

Reaction of steam and methane over novel YSZ –LaB₆ composites and nickel-YSZ cermets

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Aims

Current SOFC Ni-YSZ cermet anodes suffer from a number of problems when exposed to methane-containing fuels at typical operating temperatures. These include; carbon deposition, nickel sintering and poisoning by sulfur present in the methane supply; ultimately these processes result in degradation in fuel cell performance.

In this study our goal is to explore an alternative anode material that is resistant to carbon deposition and sintering. The system under investigation is a composite that is fabricated from sintering LaB₆ and 8mol%YSZ under an argon atmosphere. A comparison in catalytic activity is made with a number of Ni-8mol %YSZ cermets using temperature programmed methods under CH₄ and CH₄-H₂O atmospheres.

Material fabrication

The Ni-YSZ cermets were fabricated using Ni electroless plating (EP), with either N₂H₄ or NaH₂PO₂ as reducing agent, and Ni nano powder with a commercial YSZ powder. The Ni content was around 40% following sintering under 5% H₂/Ar at 1000°C for 2 hrs (Table 1). The YSZ-LaB₆ composites were made by sintering required mixtures of commercial YSZ and LaB₆ powders in Ar at 1350°C for 2 hrs (Table 2). XRD of the as-made composites indicate that they are not single phase; ZrB₂ is present, unreacted LaB₆ and LaBO₃/La(BO₂)₃ type phases depending on the proportions of starting materials used to fabricate the composite, while the Ni cermets showed metallic Ni and the support (patterns not shown).

Material catalytic testing

Catalytic tests were carried on an automated catalytic testing rig comprising of; gas-supply and control, microreactor and online mass spectrometer. Dry CH₄ was supplied at 5 kPa (in He) for the CH₄-TPR tests (600-1000°C) and 0.8 kPa CH₄ and 0.8 kPa H₂O were co-fed (in He) for steam reforming (50-1000°C). Typically 50 ±3 mg of fresh sample was used and a heating rate of 10°C min⁻¹ to the final set point temperature. The sample was then cooled to room temperature in He for post operation analysis.

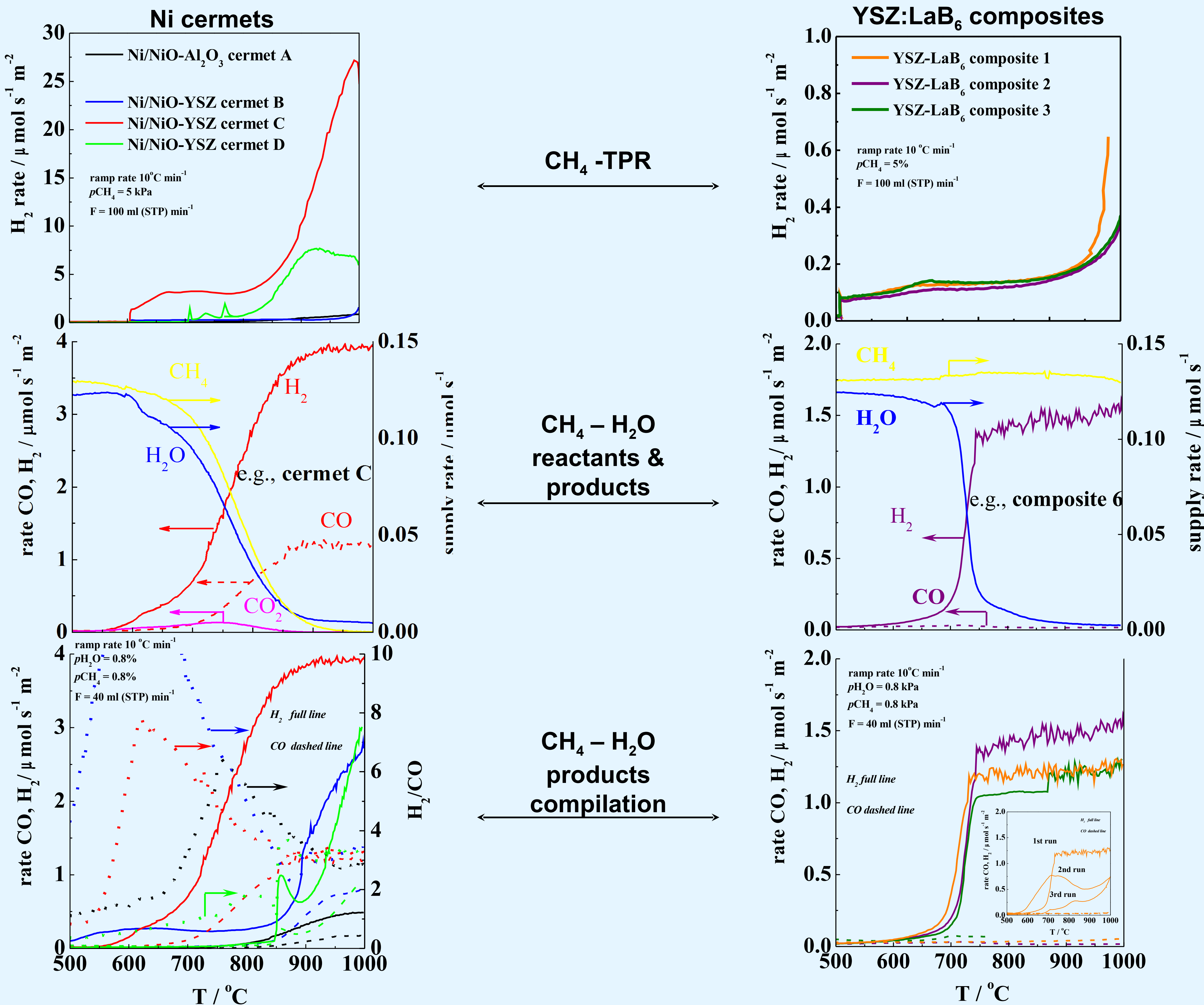
Table 1. 40% Ni cermets

cermet A	Ni/NiO- γ-Al ₂ O ₃ EP (N ₂ H ₄)	34.4 m ² g ⁻¹
cermet B	Ni/NiO-YSZ EP (NaH ₂ PO ₂)	BET 4.2 m ² g ⁻¹
cermet C	Ni/NiO-YSZ EP (N ₂ H ₄)	BET 4.5 m ² g ⁻¹
cermet D	Ni/NiO-YSZ (Ni nano powder)	4.0 m ² g ⁻¹

Table 2. YSZ-LaB₆ composites

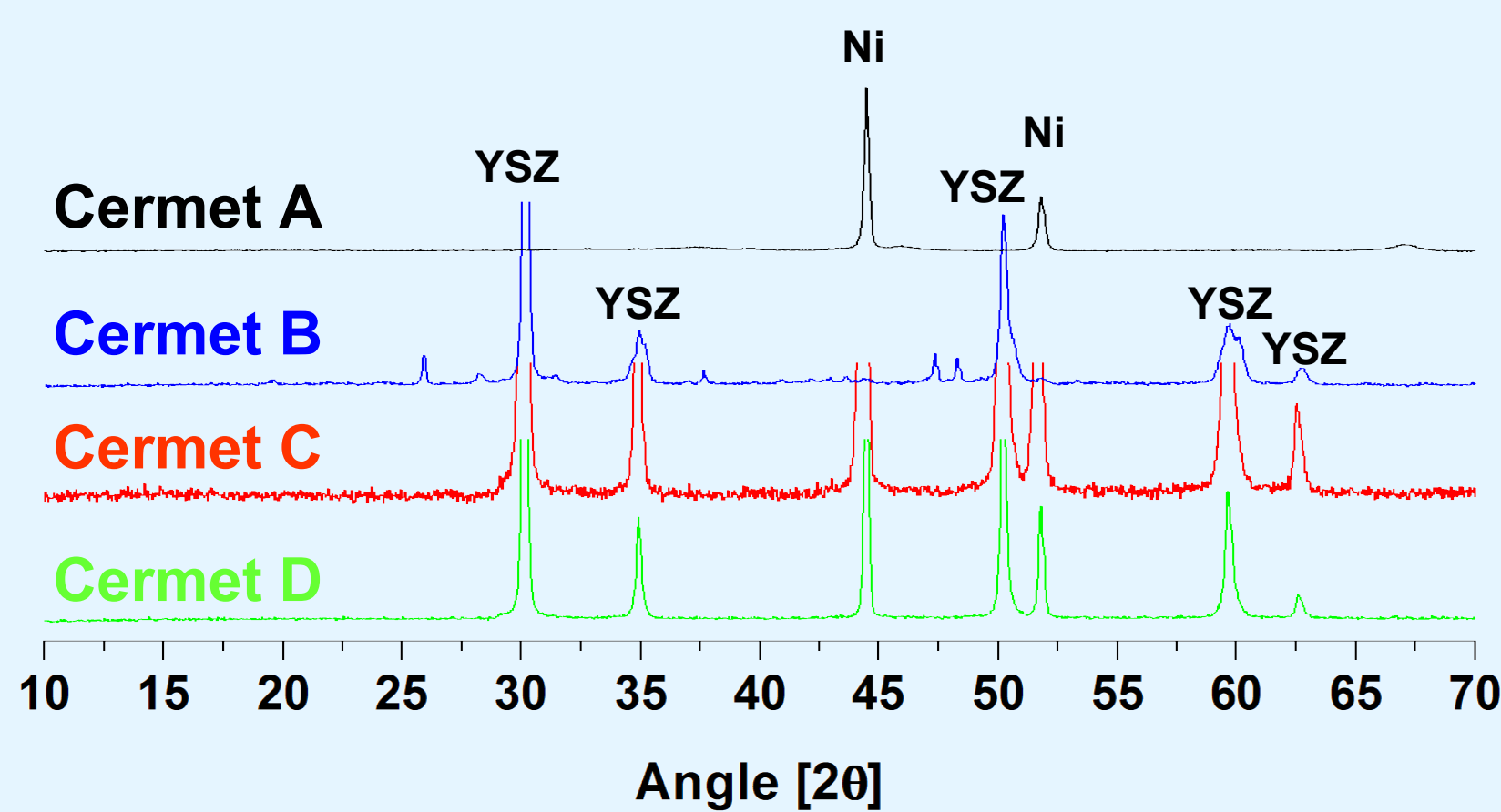
COMP1	YSZ:LaB ₆ 10:90	0.9 m ² g ⁻¹
COMP2	YSZ:LaB ₆ 50:50	1.3 m ² g ⁻¹
COMP3	YSZ:LaB ₆ 70:30	2.2 m ² g ⁻¹

Results on dry and steam methane reforming

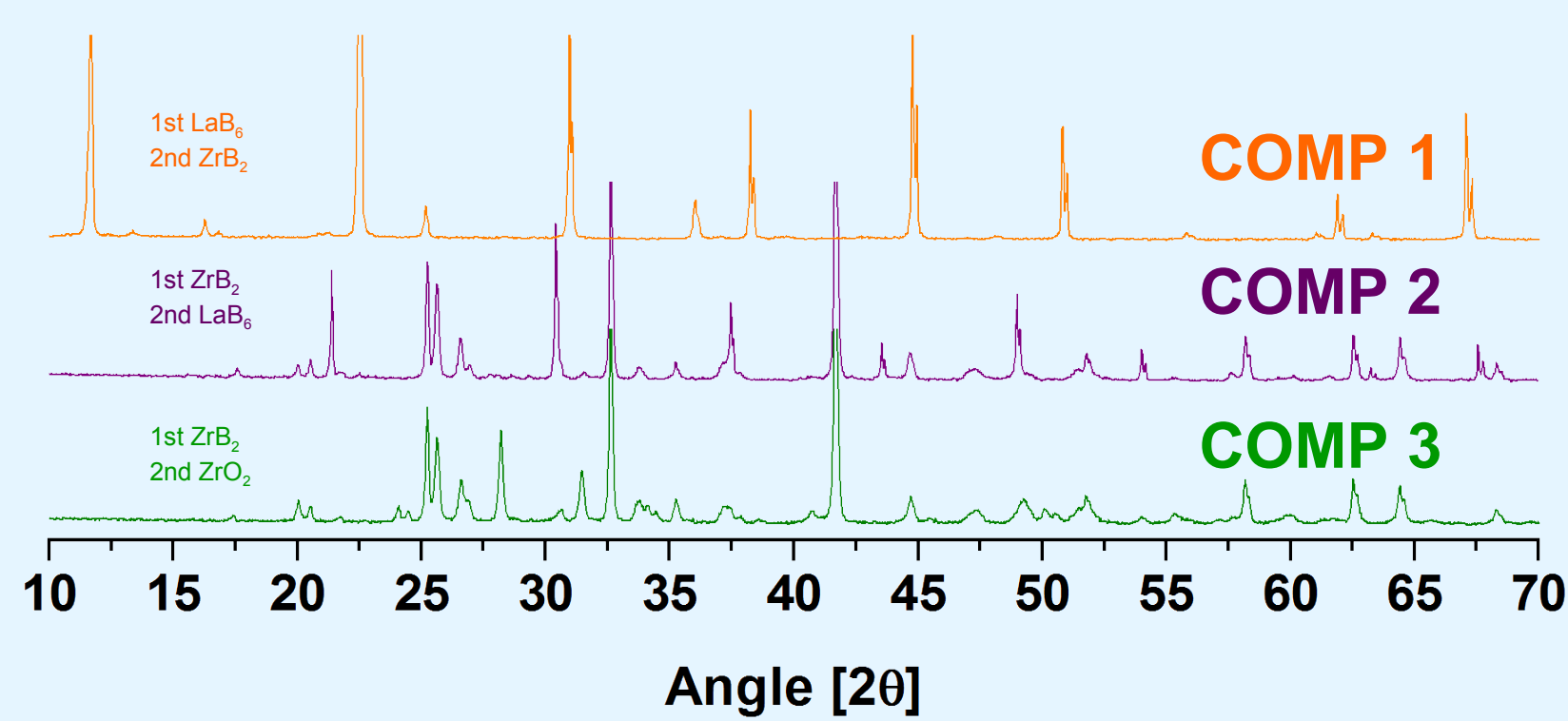


Powder x-ray diffraction

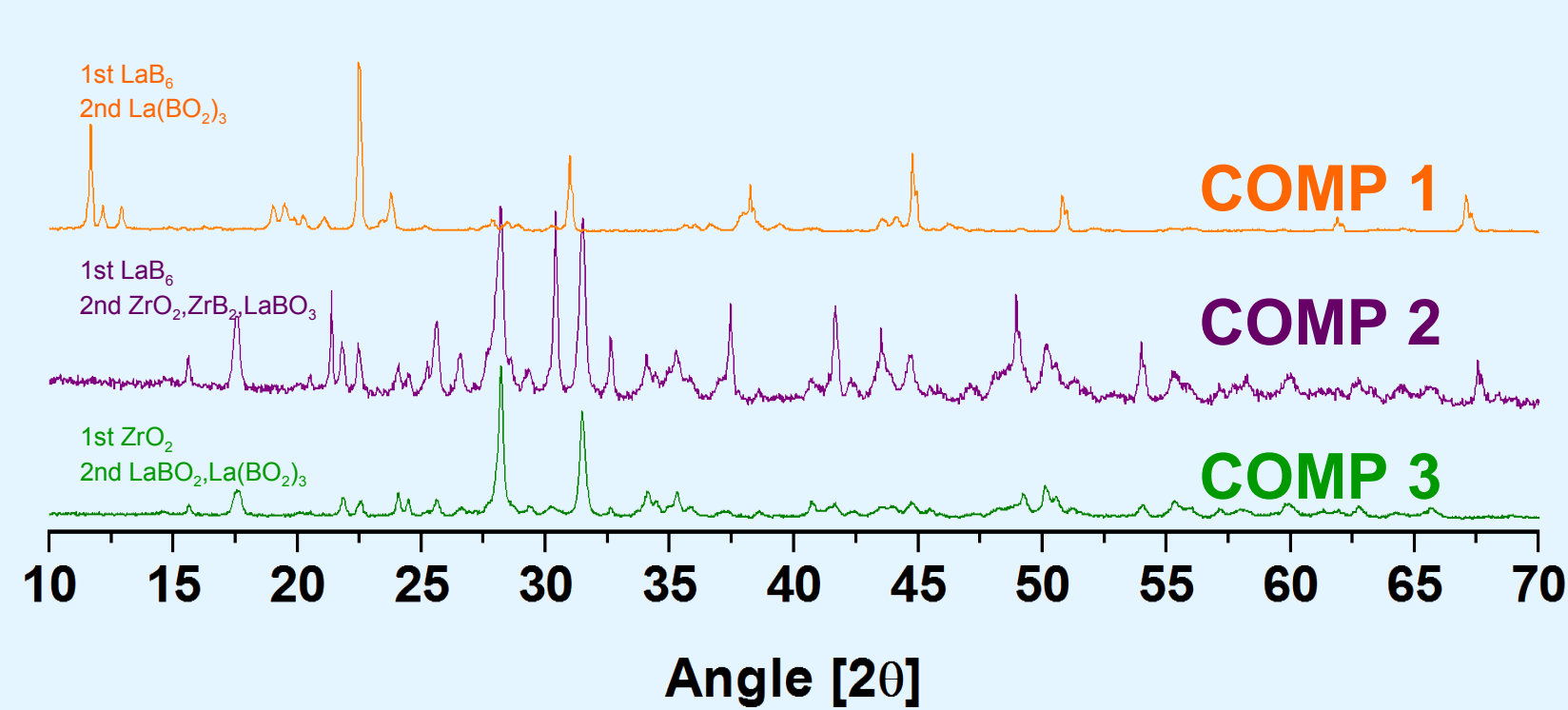
Ni Cermets – Post-op'



YSZ:LaB₆ – As prepared



YSZ:LaB₆ – Post-op'



Discussion

The initial investigation with CH₄-TPR indicated that cermets B and D would be the best candidates for steam reforming with methane. The Ni cermets steam reform the methane to mostly H₂ and CO with some coking at lower temperature as indicated by the H₂ to CO ratio. Using N₂H₄ as reducing agent in the EP deposition of Ni onto the YSZ crystals produced the most active cermet of those studied here. The YSZ-LaB₆ composites in comparison are poor at cracking the CH₄ molecule to produce H₂ but are very active for water splitting to give H₂ as the only gas-phase product. The methane during the reforming tests is inert although some coke deposition at high temperature is likely. During three methane-steam cycles there was still sign of activity for water splitting but progressively this reduced. XRD indicates “unzipping” of the composites.

