compounds

MDPI

Supporting Information

Perovskite-type oxide catalysts in CO_2 utilization: A principal study of novel Cu-doped perovskites for methanol synthesis.

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Exact Masses

Table S1. Masses of the catalysts used for each test.

Catalyst	Preliminary Test	Pressure Test
NCF	29.9 mg	-
NCF-Cu	30.5 mg	1.00 g
STF	29.7 mg	-
STF-Cu	30.0 mg	1.00 g
CCM	28.7 mg	-
CCM-Cu	34.2 mg	1.00 g

Calculations

For the calculations of yield and selectivity, the total amount of all detected compounds containing carbon was calculated according to equation S1.

$$C_{sum} = \sum x(\text{carbon containing compound}) \quad \text{(S1)}$$

The total conversion occurring at each datapoint was calculated by comparing the amount of CO_2 remaining according to equation S2.

$$\text{conv} = 1 - \frac{x_{CO_2}}{C_{sum}} \quad \text{(S2)}$$

The yield for each compound was determined by dividing the detected amount of the respective compound by the sum of all carbon containing compounds.

$$\text{yield}_i = \frac{x_i}{C_{sum}} \quad \text{(S3)}$$

The selectivity was calculated by comparing the yield of the respective the compound with the total conversion as seen in equation S4.

$$\text{select}_i = \frac{\text{yield}_i}{\text{conv}} \quad \text{(S4)}$$

Preliminary Tests

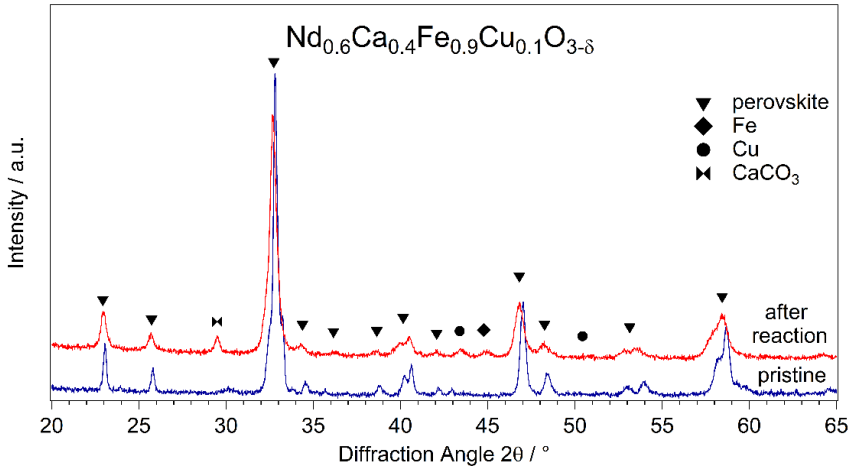

Figure S1: XRD measurements before (bottom track) and after (top track) the reaction at ambient pressure. Newly formed phases include metallic Fe and Cu as well as $CaCO_3$. The perovskite phase remained intact during the reaction

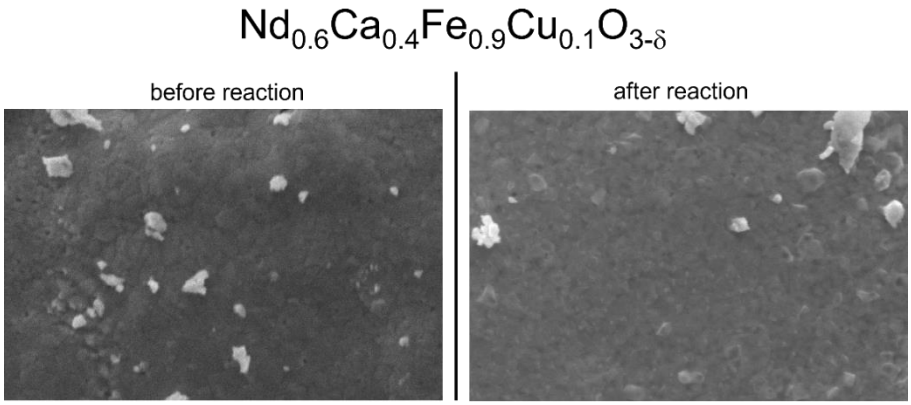

Figure S2: Comparison of SEM images of NCF-Cu before and after the reaction at ambient pressure. Some slight deactivation is visible after the reaction (right), due to the formation of $CaCO_3$. However, exsolved nanoparticles could not be detected, pointing to the particles either being too small for SEM resolution or still being located inside the catalyst.

Pressure Tests

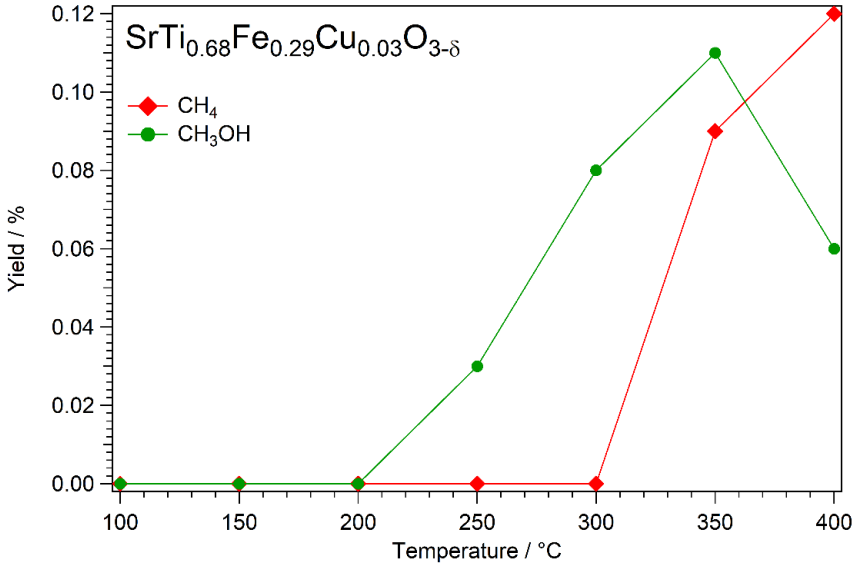

Figure S3: The progression of the yields for CH_4 and CH_3OH across the temperature steps for the case of the STF-Cu catalyst. The measurement was performed after oxidizing (600 °C, O_2) and reducing (700 °C, H_2/H_2O) pre-treatments at 21 bar. During the measurement, the temperature was raised stepwise from 100 °C to 400 °C in 50 °C steps. Each step was held until an equilibrium was reached. The educt gas flow consisted of 1 mLN min^{-1} He + 3 mLN min^{-1} H_2 + 1 mLN min^{-1} CO_2. Starting at 250 °C, methanol could be detected in small amounts.increased up to 350 °C to a maximum value of 0.11 %. At 400 °C, the CH_3OH yield dropped significantly (back to 0.06 %). CH_4 could be detected at 350 °C for the first time, afterwards the CH_4 yield increased with the temperature and became the dominant of the shown products at 400 °C with 0.12 % yield.

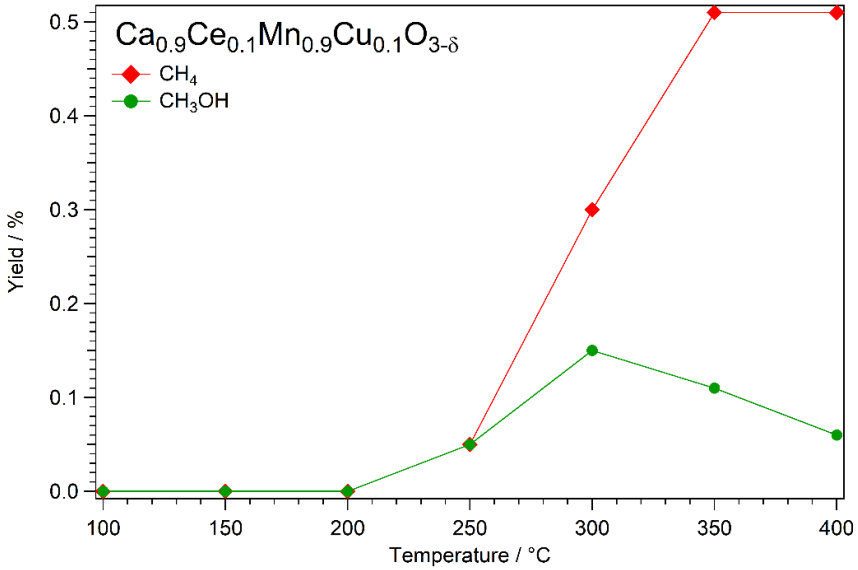

Figure S4: The progression of the yields for CH_4 and CH_3OH across the temperature steps for the case of the CCM-Cu catalyst. The measurement was performed after oxidizing (600 °C, O_2) and reducing (300 °C, H_2/H_2O) pre-treatments at 21 bar. During the measurement, the temperature was raised stepwise from 100 °C to 400 °C in 50 °C steps. Each step was held until an equilibrium was reached. The educt gas flow consisted of 1 mLN min^{-1} He + 3 mLN min^{-1} H_2 + 1 mLN min^{-1} CO_2. Starting at 250 °C, methanol could be detected in small amounts. The yield remained increased up to 300 °C to a maximum value of 0.15 %. At 400 °C, the CH_3OH yield dropped back to 0.06 %. CH_4 could be detected at 250 °C for the first time, afterwards the yield increased with the temperature and became the dominant of the shown products at 300 °C and above.

XRD measurements

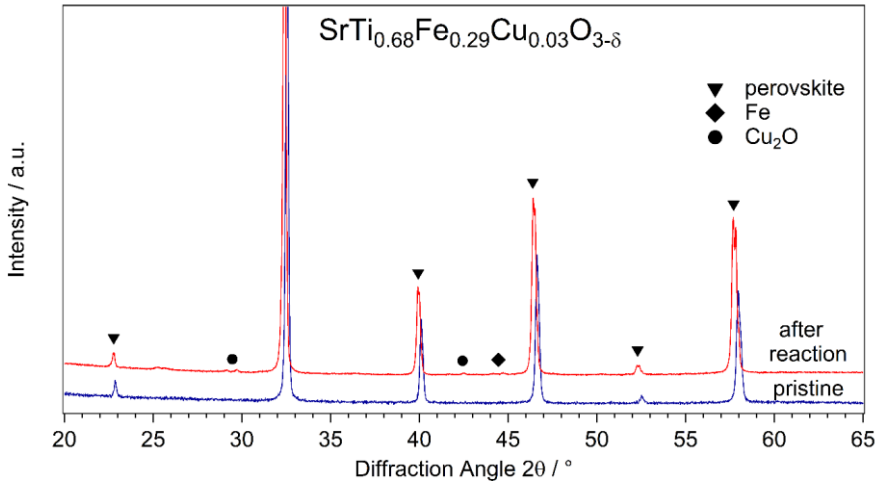

Figure S5: XRD patterns of STF-Cu before (bottom track) and after (top track) the reaction. The main perovskite peaks (marked with a triangle) were still present after the reaction. This shows that the backbone of the catalyst is stable throughout the reaction. Additionally, Fe (denoted with a diamond) emerged from the catalyst as the main reflex at 44.5° shows. Moreover, a phase containing Cu, most likely Cu_2O, was present after the reaction with the main reflexes at 42.2° and 29.6°. The perovskite reflexes were shifted about 0.2° to the left after the reaction, indicating a change in the base perovskite lattice during the reaction.

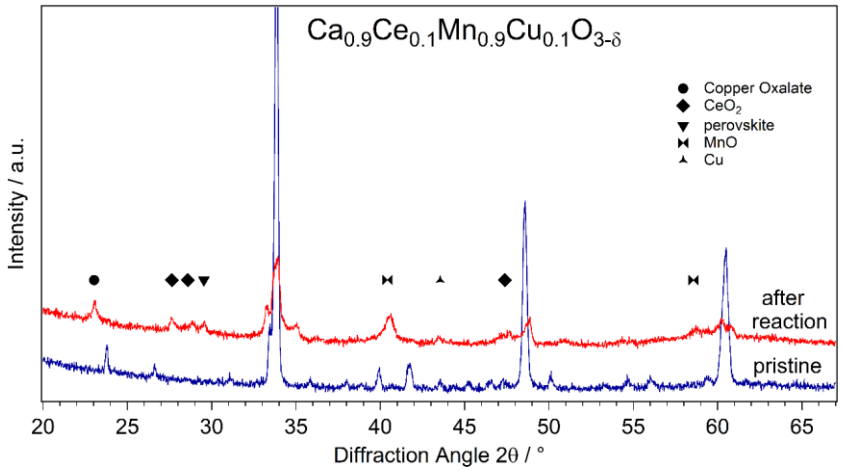

Figure S6: XRD patterns of CCM-Cu before (bottom track) and after (top track) the reaction. The perovskite lattice was mostly destroyed during the reaction. Instead, copper oxalate (marked with a circle, 23.0°), CeO_2 (marked with a diamond, 27.6°, 28.8°, 47.6°), MnO (marked with two triangles, 40.5°, 58.7°) and Cu (marked with a star, 43.5°) formed in the sample.

SEM images

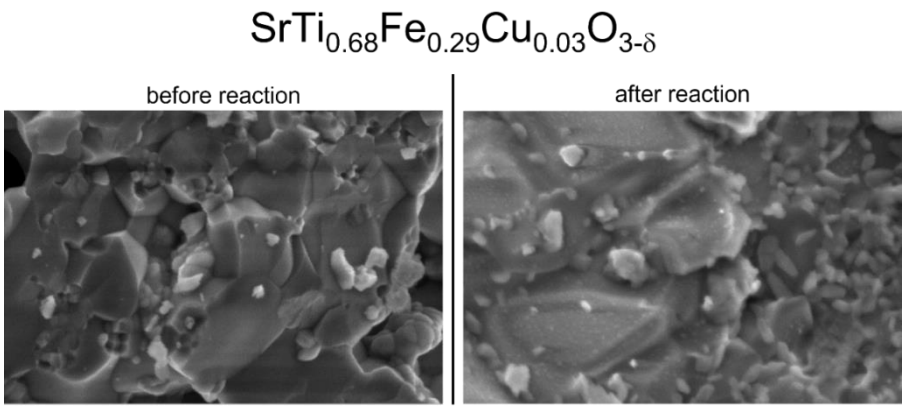

Figure S7: Comparison of SEM images of STF-Cu before and after the reaction with a reductive pretreatment. Before the reaction (left), the surface of the catalyst is smooth with a few flakes sitting on top. After the reaction (right), nanoparticles were formed in the range of 10 nm to 30 nm.

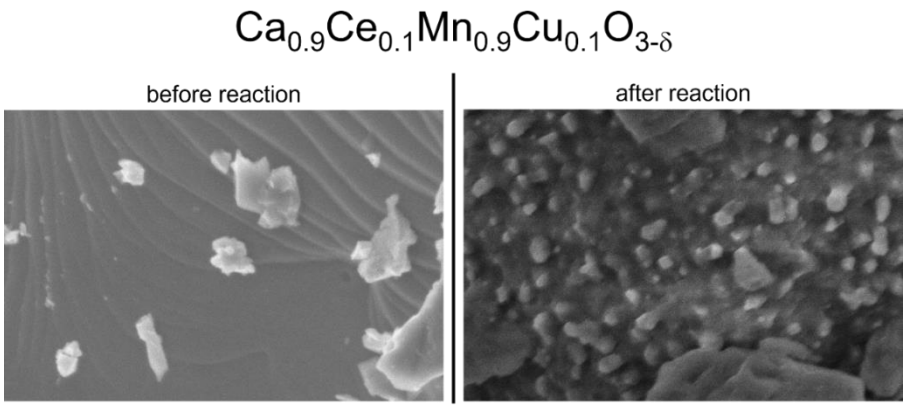

Figure S8: Comparison of SEM images for CCM-Cu before and after the reaction with a reductive pretreatment. Before the reaction (left), the catalyst showed a very flat and uniform surface likely due to sintering. After the reaction (right), the catalyst surface appears to be very rough. As other measurements have shown, the catalyst decomposed during the reaction, indicating the particles formed during the reaction are decomposition products.