Supporting information

Highly Active Ceria Supported Ru Catalyst for the Dry Reforming of Methane: In-situ Identification of $Ru^{\delta+}$-Ce^{3+} Interactions for Enhanced Conversion

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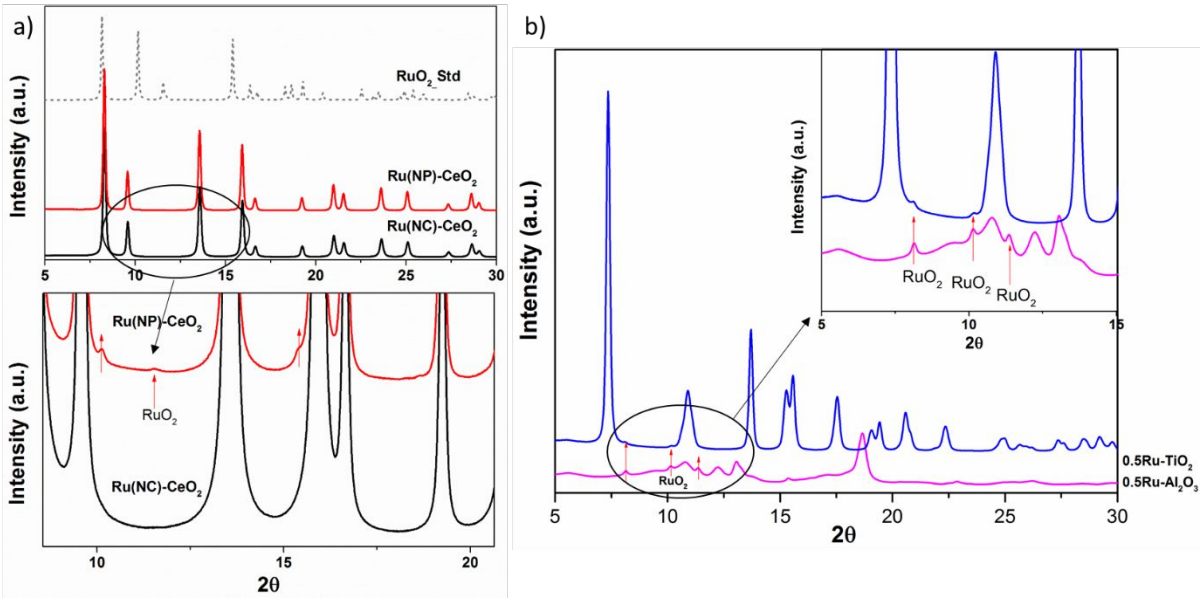

Figure S1. XRD pattern of the as-prepared samples: a) Ru(NP) and Ru(NC) on ceria, b) Ru-TiO_2 and Ru-Al_2O_3. The RuO_2 diffraction regions were magnified for a clear view.

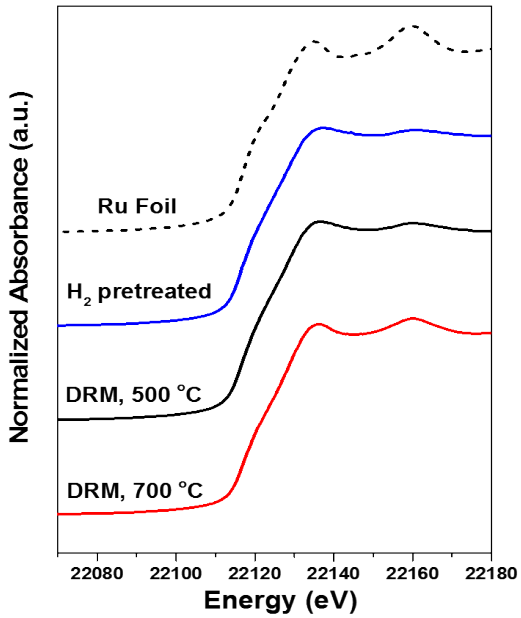

Figure S2. *In-situ* Ru K-edge XANES data of 0.5 wt% Ru(NC)-CeO_2 under H_2 pretreatment (400 °C) and dry reforming of methane (500 °C and 700 °C).

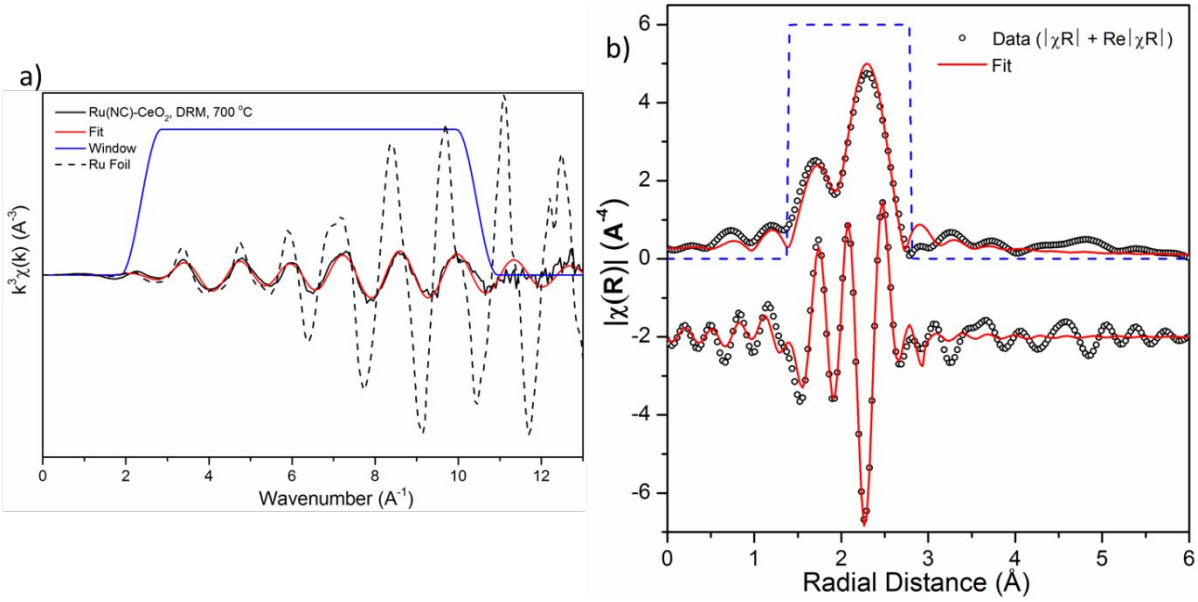

Figure S3. EXAFS Fittings of the 0.5 wt% Ru(NC)-CeO_2 catalyst at 700 °C under DRM reaction conditions, a) K space, b) R space.

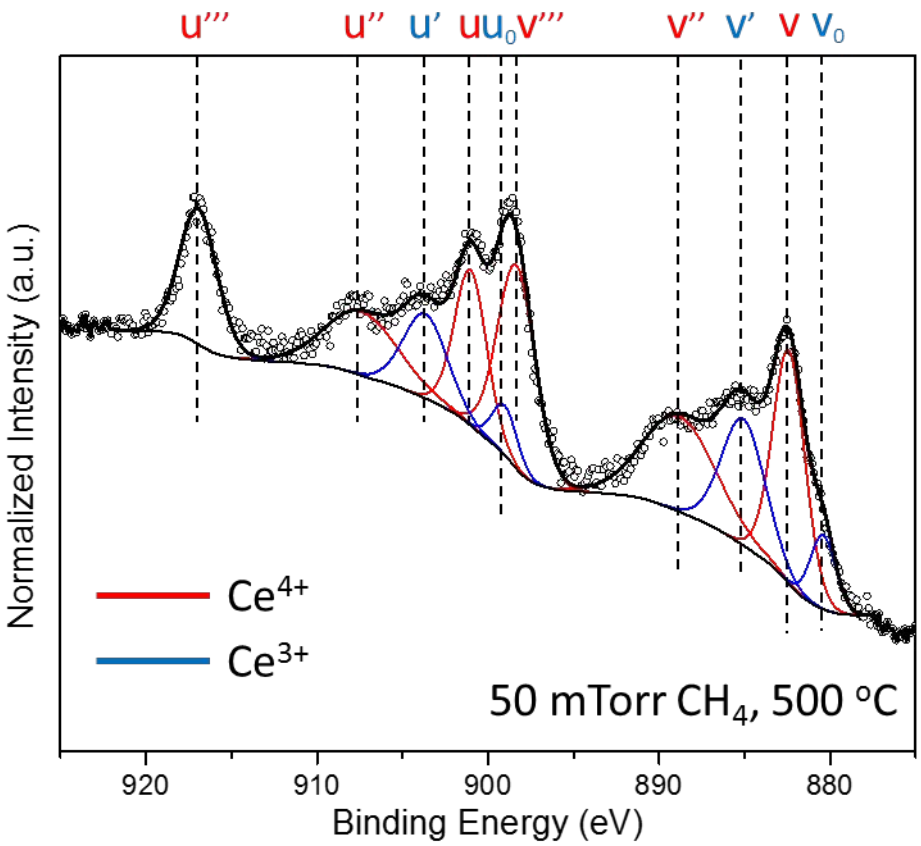

Figure S4. One example of the peak deconvolution for the Ce 3d region of the in-situ AP-XPS data, reaction condition: 50 mTorr CH_4 at 500 °C. The $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ concentration were derived by taking ratio of the total peak areas of each component.[1-2] Open circles represent the experimental data.

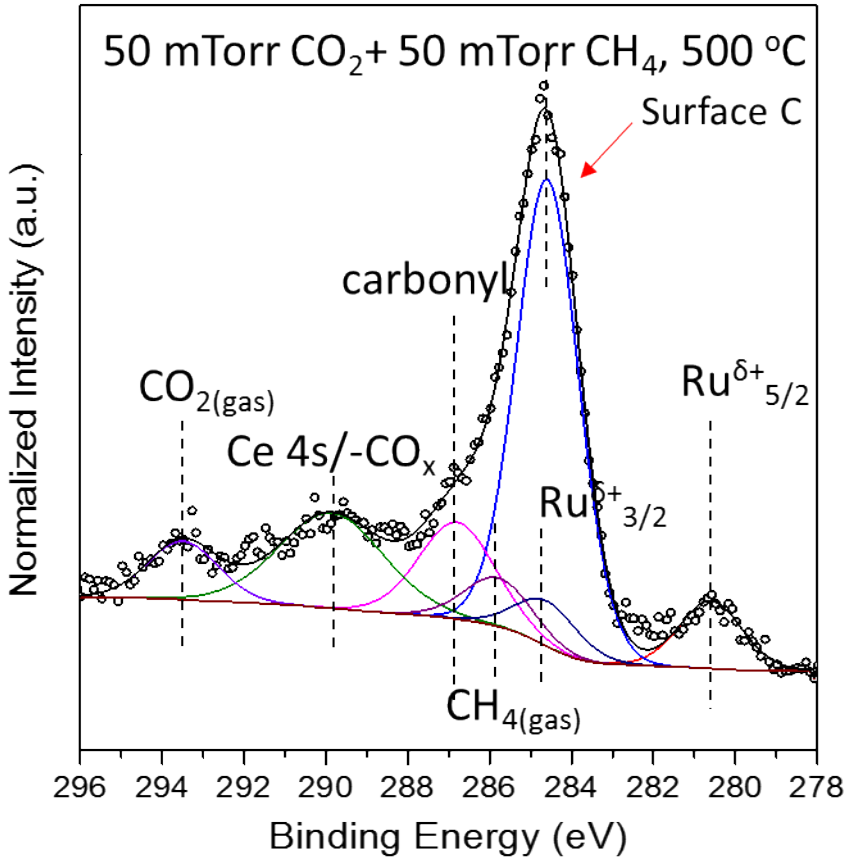

Figure S5. One example of the peak deconvolution for the C 1s + Ru 3d region of the AP-XPS data, reaction condition: 50 mTorr CO_2 + 50 mTorr CH_4 at 500 ^oC. The C peak areas (284. 6 eV) were then used to estimate the development of surface carbon. Open circles represent the experimental data.

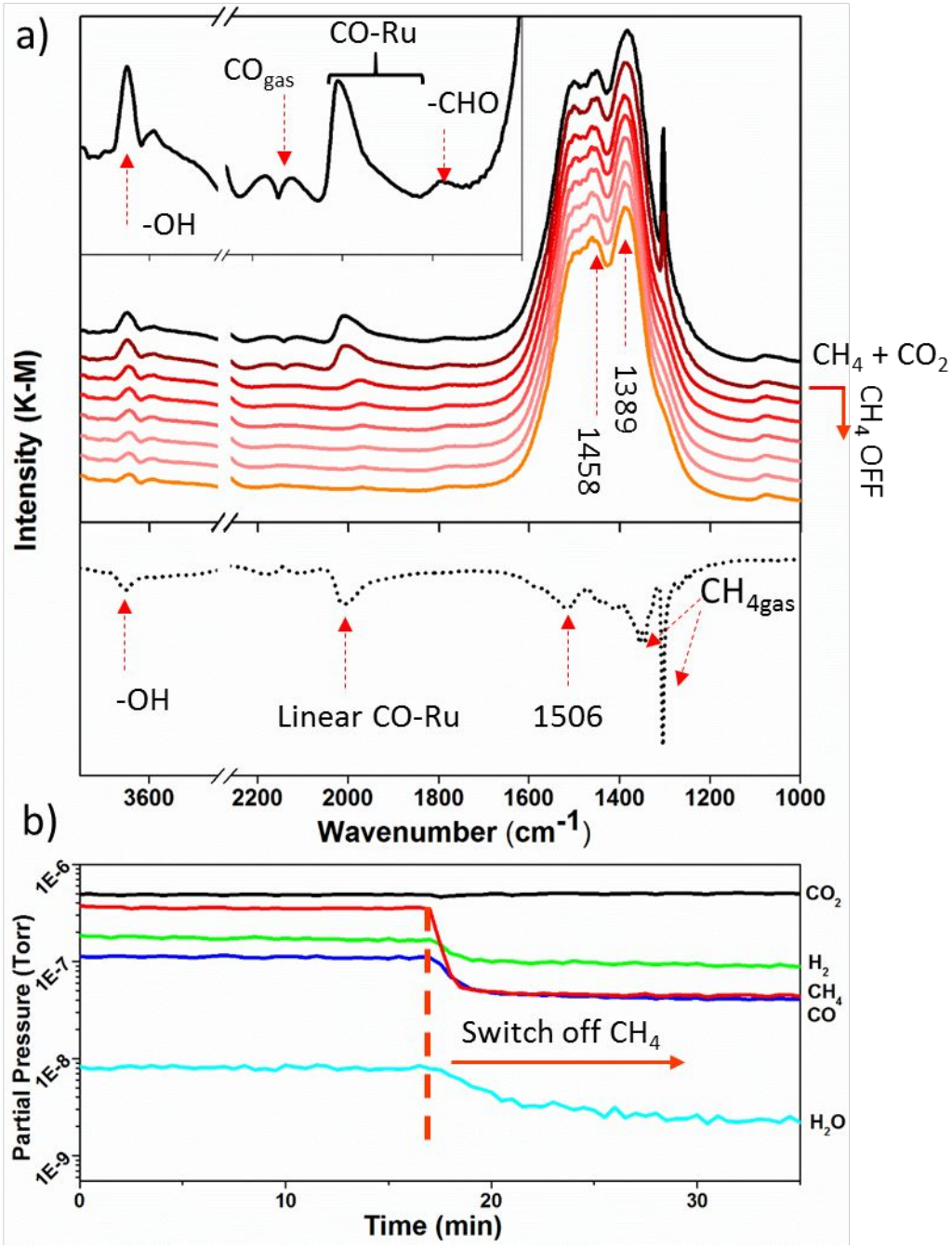

Figure S6. a) In-situ DRIFTS spectra collected over the 0.5 wt% Ru(NC)-CeO_2 sample under steady-state reaction conditions (CH_4/CO_2/He=5/5/30 ml/min) at 500 ^oC with subsequently switching off CH_4. Spectra were recorded per minute and plotted every third of them. The inset figure shows the blow-up region between 3700-1600 cm^{-1}. The bottom dash line was obtained by subtracting the '$CH_4 + CO_2$' spectrum (black line) from the last 'CO_2-only' spectrum (orange line)

to get the dynamic variation of the surface adsorbed species. b) The corresponding gas phases evolution monitored by a mass spectrum.

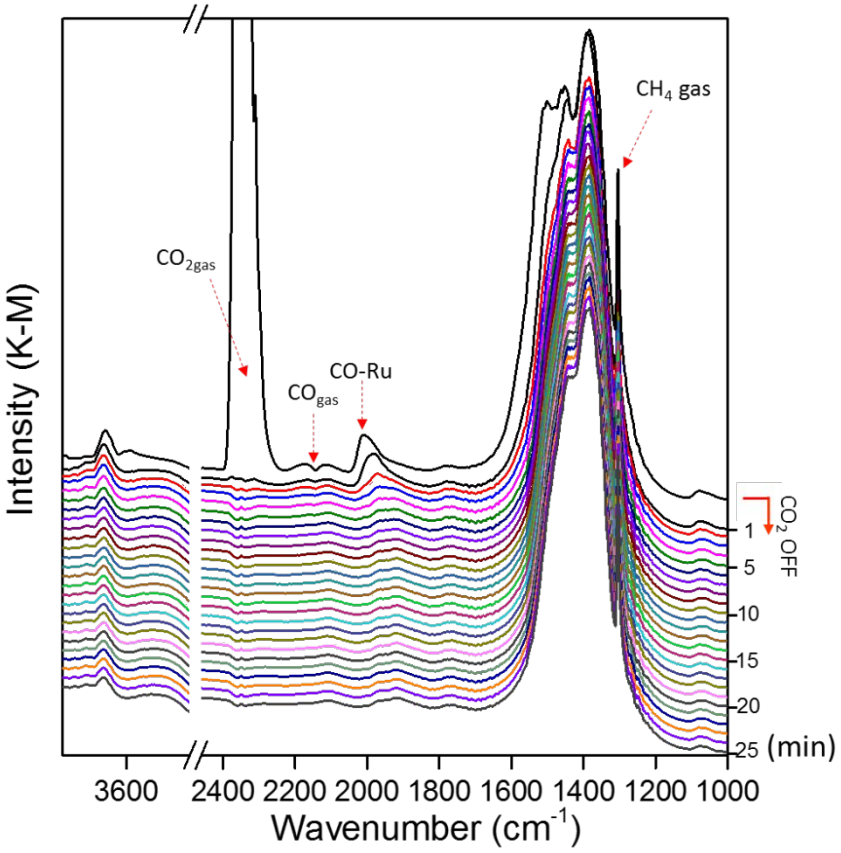

Figure S7. The full set of in-situ DRIFTS spectra collected as a function of time for the experiment in Figure 9.

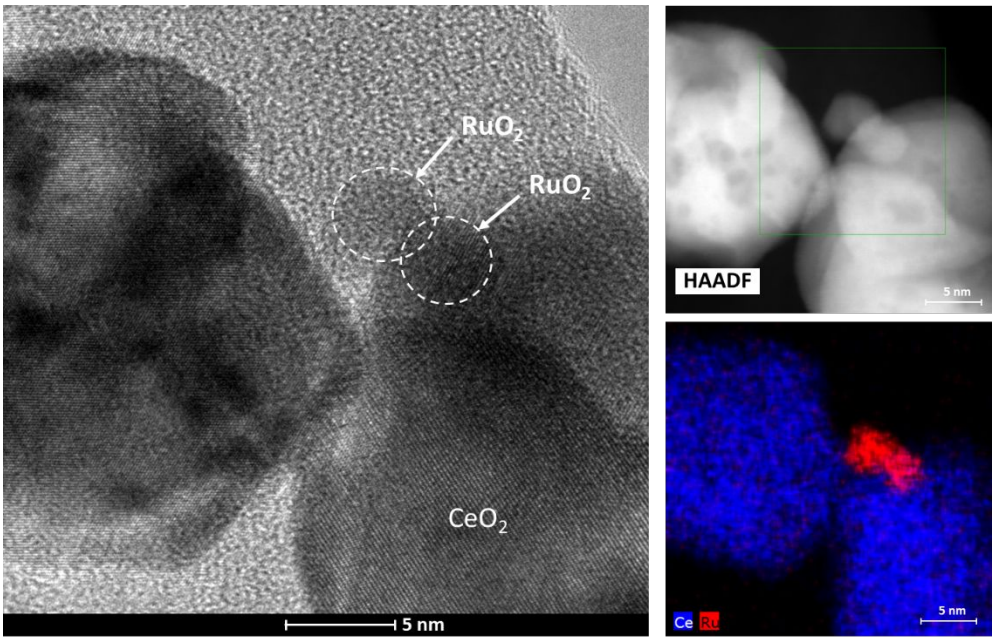

Figure S8. a) TEM image, b) HAADF-STEM image and c) EDX elemental mapping of the as-prepared 0.5 wt% Ru(NP)-CeO_2 catalyst.

Reference

(1) Mullins, D. R.; Overbury, S. H.; Huntley, D. R. Electron Spectroscopy of Single Crystal and Polycrystalline Cerium Oxide Surfaces. *Surf. Sci.* **1998**, *409*, 307-319.

(2) Sohn, H.; Soykal, I. I.; Zhang, S.; Shan, J.; Tao, F.; Miller, J. T.; Ozkan, U. S. Effect of Cobalt on Reduction Characteristics of Ceria under Ethanol Steam Reforming Conditions: Ap-Xps and Xanes Studies. *J. Phys. Chem. C* **2016**, *120*, 14631-14642.