

Supplementary Information

Enhanced Catalytic Methane Coupling using Novel Ceramic Foams with Bimodal Porosity

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Foaming Process

For the preparation of the ceria and samaria foams, we used commercially available isocyanate PAPI 27 (DOW Chemical). All syntheses were performed using 27.5 %vol of ceramic powder, 0.4 mL polyethylene glycol - 200, 0.1mL Tween 80 and 0.8 mL of isocyanate. 1 mg of Diazabicyclo[2.2.2]octane was added to start the foaming process. To ensure fast and proper homogenisation of the slurry, we used a drill equipped with a PTFE spatula for mixing. To increase the amount of gas released during the foaming process, 12 µL of water were added before the end of the mixing. 24 hours after the preparation, the hybrid-foams were cut into the desired shape and sintered in a furnace. The maximum temperature of 1300 °C for the samaria and 1650 °C for the ceria was held for only 2 hours to obtain a high surface area monolith. To ensure slow burning of the PU without destroying the foam, we selected a heating rate of 1°C/min up to 600 °C and increased the heating rate afterwards to 2 °C/min. The selected cooling rate was 3 °C/min.

Powder X-ray Diffraction (p-XRD)

The powder diffraction was performed using a X'PertPro MPD diffractometer (PANalytical) with Cu $K\alpha_{1,2}$ radiation. The 2θ scanning region was 5-120°. The experiment shows that the samaria has monoclinic structure, while the ceria is cubic.

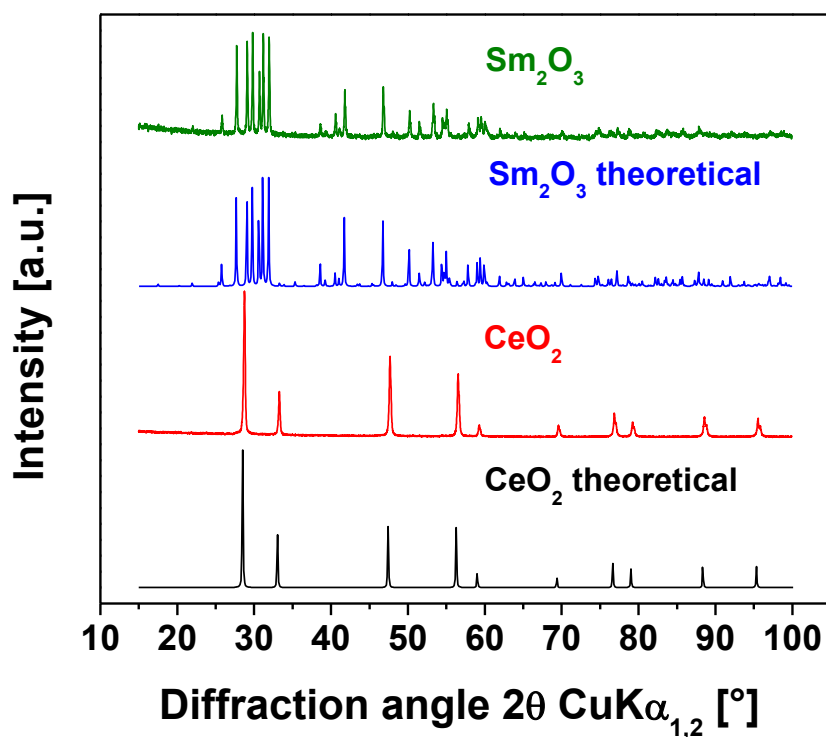


Figure 1: X-ray diffractograms of a samaria and a ceria foam. The samaria exhibits the monoclinic high temperature phase, the ceria is cubic.

Mercury Porosimetry

Hg-Porosimetry was performed using a Quantachrome Autoscan-60 Mercury Porosimeter and the Quantachrome filling apparatus (Boynton Beach, FL).

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) of the oxides was performed at a heating rate of 5 K/min in air using a STA 449 F3 Jupiter® Netzsch Germany.

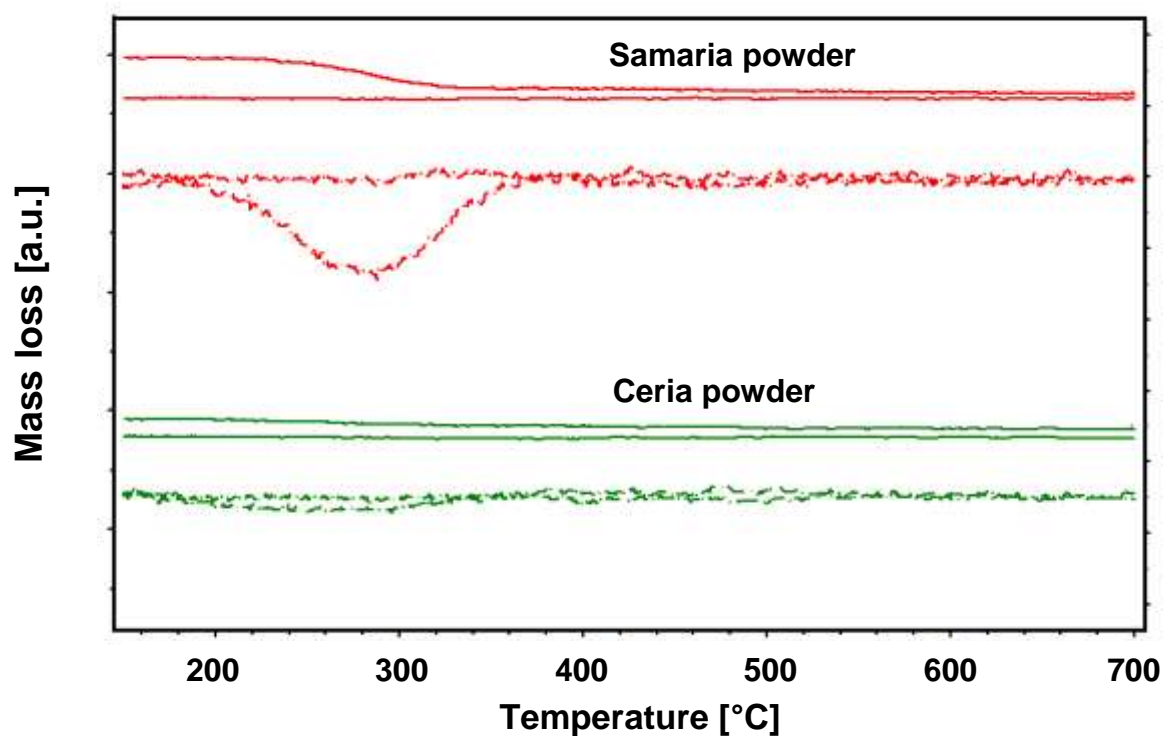


Figure 3: Thermogravimetric analysis of the samaria (upper 2 curves) and the ceria (lower 2 curves) ceramic powders used as a starting material for the foam synthesis. The analysis was carried out during heating and cooling, showing that the weight loss is irreversible. The dashed lines show the first derivative of the mass loss of the two powders. The ceria does not show a specific weight loss while the samaria shows a weight loss between 200-350 °C due to the higher amount of adsorbed water on the surface of the powder.

Diffusive Reflection Fourier Transform Spectroscopy (DRIFTS)

The DRIFTS experiments were performed using an Agilent Cary 670 equipped with a MCT Detector and a Praying Mantis Diffuse Reflection Cell from Harrick. The collected spectra were referenced to samaria heated to 140 °C (to remove adsorbed water from the cell and the surface of the powder).

The reflectivity (R) of each spectrum was corrected by referencing the reflectivity by the reflectivity of KBr at the specific temperature (Equation 1).

$$-\log(R') = \frac{R(\text{Samaria } T1) * R(\text{KBr } 140^\circ\text{C})}{R(\text{Samaria } 140^\circ\text{C}) * R(\text{KBr } T1)} \quad \text{Eq. 1}$$

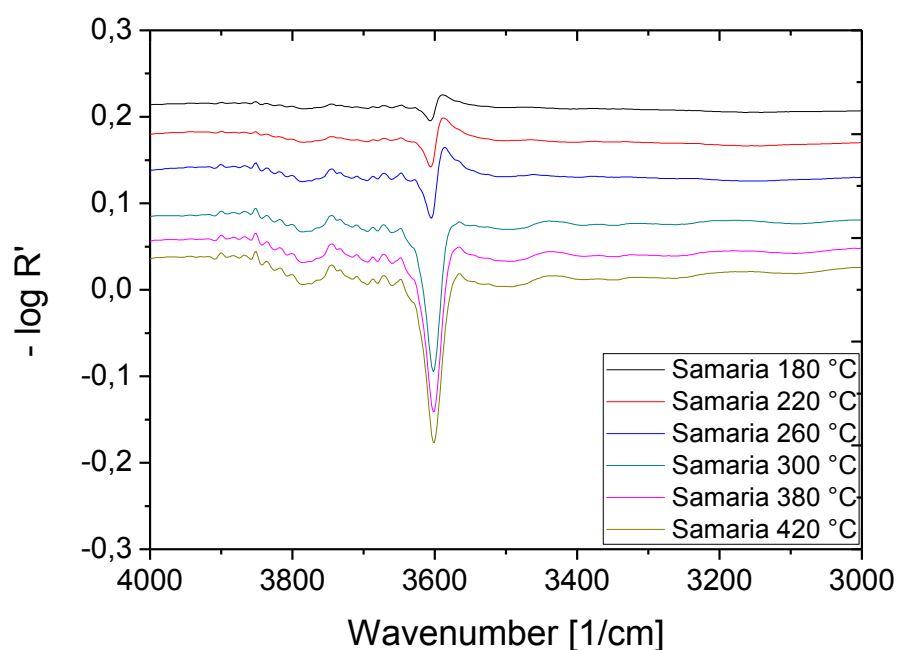


Figure 4: The diffuse reflectance infrared spectra of samaria are presented. Spectra were acquired at different temperatures between 180 °C and 420 °C. It is clearly visible that the main loss of OH groups takes place between 260 °C and 300 °C (represented by the increasing reflectivity in the OH vibration region at $\sim 3600 \text{ cm}^{-1}$) already indicated by the TGA data.

The series of spectra reveal that the weight loss observed with TGA at around 280 °C is connected with the loss of OH groups from the surface of the samaria powder used for the foam synthesis.

Scanning Electron Microscopy (SEM) The microscopic structure and the shape of all foams were characterized with a benchtop scanning electron microscope (Neoscope JCM 5000 M, JEOL-Nikon) operated at 15 kV with a working distance of 12 mm. To decrease charging effect during the acquisition a thin gold layer was sputtered onto the investigated foams.

Magnet Resonance Imaging (MRI)

All magnetic resonance imaging (MRI) experiments were performed using a 7-Tesla BrukerBiospec 70/20 system (Bruker-Biospin, Ettlingen, Germany) equipped with self-shielded gradients (maximum strength 400 mT/m, slew rate 4000 mT/m/ms). A quadrature volume coil (72 mm inner diameter) was employed for both radiofrequency (RF) excitation and signal reception. For the experiments, an optimized sample holder was machined using Teflon for all parts that are inserted into the RF coil, ensuring that proton signals exclusively originate from the sample. MRI measurements were performed using the proton signal of water in which the porous structures were inserted. As rather short effective transverse relaxation times T_2^* were observed in the porous samples, a zero-echo time (ZTE) pulse sequence was applied for 3D MRI. In the ZTE sequence, the read gradient used for spatial encoding is switched on prior to RF excitation achieved by a short rectangular RF pulse. Signal detection is started immediately after RF excitation, thus minimizing signal losses by T_2^* relaxation. The ZTE pulse sequence supplied by the manufacturer was modified by adding outer volume suppression pulses to saturate signals originating from parts of the RF coil. The parameters of the ZTE pulse sequence were as follows: RF excitation by a 2 μ s rectangular pulse with a flip angle of 4°, repetition time (TR) 10.75 ms, 224 complex data points per TR, spectral width 150 kHz, radial sampling using 158026 projections without polar undersampling, image matrix size 224x224x224, field-of-view 32³ mm³, 4 averages yielding in a total measurement time of about 113 minutes. In principle, all MRI pulse sequences known from standard MRI applications could be applied. However, since within the porous structures rather short transverse relaxation times are observed for the protons of water¹, MRI measurements with ultrashort echo times (TE) are required to minimize signal losses. Using other pulse sequences may lead to misinterpretations as the absence of NMR signals

could not only be due to the absence of water, but also to very short transverse relaxation times caused by the interaction of the water with the foam. However, using MRI with ultrashort TE allows the detection of the water signal within the pores of the foam.

Catalytic Activity of Oxidative Methane Coupling

Product analysis was performed by an on-line Agilent 6890N gas chromatograph equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID) in series along with two packed columns, a polar Porapak Q capillary column and a molecular sieve, also in series with a column isolation valve in between the columns. The former was used to separate the CO₂, C₂H₆, and C₂H₄ and the latter for CH₄, O₂, N₂, CO, H₂ separation. Calibration curves for product formation and methane conversion were taken by feeding a known flowrate of the calibration gas to the GC and measuring the calibration gas to N₂ TCD peak ratio. All calibration curves were linear and regression analysis resulted in fit values of >98%. Measurements were taken at each reaction parameter after 20 minutes to allow for the reaction to reach steady state and a repeat was taken to ensure reproducibility. The water produced during the reaction was separated from the gas phase products prior to entering the GC using a condenser trap emerged in an ice-water bath.

References:

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- [2] Jones, S; Neal, L; Hagelin-Weaver H. *Applied Catalysis B* 2008, 84, 631-642.
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