Catalytic reverse water gas shift reaction assisted by an electric field over cerium- and zirconium-based materials

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Highlights

- Ce- and Zr- based materials appear active semiconductors for RWGS reaction under electric field.
- $Ce_{0,5}Zr_{0,5}O_2$ prepared by sol-gel method showed a good catalytic activity with only CO.
- Addition of nickel to the CeO_2 resulted in both CH_4 and CO formation.
- Bare CeO_2, ZrO_2 and $Ce_{0,5}Zr_{0,5}O_2$ supports showed a plasma discharge generation during the test.

1. Introduction

Reducing CO_2 emissions derived from fossil fuels has attracted significant attention in recent decades due to global warming concerns. To address this challenge, several carbon capture and utilisation technologies have emerged, including the conversion of CO_2 into added-value chemicals using renewable energies. In this context, the reverse water gas shift (RWGS) [1] reaction is considered a promising approach for CO_2 reduction to CO, which can be used to form hydrocarbons or oxygenated compounds either through the Fischer-Tropsch or through industrial processes.

In this project, we are interested in RWGS reaction assisted by electric field, a technology that has been recently reported in the literature but which is currently the subject of less studies compared to plasma RWGS. It is also important to mention that no correlation has been developed between the physicochemical properties of catalysts and catalytic performance. The objective of this research is to carry out a parametric study to identify and optimize the catalytic system for CO production via CO_2 reduction using RWGS over cerium- and zirconium-based semiconductors. In addition, various structural, chemical and electrical analyses were performed before and after the test in order to better understand and explain the catalytic activity behaviour.

2. Methods

CeO_2, ZrO_2 and $Ce_{0,5}Zr_{0,5}O_2$ catalysts were synthesised using sol-gel method. 15%wtNiO/support were prepared by impregnation. The nickel precursor $Ni(NO_3).6H_2O$ was impregnated onto the sol-gel prepared supports, then calcined in a static muffle furnace for 3 hours at a rate of 5 °C/min at 450 °C or 500 °C, depending on the compound. The obtained samples were then reduced under 50% H_2 and 50% N_2 atmosphere to get 15%wtNi/support. All the prepared catalysts were pressed, crushed and sieved to 355 - 630 um before being introduced into the setup. The reactor [2] employed is a fixed-bed reactor with two electrodes (high voltage electrode and working electrode) with point to plane configuration, with a gap distance of 2 mm where the catalyst is placed. The experimental device was designed to withstand high temperatures and maintain long term durability at 200°C. The reaction protocol was based on the work of Sekine's group [3]. A pre-treatment was first carried out to remove any impurities at 200°C for 1h under 30 mL/min of Ar, followed by the experiment at CO_2:H_2:Ar 1:1:2 (60 mL/min total flow rate) and N_2 (10 mL/min) as a trace gas. The tests were then conducted under an electric field with a direct current of 9 mA at the same temperature (200 °C) for 1 hour. Each catalyst was subjected to at least 2 reproducibility tests to ensure repeatability. The prepared samples were characterized using H_2-TPR, XRD, Raman, BET and UV-visible spectroscopy measurements before and after the catalytic test.

3. Results and discussion

Experiments were conducted on bare CeO_2 and ZrO_2, as well as on the impregnated supports with nickel oxide and metallic nickel. The effect of doping Zr on the ceria-based material was also investigated using $Ce_{0,5}Zr_{0,5}O_2$. Among all the tested catalysts, $Ce_{0,5}Zr_{0,5}O_2$ resulted interesting results with a CO_2 conversion of 20% and a CO yield of 18,2 % (Figure 1). More importantly, only CO was detected, unlike nickel-impregnated CeO_2 materials that showed both CO and CH_4 production. According to the literature [4], it has been demonstrated that doping Ce-based compound with Zr preserves the cerium structure throughout the thermal treatment and increases the oxygen mobility in the material. Moreover, $Ce_{0,5}Zr_{0,5}O_2$ exhibited a direct band gap of 3.4 eV, much lower than that of ZrO_2 and comparable to that of CeO_2. The absorption analysis revealed less defects compared to CeO_2 supported by Ni and NiO. This is linked to the stabilizing effect of Zr on the cerium structure, that decreases the Ce^{3+} production [4,5]. All of this suggests a low conductivity and a semiconductor behaviour with a wide band gap. Additionally, Raman spectroscopy on the catalysts demonstrated oxygen defects generation, nevertheless, high oxygen vacancies on the material could result in CH_4 alongside CO. Similarly to CeO_2 and ZrO_2, a plasma discharge was formed during the test due to the low dielectric constant [6], which was not observed with impregnated supports, indicating only electric field operation.

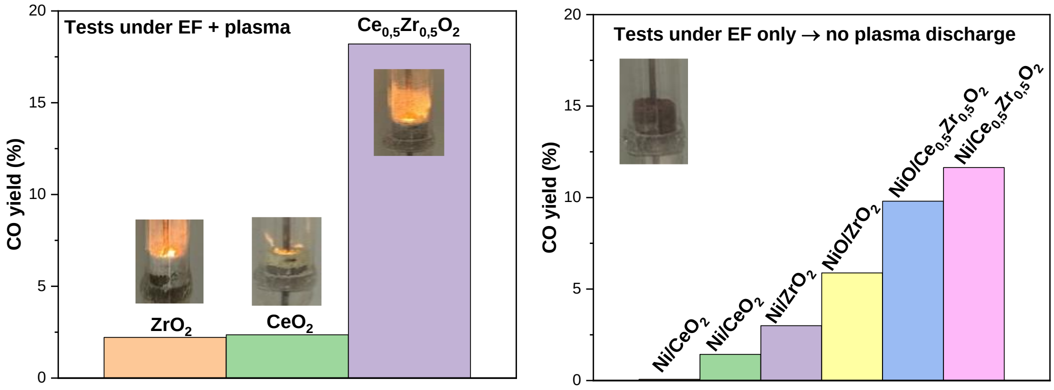

Figure 1. Catalysts comparison in term of CO yield (%), divided into two groups; catalysts under electric field + plasma discharge and catalysts under electric field only.

4. Conclusions

To conclude, RWGS reaction under electric field was investigated over Ce and Zr based semiconductors prepared by sol-gel method. Bare supports and impregnated supports with NiO and Ni were also examined, in addition to the effect of Zr doping in the Ce-based material. As a result, $Ce_{0,5}Zr_{0,5}O_2$ outperformed all the prepared catalysts and achieved a CO yield of 18,2% at 200°C, demonstrating significant activation at low temperature.

References

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Keywords

RWGS; electric field; ceria-based catalysts; semiconductor