Electronic Supplementary Information (ESI) †

CO Oxidation Activity of Thermally Stable Fe-Cu/CeO₂ Catalysts

Prepared by Dual-mode Arc-plasma Process

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Figure captions

Figure S1 XRD patterns of the Fe/CeO₂(AP), Cu/CeO₂(AP), Fe–Cu/CeO₂(AP), Fe–Cu/CeO₂(AP), Fe–Cu/CeO₂(imp) before and after thermal aging. CeO₂ is shown as a reference.

Figure S2 Ce 3d XPS spectra of (left) Cu/CeO₂ and (right) Fe–Cu/CeO₂ prepared by (a, b) the AP and (c, d) wet-impregnation processes; spectra were collected (a, c) before and (b, d) after the catalysts were thermally aged at 900 °C for 25 h.

Figure S3 Catalytic CO conversion versus the reaction time. CO conversion for thermally aged Fe–Cu/CeO₂(AP) and Fe–Cu/CeO₂(imp) measured at 150 °C. Reaction conditions: 0.1% CO, 1.25% O₂, He balance, W/F = 5.0×10^{-4} g·min·cm⁻³.

Figure S4 In situ FT-IR spectra of CO adsorbed on as-prepared Fe, Cu and Fe–Cu/CeO₂(AP) at 50 °C. The spectra were measured in gas feeds of (a) 1% CO and He balance, followed by (b) He and (c) 2.5% O₂ and He balance.



Figure S1 XRD patterns of the Fe/CeO₂(AP), Cu/CeO₂(AP), Fe–Cu/CeO₂(AP) and Fe–Cu/CeO₂(imp) before and after thermal aging. CeO₂ is shown as a reference.

The XRD patterns of the as-prepared Fe/CeO₂, Cu/CeO₂ and Fe–Cu/CeO₂ using AP and wetimpregnation processes exhibited peaks assignable to CeO₂ with a cubic fluorite-type structure. After the samples were thermally aged at 900 °C, the diffraction peaks of CeO₂ became intense and sharp because of sintering, whereas other diffraction peaks associated with Fe, Cu and Fe–Cu were not observed because of their low loading levels of 0.1–0.2 wt%.



Figure S2 Ce 3d XPS spectra of (left) Cu/CeO₂ and (right) Fe–Cu/CeO₂ prepared by (a, b) the AP and (c, d) wet-impregnation processes; spectra were collected (a, c) before and (b, d) after the catalysts were thermally aged at 900 °C for 25 h.

The peak deconvolution of the Ce 3d XPS spectra yielded two sets of peaks, which were assigned to Ce^{3+} (V⁰, V', U⁰, and U' shown as dashed lines) and Ce^{4+} (V, V'', V''', U, U'', and U''' shown as solid lines). The surface concentration ratio (Ce^{3+}/Ce) of the CeO_2 was in the range of 17–25%, which was the same as that for the neat CeO_2 (Table S1). The spectra were thus not affected by loading the small amount of Fe and Cu (0.2 wt%, respectively) used in the present system.



Figure S3 Catalytic CO conversion versus the reaction time. CO conversion for thermally aged Fe–Cu/CeO₂(AP) and Fe–Cu/CeO₂(imp) measured at 150 °C. Reaction conditions: 0.1% CO, 1.25% O₂, He balance, W/F = 5.0×10^{-4} g·min·cm⁻³.

The stability of aged Fe–Cu/CeO₂(AP) was tested at 150 °C, but no indication of noticeable deactivation was observed during 2 h of reaction.



Figure S4 In situ FT-IR spectra of CO adsorbed on as-prepared Fe, Cu and Fe–Cu/CeO₂(AP) at 50 °C. The spectra were measured in gas feeds of (a) 1% CO and He balance, followed by (b) He and (c) 2.5% O₂ and He balance.

In situ FT-IR spectra of CO adsorbed on the catalysts as prepared by AP were measured. The three catalysts showed only very weak CO bands in a flow of 1% CO and He. However, these bands soon disappeared after the gas feed was changed to He. Because these results were completely different from those of thermally aged catalysts shown in Figure 5, we concluded that a highly dispersed Cu⁺, which formed on the surface of CeO₂ by thermally aging at 900 $^{\circ}$ C, plays a role of active site for CO adsorption and reaction.

thermal aging	crystal	S _{BET}	primary particle	Ce ³⁺ /Ce ^b	T ₅₀
	structure	$/ m^2 \cdot g^{-1}$	size ^a / nm	/ %	/ °C
none	fluorite	173	1–3	24	403
900 °C, 10% H ₂ O/air	fluorite	6	>100	25	532

Table S1 Physicochemical properties of CeO_2 powders before and after aging at 900 °C

^{*a*} Determined by TEM images.

^b Determined by Ce 3d XPS spectra.