Electronic Supplementary Information

Preparation and Oxygen Storage of Cadmium-modified Zeolites with Superior Electron Transfer Capacities

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1. Materials

The O_2 gas (> 99.999%) was supplied by Shanghai Chengkung Gas Co., Ltd. Metallic Cd (A.R.), cadmium nitrate hexahydrate (A.R.) was purchased from Sinopharm Chemical Reagent Co., Ltd. The zeolite NaZSM-5 was prepared by the procedure described in the literature.[S1] The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of the NaZSM-5 was approximately $Na[AlSi_{14.8}O_{31.6}]$.

2. Experimental Section

2.1 Preparation of HZSM-5

The protonated zeolite ZSM-5 (HZSM-5) samples were prepared by calcining their corresponding NH_4-forms in oxygen. First, the NH_4-form zeolite ZSM-5 was obtained through an ion exchange process. 1.0 g of the corresponding Na-form zeolite ZSM-5 was added to 50 mL of 1.0 M ammonium chloride aqueous solution with stirring. After stirred for 24 hours, the NH_4-ZSM-5 material was filtered, washed with deionized water and dried in an oven at 110 ºC for five hours. The ion exchange experiment was repeated four times. Subsequently, the NH_4-ZSM-5 was calcined at 500 ºC in oxygen for 10 hours, generating the corresponding protonated HZSM-5. The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of the HZSM-5 was approximately $H[AlSi_{14.8}O_{31.6}]$.

2.2 Preparation of CdZSM-5

The electron-rich CdZSM-5 material was prepared by vapor chemical reaction of metallic cadmium in the cages of the HZSM-5 zeolite. First, 0.5 g of the HZSM-5 sample and 0.2 g of the metallic cadmium were loaded into different positions of a one end sealed glass tube. The tube was then evacuated at 400 °C for 2 hours to remove the water and other molecules adsorbed in the zeolite. Afterwards, the tube with both ends sealed was heated at about 450 °C so that the metallic cadmium vaporizes to react with the protons in the HZSM-5 zeolite. Following this treatment for about 40 hours, the glass tube was evacuated at 420 ºC for another 6 hours to remove the physically adsorbed Cd atoms (See the schematic preparation procedure). The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of CdZSM-5 was approximately $Cd_{0.69}[AlSi_{14.8}O_{31.6}]$.

2.3 Preparation of Cd^{2+}-ZSM-5

The ion-exchanged Cd^{2+}-ZSM-5 sample was prepared by introducing Cd^{2+} cations into the channels of zeolite ZSM-5 *via* ion exchange. The ion exchange process was repeated four times. 0.5 g of HZSM-5 was dispersed into 30 mL of 1.0 M cadmium nitrate aqueous solution. After stirred for 24 hours, the ion-exchanged zeolite ZSM-5 was filtered, washed with deionized water and dried in an oven at 110 ºC for five hours. Finally, the ion-exchanged Cd^{2+}-ZSM-5 sample was obtained through calcination in oxygen at 450 ºC for 10 hours. The ICP analysis and ^{29}Si MAS NMR spectroscopy indicated that the molar composition of Cd^{2+}-ZSM-5 was approximately $Cd_{0.49}[AlSi_{14.8}O_{31.6}]$.

2.4 The O_2 storage/release capacity

O_2 storage/release experiment was conducted in a glass tube reactor loaded in a tube furnace. In order to prevent the electron-rich CdZSM-5 sample from deactivation by air and moisture, the experiments were performed under dry Ar atmosphere or vacuum using the 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 evolved O_2 from the zeolite was collected with a syringe and analyzed on a Shimadzu GC-2014 gas chromatograph with a Paropak Q, column; column temperature, 70 ºC; carrier gas, He; total flow, 30.0 mL/min; injection detector temperature, 100 ºC; thermal conductivity detector (TCD) temperature, 120 ºC.

2.5 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 temperature, 25 ºC. 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 UV-vis diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 20 UV-vis spectrometer.

The X-ray absorption data at the Cd K-edge (26711 eV) 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 cadmium metal foil. Data processing was performed using the program ATHENA. All fits to the EXAFS data were performed using the program ARTEMIS.

References

S1. L. Li, G. D. Li, C. Yan, X. Y. Mu, X. L. Pan, X, X, Zou, K. X. Wang and J. S. Chen, *Angew. Chem. Int. Ed.*, 2011, 50(*36*), 8299-8303.

3. Results and discussion

3.1 Proportion of Cd atoms reducing one proton each in the CdZSM-5 sample

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

$$R_{(Cd/Al)} = \frac{1}{x\% + 2\,(1-x\%)} = 0.69 \qquad ES1$$

$R_{(Cd/Al)}$ is the measured atomic ratio of Cd/Al on the basis of the ICP analysis. x% is the percentage of the Cd atoms reducing one proton each whereas (1-x%) the percentage of the Cd atoms reducing two closely-positioned protons each among the total cadmium atoms incorporated in the cadmium-modified zeolite ZSM-5.

The value of x % is calculated to be about 55 % in our CdZSM-5 sample.

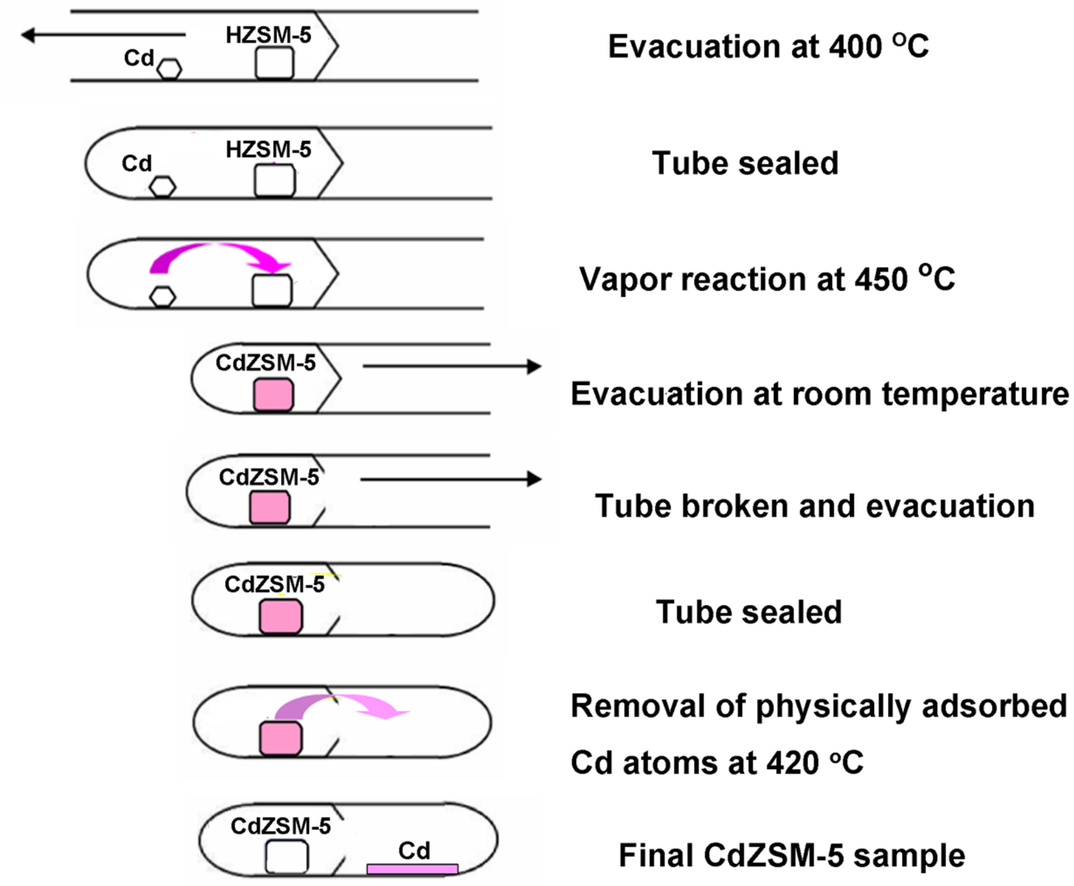

Figure S1. Schematic preparation procedure for the electron-rich CdZSM-5 sample under vacuum.

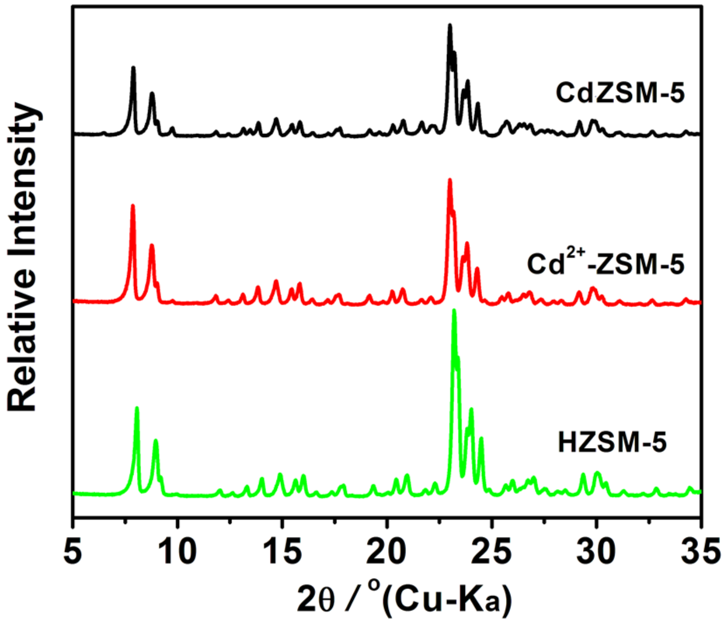

Figure S2. XRD patterns for the samples of zeolite HZSM-5, Cd^{2+}-ZSM-5, and CdZSM-5.

Table S1. Structural parameters obtained from the analysis of the EXAFS spectra at Cd K-edge for samples.[a]

Sample	**Shell**	***N***	***R*(Å)**	**σ^2(×10^{-3} Å^2)**	**ΔE_0(eV)**
Cd^{2+}-ZSM-5	Cd-O	3.3 ± 0.5	2.27 ± 0.01	7.1 ± 3.2	-0.72
	Cd-Si/Al	1.7	2.91 ± 0.02	6.3 ± 2.9	11.0
	Cd-Cd	7.6 ± 1.2	3.04 ± 0.02	15.8 ± 2.9	4.5
CdZSM-5	Cd-O	3.9 ± 0.5	2.25 ± 0.01	5.3 ± 2.8	-0.72

[a] *N*, coordination number; *R*, bond distance; σ^2, Debye-Waller factor; ΔE_0, inner potential shift.

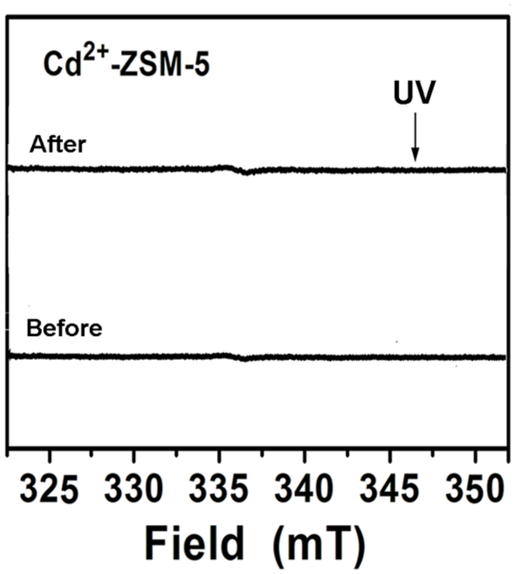

Figure S3. *In situ* EPR spectra for the ion-exchanged Cd^{2+}-ZSM-5 sample before and after the irradiation of UV light under room temperature.

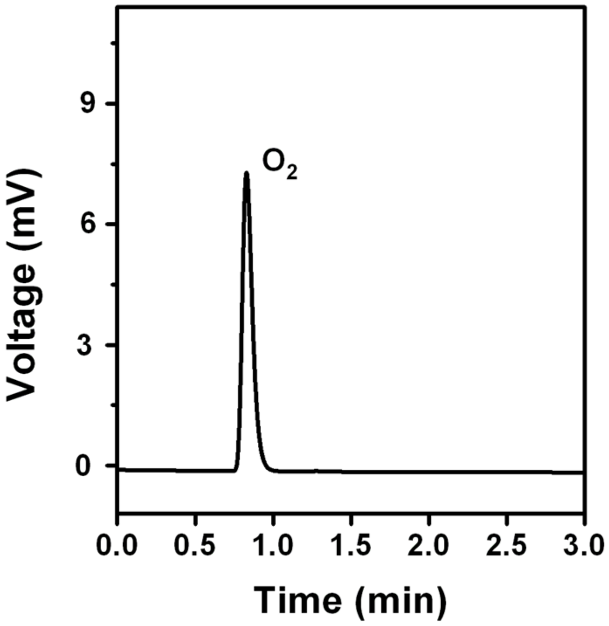

Figure S4. The release of O_2 at 300 °C on the basis of gas-cheomatographic (GC) traces for the electron-rich CdZSM-5 sample. The product of O_2 released was measured by GC with a thermal conductivity detector (TCD).

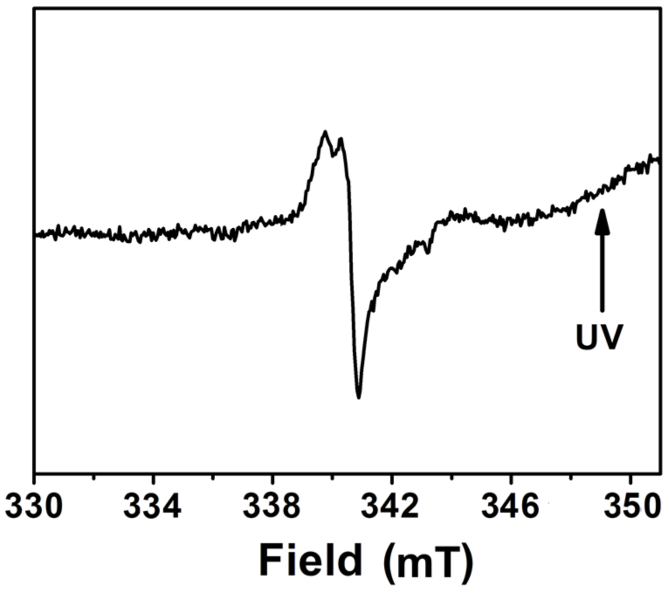

Figure S5. Room temperature *in situ* EPR spectra for the CdZSM-5 sample under the irradiation of UV light after the removal of the $^{\bullet}O_2^-$ radicals.

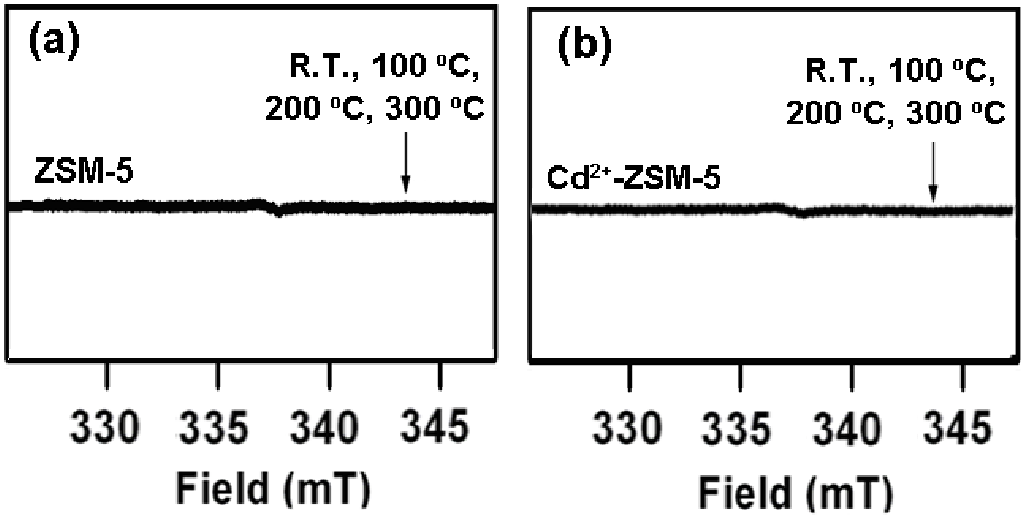

Figure S6. *In situ* EPR spectra for the samples of pristine ZSM-5 and ion-exchanged Cd^{2+}-ZSM-5 after exposure to O_2 at different temperature between R.T. and 300 °C.

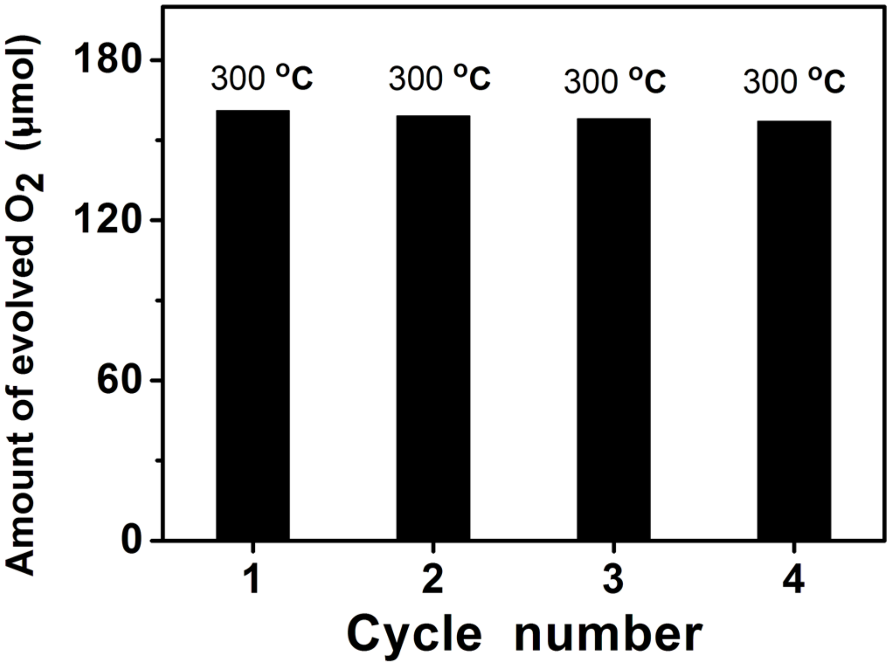

Figure S7. The recycling results of storage O_2 for the electron-rich CdZSM-5 sample. Typical reaction conditions: 0.5 g CdZSM-5 sample, reactor volume, 100 cm^3, 300 ºC. Under the temperature of 300 ºC, the evolved O_2 from the CdZSM-5 sample was collected with a liquid-N_2 trap, and analyzed by GC. Afterwards, the reactor was evacuated at 300 ºC for 2 hours to remove the residual O_2 from reaction system. Finally, the CdZSM-5 sample without containing oxygen in the reactor was reused for the next run and pure O_2 was introduced into the reactor again under the room temperature. The result unambiguously demonstrates that the CdZSM-5 sample can retain oxygen storage activity after the extraction treatment.

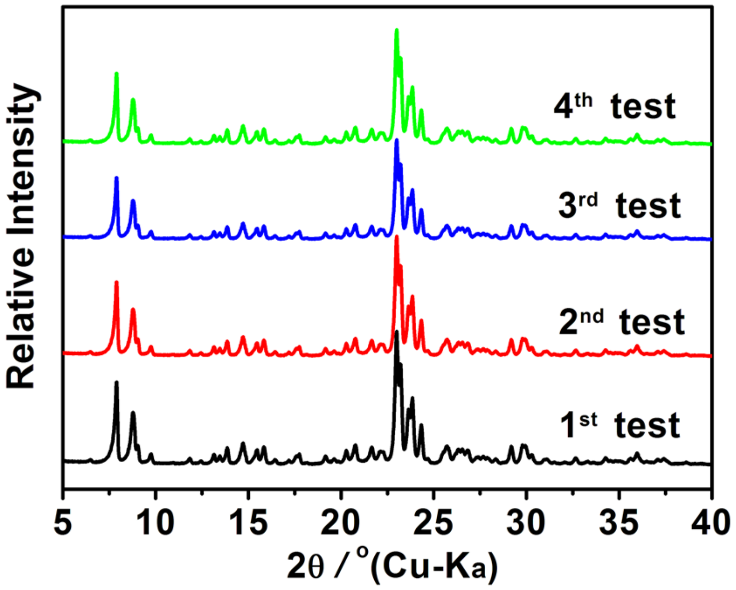

Figure S8. XRD patterns of the electron-rich CdZSM-5 sample after oxygen storage cycle test. This result demonstrates that the crystal structure of the Cd-containing zeolite ZSM-5 material remained intact.