



Short communication

Nano-scale sulfur-tolerant lanthanide oxysulfide/oxysulfate catalysts for water–gas-shift reaction in a novel reactor configuration

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ABSTRACT

We synthesized and tested nano-scale lanthanide oxysulfide/oxysulfate catalysts for water–gas-shift (WGS) reaction. No existing literature has applied these nanoparticles with unique morphologies as heterogeneous catalysts in WGS. The motivation behind our endeavor is to investigate whether the unique morphologies from the synthesis approach can increase catalyst activity of lanthanide oxysulfide/oxysulfate catalysts, which are good catalysts for WGS in both sulfur-free AND sulfur-laden environments, but face the challenge of low activity in micro-scale regime. All three nanocatalysts showed significantly enhanced catalyst activity. Finally, sulfur tolerance testing with Eu₂O₂S demonstrated dampened, but still high CO conversion, which recovered from sulfur influence rapidly.

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1. Introduction

Both theoretical and experimental research has demonstrated that lanthanide-coordinated complexes have applications in basic and applied research and commercial processes ranging from semiconductors to catalysis owing to their magnetic, catalytic and optical properties arising from 4f electrons in lanthanides [1–4]. Among these complexes, lanthanide oxysulfide/oxysulfate (Ln₂O₂S/Ln₂O₂SO₄, Ln = lanthanum, praseodymium, samarium and neodymium) transition systems exhibit oxygen capacity between Ln₂O₂S (S^{−2}) and Ln₂O₂SO₄ (S⁺⁶), which is eight times higher than that of the commercial CeO₂ [5,6]. The sulfur redox capacity contributes to the catalytic property in dehydrogenation processes, such as the water–gas-shift (WGS) reaction with lanthanum (La)- and praseodymium (Pr)-based candidates [4]. For applications in catalysis, the sulfur capacity provides Ln₂O₂S/Ln₂O₂SO₄ (Ln = La and Pr) with a strong sulfur-tolerant capability in reactions such as the WGS, especially for sour gas conditions [4,7]. Without the need for strict sulfur removal, pre-treatment of syngas for WGS can be alleviated or eliminated, reducing operation and capital costs.

Currently, commercial high-temperature shift (HTS) catalysts, such as iron (Fe)-chrome (Cr)-oxide, can lose half of their full activity at moderate feed gas sulfur concentrations (168–250 ppm) [8]. Cr- and Co-doped Fe/Cerium (Ce) catalysts were reported to possess sulfur resistance, but required careful pre-treatment to prevent over-reduction to oxides, carbides or metallic iron phases [9].

Commercial low-temperature shift (LTS) catalysts, such as copper-zinc (Cu–Zn), are extremely sensitive to less than 0.1 ppm sulfur, resulting in almost 100% activity loss [10]. Other metal WGS catalysts, such as Pt/CeO₂ [11] and Rh/CeO₂ [12] also become poisoned and lose active surface area at low sulfur concentrations. Pre-sulfided catalysts, such as cobalt–molybdenum-sulfide (CoMoS) [13] and CoCr₂O₄-sulfide [14], have no obvious activity loss in sulfur-laden environments, but they face challenges in sulfur-free conditions including low activity, sulfur loss during the WGS reaction and methane byproduct formation. In contrast, it was recently reported that micro-scale Ln₂O₂S/Ln₂O₂SO₄ (Ln = La and Pr) demonstrated stable WGS reaction conversion in both sulfur-free and sulfur-laden feed gas streams with up to 700 ppm sulfur [4]. However, the reported activity of these micro-scale lanthanide oxysulfides (La and Pr) in a packed-bed reactor (Fig. 1A) was 3–4 times lower than commercial Fe–Cr-oxide catalysts (FeCrO_x) [14].

It is well-known that catalyst performance can vary dramatically with particle size due to modified surface structure and electronic properties [15,16]. The present study is focused on developing a series of novel nanoscale Ln₂O₂SO₄ (Ln = La, Pr) and Eu₂O₂S catalysts that possess unique morphology [17]. To support the nanocatalysts, we developed a novel reactor configuration, in which the outer layer of a tubular, nanoporous ZrO₂ layer was impregnated with nanoparticles (NPs) (Fig. 1B, C) to largely reduce the sintering effect, a well-known issue especially during high-temperature processes such as the WGS reaction and stream reforming [18,19]. Currently, a ZrO₂/stainless steel support has been used for micro-scale catalysts [20,21]. However, to the best of our knowledge, this is the first study to impregnate

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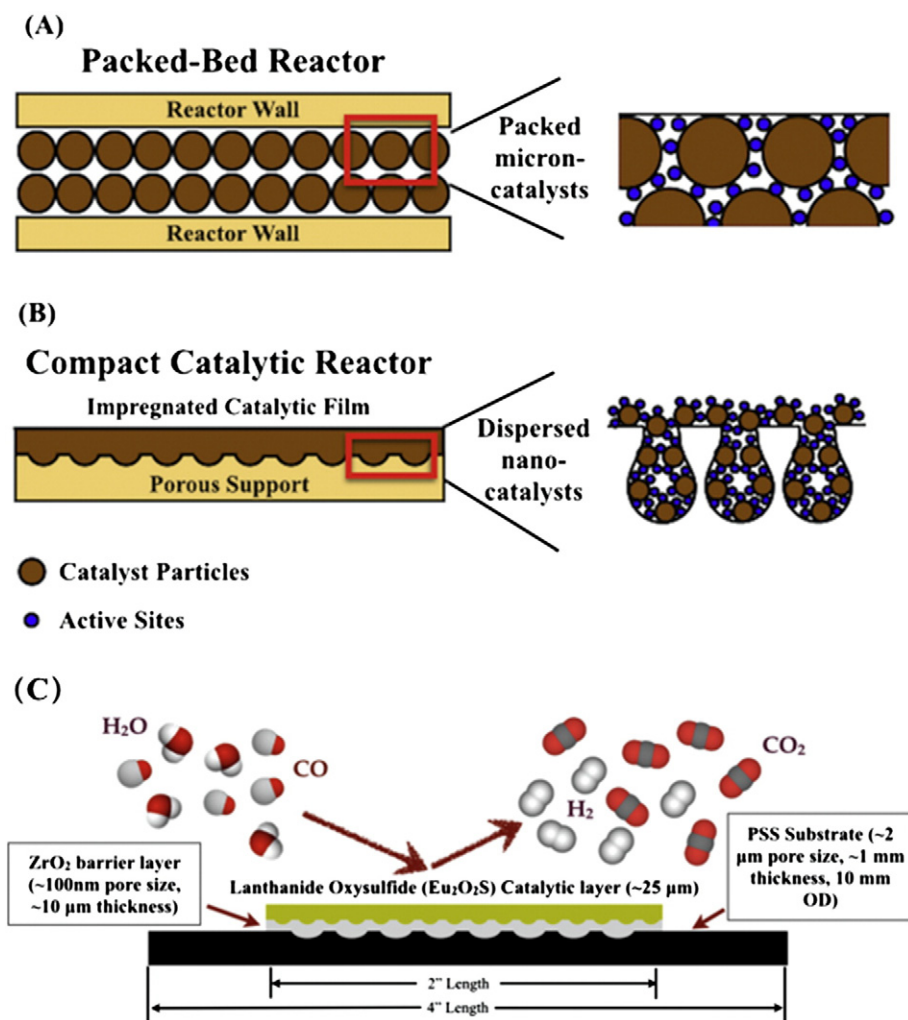


Fig. 1. Schematic of (A) micro-scale catalyst particles in a packed-bed reactor; (B) nano-scale catalysts impregnated on a porous ZrO₂/PSS support; (C) WGS reaction on the nano-Eu₂O₂S catalyst layer supported on the porous tube.

nanocatalysts onto a nanoscale porous support. Catalytic activities of the immobilized nanocatalysts outperformed micro-scale catalysts in packed-bed reactors. The nanocatalysts achieved significantly higher CO conversion than their micro-scale peers under similar operating conditions. Based on the sulfur-tolerance testing using Eu₂O₂S, nanocatalyst, slight decrease in CO conversion (~10%) was observed with 121 ppm H₂S in the feed. Impressively, the influence of H₂S was reversible and recovery time from H₂S was only 15 min. Finally, we note that the development of lanthanide nanocatalysts dovetails the rare earth elements (REE) projects in the United States that focus on exploration or development of REE in states including Wyoming, Nebraska and Texas [22].

2. Experimental

2.1. Synthesis of La₂O₂SO₄/Pr₂O₂SO₄ and Eu₂O₂S NPs

Three rare earth elements (Europium (Eu), La and Pr) were used to synthesize nano-scale catalysts via a facile synthesis approach [17, 23]. Briefly, mixed solvents and surfactants, consisting of oleylamine (OM, 70%), oleic acid (OA, 99%) and octadecene (ODE, 95%) (Sigma-Aldrich), were mixed together with Ln(dtc)₃phen (Ln = La, Pr and Eu, phen = 1,10-phenanthroline; dtc = diethyl-dithiocarbamate) precursor to synthesize the catalyst particles in suspension. Due to the difference in oxophilicity, europium oxysulfide (Eu₂O₂S) was

formed, while lanthanide sulfide (LaS and PrS) colloidal NPs were obtained instead. When the colloidal LaS and PrS NPs were heated up to 500 °C at the rate of 10 °C/min in Air, La₂O₂SO₄ and Pr₂O₂SO₄ NPs instead of lanthanide oxysulfides were formed after 5 h.

2.2. Impregnation of NPs on a porous ZrO₂/PSS tube

AccuSep® tubes (Pall Corp.) consist of a ZrO₂ layer (median pore size: 100 nm) supported on a porous stainless steel tube (PSS). Nonporous SS tubing is welded to both ends of the PSS tube (Fig. 1C), enabling the tube to be hermetically connected to other tubing. The ZrO₂ layer serves as a barrier to minimize the metallic inter-diffusion between the NPs and PSS support. Before the impregnation step, the nonporous SS ends of the tube were masked with aluminum foil, exposing only the nanoporous ZrO₂ layer for impregnation. Since visual inspection revealed white ZrO₂ support spots across the yellowish impregnated catalyst layer, the outside of the tube was treated with oxygen plasma (26.9 W) at 505 Torr to enhance the adhesion between the nanocatalyst particles and the ZrO₂ support layer [24,25]. Dispersed colloidal NPs in toluene/ethanol solvent were then used to washcoat the ZrO₂ layer. The mixture solvent was then evaporated by heating the impregnated tube in an oven at 250 °C for two hours. Above procedure was repeated 3–4 times until ~30 mg of nanocatalysts was evenly loaded onto the porous ZrO₂ layer.

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