# Supporting Information

## Enhancing Catalytic Amine Regeneration in $CO_2$ Capture Using $ZrO_xH_y$-Coated Mesoporous Silica

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### 1. Chemicals and Materials

Monoethanolamine (MEA, 99%), and zirconium(IV) oxynitrate hydrate (99%) were ordered from Sigma Aldrich. NaOH (extra pure) was ordered from ACROS Organics NV. MCM-41 (full $SiO_2$) was ordered from Nankai university catalyst co ltd. $SiO_2$ was ordered from ThermoFisher.

30 wt% MEA solution were prepared with deionized water.

### 2. Catalyst Synthesis

$ZrO_xH_y$ was synthesized by adding a proper amount of NaOH solution into 400 mL of 2.5 M $ZrO(NO_3)_2$ solution with violent stirring until the solution reached the aiming pH. The obtained mixture was aged at room temperature for 3 h with stirring. The mixture was then centrifuged and washed with distilled water, then dried at 100 °C overnight.

Zr-MCM-41 was synthesized by dispersing 5 g of MCM-41 powder into 160 mL of 0.3 M $ZrO(NO_3)_2$ solution under stirring for 10 min, followed by ultrasonication for 15 min. A NaOH solution (45 mL, 1.25 M) was then slowly added into the suspension with vigorous stirring until the pH reached 5. The resulting mixture was aged for 3 h at room temperature under stirring, centrifuged, and washed three times with distilled water. The solid product was dried at 100 °C for 24 h, yielding 8.3 g of Zr-MCM-41.

### 3. Experimental Apparatus and Procedure

The $CO_2$-rich amine solution used for desorption experiments was prepared as follows: 200 mL $min^{-1}$ 15% $CO_2/N_2$ was passed through 630 mL of 5 M MEA solution under 40 °C, 500 rpm stirring for 12 h to obtain $CO_2$-saturated MEA solution. The $CO_2$ loading in $CO_2$-saturated MEA is 0.527 mol$CO_2$ mol $_{MEA}{}^{-1}$. The absorption of AMP followed similar procedures.

An experimental apparatus for solvent regeneration (i.e. $CO_2$ desorption) consists of a 250 mL round-bottom flask equipped with a thermometer, a heater controlled by a temperature controller, a condenser, and a magnetic field stirrer (see **Figure S4.** ). For a typical $CO_2$ desorption experiment, 150 mL 5 M MEA solution with initial $CO_2$ loading of 0.527 mol$CO_2$ $mol^{-1}{}_{MEA}$ and 3 g catalyst are mixed in the reactor. A continuous $N_2$ (500 mL $min^{-1}$) flow was blowing from the top of the condenser to carry desorbed $CO_2$ out for further analysis. Then, the solution was heated to 88 °C for 50 ± 5 min and kept at this temperature for 180 min with a stirring rate of 500 rpm. The time when the temperature of the solution reached 88 °C is noted as 0 min.

The $CO_2$ loading in the solution was analyzed by Chittick equipment with an average absolute relative deviation of less than 5%. 1 mL 1.5 M $H_2SO_4$ were used for titration to ensure the complete release of $CO_2$ from amine samples. Typically, 500 μL $CO_2$-loaded amine solution samples were added to the flask by a calibrated pipette, and then 1 mL of 1.5 M $H_2SO_4$ was injected into the solution under stirring. The volume of released $CO_2$ was recorded to calculate the $CO_2$ loading of the sample. Every sample was tested three times, and the average value was adopted.

**3. Catalyst Characterization**

$N_2$ absorption measurements were performed using a Micromeritics Instruments Tristar 3000 at 77 K. The samples were degassed under $N_2$ flow at 200 °C for 6 h prior to measurement. The relative nitrogen pressure was varied between 0.01 and 0.99 (p/p0). Pore volumes were calculated by the t-plot method.

Transmission electron microscope (TEM) images were obtained using an aberration-corrected JEOL ARM200F Microscope that was operated at an electron acceleration voltage of 200 kV and equipped with a cold field-emission electron gun (FEG). High-angle angular dark field (HAADF) and Bright-field (BF) imaging were performed in Scanning TEM (STEM) mode with BF and HAADF detectors. Energy Dispersive X-ray spectroscopy analysis of Si and Zr in the sample was carried out utilizing a Centurio EDXS detector with a solid angle of 0.98 steradians from a 100 $mm^2$ detection area. To prepare the samples, a sonicated particle suspension was dropped on a holey carbon-coated TEM grid (Cu, 400 mesh, Agar Scientific).

XPS measurements were carried out on a SSI X probe spectrometer (model SSI 100, Surface Science Laboratories, Mountain View, CA) equipped with a monochromatized Al-Kα radiation (1486 eV). The pressure in the analysis chamber was around 10−6 Pa. The analysed area was ~1.4 $mm^2$ and the pass energy was set at 150 eV. A flood gun set at 8 eV and a Ni grid placed 3 mm above the sample surface

were used for charge stabilisation. Si2p peak of silicon was fixed to 103.5 eV to set the binding energy scale. Molar fractions were calculated using peak areas normalised based on acquisition parameters and sensitivity factors provided by the manufacturer.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed using an FTIR spectrometer (iS50 FT-IR, Thermo Scientific) equipped with a liquid nitrogen cooled MCT detector and a diffuse reflectance cell (Harrick Praying Mantis). KBr was used as the background material. The sample powders were finely ground and loaded into the sample cup of the DRIFTS cell without dilution. Infrared spectra were recorded in the range of 4000–650 $cm^{-1}$ with a spectral resolution of 0.241 $cm^{-1}$, averaging 64 scans for each spectrum. Prior to spectra collection, each sample was heated under a flow of $N_2$ to the desired temperature at a ramping rate of 10 °C $min^{-1}$.

## 4. Calculation

### 4.1 Calculation of $k_{cat}$

Assuming the $CO_2$ desorption is a first-order reaction,

$$ln(\frac{C_t}{C_0}) = -k_{overall} \times t$$

Where $C_0$ and $C_t$ represent the $CO_2$ loading in the MEA solvent ($molCO_2\ mol_{MEA}^{-1}$) at the beginning of the isothermal stage (0 min) and t min. Five data points (0, 30 min, 60 min, 90 min, 120 min, and 180 min) were collected to calculate $k_{overall}$.

For $CO_2$ desorption with catalysts:

$$k_{cat} = k_{overall} - k_{blank}$$

### 4.2. Weisz-Prater criterion

$$C_{WP} = \frac{kR^2}{D_{eff}}$$

Where, k is the observation First-Order Rate constant ($s^{-1}$);

R is the particle radius which is 0.125 mm (in our condition);

$D_{eff}$ is the diffusivity of the reactant in the MCM-41 pores. Calculated as below:

$$D_{eff} = \frac{\varepsilon}{\tau} D_{bulk}$$

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$D_{bulk}$ is the bulk molecular diffusivity values reported for small species in aqueous carbamate/protonated MEA ( $\approx 10^{-9}$ $m^2$ $s^{-1}$). The particle porosity $\varepsilon \approx 0.55$ was calculated from $N_2$ physisorption data and a tortuosity factor of $\tau \approx 2$ was adopted considering the ordered cylindrical pore structure of MCM-41.

## 5. Supporting Figures

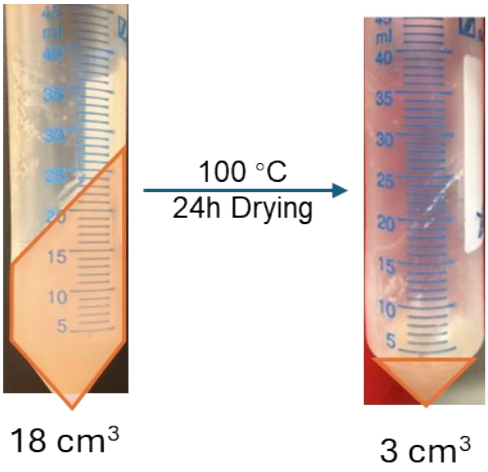


**Figure S1.** Photo of $ZrO_xH_y$ gel before and after drying process.

**Table S1. Isothermal results of $N_2$ physisorption of MCM-41 and Zr-MCM-41**

| | $S_{BET}$ ($m^2$ $g^{-1}$) | $V_{meso}$ ($cm^3$ $g^{-1}$) | BJH pore size (nm) |
|---|---|---|---|
| MCM-41 | 891 | 0.77 | 2.8 |
| Zr-MCM-41 | 825 | 0.54 | 2.5 |

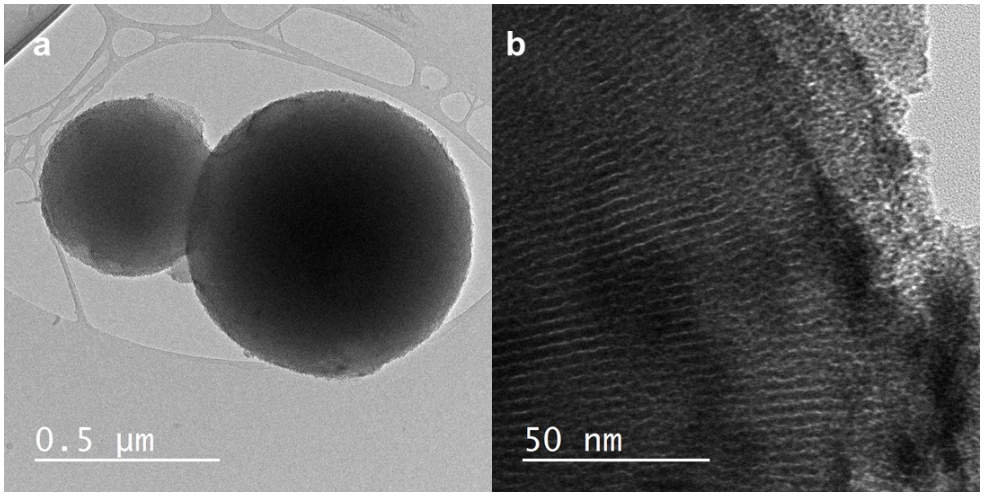


**Figure S2.** TEM images of Zr-MCM-41 (32 wt%).

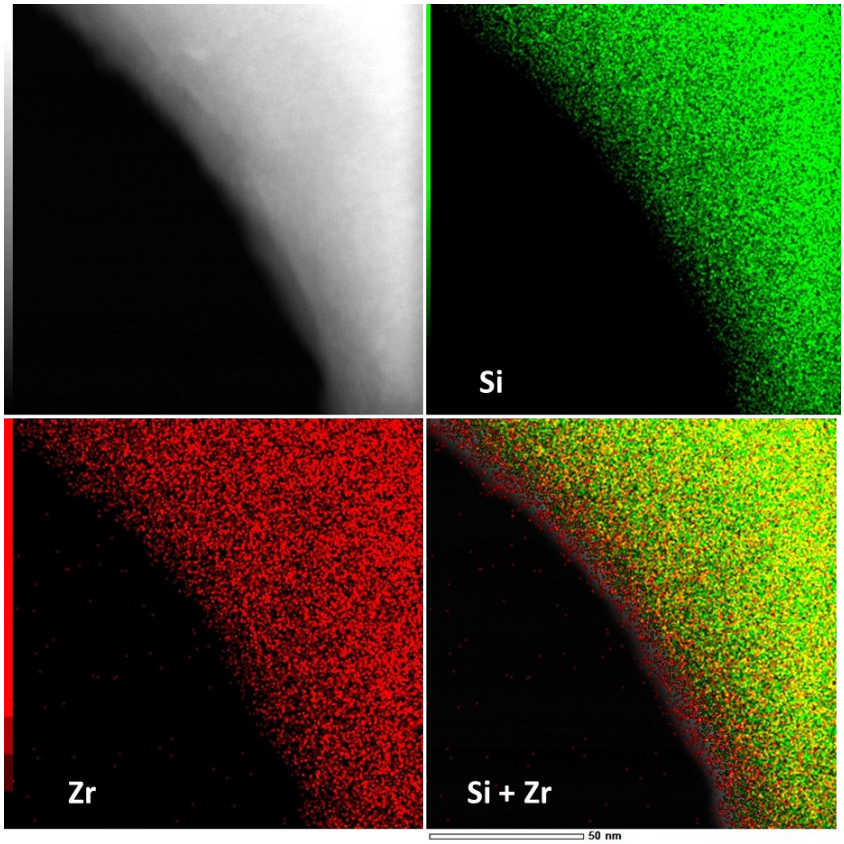


**Figure S3.** EDX mapping STEM images on Si (green), Zr(red) elements for Zr-MCM-41 (32 wt%).

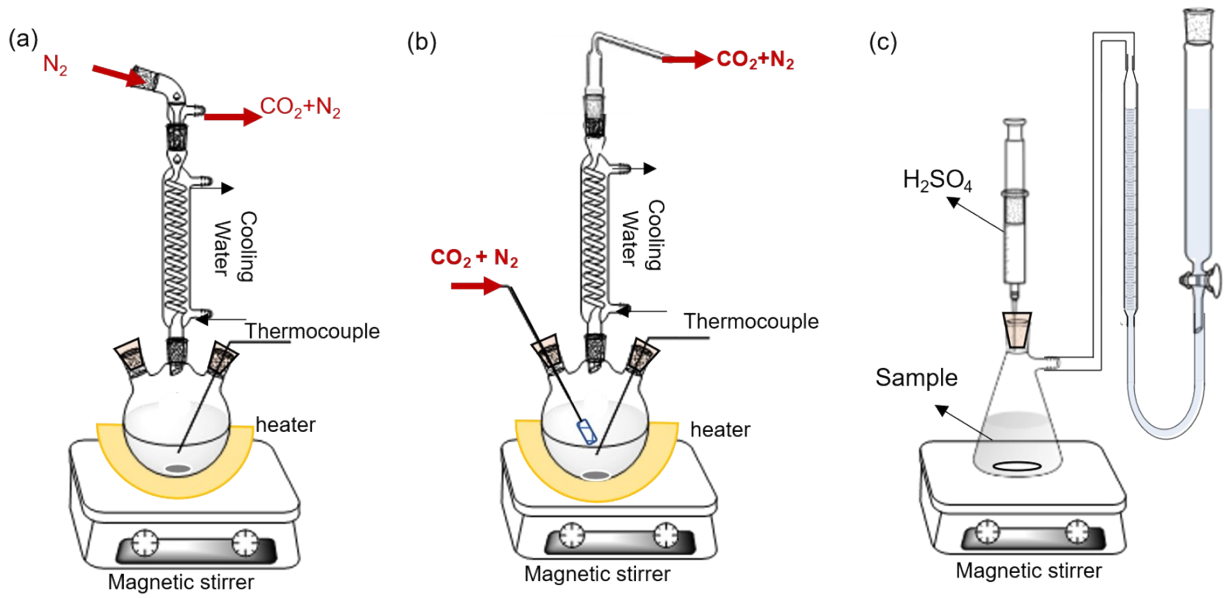


**Figure S4.** (a) the batch reactor for $CO_2$ desorption with amine solution (b) $CO_2$ absorption reactor for producing $CO_2$ saturated amine. (c) Chittick apparatus for titrating the $CO_2$ loading in the amine solution .

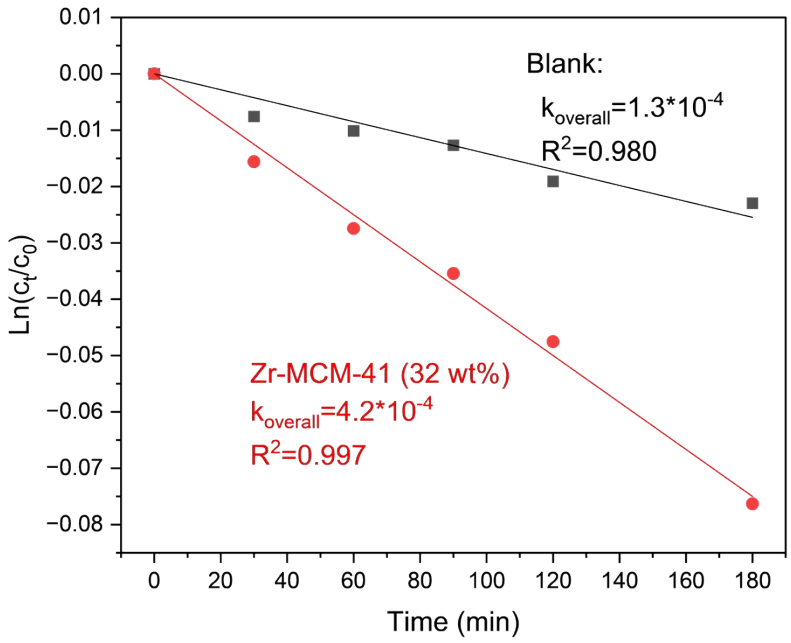


**Figure S5.** Overall kinetic constant of $CO_2$ desorption without and without catalyst. Reaction conditions: 150 mL $CO_2$-saturated 30 wt% MEA, 3 g catalyst, $N_2$ flow 0.5 L $min^{-1}$ at the condenser top, 88 °C.

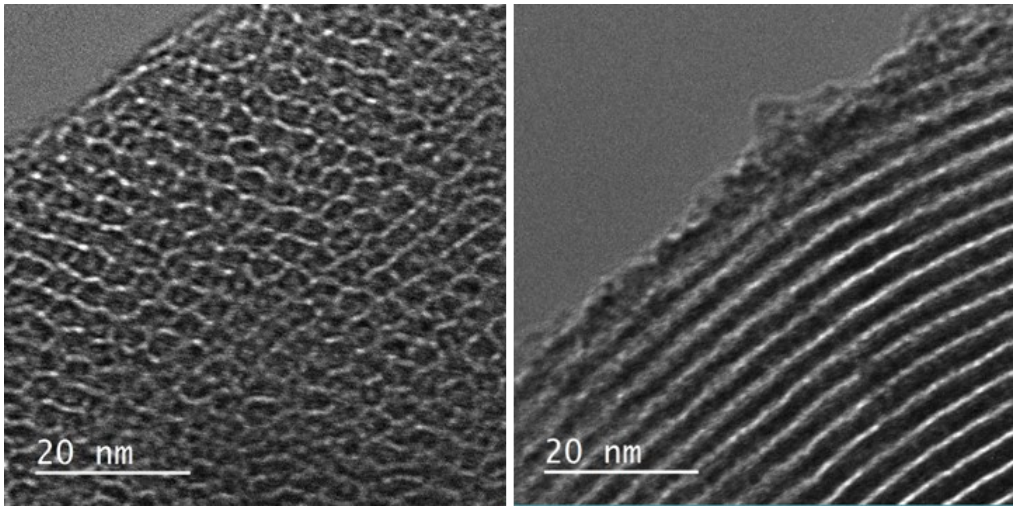


**Figure S6.** HR-TEM of Zr-MCM-41 (13 wt%).

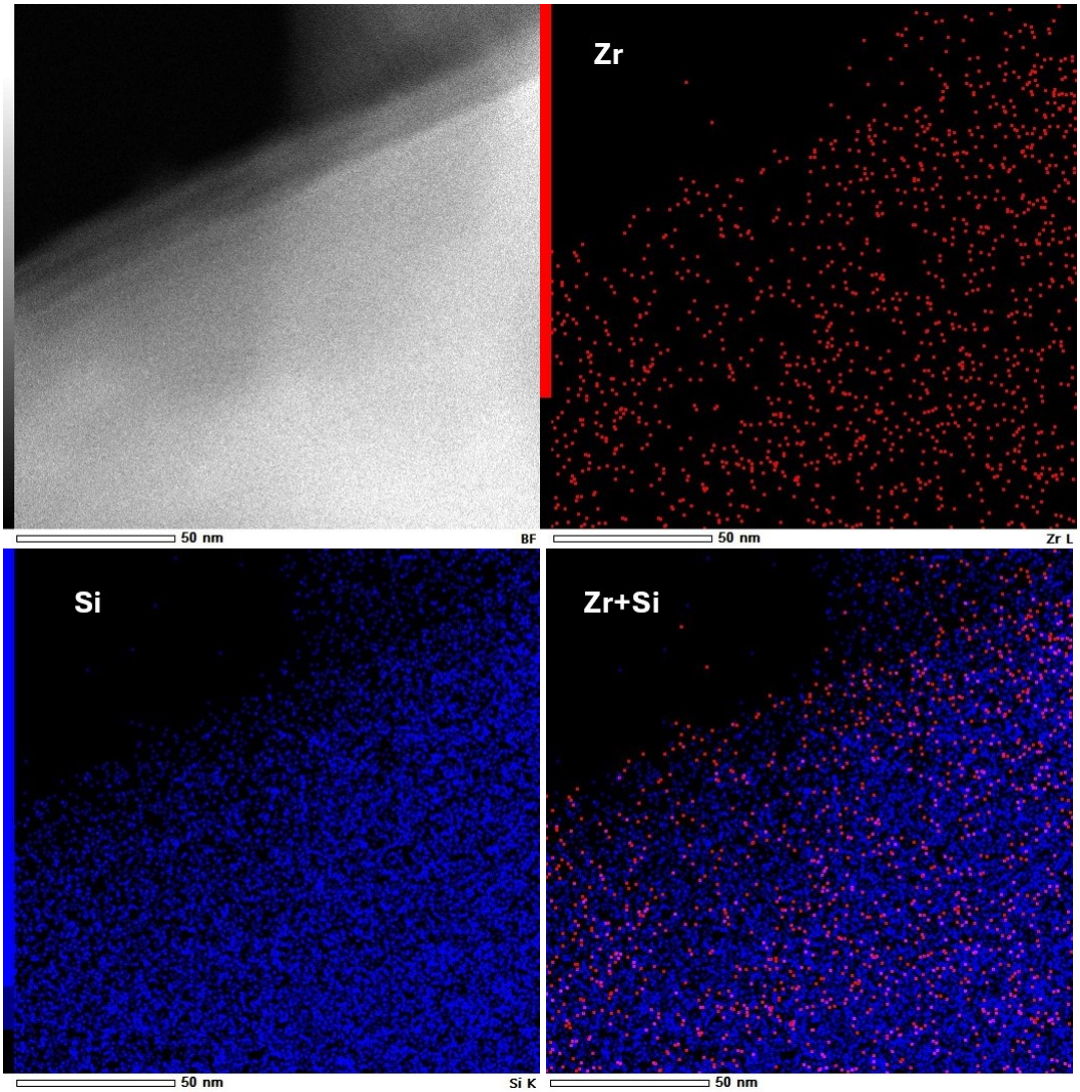


**Figure S7.** EDX mapping TEM of Zr-MCM-41(13 wt%) with element of Zr and Si.

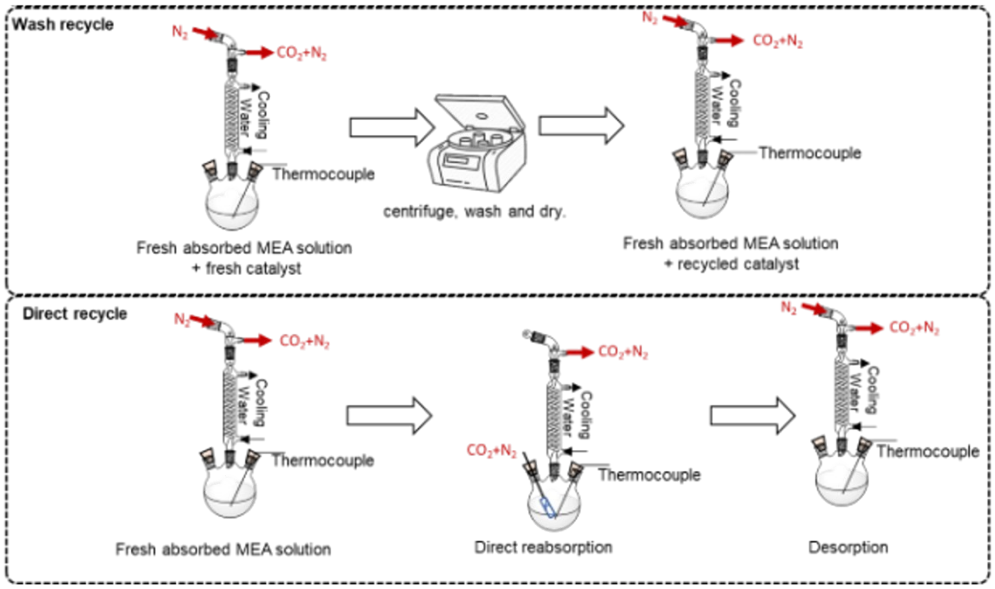


**Figure S8.** $ZrO_xH_y$ recycled through different methods.