

Dispersed Calcium Oxide as a Reversible and Efficient CO₂–Sorbent at Intermediate Temperatures

Philipp Gruene,[†] Anuta G. Belova,[†] Tuncel M. Yegulalp,[†] Robert J. Farrauto,^{†,‡} and Marco J. Castaldi^{*,†}

[†]Earth and Environmental Engineering Department, Columbia University in the City of New York, 500 West 120th Street, New York, New York 10027, United States

[‡]BASF Corporation, 25 Middlesex Turnpike, Iselin, New Jersey 08830, United States

ABSTRACT: Dispersion of calcium oxide on high surface area γ -Al₂O₃ creates a stable and reversible CO₂–sorbent that overcomes the problems associated with bulk CaO, such as limited long-term stability, slow uptake kinetics, and energy-intensive regeneration. This sorbent is a candidate for the sorption-enhanced hydrogen production via steam reforming and/or water-gas shift reactions. CO₂ uptake tests were performed in a 15% CO₂/N₂ atmosphere to evaluate the efficacy at typical hydrocarbon reformer gas partial pressure. CO₂ uptake kinetics and capacities are investigated in TGA studies, while the long-term stability is shown in multicycle experiments. The dispersed CaO is an active sorbent at low temperatures and binds CO₂ at 300 °C up to 1.7 times as efficiently as compared to bulk CaO powder. Furthermore, the sorbent can be regenerated in a CO₂-free atmosphere at intermediate temperatures between 300 and 650 °C. Multicycle CO₂ uptake and release has been tested for 84 cycles at a constant temperature of 650 °C and shows the superior long-term stability of dispersed CaO as compared to bulk CaO. The attempt to increase the uptake capacity from 0.16 to 0.22 mmol CO₂ per gram of sorbent occurred with a commensurate loss in BET area from 115 to 41 m², leading to a decline in overall uptake efficiency from 15% to 6%. Infrared spectroscopy is used to characterize the CO₂–sorbent binding interaction on a molecular level and to distinguish between CO₂ adsorbing on the bare support, on bulk CaO, and on dispersed CaO/Al₂O₃.

INTRODUCTION

Increasing energy demands coupled with a heightened awareness of human influence on the global climate system, particularly the production of greenhouse gases, has resulted in incentives to develop alternative sources of energy and chemicals and to address energy security in an environmentally benign manner. One direction that is evolving to satisfy the demand is to move toward a hydrogen economy. However, for the foreseeable future, hydrogen will be generated through the increased usage of fossil fuel reforming. This realization has raised some questions about the responsible use of fossil fuels, and consequently what is emerging is the critical need for a carbon dioxide management strategy and technology to forestall projected global warming and its impacts.^{1–5}

Hydrogen can be produced from fossil fuels or biorenewable sources through steam reforming (SR) processes, for example, fossil or biogas methane:



To enhance the hydrogen yield and remove CO from the product gas stream, the water-gas shift (WGS) reaction occurs in a subsequent reactor:



In both processes, catalysis is of fundamental importance, as it allows SR and WGS reactions to proceed at reasonably low temperatures and high rates.^{6,7} However, in both reactions, hydrogen production is ultimately limited by the thermodynamic equilibrium. This is particularly acute for the WGS reaction. To enable a more efficient reaction process and

promote complete reactant conversion, it is desirable to remove one of the products from the effluent. A significant amount of investigation has been done on hydrogen removal in situ and ex situ. Recently, the attention has been focused on the possible removal of the CO₂ product, as this can also facilitate carbon sequestration efforts. The conventional way this has been designed is CO₂-removal by using either monoethanolamine or pressure-swing adsorption on zeolites integrated in a staged reactor system.

Almost 10 years ago, it was shown experimentally that hydrogen production can be facilitated drastically by sorption-enhanced reactions (SER).^{8,9} This yields the possibility of a CO₂–sorbent added to the SR and WGS catalyst in a single reactor, thus shifting the thermodynamic equilibrium entirely toward the product side. It is known that CaO is a promising sorbent, which reacts stoichiometrically with CO₂:



Calcium minerals are also among the most abundant metal oxides in nature and are commonly found in the form of carbonates, for example, limestone and dolomite. Heating these materials to very high temperatures (>900 °C) leads to liberation of CO₂ and to the formation of calcium oxide. At lower temperature, the oxide can react again stoichiometrically with CO₂, acting as a very cheap, robust, and high-temperature sorbent with very high sorption capacities.⁴ Unfortunately, bulk CaO as a CO₂–sorbent

Received: June 8, 2010

Accepted: January 27, 2011

Published: March 04, 2011