CARBON DIOXIDE CONVERSION BY REVERSE WATER GAS SHIFT CHEMICAL LOOPING

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Abstract

A chemical looping approach to CO_2 conversion has been designed and developed to convert by reverse water gas shift chemical looping. Various formulations of perovskite oxides have been examined experimentally and computational to improve the process. Although the process requires renewable hydrogen, the reaction rates are an order of magnitude higher than other CO_2 conversion routes and occurs at much lower temperatures. This contribution focuses on structure-function relations of this class of materials.

Keywords

carbon dioxide conversion, carbon monoxide production, reverse water gas shift, perovskite oxides, chemical looping

Introduction

Carbon dioxide conversion is a major challenge because of thermodynamic limitations and the sluggish conversion rates. For example, thermodynamics do not predict CO_2 splitting until temperatures higher than 2000 K. The reverse water gas shift (RWGS) is the most established approach to convert CO_2. It requires H_2, which must be produced from renewable, non-hydrocarbon sources to be useful. In addition, the reaction is limited to high temperatures because of kinetics and thermodynamics and methane can form as a side-product. Despite these limitations, Mallapragada et al determined that thermochemical conversion of CO_2 to liquid hydrocarbon fuels, with the RWGS reaction employing a solar-heating, was efficient compared, in terms of sun-to-fuel efficiency, to other approaches.

The overall goals of this effort are to design processes and materials to enhance efficiency of futuristic CO_2 conversion processes involving redox cycles (Figure 1). In this effort, we examine the structure-function relations of various perovskite oxides to further enhance the reverse water gas shift – chemical looping (RWGS-CL) process.

Figure 1. Two step RWGS-CL process for conversion of CO2 to CO.

While this route has the inherent benefits of avoiding thermodynamic issues by using stoichiometric reactions

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and eliminating methane formation by keeping CO and H_2 separate, the achievement of higher conversion rates at lower temperatures would better thermally integrate the process with subsequent processes (i.e., fuel synthesis by CO hydrogenation).

Experimental

Perovskite oxides were prepared using the Pechini method. Their structure and properties were validated using X-ray diffraction, nitrogen physisorption, and temperature-programmed techniques. Computational studies on the structure and CO2 adsorption were conducted using density functional theory with the VASP software package.

CO_2 conversion studies via reverse water gas shift chemical looping were conducted using chemical looping studies in a packed bed reactor connected to an online mass spectrometer (MKS). CO_2 conversion amounts and rates were measured at different temperatures and partial pressures after various reduction procedures.

Results & Discussion

We have performed substantial efforts toward to applying materials toward CO_2 conversion. In our original study (Daza et al 2014), parent perovskite-type oxides with a La:Sr ratio of 3:1 were selected as optimal. In that article, Co was reduced out of the perovskite oxide structure and led to high temperature (>650°C) for conversion of CO_2 as the material was re-oxidized. Fe composition on the B-site was then studied and Fe-rich compositions were proved to be very stable and capable of converting CO_2 at lower temperatures and even the same temperature as for reduction (T = 550°C) for isothermal conversion studies (Daza et al 2015a). Other dopants and correlations to simulations have also been performed (Daza et al 2015b).

Table 1. Correlation of CO_2 conversion amount to oxygen vacancy formation amount for $La_{0.75}Sr_{0.25}FeO_{3-\delta}$ for switches at T = 550°C

Reduction time (min)	mol H_2O / mol ABO_3	mol CO / mol ABO_3
3.0	0.13	0.02
13.5	0.36	0.13
30.0	0.71	0.15

Working with Fe-rich materials, oxygen vacancies has been identified as a key parameter, as both the stoichiometric reaction is limited by it as well as is the strength of CO_2 adsorption. We have computationally determined this by linking CO_2 adsorption strengths to the number of oxygen vacancies (Daza et al 2015a) but we also report the conversion amounts relative to the reduction amounts in Table 2. Further investigations are required to prove the non-linear trends. Regardless, the performance (Table 2) indicates potential for high CO_2 conversion rates.

Table 2. Comparison of conversion amounts and operation temperatures

Material	CO yield (μmol/g/cy)	T (°C)	Reference
$(La,Sr)(Mn,Al)O_3$	140	1350/1000	McDaniel et al
$(La,Sr)(Cr,Co)O_3$	157	1200/800	Bork et al
$(La,Sr)FeO_3$	4000	550	Daza et al 2015a

Conclusions

RWGS-CL has been researched as process intensification strategy to enable CO_2 conversion using renewable hydrogen. This process may yield a justifiable conversion – operation temperature scenario for futuristic CO_2 conversion systems. Our present effort is focused on structure-function relations to deploy materials to increase reaction rates while lowering conversion temperature.

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