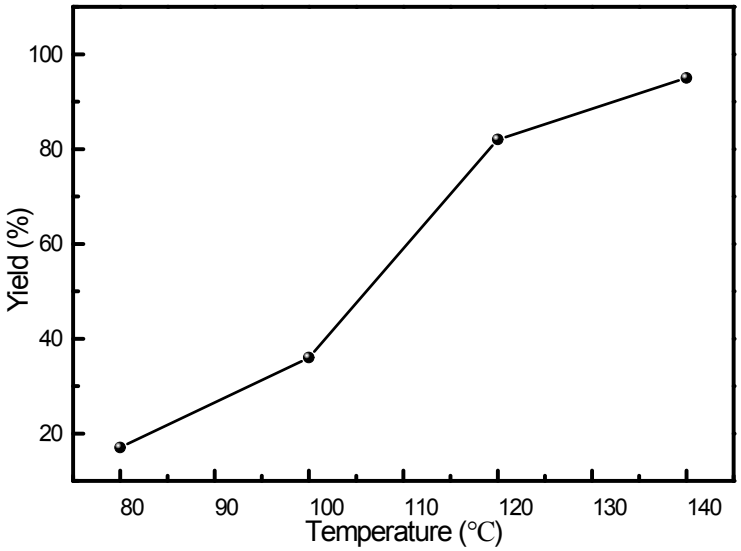

Figure S3. Effect of temperature on the yield. Reaction conditions: 10 mmol epichlorohydrin, 40mg catalyst, 4 h, 1.8 MPa CO_2.

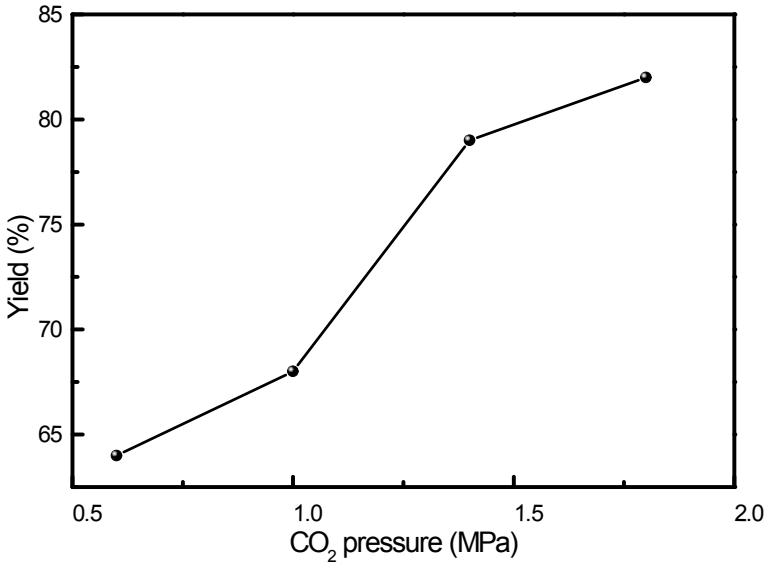

Figure S4. Effect of pressure on the yield. Reaction conditions: 10 mmol epichlorohydrin, 40mg catalyst, 4 h, 120 °C.

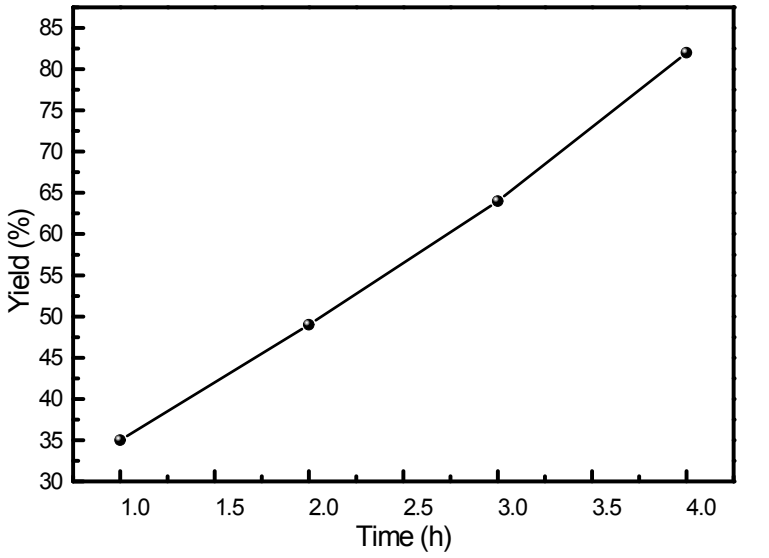

Figure S5. Effect of time on the yield. Reaction conditions: 10 mmol epichlorohydrin, 40mg catalyst, 120 °C, 1.8 MPa CO_2.

Table S2. Performance of different catalytic systems.

Entry	Epichlorohydrin (mmoL)	Catalyst	CO_2 (MPa)	t (h)	T (°C)	Yield (%)	TOF[a)] (h^{-1})	Ref.
1	50.0	SBA-15-IL1Br 1.0 moL%	2.0	2	110	99	49.5	[2]
2	34.5	TEA(2.0)/SBA-15 0.2 g	2.0	3	110	99	24.2	[3]
3	134.0	MCM-41-Imi-All/Br 0.2 g	1.5	8	150	69	24.6	[4]
4	10.0	CTA/ATP 40mg	1.8	4	120	50	543.5	This work

[a)] TOF: mole of product per mole of catalyst per hour.

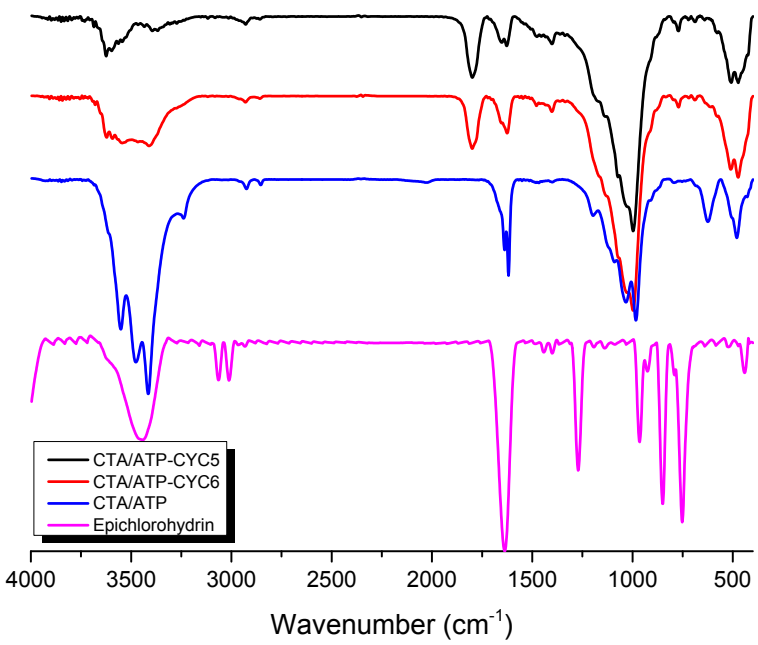

Figure S6. Infrared Spectroscopy spectrum

4. ^{1}H NMR spectra

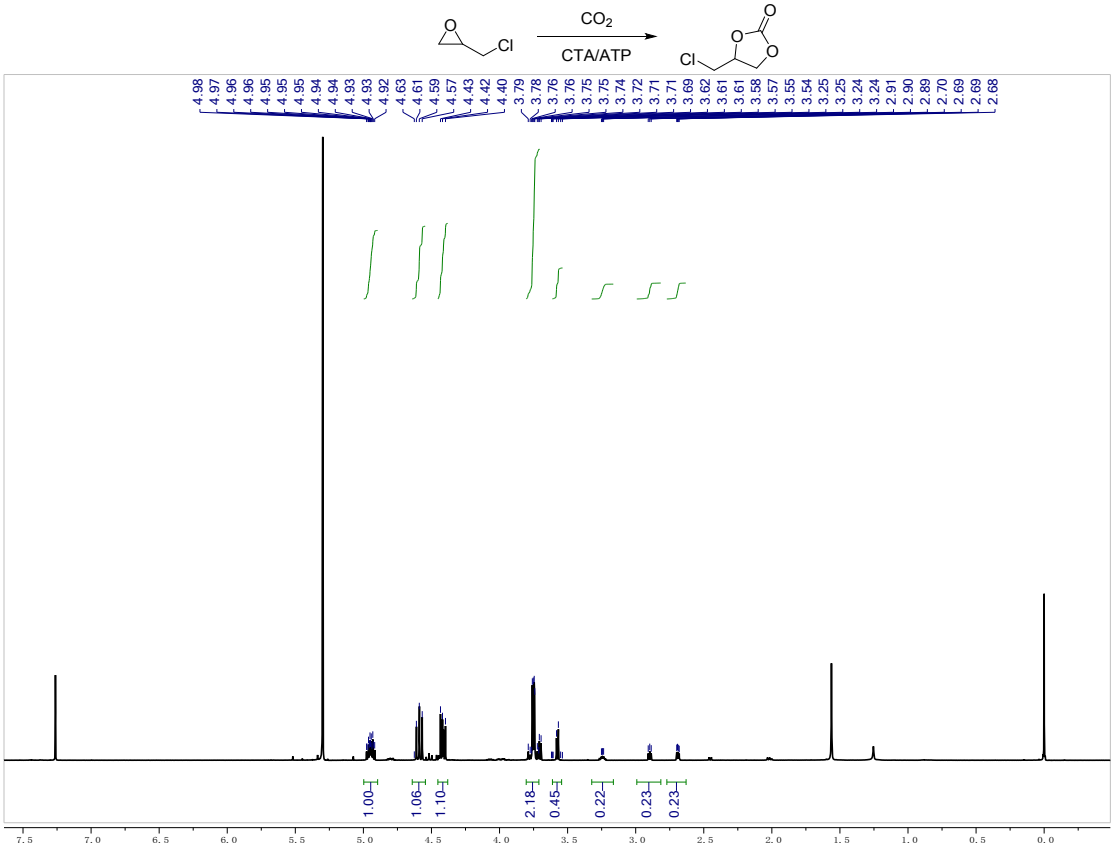

Figure S7. ^{1}H NMR spectra of the main reaction

Reactant: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.57 (d, 2H), 3.24 (dtd, 1H), 2.90 (t, 1H), 2.69 (dd, 1H).

Product: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.95 (dtd, 1H), 4.59 (t, 1H), 4.42 (dd, 1H), 3.74 (ddd, 2H).

5. References

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