



Full Length Article

Influence of surface morphology on the performance of nanostructured ZnO-loaded ceramic honeycomb for syngas desulfurization



Wen-Da Oh^{a,1,*}, Junxi Lei^{a,1}, Andrei Veksha^a, Apostolos Giannis^a, Grzegorz Lisak^a, Victor W.-C. Chang^b, Xiao Hu^c, Teik-Thye Lim^{a,d,*}

^a Residues and Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute (NEWRI), Nanyang Technological University, 1 Cleantech Loop, CleanTech One, Singapore 637141, Singapore

^b Department of Civil Engineering, Monash University, VIC 3800, Australia

^c School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

^d School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Keywords:

Nanostructured ZnO
ZnO nanosheets
Honeycomb
H₂S removal
Syngas
Gasification

ABSTRACT

A facile seeding-growth protocol was employed to immobilize nanostructured ZnO with nanorod and nanosheet morphologies (ZnO-nR and ZnO-nS, respectively) on cordierite-mullite honeycomb support. By varying the hexamethylenetetramine (HMTA) concentration, Zn precursor, and number of growth cycles during synthesis, different nanorod sizes, nanosheets textures and ZnO layers were obtained. The ZnO-loaded honeycombs were characterized using FESEM, EDX and XRD indicating that the immobilized layer of nanostructured ZnO was highly-crystalline with a thickness of $\sim 1 \mu\text{m}$. The synthesized nanostructured ZnO-loaded honeycombs and a commercial ZnO sorbent were applied for removal of sulfur compounds (H₂S and COS) from syngas at 400 °C. The ZnO-nS showed significantly longer breakthrough time (BT_{TS}) and higher total sulfur sorption capacity (48.7 mg g⁻¹ ZnO, BT_{TS} = 75.4 min) than the ZnO-nR (9–12 mg g⁻¹ ZnO, BT_{TS} = 23–25 min) and commercial ZnO sorbent (4.6 mg g⁻¹ ZnO, BT_{TS} = 6.8 min). The superior sorption capacity of ZnO-nS was attributed to the significantly better surface coverage and higher crystallinity of ZnO nanosheets on the honeycomb. The introduction of additional ZnO nanosheets layers (up to 3 layers) through repeated growth process increased the ZnO loading to $\sim 1.5 \pm 0.1 \text{ mg mm}^{-1}$ (from $\sim 0.9 \pm 0.1 \text{ mg mm}^{-1}$ in the single layer) but resulted in poorer performance (11.6 mg g⁻¹ ZnO, BT_{TS} = 24.6 min) compared to ZnO-nS. This was due to the increased internal mass transfer resistance and decreased density of the effective reactive sites. The mechanism of ZnO-nS formation is also proposed to provide further insights. Overall, the ZnO-nS showed better regenerability, lower mass transfer resistance, and higher sorption capacity compared to the commercial ZnO and ZnO-nR sorbents indicating that it has a promising potential for syngas desulfurization.

1. Introduction

The gasification process is used to convert solid waste (e.g., municipal solid waste, horticultural) into useful fuel gas called syngas, which contains predominantly carbon dioxide, carbon monoxide and hydrogen [1–3]. The syngas can be utilized in gas engines, gas turbines or fuel cells for power generation. However, raw syngas generated from solid waste gasification process contains corrosive gases (particularly sulfur compounds such as H₂S and COS) which need to be removed prior to downstream application [4,5]. The concentration of corrosive sulfur compounds from solid waste gasification is generally < 100

ppmv [6]. Although the sulfur concentration in syngas derived from solid waste gasification is significantly lower than that from the coal gasification (~ 6000 ppmv), the sulfur concentration exceeds the acceptable level for downstream application [7]. For application in gas turbines, the total sulfur concentration should be lower than 20 ppmv [8–10].

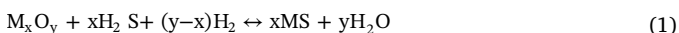
Currently, conventional methods for corrosive gas removal are scrubbing using chemical or physical sorbents at low temperature (below 40 °C) [11]. To improve the thermal efficiency of syngas, hot gas desulfurization process ($T > 200$ °C) can be carried out using metal oxide sorbents. The sulfur compounds (mainly H₂S) can be removed

* Corresponding authors at: Residues and Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute (NEWRI), Nanyang Technological University, 1 Cleantech Loop, CleanTech One, Singapore 637141, Singapore (W.-D. Oh and T.-T. Lim).

E-mail addresses: wdoh@ntu.edu.sg (W.-D. Oh), cttlim@ntu.edu.sg (T.-T. Lim).

¹ Authors 1 and 2 contributed equally to this work.

from syngas through chemisorption with the metal oxides (M_xO_y) via the following reaction [12,13]:



The Zn-, Cu-, Fe-, Mn-, and rare earth metal-based oxides are the most commonly-used sorbents for downstream syngas desulfurization [12,14–19]. The performance of each M_xO_y varies depending on the operating conditions such as syngas composition, gasification temperature, pressure and moisture content. To date, ZnO is the most widely studied metal oxide sorbent for syngas desulfurization because (i) it is thermodynamically stable and efficient under syngas environment, and (ii) it has high uptake of sulfur compounds (H_2S and COS) even at a considerably high temperature (up to 800 °C) [14,20,21].

Nanostructured ZnO sorbents demonstrated higher sulfur removal compared to ZnO with larger particle sizes. Lee et al. [22] reported that the ZnO nanoparticles have high sorption capacity towards H_2S and COS. Furthermore, the conversion efficiency and reactivity of nanosized ZnO (i.e., larger surface area, conversion to ZnS) was larger than that of the conventional pelletized ZnO. Thus, the nanostructured morphology and surface chemical composition are important criteria for the design of effective desulfurization sorbents [23]. The importance of ZnO morphology for H_2S removal was also highlighted in previous studies involving ZnO particle system [24,25]. Typically, the nanosized ZnO is prepared in powdered form and further processing (e.g., pelleting, extrusion or immobilization on a support) is required to avoid reactor plugging and pressure drop. However, the processing steps can significantly alter the ZnO morphology which is undesirable. To avoid losing the advantages of having nanostructured sorbent, direct growth of nanostructured materials on the support is preferred. By directly growing the nanostructured sorbent on the support, the morphology of the sorbent can be tuned to obtain high-performance ZnO sorbent for H_2S removal.

For efficient syngas desulfurization, it is advantageous to develop a supported nanostructured ZnO sorbent with unobstructed syngas flow (lower pressure drop) that can be applied at higher temperature (better thermal efficiency) [26]. In this study, nanostructured ZnO with various morphologies, namely nanorods and nanosheets, were immobilized on the cordierite-mullite honeycomb support via a facile seeding-growth method. The effects of various operational parameters, namely gas hourly space velocity (GHSV) and inlet H_2S concentration on desulfurization performance were investigated in a tubular fixed bed reactor. The regenerability of the ZnO supported honeycomb was also investigated.

2. Experimental

2.1. Materials

The chemicals used in this study were $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich), $Zn(CH_3COO)_2 \cdot 2H_2O$ ($Zn(Ac)_2 \cdot 2H_2O$, Sigma–Aldrich), hexamethylenetetramine (HMTA, Sigma–Aldrich), ethanol (Merck), phosphorus pentoxide (Merck), commercial ZnO sorbent (Liaoning Haitai Sci-Tech Development Co. Ltd., China) and diethanolamine (Merck). The cordierite-mullite honeycomb (Adena ceramics, Shanghai) was used as the support material for sorbent preparation. The honeycomb was 14 mm in diameter, 20 mm in height, with 1.5 mm \times 1.5 mm square channels. The total surface area of the square channels in the honeycomb was approximately 43.2 cm². All honeycombs were sonicated in ethanol and dried in an oven at 60 °C for 24 h prior to immobilization of ZnO.

2.2. Preparation and characterization of nanostructured ZnO sorbents

Two different nanostructured ZnO morphologies, namely nanorods and nanosheets, were prepared on the honeycomb multi-channel support via a general two-step seeding-growth method (Fig. 1). For the

synthesis of nanostructured ZnO nanorods, the honeycomb support was initially seeded by immersing it into a seeding solution containing 20 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ in 50 mL ethanol and 2 mL diethanolamine, dried in an electric oven at 60 °C, followed by calcination in air at 400 °C for 2 h (heating rate 2 °C min⁻¹). Once seeded, the honeycomb support was then placed in a vessel containing 25 mL of ZnO crystal growth solution with a specific HMTA concentration (0.05–0.20 M) and 0.1 M of $Zn(NO_3)_2 \cdot 6H_2O$. The vessel was tightly sealed and placed in an electric oven at 90 °C for 5 h to stimulate the ZnO crystal growth on the seeded surface. The role of HMTA is to promote direct precipitation of Zn^{2+} to form nanostructured ZnO. After 5 h, the ZnO-loaded honeycomb support was removed from the vessel, immediately washed with DI water to remove the loosely attached ZnO, and dried in the oven at 60 °C. For the synthesis of nanostructured ZnO nanosheets, similar protocol was employed except that (i) $Zn(Ac)_2 \cdot 2H_2O$ was used as the precursor, and (ii) aging for 18 h in the same solution (at 25 °C) was employed after the 5 h of crystal growth process. During the synthesis, the HMTA concentration (0.01–0.6 M), reaction time, and number of growth cycles (1–3) were varied.

The field emission scanning electron microscopy (FESEM JEOL 7600F) equipped with the energy dispersive X-ray spectroscopy (EDX, Oxford Xmax80 LN₂ Free) was used to investigate the surface morphology and elemental distribution of the ZnO-loaded honeycomb. The X-ray diffractometer (Bruker AXS D8 Advance, operated with Cu-K α source at $\lambda = 1.5418 \text{ \AA}$) was employed to obtain the X-ray diffraction (XRD) pattern.

2.3. Experimental setup and procedure

Fig. 2 presents the schematic illustration of the experimental setup for the desulfurization study. The desulfurization process was carried out in a vertical fixed-bed quartz reactor with 15 mm inner diameter. The as-prepared nanostructured ZnO-loaded honeycomb was wrapped by a thin layer of ceramic fibre and fixed in the middle of the reactor. The fibreglass was seamlessly contacted the reactor wall to avoid by-pass of gas flow. The commercial ZnO sorbent was prepared by mixing commercial ZnO particles (~18–20 mg, particle size 0.212–0.56 mm) and cordierite-mullite particles (~3 g, particle size 0.212–0.56 mm) uniformly. The total weight was equivalent to nanostructured ZnO honeycomb sorbent to maintain a consistent space velocity during experiments. Prior to the commencement of each experiment, the reactor was purged with N_2 gas at 100 mL min⁻¹ for 10 min to remove air. The model syngas contained CO, CO₂, H₂, N₂ and H₂S (500 ppmv)/N₂ and was supplied from individual gas cylinders using mass flow controllers. The steam was generated from DI water supplied by a syringe pump. All the gas lines before and after the fixed-bed tubular reactor were pre-heated to 120–150 °C to avoid moisture condensation and H_2S absorption by liquid water.

The model syngas composition was 30–100 ppmv H_2S , 8 vol% CO, 15 vol% CO₂, 10 vol% H₂, 26 vol% H₂O and N₂ balance, which is typical to syngas composition from municipal solid wastes. The total flow rates of model syngas were set at 100, 150 and 200 mL min⁻¹ at STP, resulting in a gas hourly space velocities (GHSV, volume based) of 4615, 6923 and 9230 h⁻¹, respectively. All desulfurization studies were carried out at 400 °C and a pressure range of 20–21 psi. After desulfurization, the syngas was passed through a P₂O₅ trap to remove the moisture and analysed by gas chromatograph (GC) equipped with a Flame Photometric Detector (FPD) (Agilent 7890 GC, USA). There was no significant absorption of H_2S and COS by the P₂O₅ in the control study. Before and after desulfurization experiments, the gas was purged through the by-pass until stable response of GC was obtained to measure the H_2S content. The inlet H_2S concentration was calculated as an average of two measurements (i.e. one before and one after desulfurization).

In this study, the concentrations of H_2S and total sulfur (sum of H_2S and COS) were reported. The H_2S (and total sulfur) removal was

Download English Version:

<https://daneshyari.com/en/article/6473553>

Download Persian Version:

<https://daneshyari.com/article/6473553>

[Daneshyari.com](https://daneshyari.com)