

Electronic Supplementary Information

Facile fabrication of heterogeneous Co-modified pyridinecarboxaldehyde-polyethylenimine catalyst for efficient CO₂ conversion under mild conditions

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Experimental Section

Materials

Branched polyethyleneimine (PEI, M_w of 10000), 2-Pyridinecarboxaldehyde (Py), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, KCl, Bu_4NBr , Bu_4NI and epoxides were all obtained from Aladdin Chemical Co. KBr was acquired from Sinopharm Chemical Reagent Co. Ltd. KI was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. Bu_4NCl was supplied by Shanghai Macklin Biochemical Co. Ltd. Ethanol, acetonitrile and ethyl acetate were provided from Tianjin Fuyu Fine Chemical Co. Ltd. Carbon dioxide (99%) was purchased from Harbin Liming Gases Co. Ltd.

Synthesis of M-Py-PEI catalyst

The Py-PEI was prepared through the Schiff base reaction and the synthetic method was shown in **Scheme 2**. PEI (0.250 g, containing 1.9 mmol $-\text{NH}_2$ based on ^{13}C NMR result and elemental analysis), Py (0.208 g, 1.9 mmol) and 30 mL acetonitrile were mixed in a 100 mL three-necked flask. The flask was mildly stirred and heated at 80 °C for 24 h. After cooling to room temperature, the resultant precipitates were obtained by simple centrifugation. The products were washed with acetonitrile and ethyl acetate for several times, then dried at 100 °C for 24 h.

Taken the Co-Py-PEI as an example, PEI (0.250 g, 1.9 mmol $-\text{NH}_2$), Py (0.208 g, 1.9 mmol) and 30 mL acetonitrile were mixed in a 100 mL three-necked flask. The flask was mildly stirred and heated at 80 °C for 24 h. Subsequently, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.476 g, 1.9 mmol) was then added into the above mixture and stirred at 80 °C for 48 h. After cooling to room temperature, the brown powders were collected by simple centrifugation. Then powders were washed with acetonitrile and ethyl acetate for several times, then dried at 100 °C for 24 h. The synthetic step for other M-Py-PEI was similar, the main difference was that the corresponding $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.384 g, 1.9 mmol) or $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.474 g, 1.9 mmol) were used to replace $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$.

Characterization

FT-IR spectra were performed on PerkinElmer Spectrum 100. Solid-state ^{13}C NMR was detected by a Varian Infinity Plus 400 NMR spectrometer. Liquid-phase ^{13}C NMR was collected by Bruker AV-400 MHz spectrometer. TGA data was acquired on a

NETZSCH STA449F3 simultaneous thermogravimetric analyzer under N₂ atmosphere. X-ray photoelectron spectroscopy (XPS) was conducted by a Thermo Fisher Scientific Escalab 250Xi. Elemental Analysis (EA) was performed on the Vario MICRO cube CHN analyzer. Inductively coupled plasma optical emission spectrometer (ICP-OES) analysis was conducted by PerkinElmer 8300 instrument. Scanning electron microscopy (SEM) equipped with Energy Dispersive Spectrometry (EDS) was detected by a Hitachi SU8000. GC analyses were measured on an Agilent GC-7890A.

Catalytic cycloaddition of epoxide and CO₂ to cyclic carbonate

All the experiments for CO₂ cycloaddition reactions were performed in a stainless-steel autoclave. Typically, propylene oxide (PO, 34.5 mmol), Co-Py-PEI (0.200 g) and cocatalyst Bu₄NBr (2 mol% to PO) were added into the autoclave. Thereafter, the autoclave was heated to the target temperature and then CO₂ was injected to required pressure for a desired time. After the reaction, the autoclave was cooled to room temperature and depressurized slowly. The mixtures were diluted with ethyl acetate and calculated by Agilent GC-7890A. The spent catalyst Co-Py-PEI was centrifuged, and washed with ethyl acetate, the resulted powders were dried at 100 °C for 12 h and reused directly for the next run.

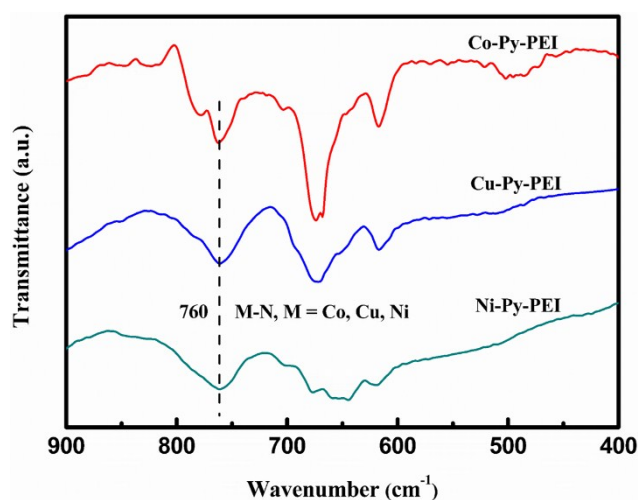


Fig. S1 FT-IR spectra of M-Py-PEI

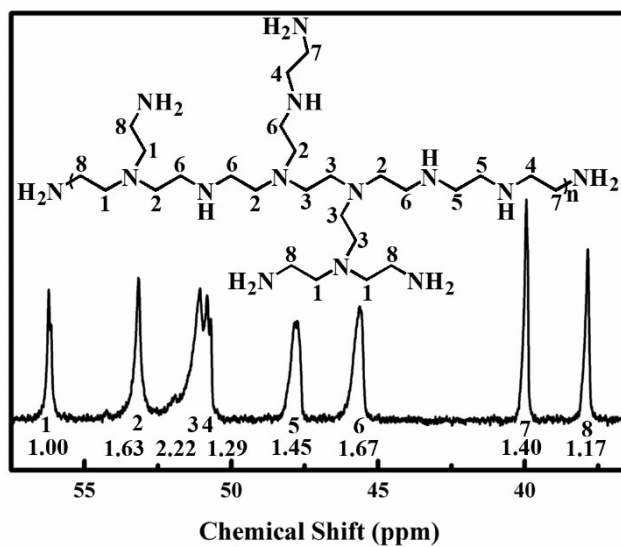


Fig. S2 Liquid-phase ^{13}C NMR spectrum of pure PEI, the sample was dissolved in D_2O .