Supplementary material

Temperature dependence of Cu-Al spinel formation and its catalytic performance in methanol steam reforming

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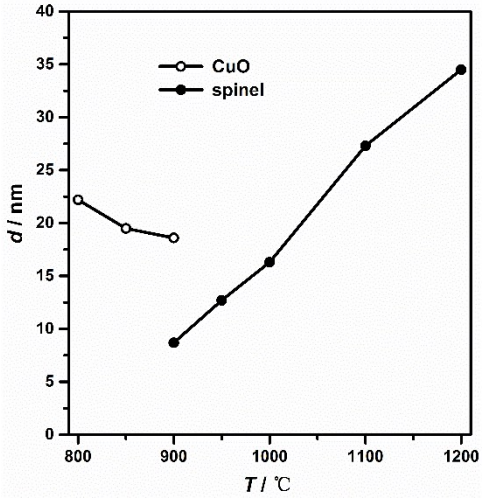

Fig. S1. Crystallite size of CuO and of spinel phase as a function of calcination temperature for CA*T* samples. (Average crystallite diameter of spinels, which were calculated by means of the Scherrer equation applied to the six main diffraction peaks, showing a nearly linear increase from 8.7 to 34.5 nm between 900-1200 ℃. The size of CuO decreases from 800 to 900 ℃, and the CuO phase disappears from XRD patterns at 950 ℃ and above)

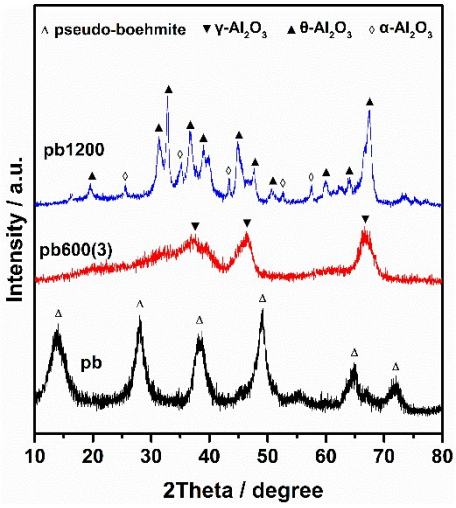

Fig. S2. XRD patterns of pseudo-boehmite (pb) and its heated products. (pb600(3) represented that pseudo-boehmite was calcined from *RT* to 600 ℃ and kept for 3h, and pb1200 indicated pseudo-boehmite was calcined from *RT* to 1200 ℃ and cooled down naturally.)

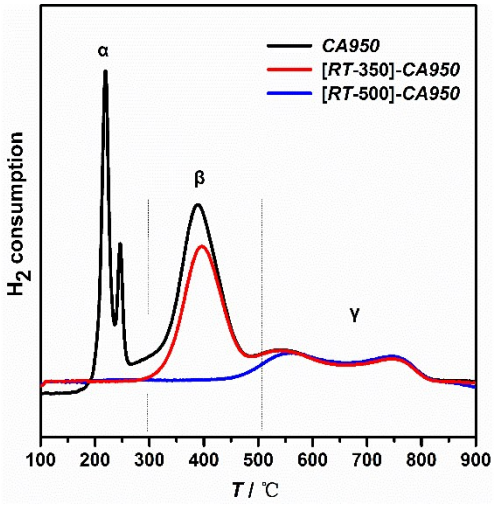

Fig. S3. H_2-TPR profiles of CA950 and treated ones under different conditions for the purpose of identifying the possible formation of $CuAlO_2$ phase as an intermediate during spinel reduction. (CA950 represented non-treated CA950 reduced from *RT* to 900 ℃. [*RT*-350]-CA950 represented that CA950 was reduced from *RT* to 350 ℃ followed by a formal TPR from *RT* to 900 ℃, and similarly [*RT*-500]-CA950 indicated the pre-reduction was performed from *RT* to 500 ℃. The obtained profiles show nearly the identical γ-peak, suggesting γ-peak is not a secondary reduction of an intermediate, which is supported by XRD data as shown in Fig. S4)

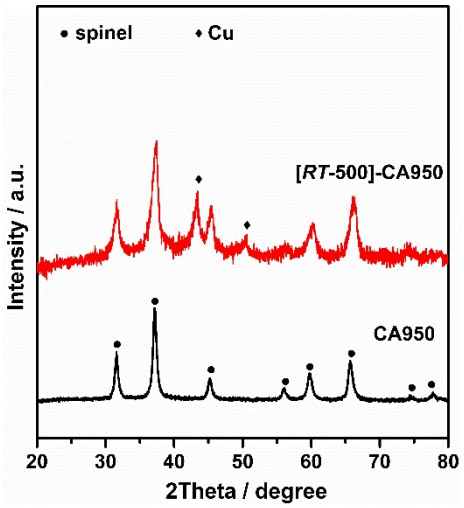

Fig. S4. XRD patterns of CA950 and [*RT*-500]-CA950, indicating the absence of $CuAlO_2$ phase in Cu-Al spinel solid solution.

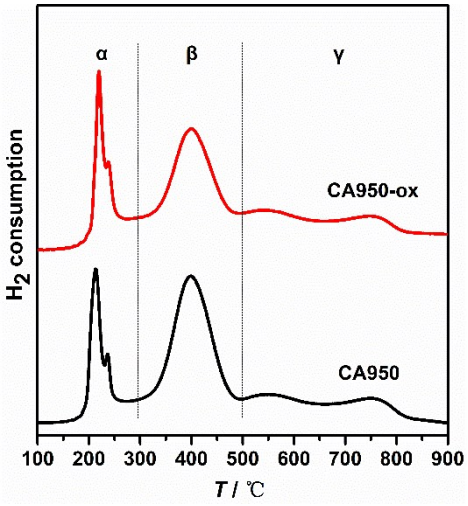

Fig. S5. H_2-TPR profiles of CA950 and CA950-ox, indicating the absence of $CuAlO_2$ phase in Cu-Al spinel solid solution. (CA950-ox represented that CA950 was oxidized in 80% O_2/N_2, the oxidation temperature condition was same as calcination of CA950 in air)

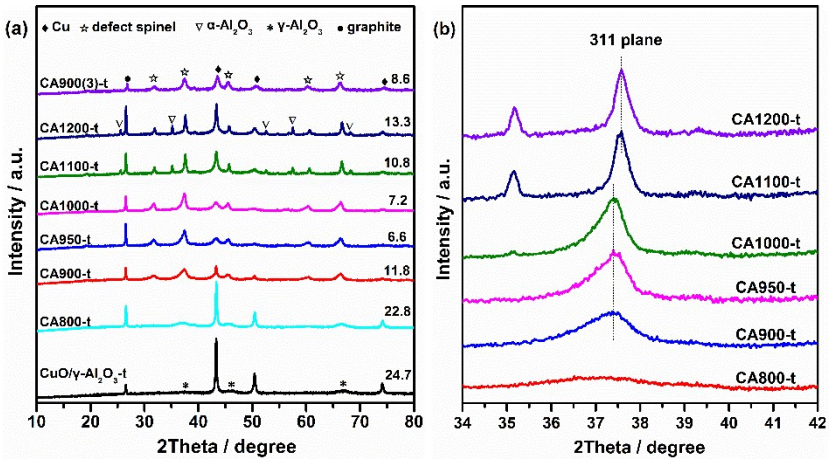

Fig. S6. XRD patterns of tested Cu-Al spinel catalysts **(a)** and details of 311 plane of Cu-Al defect spinel **(b)**. (The CA950 generates the smallest copper particles (6.6 nm) after MSR test. The 2theta values of CA900-t, CA950-t and CA1000-t almost peak at the same position with broadened peak width but higher values with narrowed peak width for CA1100-t and CA1200-t. This indicates that the content of remaining Cu in spinel structure after MSR is higher for low temperature calcined samples)

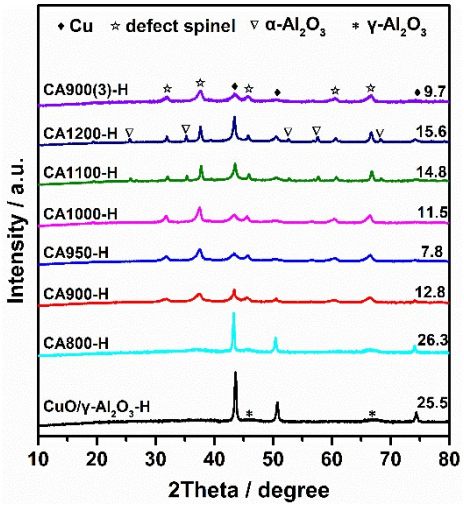

Fig. S7. XRD patterns of reduced Cu-Al spinel catalysts and copper particle size in nm calculated by the Scherrer equation. (CA*T*-H represented that the sample CA*T* was reduced in H_2 from *RT* to 500 ℃ and kept for 20 min. The CA950-t produces the smallest copper particles (7.8 nm) after reduction treatment.)

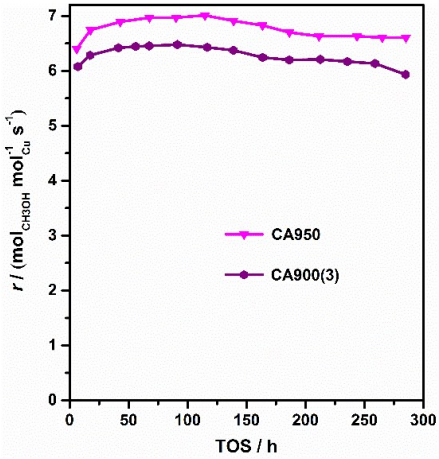

Fig. S8. Comparison of CH_3OH conversion rate in MSR over CA*T* catalysts that contained nearly the same content of Cu-Al spinel. (As CA900(3) owns the same spinel content and similar reducibility with CA950, but a lower catalytic activity. Thus, it can be concluded that a large surface area may also contribute to the catalytic action.)

Table S1. Comparison of the conversion rate (r_1) and intrinsic activity (r_2)

TOF	CA800	CA900	CA950	CA1000	CA1100	CA1200	CA900(3)
r_1 [mol_{CH3OH} mol-1 Cu h^{-1}]	3.08	4.47	6.53	5.85	5.55	5.39	5.87
$r_2 \times 10^3$ [mol_{CH3OH} m-2 NPs h^{-1}]	7.10	5.56	4.60	4.45	5.99	7.08	5.32