Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPLEMENTARY INFORMATION

Reactivity of methanol over copper supported on well-shaped CeO_2: A *TPD-DRIFTS* study

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I. Electron microscopy images (TEM and SEM) of well-shaped ceria

The morphology of the ceria supports (Ce-X) was verified by TEM-SEM. Figure S1 shows representative images of polyhedra (S1A), rod (S1B) and cube-like (S1C) ceria morphologies. Polyhedra particles present an average size of 10 nm, rods are about 15 nm wide and 275 nm long and cubes are around 36 nm. These values were obtained from measurement of about 120 particles in each case. For Cu/Ce-X catalysts all samples kept the observed shape of the corresponding support and no copper particles could be resolved from TEM images (not shown).

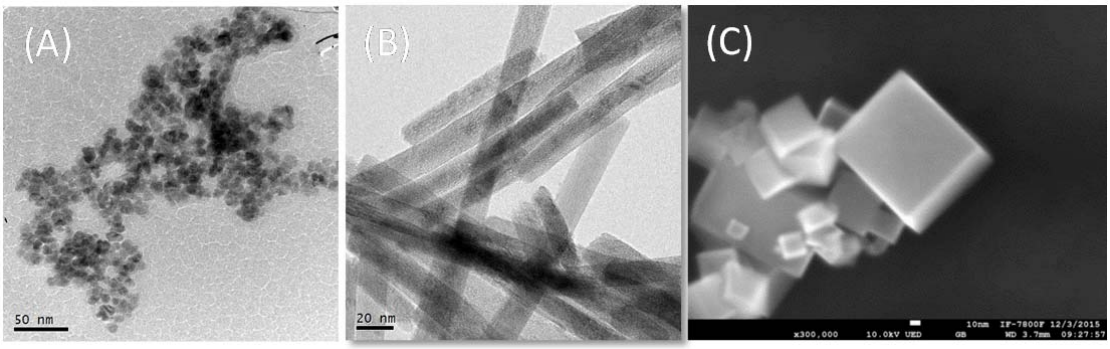

Figure S1 Typical TEM and SEM images of well-shaped CeO_2 supports: (A) Ce-P, (B) Ce-R and (c) Ce-C.

II. Thermal treatment of materials under hydrogen atmosphere prior reactivity tests.

To evaluate the state of the materials (supports and catalysts) after the activation treatment in hydrogen atmosphere prior reactivity tests, *ex-situ* experiments were followed by TCD. Figure S2A shows results for ceria support and Figure S2B for its corresponding Cu/CeO_2 catalyst. Since all samples behave similar, only rods are presented. In the bare ceria, the negative peak at the heating stage indicates desorption of adsorbed species from ceria surface; once at 300 °C, at isothermal conditions for 1 h a slight H_2 consumption is detected. In summary, activation treatment of ceria supports only helps to clean the surface and slightly reduces it. The Cu/CeO_2 catalyst presents hydrogen consumption from ca. 100-300 °C related to complete copper oxide reduction and some surface ceria reduction. Even though desorption of adsorbed species are not discarded; the rate of H_2 consumption is higher. At the isothermal stage (300 °C) no significant events are observed.

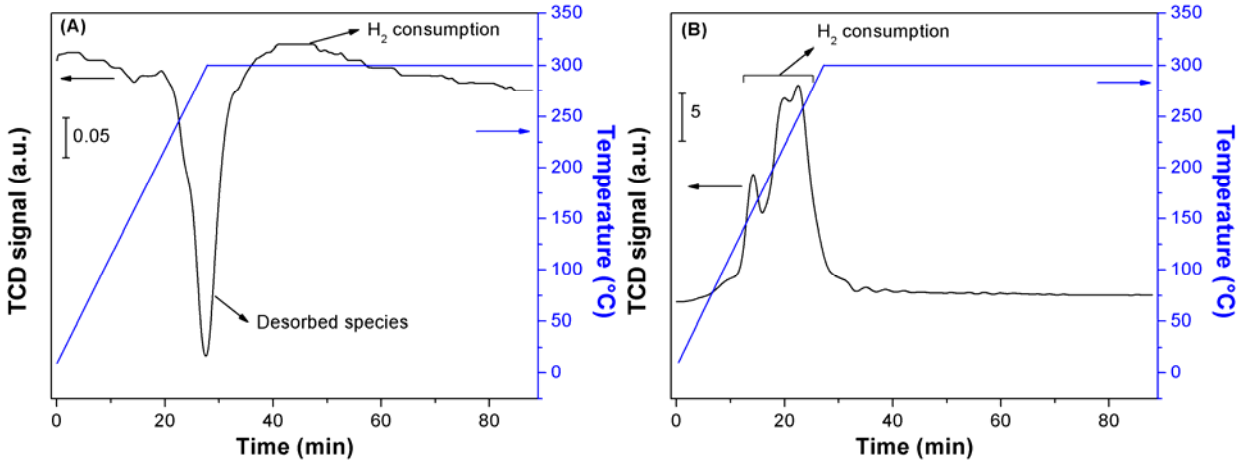

Figure S2 Activation treatment in hydrogen atmosphere followed by TCD: $5\%H_2/N_2$ 30 ml min^{-1}; heating ramp of 10 °C min^{-1} to reach 300 °C and isothermal at this temperature for 1 h. (A) Ce-R support, (B) corresponding Cu/Ce-R catalyst.

III. Analysis of desorbed products upon MeOH-TPD monitored by QMS

Distribution of desorbed products from ceria supports (Ce-X) and copper/ceria catalysts (Cu/Ce-X) is presented in Table S1. The integrated areas for each compound were corrected by the relative sensitivity values from HIDEN mass spectrometer. These values only help to visualize the differences between supports and catalysts for each desorbed product.

Table S1. Relative integrated areas of each product released from supports and catalysts into the gas phase upon MeOH-TPD monitored by QMS.

	Area (a.u.)		Area (a.u.)		Area (a.u.)	
	Ce-P	**Cu/Ce-P**	**Ce-R**	**Cu/Ce-R**	**Ce-C**	**Cu/Ce-C**
H_2	1.32E-08	1.58E-08	9.96E-09	1.36E-08	1.55E-09	1.61E-09
CO	4.81E-09	2.25E-09	5.19E-09	1.20E-09	6.45E-10	0.00E+00
CO_2	5.60E-10	2.01E-09	4.92E-10	1.32E-09	6.19E-11	3.65E-10
H_2O	1.33E-09	1.57E-09	1.75E-09	1.05E-09	0.00E+00	0.00E+00
CH_3OH	8.38E-10	5.90E-10	9.02E-10	5.88E-10	3.17E-11	7.96E-11
HCOH	3.06E-10	2.44E-10	3.33E-10	2.50E-10	0.00E+00	2.08E-11

IV. Acid-base properties of Ce-X supports and Cu/Ce-X catalysts

Temperature-programmed desorption (TPD) profiles of NH_3 and CO_2 were obtained to estimate the acid-base properties of the materials. The sample (0.050 g) was pretreated at 300 °C in hydrogen flow (10% H_2/N_2) at 30 mL min^{-1} for 1 h, then purged for 0.5 h in an inert gas flow and cooled down to room temperature in the same inert atmosphere. For acidity measurements, adsorption of NH_3 (10% NH_3/He) at 20 mL min^{-1} for 1 h was followed by purge for 0.5 h in helium flow (30 mL min^{-1}). Base properties were determined by adsorption of CO_2 (50% CO_2/He) at 30 mL min^{-1} for 0.5 h followed by purge for 0.5 h in argon flow (30 mL min^{-1}). In both experiments, samples were heated from 30 to 700 °C at 10 °C min^{-1} under an inert gas flow. The amount of evolved NH_3 was determined using thermal conductivity detector (TCD) while the amount of evolved CO_2 was determined by mass spectrometry.

CO_2-TPD profiles are similar for Ce-X supports and Cu/Ce-X catalysts (Figures S3A and S3B); three desorption peaks are observed at low, medium and high temperature. NH_3-TPD profiles are quite similar for Ce-P and Ce-R supports (Figure S3C), with a large peak at temperatures lower than 200 °C and a small one at around 350 °C, characterizing respectively, weak and medium-strong acid sites. On their side, Cu/Ce-P and Cu/Ce-R catalysts (Figure S3D) showed a complex desorption profile with a common feature, higher number of medium-strong acid sites compared to the supports. For Ce-C sample, only strong acid sites characterized by desorption at around 450 °C is observed. The Cu/Ce-C catalyst share with their catalysts counterparts the low temperature desorption peak (weak acid sites) but in this sample stronger acid sites are present (desorption peak at 572 °C).

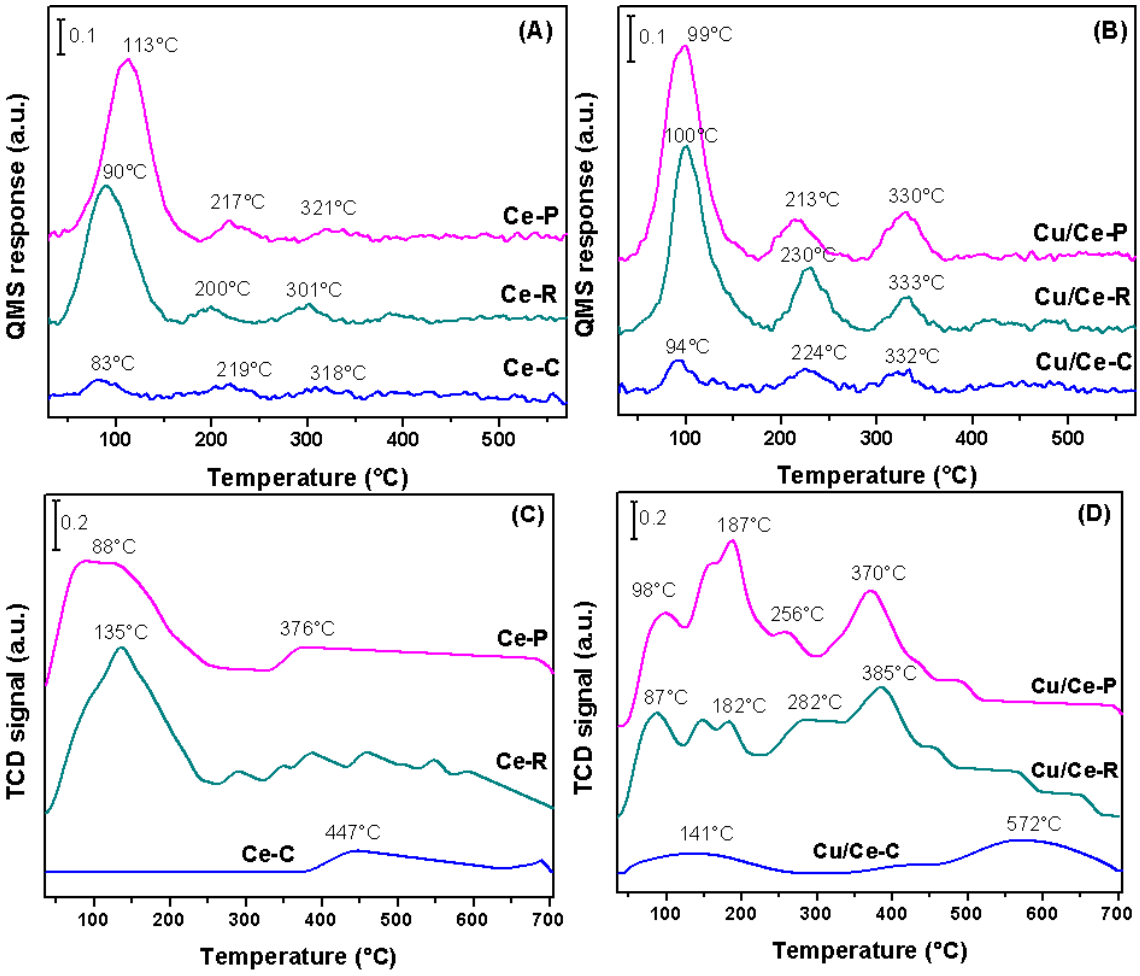

Figure S3. Acid-base properties of supports and catalysts. CO_2-TPD profiles of (A) Ce-X supports and (B) Cu/Ce-X catalysts; NH_3-TPD profiles of (C) Ce-X supports and (D) Cu/Ce-X catalysts.