Electronic Supplementary Information

Simultaneous Fabrication of Bifunctional Cu(I)/Ce(IV) Sites in Silica Nanopores Using a Guests-Redox Strategy

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Supplementary Experimental Details

Materials Characterization.

Transmission electron microscopy (TEM) was performed on a JEM-200CX electron microscope operated at 200 kV. Scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and elemental mapping were recorded on HITACHI S-4800 at 5 kV.

C_2H_4/C_2H_6 Selectivity Calculation on the Adsorption Isotherms.

In the analysis of adsorption equilibrium, the adsorption of C_2H_4 and C_2H_6 can be described well by the Double Langmuir model[1] as shown in Eq. S1.

$$q = q_c \frac{K_c P}{1 + K_c P} + q_i \frac{K_i P}{1 + K_i P} \qquad \text{Eq. (S1)}$$

where the subscripts *c* and *i* referring to the channels and intersections, respectively. The geometrical constraint gives rise to two different saturation amounts adsorbed in locations *c* and *i* and indicated by q_c and q_i. This description of adsorption equilibrium contains four parameters and their values are obtained from the experimental isotherm data by nonlinear regression.

Ideal adsorbed solution theory (IAST) is a well-known approach to predicting multi-component adsorption isotherms from experimental or simulation data for single-component adsorption.[2-3] IAST is analogous to Raoult's law for vapor-liquid equilibrium as shown in Eq. S2.

$$P_i = P_i^o(\pi_i)x_i \qquad \text{Eq. (S2)}$$

where x_i and π_i are the molar fraction and spreading pressure of component i in the adsorbed phase, respectively. At the adsorption equilibrium, the reduced spreading pressures must be the same for each component and the mixture as depicted in Eqs. S3 and S4.

$$\pi_i^* = \frac{\pi_i A}{RT} = \int_0^P \frac{q}{P} dp \qquad i = 1, 2, 3, \ldots, N \qquad \text{Eq. (S3)}$$

$$\pi_1^* = \pi_2^* = \ldots = \pi_N^* \qquad \text{Eq. (S4)}$$

where q is the pure component equilibrium capacity and P is the pure component hypothetical pressure which yields the same spreading pressure as that of the mixture.

The selectivity of ethylene over ethane on different adsorbents is calculated *via* Eq. S5.

$$S_{ij} = \frac{x_i / x_j}{y_i / y_j} \qquad \text{Eq. (S5)}$$

where x_i and x_j are the equilibrated adsorption capacity of ethylene and ethane respectively, and y_i and y_j are the molar fractions of ethylene and ethane in gas phases respectively.

References

1 W. Zhu, J. M. van de Graaf, L. J. P. van den Broeke, F. Kapteijn, J. A. Moulijn, *Ind. Eng. Chem. Res.,* **1998**, *37*, 1934-1942.

2 J. Chen, L. S. Loo, K. Wang, *J. Chem. Eng. Data,* **2011**, *56*, 1209-1212.

3 Z. Zhang, Z. Li, J. Li, *Langmuir,* **2012**, *28*, 12122-12133.

Supplementary Results and Discussion

The standard conditions refer to 273.15 K and 101.325 KPa. It is worth noting that the guests-redox strategy was conducted at the conditions of 623.15 K (350 ^{o}C) and 101.325 KPa. Thus, we calculated the free energy change at the conditions of 623.15 K (350 ^{o}C) and 101.325 KPa. The thermodynamic data were obtained from the manual as shown in Table S2. The free energy change of the Eq. (S6) was calculated with the followed Eqs.

$$\mathrm{CuCl_2{+}CeCl_3 + 2H_2O \rightarrow CeO_2 + CuCl + 4HCl} \qquad \text{Eq. (S6)}$$

$$\begin{aligned}
&\Delta_r H_\mathrm{m} = \sum \upsilon_B \Delta_f H_m(\mathrm{B}) \\
&= (\text{-}265\text{-}33\text{-}4 \times 22)\text{-}(\text{-}48\text{-}251\text{-}2 \times 58) \\
&= 29\mathrm{kcal/g}
\end{aligned} \qquad \text{Eq. (S7)}$$

$$\begin{aligned}
&\Delta_r S_\mathrm{m} = \sum \upsilon_B \Delta_f S_m(\mathrm{B}) \\
&= (17{+}58{+}4 \times 46)\text{-}(28{+}38{+}2 \times 46) \\
&= 101\mathrm{cal/g}
\end{aligned} \qquad \text{Eq. (S8)}$$

$$\begin{aligned}\Delta_r G_{\mathrm{m}}(623.15K) &= \Delta_r H_m - T\Delta_r S_m \\ &= 29000 - 623.15\times 101 \\ &< 0\end{aligned} \qquad \text{Eq. (S9)}$$

$$\begin{aligned}\Delta_r G_{\mathrm{m}}(273.15K) &= \Delta_r H_m - T\Delta_r S_m \\ &= 29000 - 273.15\times 101 \\ &> 0\end{aligned} \qquad \text{Eq. (S10)}$$

The results show that the free energy change for the process at 623.15 K is below zero. It is proved that the process could be carried out.

We also calculated the free energy change for the process at 273.15 K. The value is over zero. This indicates that the process could never occur at standard conditions.

Table S1 Fitting parameters derived from isothermal data

Adsorbent	Adsorbate	q_c (mmol·g^{-1})	q_i (mmol·g^{-1})	K_c (kPa^{-1})	K_i (kPa^{-1})	R^2
SBA-15	C_2H_4	2.09899	76.07110	0.09002	0.00206	0.99980
	C_2H_6	1.77417	92.81887	0.04024	0.00119	0.99925
4Ce/SBA-5	C_2H_4	1.77612	32.94401	0.09926	0.00295	0.99995
	C_2H_6	0.60613	25.33092	0.42080	0.00280	0.99996
4Cu/SBA-15	C_2H_4	5.33931	25.24101	1.77001	0.00754	0.99950
	C_2H_6	1.98820	24.00235	1.46670	0.00493	0.99996
4Cu-4Ce/SBA-15	C_2H_4	5.12433	35.13556	0.87088	0.00522	0.99930
	C_2H_6	1.11178	16.09248	3.04832	0.00414	0.99998
1Cu-1Ce/SBA-15	C_2H_4	4.12263	32.14155	1.47319	0.00792	0.99962
	C_2H_6	1.50235	38.45096	1.30357	0.00343	0.99995
2Cu-2Ce/SBA-15	C_2H_4	4.83942	35.49195	1.64331	0.00632	0.99949
	C_2H_6	5.17509	35.68805	0.02609	0.00236	0.99966
8Cu-8Ce/SBA-15	C_2H_4	3.33443	11.69316	1.90332	0.01255	0.99869
	C_2H_6	0.87814	28.50880	0.66742	0.00135	0.99968

Table S2 Thermodynamic parameters of chemical compounds at 101.325 KPa

Chemical Compounds	H (623.15k)-H (298.15K) (cal·g^{-1})	H (298.15K) (kcal·g^{-1})	H (623.15k) (kcal·g^{-1})	S (623.15K) (cal·g^{-1}·K^{-1})
$CeCl_3$	1304	-252	-251	38
CeO_2	825	-266	-265	17
CuCl	466	-33	-33	58
$CuCl_2$	915	-49	-48	28
H_2O (g)	423	-58	-58	46
HCl (g)	362	-22	-22	46

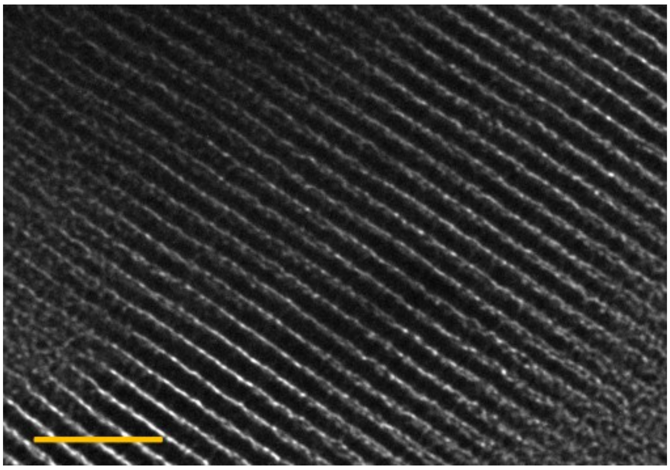

Figure S1 TEM image of the sample 4Cu-4Ce/SBA-15. The scale bar represents 50 nm.

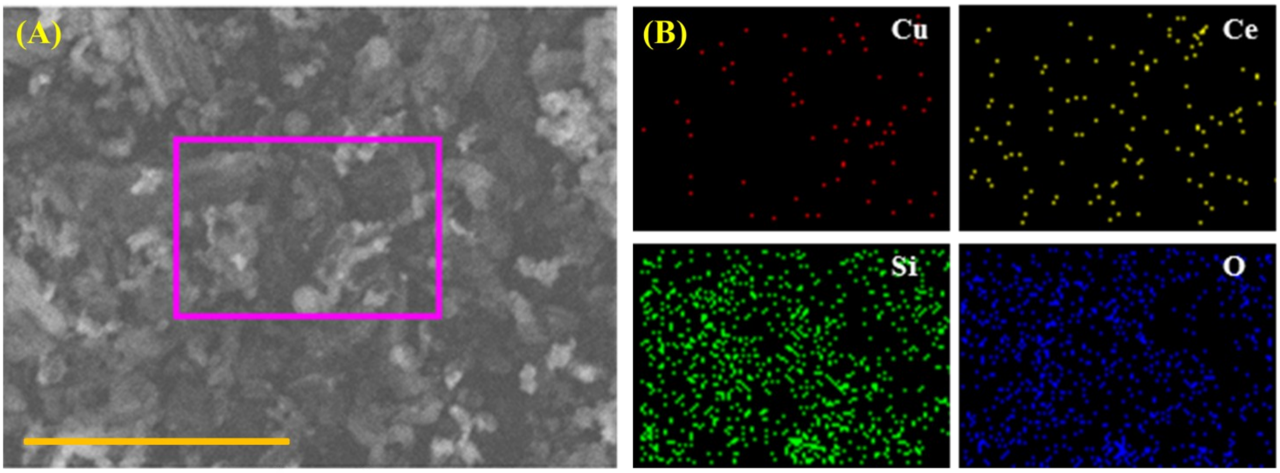

Figure S2 (A) SEM image and (B) elemental maps of the sample 4Cu-4Ce/SBA-15. The scale bar represents 10 μm.

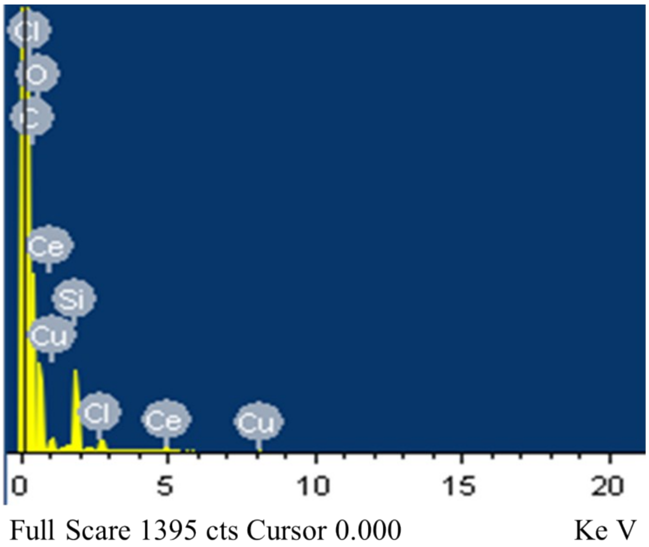

Figure S3 EDX spectrum of the sample 4Cu-4Ce/SBA-15.

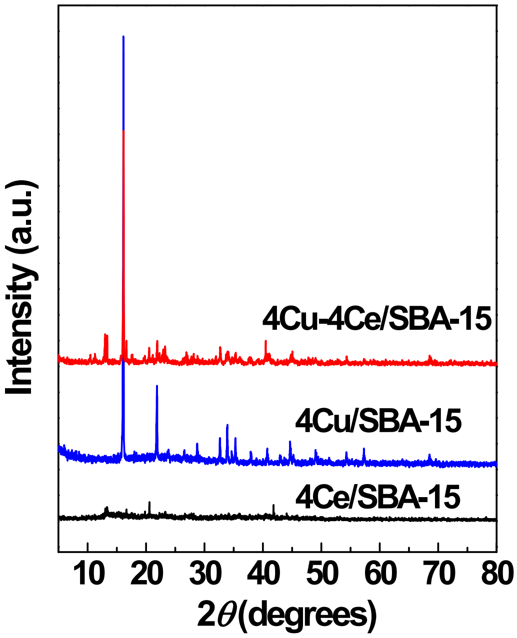

Figure S4 Wide-angle XRD patterns of the samples before thermal treatment.

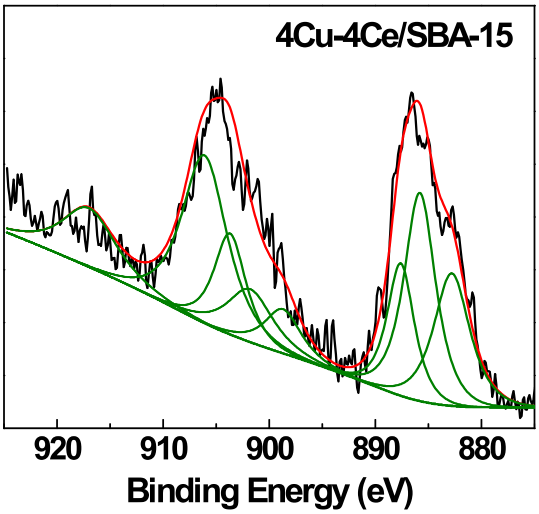

Figure S5 XPS peak fitting of Ce 3*d* spectra of the sample 4Cu-4Ce/SBA-15.

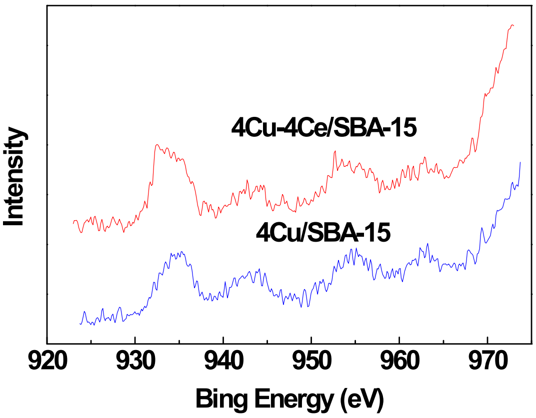

Figure S6 XPS spectra of Cu regions of the samples.