

Electronic Supplementary Information (ESI)

**Highly dispersed copper-based nano composite synthesis via spray pyrolysis:
Towards waste-to-hydrogen production through the water-gas shift reaction**

I-Jeong Jeon^{a,1}, Jae Seob Lee^{b,c,1}, Kun Woo Baek^b, Chang-Hyeon Kim^a, Ji-Hyeon Gong^d, Won-
Jun Jang^{d,e,*}, Jung Sang Cho^{b,f,g,*}, Jae-Oh Shim^{a,*}

*^a Department of Chemical Engineering, Wonkwang University, 460 Iksan-daero, Iksan-si,
Jeollabuk-do 54538, Republic of Korea*

*^b Department of Engineering Chemistry, Chungbuk National University, Chungbuk, 28644,
Republic of Korea*

*^c Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-
Gu, Seoul 02841, Republic of Korea*

*^d Department of Environmental Engineering, Ajou University, 206 World Cup-ro, Suwon-si,
Gyeonggi-do 16499, Republic of Korea*

*^e Department of Environmental and Safety Engineering, Ajou University, 206 World Cup-ro,
Suwon-si, Gyeonggi-do 16499, Republic of Korea*

*^f Biomedical Research Institute, Chungbuk National University Hospital, Chungbuk 28644,
Republic of Korea*

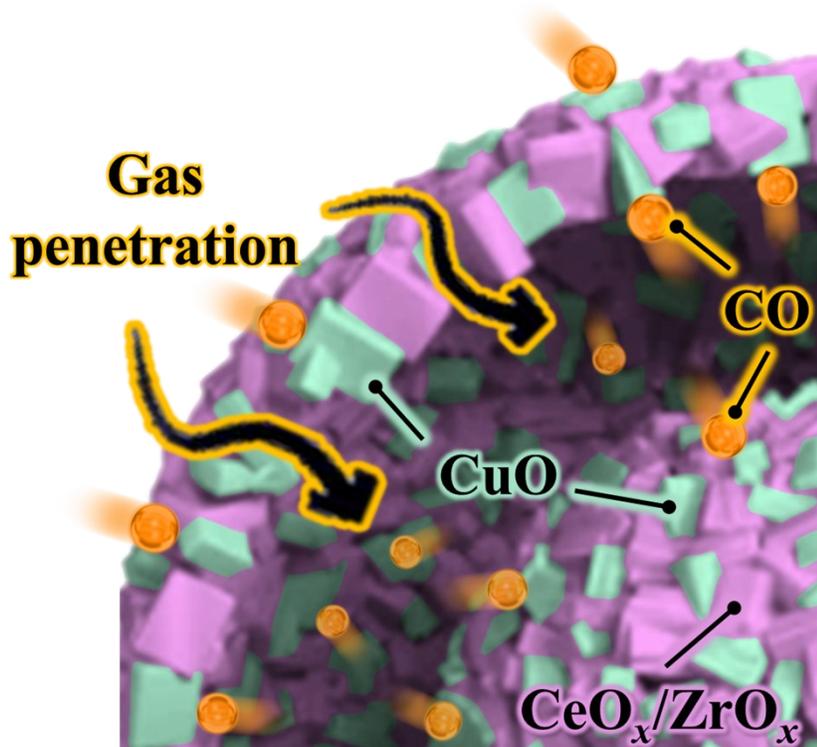
*^g Advanced Energy Research Institute, Chungbuk National University, Cheongju, Chungbuk
28644, Republic of Korea*

*Corresponding authors

E-mail address: wjjang@ajou.ac.kr (W.-J. Jang)

E-mail address: jscho@cbnu.ac.kr (J.S. Cho)

E-mail address: joshim85@wku.ac.kr (J.-O. Shim)



CuO/MeO_x yolk-shell catalyst

Scheme S1 Schematic representation of efficient gas penetration into the yolk-shell structured SPCZC and CO gas adsorption on both the yolk and shell surfaces.

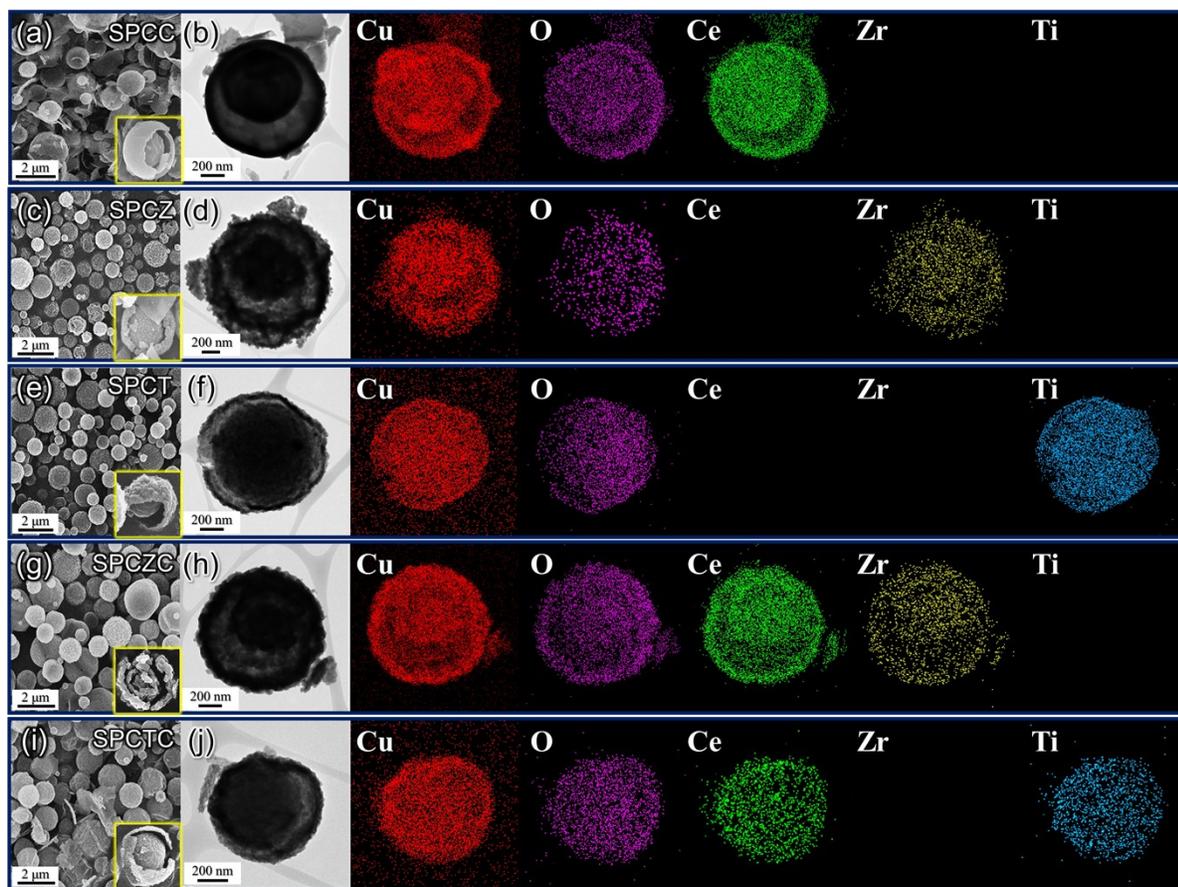
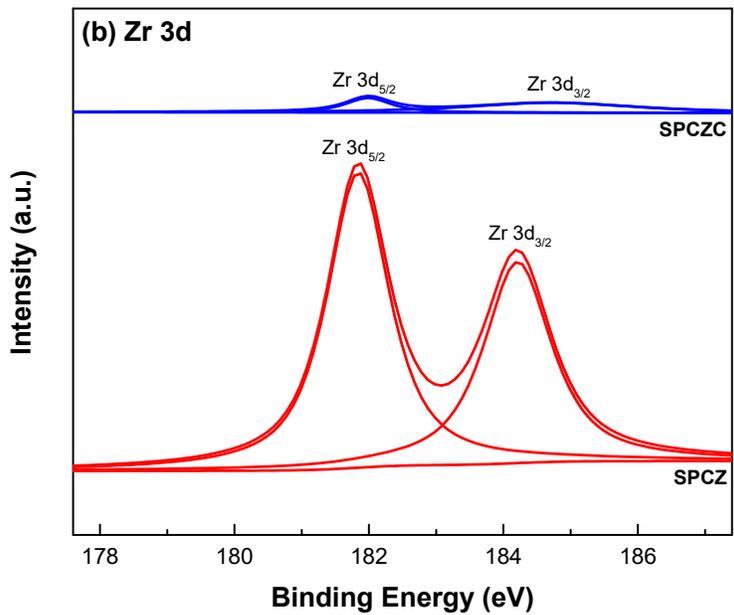
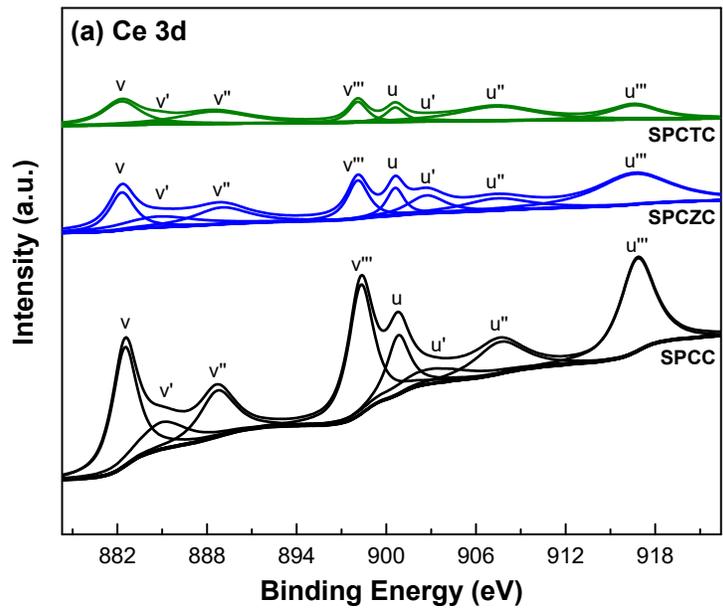


Figure S1 The FE-SEM images ((a): SPCC, (c): SPCZ, (e): SPCT, (g): SPCZC, (i): SPCTC) and TEM-EDS elemental mapping images ((b): SPCC, (d): SPCZ, (f): SPCT, (h): SPCZC, (j): SPCTC) of the fresh SPC catalysts supported on various supports.



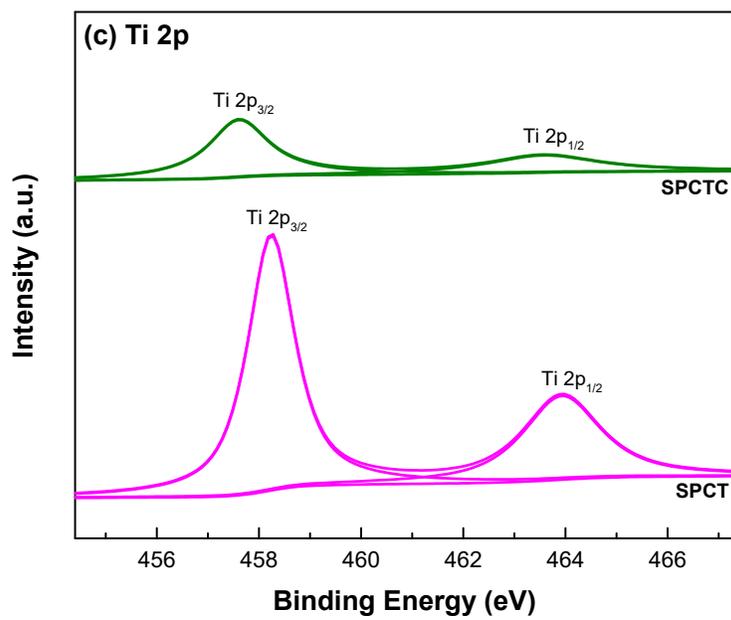


Figure S2 The XPS patterns of the fresh SPC catalysts supported on various supports ((a): Ce 3d, (b): Zr 3d, (c): Ti 2p).

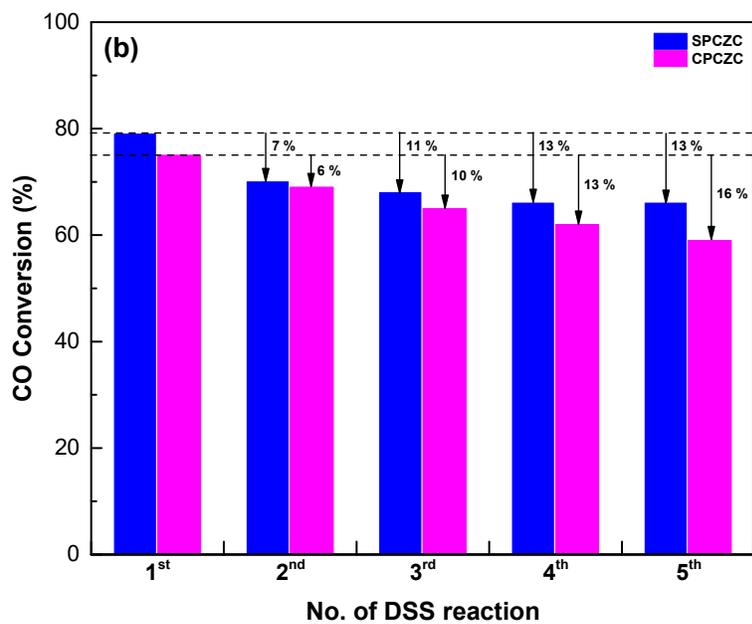
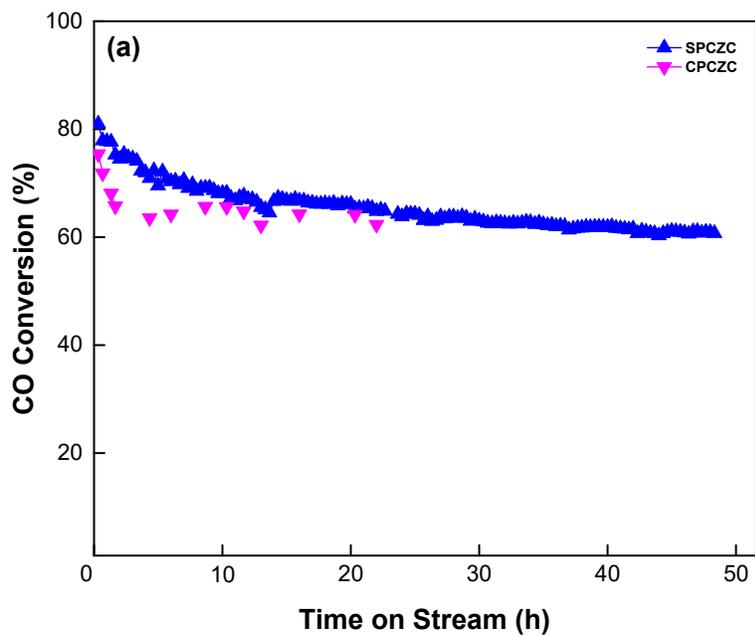
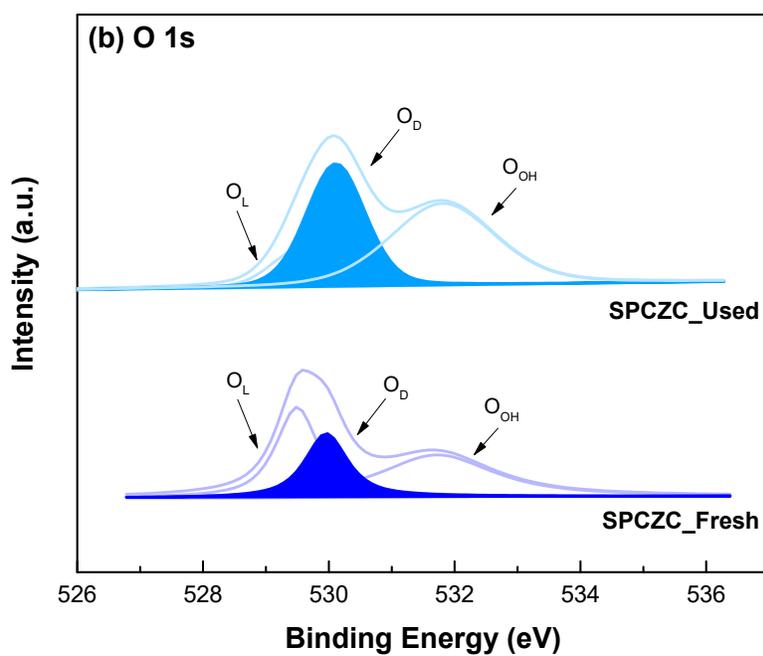
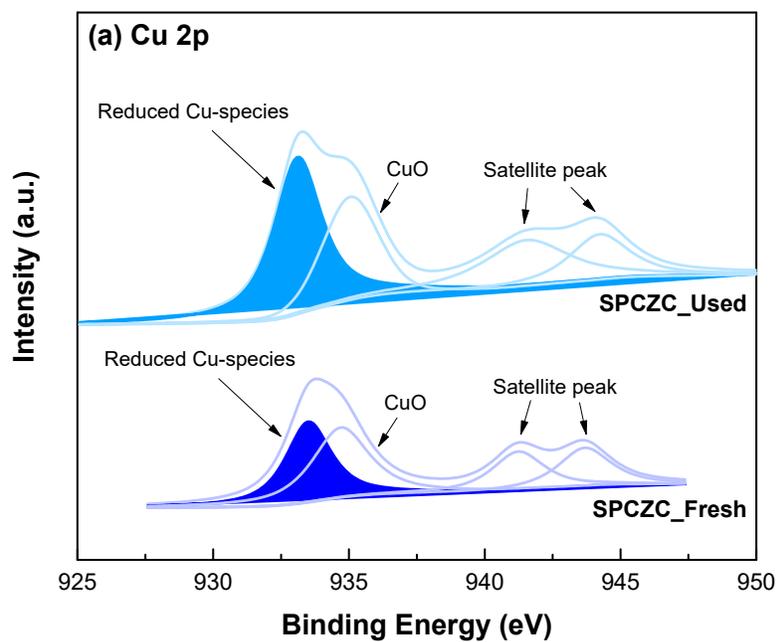


Figure S3 Comparison of the stability test and DSS reaction for SPCZC and CPCZC catalysts ((a): Stability test, (b): DSS reaction).

Additionally, the Cu-ZrCeO₂ catalyst was synthesized using the co-precipitation method (CPCZC), which is widely applied in commercial processes, and a direct comparison was conducted with other synthesis methods. The results showed that catalysts prepared by the co-precipitation method exhibited rapid deactivation initially compared to the SPCZC catalyst and had lower initial activity (Figure S3(a)). Furthermore, the daily start-up and shut-down (DSS) test showed that the CPCZC catalyst exhibited a continuous decrease in activity, showing a decline of 6%, 10%, 13%, and 16% over the course of five reactions (Figure S3(b)). Therefore, it can be confirmed that the yolk-shell structure is more stable and exhibits higher catalytic activity compared to conventional catalyst structures.

[Synthesis method of CPCZC]

The CPCZC catalyst was prepared by co-precipitation and impregnation methods. 0.15 M Ce(NO₃)₃·6H₂O (SAMCHUN, 98.0%) and 0.05 M Zr(NO₃)₂·xH₂O (Thermo Fisher Scientific, 99.5%) were dissolved in 500 mL of distilled water. A 15 wt.% KOH (95%, SAMCHUN) solution was added dropwise to this solution at 80 °C to adjust the pH to 10.5. The precipitate was aged at 80 °C for 3 days, then washed five times with distilled water and air-dried at 110 °C for 1 day. The dried precipitate was calcined in air from room temperature to 500 °C at a heating rate of 1°C/min and maintained at that temperature for 6 hours. The prepared ZrO₂-CeO₂ was impregnated with 0.1 M Cu(NO₃)₂·3H₂O (DAEJUNG, 99.0%) to obtain the CPCZC catalyst.



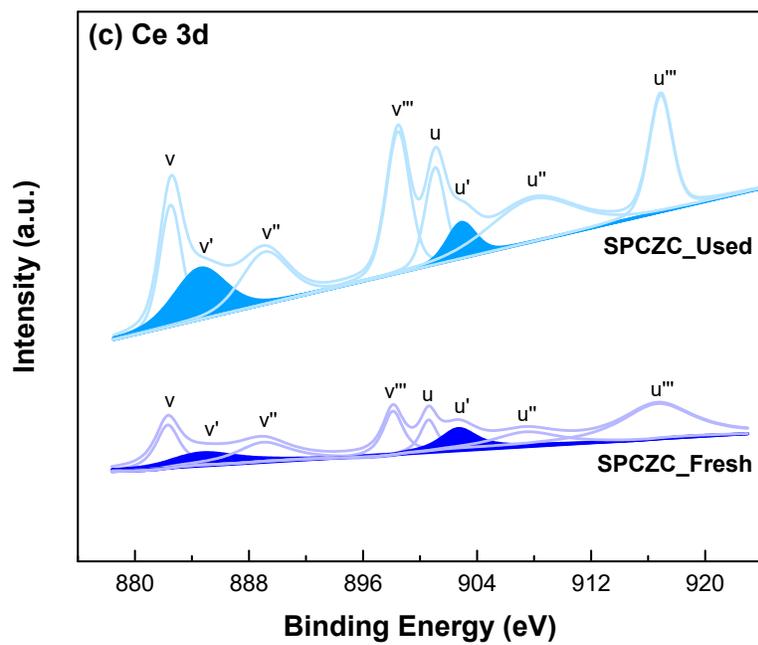


Figure S4 The XPS patterns of the fresh and used SPCZC catalysts ((a): Cu 2p, (b): O 1s, (c): Ce 3d).

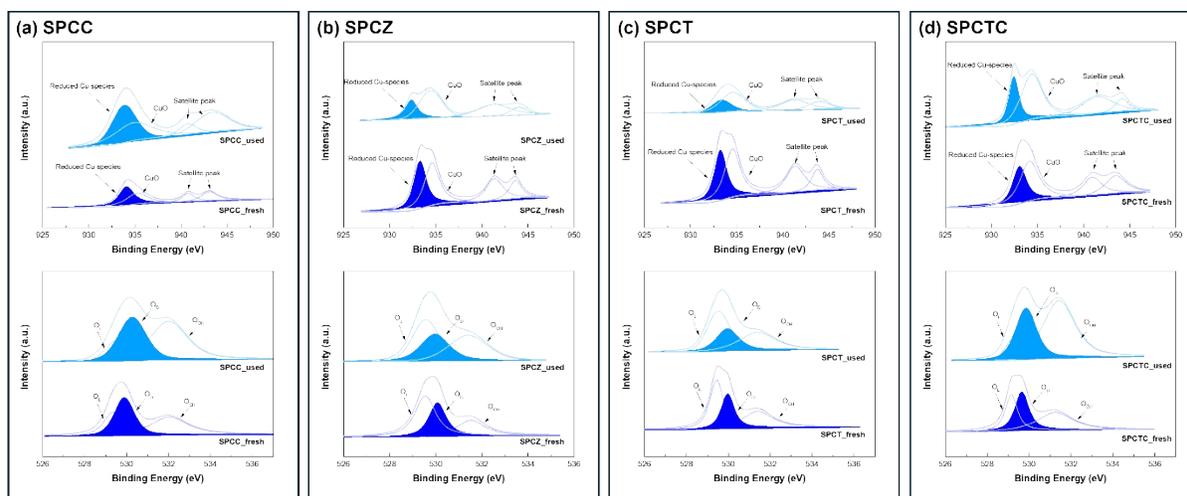


Figure S5 The Cu 2p and O 1s spectra of the fresh and used SPC catalysts ((a): SPCC, (b): SPCZ, (c): SPCT, (d): SPCTC).

[XPS analysis of SPC catalysts]

Except for the SPCC catalyst, the fresh and used samples of the SPC catalysts were analyzed by XPS, as shown in Figure S5, and the surface atomic ratios calculated from the XPS data are presented in Table S2. All catalysts exhibited a decrease in the reduced Cu species after the reaction. Interestingly, the distribution of reduced Cu species followed the same trend as the catalyst deactivation rates after 50 hours of stability test. In contrast, oxygen defects did not show a significant reduction, even after 50 hours of time-on-stream reactions.

Table S1 The surface atomic ratios and OSCC value of fresh and used SPCZC catalysts

Catalyst	The surface atomic ratios by XPS (%)				OSCC value ($\mu\text{mol O}_2/\text{g}_{\text{cat}}$)
	Reduced Cu	CuO	$\text{O}_D/(\text{O}_L+\text{O}_D+\text{O}_{\text{OH}})$	$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$	
SPCZC_Fresh	63.23	36.77	39.49	19.10	1,002
SPCZC_Used	62.49	37.51	39.51	18.04	1,018

Table S2 The surface atomic ratios of fresh and used SPC catalysts

Catalyst		The surface atomic ratios by XPS (%)		
		Reduced Cu	CuO	$O_D/(O_L+O_D+O_{OH})$
SPCC	Fresh	54.79	45.21	38.08
	Used	52.52	47.48	37.79
SPCZ	Fresh	47.95	52.05	30.99
	Used	34.29	65.71	29.84
SPCT	Fresh	45.01	54.99	27.89
	Used	33.06	66.94	26.46
SPCTC	Fresh	40.51	59.49	34.08
	Used	36.28	63.72	33.48