



## Research Paper

# Enhancing catalytic activity of lanthanide oxysulfate ( $\text{La}_2\text{O}_2\text{SO}_4/\text{Pr}_2\text{O}_2\text{SO}_4$ ) via facile manipulation of nanoscale catalyst synthesis process and reactor configuration



Shuai Tan, Dongmei Li\*

Department of Chemical Engineering, University of Wyoming, Laramie, WY 82071, USA

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## ABSTRACT

We recently reported that a facile colloidal synthesis approach can be used to synthesize nanoscale  $\text{Eu}_2\text{O}_2\text{S}$  to significantly enhance activity of rare-earth based catalysts. While extending this method to synthesize other coordinated lanthanide complexes (La and Pr), we discovered that mixed phases of lanthanide monosulfide (LnS) and lanthanide oxysulfate ( $\text{Ln}_2\text{O}_2\text{SO}_4$ ) (Ln = La, Pr) co-existed in the product, instead of the desired single-phase complex. Utilizing the high oxophilicity of sulfur and Ln elements, we successfully converted LnS impurity to  $\text{Ln}_2\text{O}_2\text{SO}_4$  nanoparticles with unique morphologies by simply heating them in air. By impregnating the resultant nanocatalysts onto a commercial tubular oxide support (referred to as CCR), CO conversion of nanoscale  $\text{La}_2\text{O}_2\text{SO}_4$  for high temperature water-gas-shift (HTS) reaction increased from nearly zero in fixed-bed reactor (FBR) to 35% in CCR module at 500 °C. Reactivity comparison among different catalyst size, morphology and type suggests that the enhanced catalytic activity of  $\text{La}_2\text{O}_2\text{SO}_4/\text{Pr}_2\text{O}_2\text{SO}_4$  nanocatalysts in CCR derives from the increased surface area and minimized aggregation.

## 1. Introduction

Water-gas-shift (WGS) reaction ( $\text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2$ ) is widely used in industrial  $\text{H}_2$  production from different feedstocks, such as syngas after coal gasification and steam reforming, or as a probe reaction for new catalysts developed for methanol synthesis, ammonia synthesis and catalytic combustion [1–4]. Generally, WGS reactors are the largest component in most hydrocarbon processes due to its slow kinetics [5]. It is also well known that CO conversion at high temperature is bounded by thermodynamic equilibrium. To overcome these limits, it is essential to search for more efficient reactor configurations and innovative heterogeneous WGS catalysts with higher activity at lower reaction temperature [6,7]. Besides the widely used high-temperature-shift (HTS)  $\text{FeCrO}_x$  [8–10] and low-temperature-shift (LTS) Cu/Zn [11–14] catalysts for high-volume  $\text{H}_2$  production, metal-doped [15–18], oxide/alkali-promoted [19–22] or supported heterogeneous [23–26] WGS catalysts were recently reported, showing relatively enhanced catalytic performances. Among these catalysts, cerium oxide ( $\text{CeO}_2$ ) was investigated extensively as an efficient catalyst LTS due to its redox cycle ( $\text{Ce}^{+3} \leftrightarrow \text{Ce}^{+4}$ ) [27–30] and an active support for platinum (Pt) or gold (Au) nanoparticles (NPs) [31–36].

Despite progresses in research and development, catalyst poisoning

issue persists from contaminants in industrial hydrocarbon processes. Among them, sulfur remains the persistent poisoning source that shortens the lifetime of WGS catalysts, resulting from its strong absorbance to catalyst surface, which consequently blocks active sites, or permanently bonding with precious metals to form coordinated sulfide state [37–39]. Even though desulfurization units are used before WGS reactors to remove sulfur from hydrocarbon fuels, trace amount of sulfur remains in the feed to WGS reactors, deactivating catalysts, especially the susceptible metals, such as Cu, Pt and Au [40,41]. Although pre-sulfided catalysts, such as cobalt-molybdenum-sulfide ( $\text{CoMoS}$ ) and  $\text{CoCr}_2\text{O}_4$ -sulfide, demonstrated good sulfur tolerance in sulfur-laden environments, they face challenges in sulfur-free conditions including low activity, sulfur loss during the WGS reaction and methane byproduct formation [42,43]. Cr- and Co-doped  $\text{Fe/CeO}_x$  catalysts achieved steady CO conversion with 400 ppm of sulfur in the feed at much lower steam to carbon ratio ( $\sim 1.5$ ) than what is typically desired to reduce the operating cost [44]. However, careful pre-treatment is needed to avoid the over-reduction of magnetite ( $\text{Fe}_3\text{O}_4$ ) to lower carbides, oxides or metallic iron phases and further stability study is still required in long term running.

Recently, a new category of micro-scale lanthanide oxysulfide/oxysulfate ( $\text{Ln}_2\text{O}_2\text{S}/\text{Ln}_2\text{O}_2\text{SO}_4$ , Ln = La and Pr) was reported to have

\* Corresponding author.

E-mail address: [dli1@uwyo.edu](mailto:dli1@uwyo.edu) (D. Li).

stable catalytic activity in both sulfur-free and sulfur-laden gas stream with up to 700 ppm H<sub>2</sub>S. The redox pair of sulfur ion (S<sup>-2</sup> ↔ S<sup>+6</sup>) instead of the metal pair, such as Ce<sup>+3</sup> ↔ Ce<sup>+4</sup>, provides much higher OSC [45–47]. However, the reported Ln<sub>2</sub>O<sub>2</sub>S/Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> catalysts require higher operating temperature (400 °C–800 °C), with catalytic activity in a fixed-bed reactor (FBR) 3–4 times lower than commercial FeCrO<sub>x</sub> catalysts in the typical WGS operating temperature range of 300 °C–500 °C [39]. The low catalytic activity and higher operating temperature requirement limits the application of the micro-scale Ln<sub>2</sub>O<sub>2</sub>S/Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> catalysts to industrial processes. Nanoscale Ln<sub>2</sub>O<sub>2</sub>S (Ln = Eu and Gd) was recently synthesized via a facile colloidal synthesis method with unique morphologies (nanowire, nanorods and nanoplate) by tuning the mixed surfactant ratios for applications in optics [48,49]. We recently reported that Eu<sub>2</sub>O<sub>2</sub>S/Eu<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> synthesized via this colloidal synthesis approach can have very high CO conversion in sulfur-laden and sulfur-free feed streams for WGS [50].

In this paper, the colloidal synthesis method was firstly extended to the low cost of La/Pr from costly Eu and Gd elements. De Crom et al reported that high purity Ln(ddtc)<sub>3</sub>Phen precursors were obtained (Ln = Y–Lu) by using diethylammonium diethyldithiocarbamate (Et<sub>2</sub>NH<sub>2</sub>)(Et<sub>2</sub>dtc), Phen–H<sub>2</sub>O with CH<sub>3</sub>CN as solvent [51]. But due to the toxicity of CH<sub>3</sub>CN, this method is not environmentally friendly. Another relatively simple synthesis method was reported by Ivanov et al, involving utilization of Na(ddtc)·H<sub>2</sub>O, LnCl<sub>3</sub>·H<sub>2</sub>O and Phen–H<sub>2</sub>O in aqueous solution. It is worth noting that Ln(ddtc)<sub>3</sub>Phen products were only applied to Eu and Gd for optical applications [52]. We note that Ding et al. indicated it may be difficult to extend this synthesis approach to lanthanide elements other than Sm, Eu and Gd, due to challenges associated with synthesizing the corresponding single-source precursors (Lanthanide diethyldithiocarbamate with o-phenanthroline, or Ln(ddtc)<sub>3</sub>Phen) [53]. However, by characterizing precursor components via FT-IR and elemental analysis, we have successfully synthesized high purity Ln(ddtc)<sub>3</sub>Phen compounds (Ln = La and Pr) without the need of further purification. Interestingly, due to the difference in oxophilicity, the Ln(ddtc)<sub>3</sub>Phen precursors (Ln = La, Pr and Eu) did result in different morphologies when the same process was used for these three elements.

In addition to surface/crystallinity characterization, effect of reactor type and particle size on catalytic activity was evaluated using HTS as a probe reaction. In contrast to FBR, the resultant nanocatalysts were impregnated onto outer surface of a commercial tubular support to form a thin catalytic layer, referred as compact catalytic reactor (CCR), which can obtain optimized catalyst dispersion and mechanical strength [54–57]. Similar to monolith [58–60] and hollow fibers [61,62], these two popular modules used in micro-reactor with coated catalysts, the CCR configuration in this paper utilizes porous stainless steel (PSS) tube coated with a thin layer of a porous ZrO<sub>2</sub> layer (median pore size: 100 nm). We hypothesize that nanoscale Ln<sub>2</sub>O<sub>2</sub>S/Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> particles may have more exposed active sites than their micro-scale peers. Combining with optimized dispersion, the increased number of active sites provides a feasible pathway to significantly increase the low catalytic activity observed in microscale lanthanide oxysulfides. The tubular CCR configuration may be easily bundled up for high-volume H<sub>2</sub> generation and separation processing from sour gas stream.

## 2. Experimental

### 2.1. Sample preparation

#### 2.1.1. Synthesis of Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> NPs (Ln = La and Pr)

First, Ln(ddtc)<sub>3</sub>Phen (Ln = La and Pr) precursors were synthesized in aqueous solution by mixing Phen–H<sub>2</sub>O, Na(ddtc)·H<sub>2</sub>O and LnCl<sub>3</sub>·H<sub>2</sub>O from Sigma-Aldrich [52]. Specifically, 1 mmol Phen–H<sub>2</sub>O in 10 mL boiling water was added into a solution of LnCl<sub>3</sub>·H<sub>2</sub>O (1 mmol, 10 mL) under vigorous stirring. Then, an aqueous solution of Na(ddtc)·H<sub>2</sub>O (3 mmol, 20 mL) was added dropwise to the mixture solution under

constant stirring. The colored solids (yellow for La and apple green for Pr) that precipitated from the solution were separated via centrifuge (4000 rpm for 10 min) and dried in a vacuum desiccator at room temperature.

Following the colloidal synthesis method in open literature [48], 0.48 mmol Ln(ddtc)<sub>3</sub>Phen precursors were dissolved into a surfactant solvent mixture at 70 °C consisting of 9.17 g of 70% oleylamine (OM, 24 mmol), 2.98 g of 90% oleic acid (OA, 9.5 mmol) and 2.67 g of 90% octadecene (ODE, 9.5 mmol) until a homogeneous and clear solution was formed in a three-neck flask. OM, OA and ODE are all from Sigma-Aldrich and used as received without further purification. The resultant solution was rapidly heated to 300 °C in 10 min, following by vigorous stirring for over 50 min. Since La and Pr have higher oxophilicity values than Eu [63], oxygen level during synthesis need to be carefully controlled. Briefly, one neck of a three-neck flask was capped by a wooden plug. One of the remaining two was plugged with a thermocouple, with the third neck being capped by a wooden plug that has a small hole for vaporous reaction exhaust to escape. As such, less air will be present in the flask as this heated reaction proceeded in order to minimize oxide phase formation. NPs were present in the colloidal solution after cooling down to 70 °C and, subsequently, precipitated out when 30 mL hexane/acetone solvent (1:5) in 30 mL was added into the resulting colloidal solution. The suspension was centrifuged at 4000 rpm for 10 min. The colored NPs (La: gray white, Pr: pale green), were re-dissolved in 15 mL toluene. After adding excessive amount of ethanol to the toluene solution to reprecipitate the NPs, the final products were separated from the mixed toluene/ethanol solvents and dried in a vacuum desiccator. Finally, the dried powders were grinded and heated in air at 500 °C for over 5 h (10 °C/min) to obtain Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> NPs (Ln = La and Pr).

#### 2.1.2. Synthesis of micro-scale La<sub>2</sub>O<sub>2</sub>SO<sub>4</sub>

Micro-scale of high surface area La<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> was synthesized as reported by Machida et al. [64] Briefly, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (7.96 g), C<sub>12</sub>H<sub>25</sub>O<sub>5</sub>O<sub>3</sub>Na (10.89 g), 28% aqueous NH<sub>3</sub> (37.5 mL) and water (20 mL) were mixed and constantly stirred at 40 °C for one hour. This mixture was then heated up to 60 °C and continuously agitated for more than 10 h to encourage precipitation at pH 11. Subsequently, the precipitate was separated from the solution via centrifuge. After washing the precipitate in deionized (DI) water three times, it was dried in desiccator at room temperature. Finally, the dry powder was ground in a mortar and heated up to 500 °C in air over four hours (2 °C/min) to obtain micro-scale La<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> [64].

#### 2.1.3. The preparation of CCR with impregnated Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> NPs

The support used for CCR is an AccuSep<sup>®</sup> tube (Pall Corp., O.D. = 10 mm), which consists of a ZrO<sub>2</sub> layer (median pore size: 100 nm, 20 μm thickness) coated on a porous stainless steel (PSS) (2 mm thickness). Nonporous SS tubing is welded to both ends of the PSS tube, enabling the tube to be hermetically connected to other fittings. The ZrO<sub>2</sub> layer serves as a barrier to minimize metallic inter-diffusion between impregnated NPs and PSS support. Before the impregnation step, the nonporous SS ends of the tube were masked with aluminum foil, exposing only the nanoporous ZrO<sub>2</sub> layer for impregnation. In order to gain better NP dispersion and stronger adhesion to the ZrO<sub>2</sub> layer, AccuSep<sup>®</sup> tubes were pretreated in O<sub>2</sub> plasma (26.9 W) under 505 Torr over 25 min. Sequentially, highly viscous NPS suspension in the mixed solvent of toluene/ethanol were used to wash-coat the AccuSep<sup>®</sup> tube for 3–4 times to obtain a uniform, smooth catalyst coating layer. Finally, the coated tube was heated up to 500 °C in an oven for more than two hours. Fig. 1 shows the color change before and after the wash-coat procedure.

### 2.2. Catalyst performance testing procedure

For CCR, the coated AccuSep<sup>®</sup> tube with 35 mg Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> NPs

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