

# Supporting Information: Oxygen activation in oxidative coupling of methane on calcium oxide

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Journal of Physical Chemistry C:

Festschrift Hans-Joachim Freund and Joachim Sauer

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## ISOTOPIC SCRAMBLING

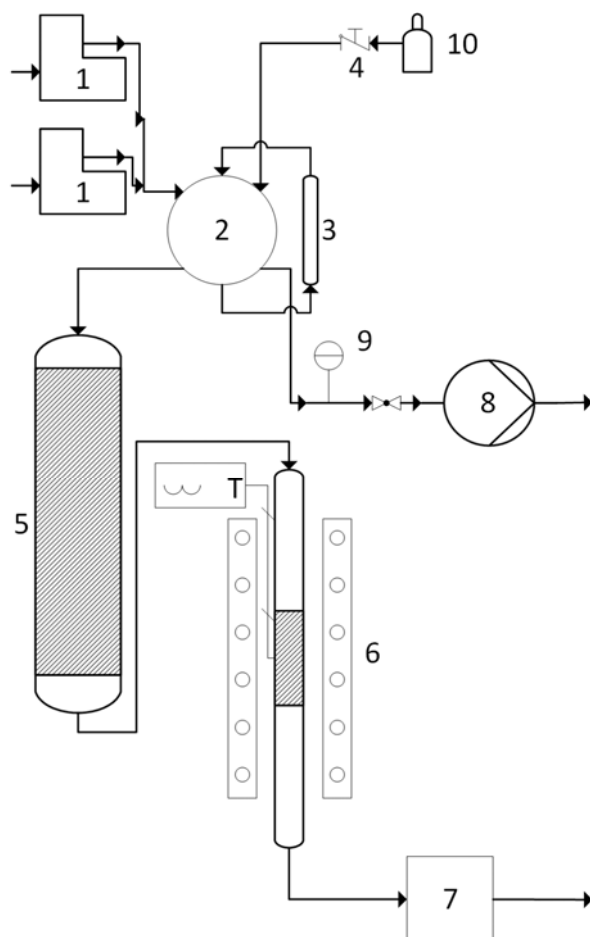


Figure S1: Scheme of experimental

setup for oxygen scrambling

experiments: 1: mass flow controller for

feed gases (helium, oxygen, carbon

dioxide), 2: Valvo VICI 6-port diaphragm

valve, 3: sample loop 250 ml-2 ml, 4:

needle valve, 5: optional drying column

(20 g CaO activated at 950°C for 24 h),

6: quartz tube reactor (6 mm outer

diameter, 4 mm inner diameter), 7: mass

spectrometer, 8: vacuum pump, 9:

pressure indicator, 10: pressure vessel

for labeled synthetic air (20%  $^{36}\text{O}_2$  and  
80% He).

Figure S1 shows a scheme of the used setup for the oxygen scrambling experiments. The CaO column for impurity trapping can be removed and for the experiments with water a saturator was installed instead.

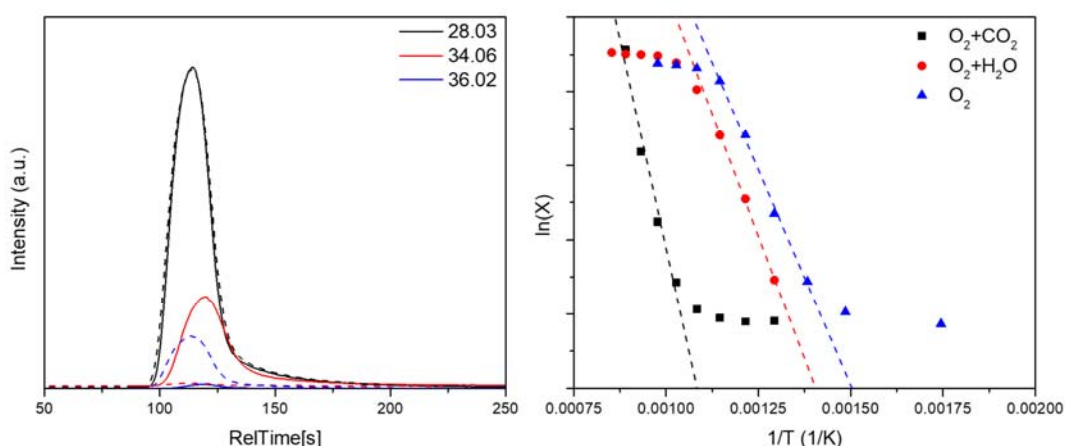


Figure S2: Mass spectrometer responses after dosing a pulse of 500  $\mu\text{l}$  of labeled synthetic air (80% N<sub>2</sub> and 20% <sup>36</sup>O<sub>2</sub>) into 30 ml/min unlabeled synthetic air (80% He and 20% <sup>32</sup>O<sub>2</sub>) at 750°C (solid lines) and 300°C (dashed lines) over 27.7 mg CaO (25763) diluted in 730 mg SiC (left), Arrhenius plots of the oxygen scrambling experiments over a temperature range of 500 to 900°C (right).

In Figure S2 (left), the mass spectrometer responses of exemplary isotope scrambling experiments at 300°C and 750°C are shown. At the low temperature almost no <sup>34</sup>O<sub>2</sub> is being observed, whereas at the higher temperature the signal for <sup>36</sup>O<sub>2</sub> is almost completely gone. Figure S2 (right) shows the Arrhenius plots used for determining the activation energy for the reaction.

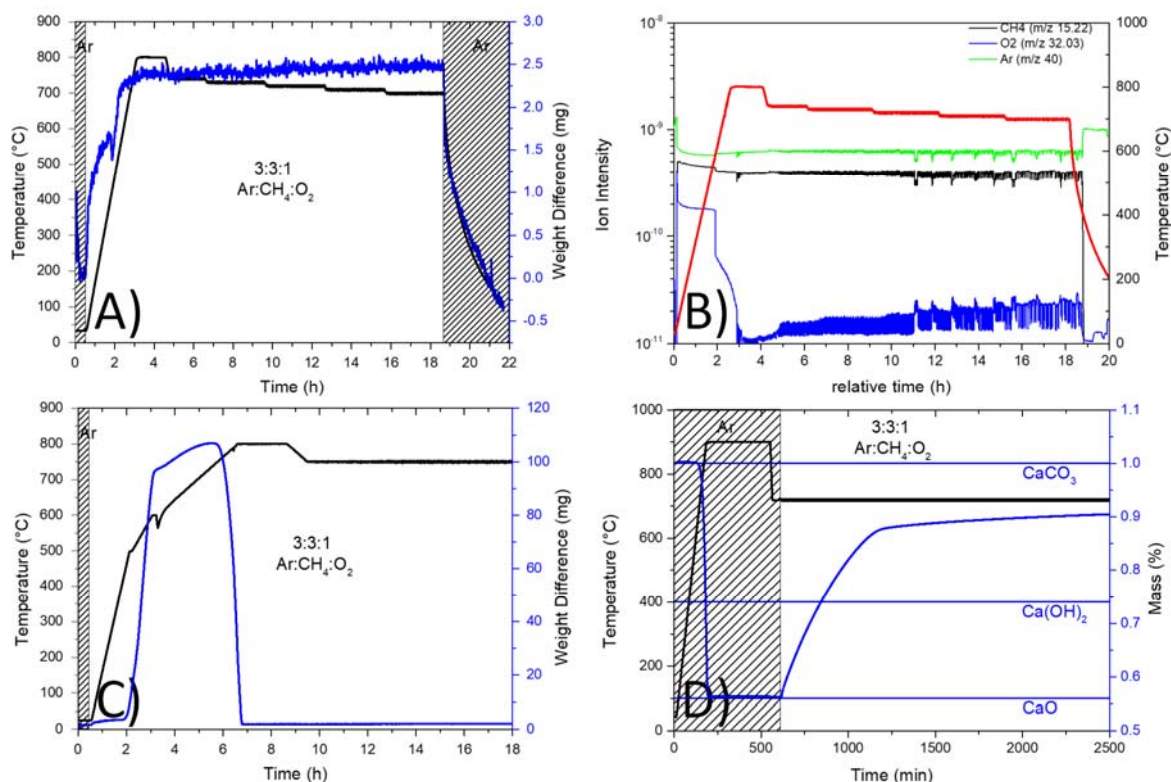


Figure S3: Blank experiment with 500 ml/min OCM feed (3:3:1, Ar:CH<sub>4</sub>:O<sub>2</sub>) A) mass change between 800°C and 700°C, B) ion intensities for educts. Mass change for 500 mg CaCO<sub>3</sub> in 500 ml/min OCM feed (3:3:1, Ar:CH<sub>4</sub>:O<sub>2</sub>) after sample activation at 750°C, D) at 720°C.

In Figure S3A the mass change in a blank experiment is shown. Due to buoyancy changes because of feed change (Ar to OCM feed (3:3:1, Ar:CH<sub>4</sub>:O<sub>2</sub>)) and thermal expansion, mass changes can be observed during feed switching and heating. The constant positive drift in the mass at elevated temperatures can be explained by coking of metal parts in the suspension balance. The obtained mass evolution was used to correct the data shown in Figure 5A in the main text. In Figure S3B the mass spectrometer signals for the products are shown during the blank experiment. The methane signal is almost constant at all temperatures above 700°C and the oxygen signal is always less than 10% of the original signal before heating indicating a strong

activity even without catalyst. In Figure S3C, the mass change at 750°C is shown, exhibiting no drift. Coking here has little influence on the obtained data. Figure S3D shows the decomposition of 500 mg  $\text{CaCO}_3$  in Ar at 900°C and the mass change switching to 740°C and OCM feed (3:3:1,  $\text{Ar}:\text{CH}_4:\text{O}_2$ ).  $\text{CaCO}_3$  was quantitatively decomposed, the mass gain during OCM is higher compared to what is expected for hydroxide formation but less compared to full conversion to carbonate. The  $\text{CO}_2$  uptake could be separated in 2 regimes: the first being dominated by adsorption (steep slope at the beginning of experiment) and a second regime dominated by bulk diffusion (constant slow mass gain). XRD analysis of the catalyst after the experiment is shown in Figure 5B proving the formation of a calcite phase in addition to the CaO phase, but no hydroxide phases. Changing the temperature from 800°C to 740°C a mass gain of 25 $\mu\text{g}$  was observed, which is most likely due to an error in the buoyancy correction (Figure S4).

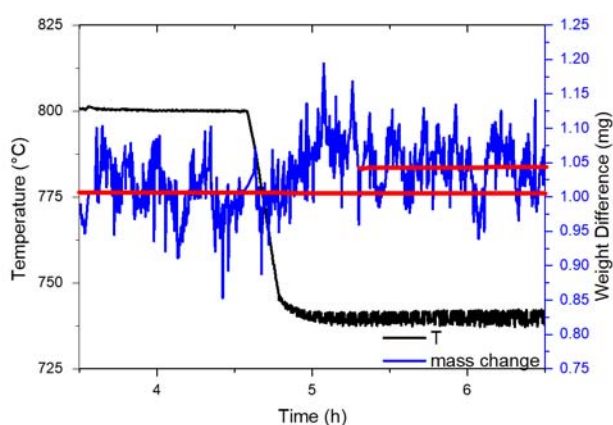


Figure S4: Mass change between 800°C and 750°C in OCM feed (500 ml/min 3:3:1,  $\text{Ar}:\text{CH}_4:\text{O}_2$ ) of 500 mg  $\text{CaCO}_3$  decomposed at 900°C in Ar.

## RAMAN SPECTROSCOPY

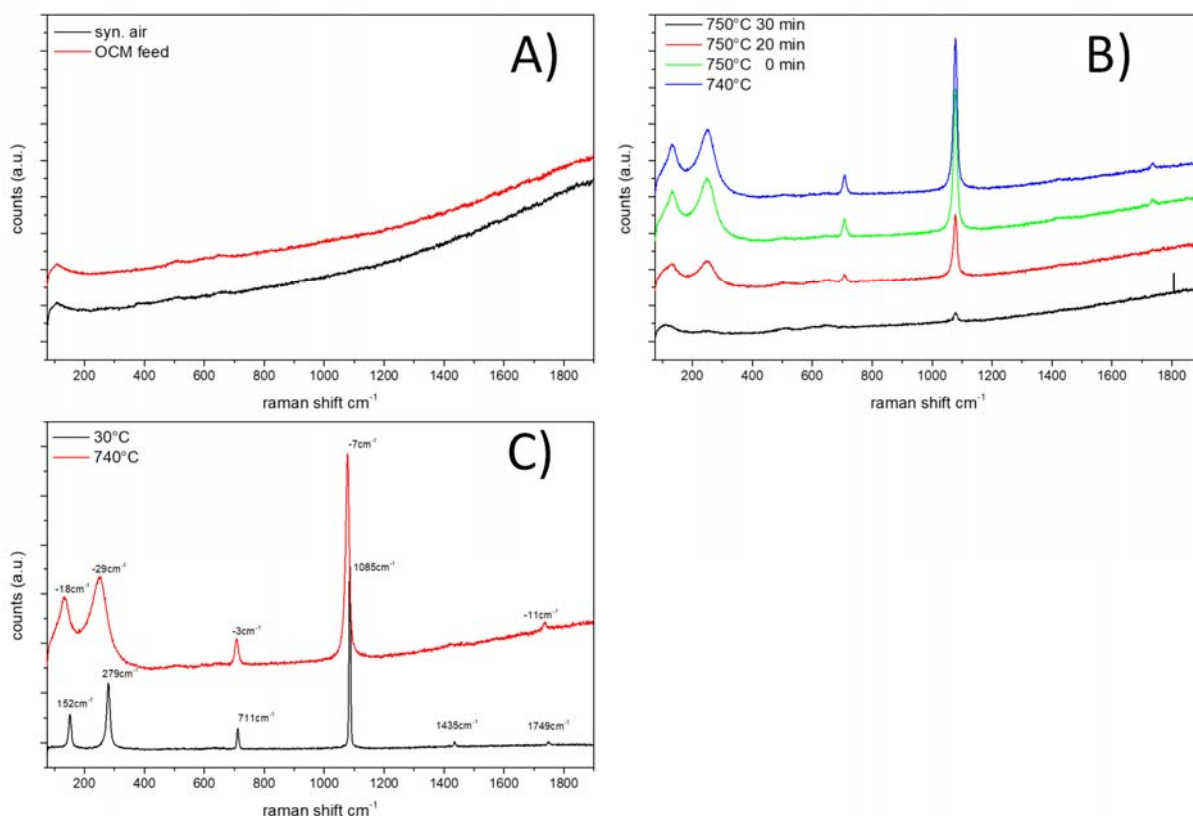


Figure S5: Raman spectra of CaO catalyst (25763) obtained with 532 nm laser A) after switching feed from synthetic air (10 ml/min, 20%  $\text{O}_2$  in He) to OCM feed (10 ml/min, 3:3:1, He:CH<sub>4</sub>:O<sub>2</sub>) at 800°C, B) after changing the temperature from 740°C to 750°C under OCM feed and recording spectra after 0, 20 and 30 min, C) at 750°C and after cooling down to room temperature under OCM feed.

In Figure S5A Raman spectra are shown obtained at 800°C under OCM red (red) and synthetic air (black). No significant change was observed, indicating a consumption of surface oxygen species or surface adsorbates formed during the reaction. In Figure S5B the decomposition of the formed calcite phase below 740°C under OCM feed after heating to 750°C is shown. After 30 minutes the calcite phase was almost completely vanished. The calcite peaks at elevated temperatures were slightly shifted and broadened compared to the spectra obtained at 30°C (Figure

S5C). The peak positions obtained at room temperature (152, 279, 711, 1085, 1435 and 1749  $\text{cm}^{-1}$ ) correspond well with what is reported in the literature for calcite (see references 38 and 39 in the main manuscript).

## PULSED CATALYTIC EXPERIMENT

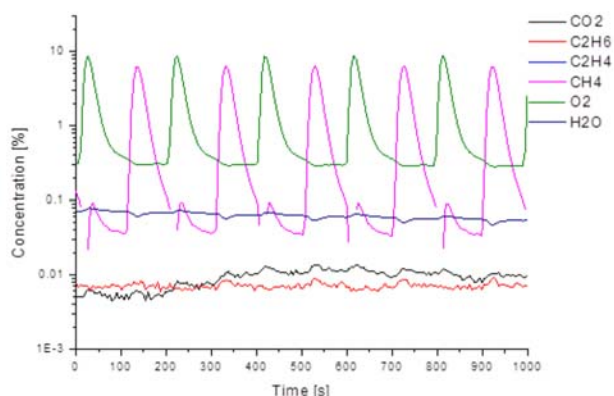


Figure S6: Time-delayed methane and oxygen pulses on a CaO catalyst at 800°C, with 30 ml/min He, 400 mg CaO and 1 ml alternating O<sub>2</sub> and CH<sub>4</sub> every 90 s.

To exclude redox processes or stable surface species being responsible for the catalysis, 1 ml of oxygen and methane were fed alternating to a constant carrier gas stream of 30 ml/min helium over a CaO catalyst with a time delay of 90 s at 800°C (Figure S6). No formation of products can be observed, proving, that the catalysis involves instable surface species. For this experiments a similar setup was used as shown in Figure S1, replacing the quartz reactor with a 8 mm inner diameter quartz reactor with internal thermocouple.