Supporting Information

Decomposition of CO_2 to Carbon and Oxygen under Mild Conditions over a Zinc-modified Zeolite

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1. Materials

The gases CO_2 (> 99.997%) and O_2 (> 99.999%) were supplied by Shanghai Chengkung Gas Co., Ltd. Metallic Zn (A.R.), zinc nitrate hexahydrate (A.R.) and zinc acetate dihydrate (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. The NaY zeolite was prepared by the procedure described in the literature. (L. Li, X. S. Zhou, G. D. Li, X. L. Pan and J. S. Chen, *Angew. Chem. Int. Ed.*, 2009, ***48***, 6678.) The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of the NaY was approximately $Na[AlSi_{2.46}O_{6.92}]$.

2. Experimental Section

2.1 Preparation of HY

The protonated zeolite Y (HY) samples were prepared by calcining their corresponding NH_4-forms in oxygen, whereas the NH_4-form Y materials were obtained through a four-fold ion exchange process from the corresponding Na-forms at 80 ºC in a 1.0 M aqueous solution of ammonium chloride. When an ion-exchange degree of 86 % for zeolite Y was reached, the material was washed in deionized water and dried in an oven at 110 ºC for five hours. Subsequently, the NH_4-form zeolite sample was calcined in oxygen at 500 ºC for 10 hours to achieve the corresponding protonated form. The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of the HY was approximately $H_{0.86}Na_{0.14}[AlSi_{2.46}O_{6.92}]$.

2.2 Preparation of Zn^{2+}-Y

The Zn^{2+}-Y sample was prepared by calcining in oxygen at 500 ºC the Zn^{2+}-exchanged Y which was obtained through a four-fold ion exchange process from the corresponding Na-form Y zeolite at 80 ºC in a 1.0 M aqueous solution of zinc nitrate. The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of Zn^{2+}-Y was approximately $Zn_{0.43}Na_{0.14}[AlSi_{2.46}O_{6.92}]$.

2.3 Preparation of Zn^{2+}-Y^-

The electron-rich Zn^{2+}-Y^- material was prepared by vapor chemical reaction of metallic zinc in the cages of the HY zeolite. First, the HY sample and the metallic zinc were loaded into a Pyrex® (a registered trademark of Corning Incorporated) glass tube at different locations, and the tube system was then evacuated at 500 °C (at the zeolite location) for two hours to remove the water and other molecules adsorbed in the zeolite. Afterwards, the tube with both ends sealed was heated at about 500 °C so that the metallic zinc vaporizes to react with the protons in the HY material. Following this treatment for about 40 hours, the Pyrex® glass tube was evacuated at 450 ºC for another six hours to remove the physically adsorbed Zn atoms (See the schematic preparation procedure). The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of Zn^{2+}-Y^- was approximately $Zn_{0.53}Na_{0.14}[AlSi_{2.46}O_{6.92}]$.

2.4 CO_2 decomposition

The decomposition of CO_2 was conducted in a Pyrex® glass tube reactor loaded in a tube furnace. In order to prevent the electron-rich Zn^{2+}-Y^- sample from deactivation by air and moisture, the experiments were performed under dry Ar atmosphere or vacuum using Schlenk glassware, glove box or vacuum line techniques. After reaction, the resulting zeolite sample was taken out from the reactor in the glove box, and for the following characterization the sample was always under the protection of argon gas. The gas reactant and product were collected from the reaction system with a syringe and analyzed on a Shimadzu GC-2014 gas chromatograph with a Paropak Q, TDX-01 column; column temperature, 70 ºC; carrier gas, H_2; total flow, 30.0 mL/min; injection detector temperature, 100 ºC; thermal conductivity detector (TCD) temperature, 120 ºC. The carbon content in the solid after the decomposition reaction was obtained on a Vario EL III CHNS/O elemental analyzer.

3. Characterization Results, Figures and Table

3.1 Material characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer with Cu Kα radiation (λ =1.5418 Å). The electron paramagnetic resonance (EPR) spectra were obtained on a JES-FA 200 electron paramagnetic resonance spectrometer, and the instrumental parameters were as follows: scanning frequency, 9.45 GHz; central field, 3360 G; scanning width, 8000 G; scanning power, 0.998 mW; scanning temperature, 25 ºC. The magnetic susceptibility data were recorded on a Quantum Design MPMS-5T SQUID magnetic property measurement system. A Perkin-Elmer Optima 3300DV inductively coupled plasma (ICP) spectrometer was used for the ICP elemental analysis. The ^{29}Si MAS NMR measurements were performed on a Varian Infinity plus 400 NMR spectrometer.

The X-ray absorption data at the Zn K-edge of the samples were recorded at room temperature in transmission mode using ion chambers at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The station was operated with a Si (111) double crystal monochromator. During the measurement, the synchrotron was operated at 3.5 GeV and the current was between 150-210 mA. The data for each sample were collected three times and calibrated with standard zinc metal foil. Data processing was performed using the program ATHENA. All fits to the EXAFS data were performed using the program ARTEMIS.

3.2 Proportion of Zn atoms reducing one proton each in the Zn^{2+}-Y^{-} sample

The proportion (x%) of the Zn atoms that reduced one proton each among the total incorporated Zn atoms can be calculated through Equation-S1 derived from charge balance requirement.

$$R_{(Zn/Al)} = \frac{1-R_{(Na/Al)}}{x\% + 2\,(1-x\%)} = 0.53 \qquad \text{Eq.-S1}$$

$R_{(Zn/Al)}$ and $R_{(Na/Al)}$ are the measured atomic ratios of Zn/Al and Na/Al, respectively, on the basis of the ICP analysis. x% is the percentage of the Zn atoms reducing one proton each whereas (1-x%) the percentage of the Zn atoms reducing two closely-positioned protons each among the total zinc atoms incorporated in the zinc-modified zeolite Y.

The value of x % is calculated to be about 38 % in our Zn^{2+}-Y^{-} sample.

3.3 Carbon Mass Balance

The calculation of the carbon balance during the decomposition of CO_2 was performed based on the ratio of carbon output (carbon or CO) to carbon input (CO_2), as shown in Equation-S2:

$$\text{Carbon balance} = \frac{\text{Moles of products in terms of carbon}}{\text{Moles of the inital reactant in terms of carbon}} \times 100\ \% \qquad \text{Eq.-S2}$$

As an example, Entry 1 of Table 1 in the main text presents the amount variation for the reactant (CO_2) and for the products (C and O_2) during the reaction. The data indicate that after 8 hours, the amount of CO_2 varied from the initial 4,000 to 3,580 μmol, and none of carbon monoxide (CO) was detected in our system. The deposited carbon amount was 425 μmol. Therefore, according to Equation-S2, the value of the carbon balance under this condition is calculated to be:

$$\text{Carbon balance} = [(3580 + 425)/4{,}000] \times 100\ \% = 100.1\%$$

Figures and Table

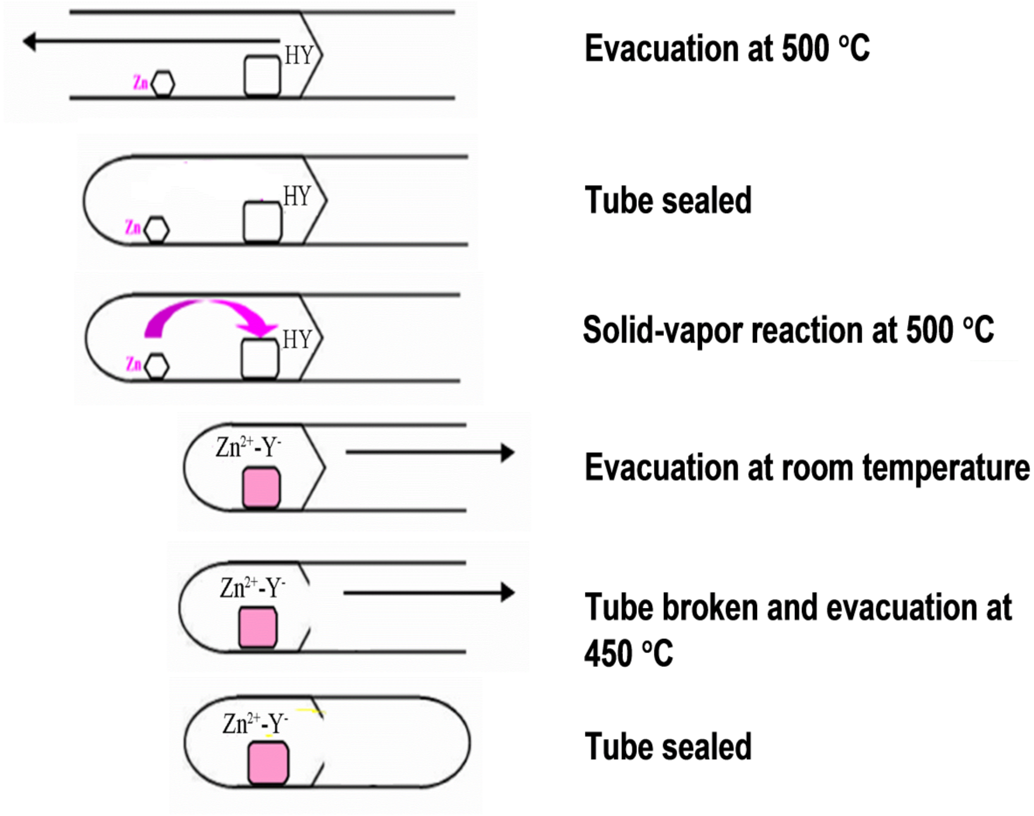

Figure S1. Schematic preparation procedure for the Zn^{2+}-Y^{-} sample.

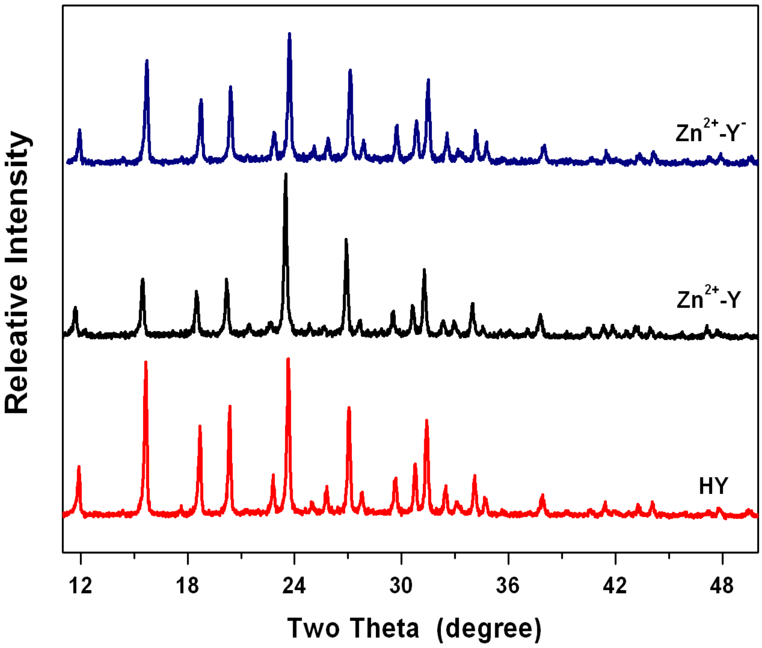

Figure S2. XRD patterns for the samples of zeolite HY, Zn^{2+}-Y , and Zn^{2+}-Y^-.

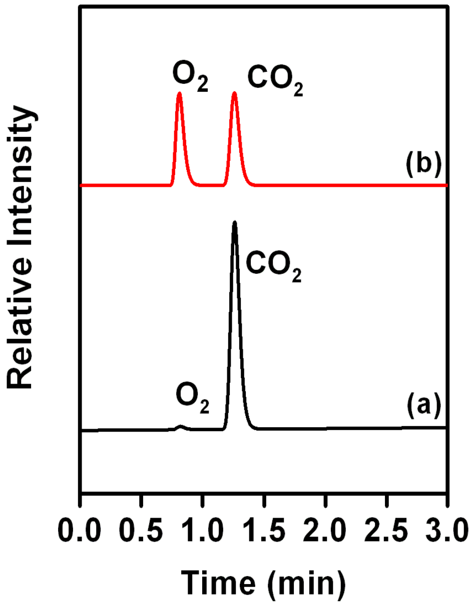

Figure S3. Gas chromatographic (GC) profiles of gases in the reaction system (a) before and (b) after reaction with Zn^{2+}-Y^- sample. The tiny O_2 peak in (a) is attributed to air in the gas chromatograph or injector. These results unambiguously demonstrate that the evolved O_2 molecules are generated from the consumed CO_2 molecules.

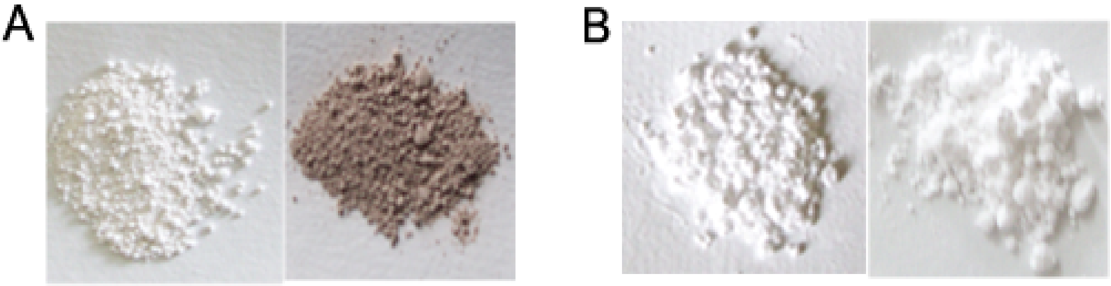

Figure S4. Color changes for Zn^{2+}-Y^- and Zn^{2+}-Y samples during the decomposition of CO_2 at 300 ºC for 24 hours. (A) Zn^{2+}-Y^- before (left) and after the CO_2 decomposition reaction (right); (B) Zn^{2+}-Y before (left) and after (right) the CO_2 decomposition reaction.

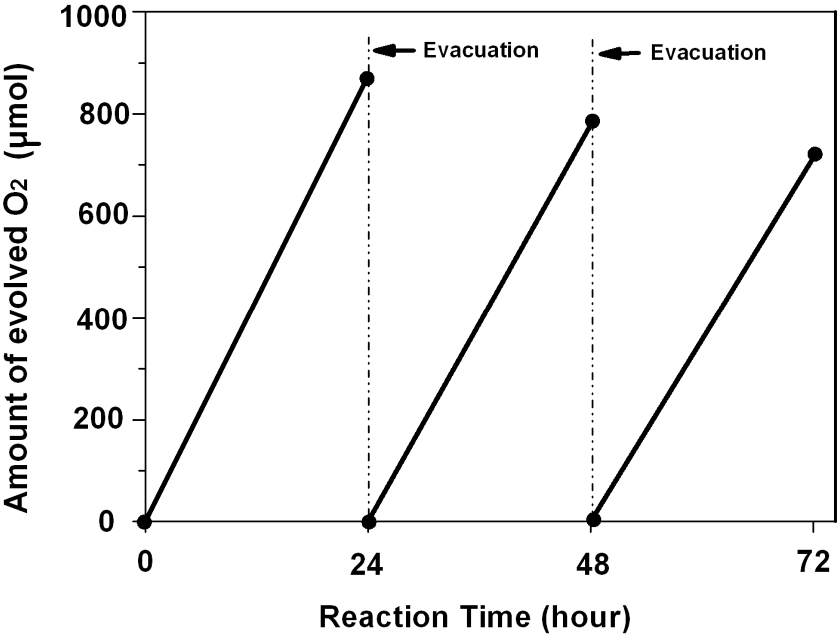

Figure S5. The activation performance of the Zn^{2+}-Y^- sample on the basis of gas-chromatographic (GC) traces. Typical reaction conditions: CO_2, 4,000 μmol; Zn^{2+}-Y^- sample, 1.0 g; reaction temperature, 300 ºC; reaction time, 24 hours; reactor volume, 90 cm^3. When the reaction was terminated after 24 hours, the product O_2 and the reactant CO_2 were both extracted from the Schlenk glassware reactor at 300 ºC. Afterward, the amount of 4,000 μmol reactant CO_2 was introduced into the reactor again for the following decomposition reaction. The result unambiguously demonstrates that the Zn^{2+}-Y^- sample retained its oxygen evolution activity after the extraction treatment.

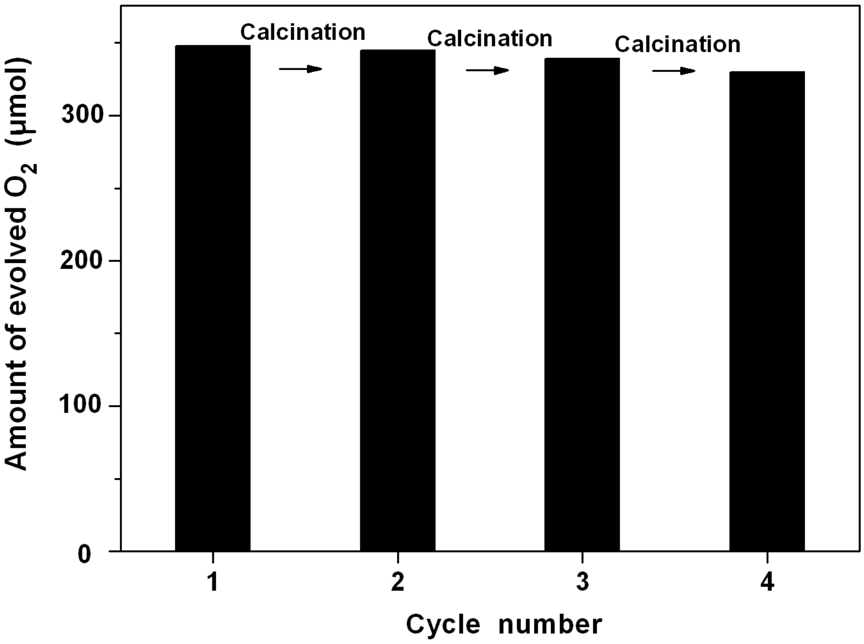

Figure S6. The recycling results of the Zn^{2+}-Y^- sample by removing carbon. Typical reaction conditions: 4,000 μmol CO_2, 1.0 g Zn^{2+}-Y^- sample, 300 ºC, 8 hours. After the reaction, the product O_2 and the reactant CO_2 were both extracted from the Pyrex® reactor at 300 ºC. Then the Zn^{2+}-Y^- sample in the reactor was calcined to remove the carbon entirely at 500 ºC for 6 hours in an O_2 flow. Afterward, the O_2 was evacuated completely from the Pyrex® reactor at 500 ºC for 2 hours. The Zn^{2+}-Y^- sample without carbon and oxygen in the reactor was reused for the next run. The result demonstrates that the activity of the Zn^{2+}-Y^- material can be recovered if the deposited carbon species are removed by calcination.

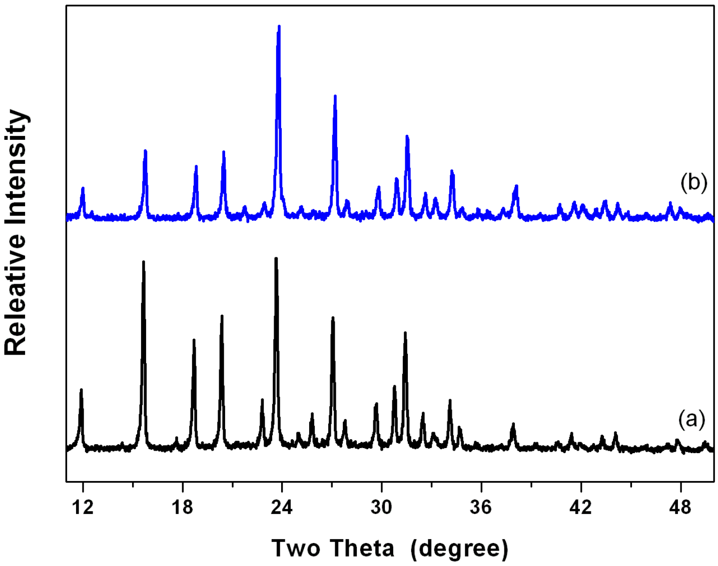

Figure S7. XRD patterns for the Zn^{2+}-Y^- sample (a) before and (b) after the decomposition reaction.

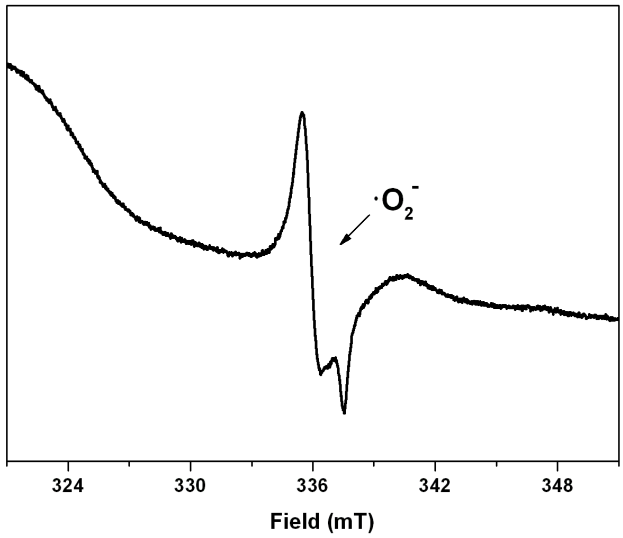

Figure S8. A typical EPR spectrum of the superoxide radical anions registered for the Zn^{2+}-Y^- sample after adsorption of pure O_2.

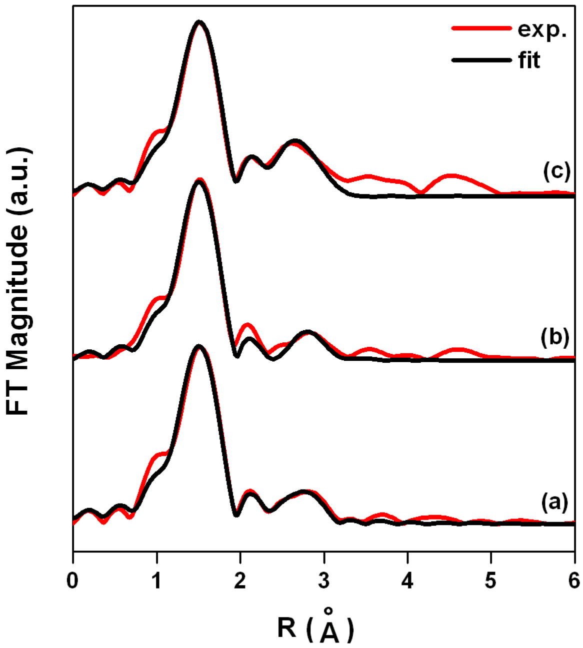

Figure S9. Fourier-transformed results of Zn K-edge EXAFS spectra for the Zn^{2+}-Y^- sample during the reaction. Zn^{2+}-Y^- sample (a) before the reaction, (b) after the reaction for eight hours, and (c) followed by evacuation of O_2 at 300 °C for four hours.

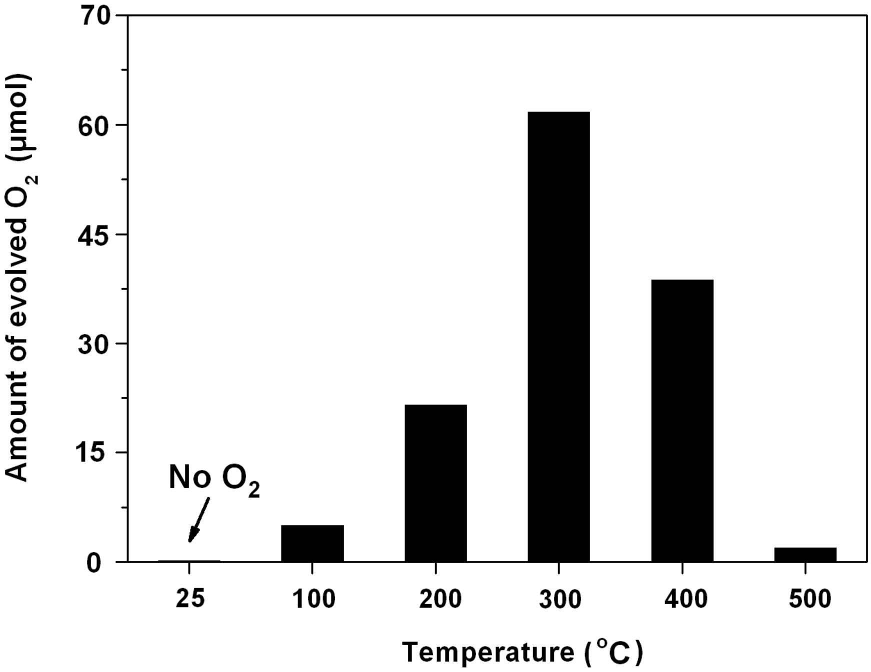

Figure S10. Amount of evolved O_2 based on gas chromatographic (GC) trace versus temperature. Reaction conditions: 800 μmol CO_2, 0.2 g Zn^{2+}-Y^- sample, 8 hours.

Table S1. EXAFS results of Zn K-edge for the Zn^{2+}-Y^- sample during the reaction[a]

Zn^{2+}-Y^- sample	**Shell**	**CN**	**R (Å)**	**$10^3\ \Delta\delta^2$ (Å)^2**	**ΔE_0(ev)**
a	O	3.6	1.98	7.2	1.4
b	O	4.1	1.98	8.4	0.2
c	O	4.2	1.98	8.8	4.7

[a] The accuracies of these parameters are estimated to be as follows: coordination number (CN), ± 10%, distance R, ± 0.02 Å; Debye-Waller factor $\Delta\delta^2$, ± 10%; and inner potential ΔE_0, ± 10%.