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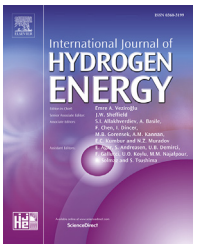

Reactivity of Ni, Cr and Zr doped ceria in CO_2 splitting for CO production via two-step thermochemical cycle

Liya Zhu, Youjun Lu, Feng Li*

State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

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ABSTRACT

This work focuses on modification and screening of ceria-based oxides for solar H_2O/CO_2 splitting via two-step thermochemical cycle. $Ce_{1-x}M_xO_{2-\delta}$ (M = Zr, Ni, Cr; x = 0, 0.05, 0.10, 0.15, 0.20) were synthesized via sol-gel method and tested for CO_2-splitting via two-step thermochemical cycles. Reduction was conducted at 1500 °C through a ramp rate of 10 °C/min and oxidation was performed at 1000 °C isothermally. Both Ni and Cr showed low solubility in ceria and no or very limited promoting effect on CO productivity. Cr could be reduced in the first reduction step but cannot be oxidized by CO_2 in the following oxidation step. Zr doped sample showed advantages in both CO productivity and lattice stability. 15% Zr doped exhibited the best performance with the CO productivity of 315.40 μmol/g. However, the oxidation rate of Zr doped samples was much lower than that of pure ceria. Compromise between fuel productivity and fast kinetics should be made in practical application.

Introduction

Solar fuel production via two-step thermochemical cycle is a promising path for solar energy conversion [1–5]. Usually it is based on the redox reactions of metal oxides. As depicted in Fig. 1, the metal oxide is reduced at first, in which process concentrated solar energy could be used to drive the reaction. Thus the solar energy is converted into chemical energy. In the following step, the reduced metal oxide is exposed to H_2O or CO_2 and oxidized back to the initial state, closing the cycle. The oxidation step is exothermic so no energy input is needed [6]. Overall, CO_2/H_2O is split into O_2 and CO/H_2 separately in two steps with no side reaction. The H_2 and CO produced could be further synthesized into liquid fuels [7], which could be conveniently used in vehicles and industries.

A lot of redox materials have been investigated for this application [8–16]. Among them, ceria has drawn a lot of interests due to its good stability, prominent oxygen storage capacity, and fast kinetics [17–19]. Different from some other metal oxides, the cycle of ceria could be a nonstoichiometric process. Oxygen vacancies could be created in the crystal lattice without changing the crystalline phase. They could be seen as one kind of lattice defect. The amount of oxygen vacancies is dependent on the (T, p_{O_2}) condition. The thermochemical is based on the defect equilibrium, and could be expressed as:

* *Corresponding author.*
E-mail address: yjlu@mail.xjtu.edu.cn (Y. Lu).

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Nomenclature

Mx	ceria doped with x% of M
T	temperature, °C
p_{O_2}	oxygen partial pressure
x	molar ratio
a	lattice constant
k	rate constant
A	Arrhenius constant
E_a	activation energy
R	gas constant
red	reduction step
ox	oxidation step

$$\text{reduction: } CeO_{2-\delta_i} \rightarrow CeO_{2-\delta_f} + \frac{\delta_f - \delta_i}{2} O_2 \quad (1)$$

$$\text{oxidation: } CeO_{2-\delta_f} + (\delta_f - \delta_i)CO_2 \rightarrow CeO_{2-\delta_i} + (\delta_f - \delta_i)CO \quad (2a)$$

or

$$CeO_{2-\delta_f} + (\delta_f - \delta_i)H_2O \rightarrow CeO_{2-\delta_i} + (\delta_f - \delta_i)H_2 \quad (2b)$$

Investigation on ceria in this area was firstly conducted by Abanades et al. [20], in whose research, ceria experienced stoichiometric change (from CeO_2 to Ce_2O_3) at a very high temperature (~2000 °C) and were oxidized by water at moderate temperatures (400–600 °C). In 2007, Kaneko et al. [21] developed and fabricated a kind of rotary-type solar reactor, in which continuous production of hydrogen is demonstrated using CeO_2 through nonstoichiometric change. After that, Chueh et al. [19] discussed the feasibility of fuel production by splitting both CO_2 and H_2O using ceria as a reaction medium. The two-step reactions were further analyzed from two aspects of thermodynamics and kinetics [18], and 500 cycles was conducted by using a solar cavity-receiver reactor [17].

However, for pure ceria, the reduction temperature is still too high and the gas fuel productivity is relatively low [22], resulting in limited energy conversion efficiency [23]. Doping is generally considered as an effective method to alleviate these problems. Through comparing water-splitting performances of ceria-based oxides doped with a series of elements (Al, Mn, Fe, Co, Cu, Zn, Zr, Zr3Y, Zr8Y), Abanades et al. recommended Zr doping as a preeminent choice [24]. After that, the influences of synthesis method, material morphology and oxidation temperature were studied [25–27]. They also tested some ternary ceria-based oxides doped with both Zr and a third cation (Y, La, Pr, and Gd) and it turned out that the thermal stability during repeated cycles could be enhanced [28,29].

Tada et al. [30] and Lee et al. [31] found that both ionic radius and iconicity play important role in the reduction reaction. Meng et al. suggested that dopants with higher valences and smaller ionic radii could make the Ce–O bonds around easy to break [32]. Dopants with lower valences could introduce oxygen vacancies, which may promote bulk oxygen diffusion since the lattice oxygen diffuses through oxygen

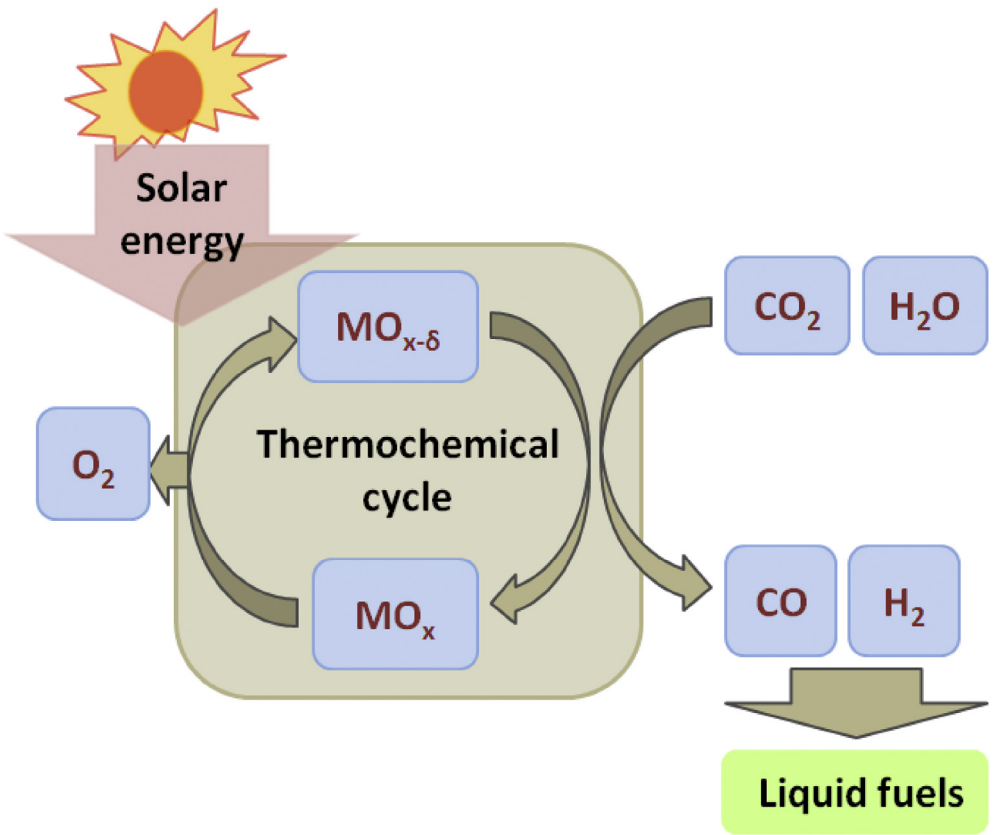

Fig. 1 – General schematic of two-step thermochemical cycle for solar fuel production [6].

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