

Promoted ZnO/Silica For Wide Temperature Range H₂S Removal, While Inhibiting COS Formation

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Introduction

High efficiency desulfurization is critical to maintain the activity of fuel processing catalysts and high-value membrane electrode assemblies in logistic PEM fuel cell systems [1]. Packed beds provide enough volume to remove sulfur from several thousands ppmv to sub-ppmv levels generally use sorbent particles sizes, ca. 1-5 mm, which demonstrate low sorbent utilization and poor regenerability, owing to low contacting efficiency, intra-particle and lattice diffusion limitations [2]. Small particle size (100-200 microns) allows entrapment in the microfibrinous media viable for composite bed design. Those microfibrinous media offer enhanced contacting efficiency and mass transfer without significant pressure drop [3]. ZnO is preferred metal oxide because of favorable sulfidation thermodynamics [4] but is not efficient to remove COS [5]. Addition of dopant not only stabilizes the active sorbent by increasing active surface area and decreasing crystallite size, but may introduce defects with promoter behavior [6].

Materials and Methods

Promoted ZnO sorbents were made by incipient impregnation method on SiO₂. The challenge gas was chosen to mimic the model reformate gases as 1 vol% H₂S-33 vol% CO/CO₂-H₂, outlet gases were analyzed by TCD-GC (Varian CP3800). Desulfurization was carried out at various temperatures, 20 to 400 °C, at 1 atm. Regeneration was carried at 550 °C in air. Surface area and pore volume of sorbents were measured by the N₂ adsorption/desorption, on Autosorb 1C (Quantachrome). The model Cu-ZnO/SiO₂ sorbents were prepared *ex-situ* under controlled conditions by pneumatic chemical spray pyrolysis technique on oxidized Si wafers. SEM and SEM-EDX micrographs of the sorbents were obtained by a Zeiss DSM 940 and Zeiss EVO 50 microscopes. XPS measurements were done on Leybold-Heraeus LHS-10 XPS system. Studies of dopant ions were done on Bruker EMX-6/1 X-band EPR spectrometer. Desulfurization and sorbent regeneration were studied by Temperature Programmed Oxidation (TPO), with RHK's TM310 and HP 6456B controllers, with desorbed gas measured by QMS 3F/PIC 1-300 amu (Hidden Analytical).

Results and Discussion

The un-promoted ZnO/SiO₂ shows 5-12 fold increase in H₂S saturation capacity over BASF and Sud-Chemie ZnO extrudates. On doping the sorbent with 5 mol % transition metal, H₂S capacity further goes up by 27%. Transient COS is not detected in the reaction products, if desulfurization is done at room temperature with doped sorbents as shown in Figure 1. The Cu-ZnO/SiO₂ sorbent shows >70% capacity recovery when regenerated over 10 cycles in air. Spatial dispersion of the dopant element (ions vs clusters vs domains) and diffusion of S ions in the “spent” Metal-ZnO/SiO₂ sorbent depends on the dopant ion, concentration and sample temperature. Results obtained on the model sorbents are in

reasonable agreement with those obtained with the “real” sorbents. The dispersion and relative amount of dopant elements on the surface of the doped sorbent do not change significantly after multiple oxidative regenerations of the “spent” sorbent in air.

Table 1. Comparison of the 5% mol. doped supported vs. undoped granulated sorbents:

Sorbent	Measured Capacity, g S/g ZnO	Theoretical Capacity, %
Cu-ZnO/SiO ₂	0.367	90.63
Fe-ZnO/SiO ₂	0.328	81.25
Co-ZnO/SiO ₂	0.304	75.00
Ni-ZnO/SiO ₂	0.252	62.51
Mn-ZnO/SiO ₂	0.24	59.31
ZnO/SiO ₂	0.253	62.51
ZnO (BASF [*])	0.019	4.96
ZnO (Sud-Chemie [*])	0.038	9.8

^{*}crushed to 100-200 microns

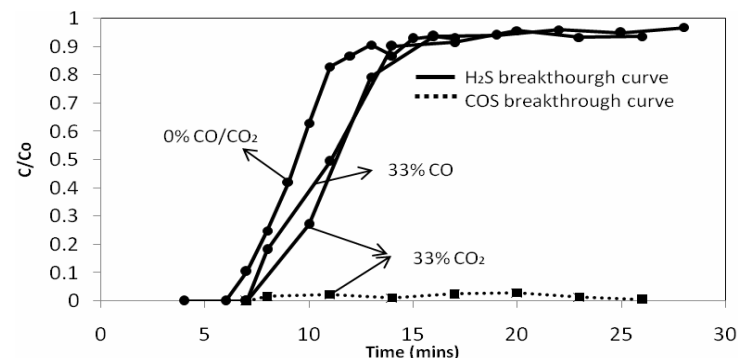


Figure 1. Breakthrough curve for H₂S/COS in presence of CO/CO₂ room temperature.

Significance: The objective of the present work is to develop supported doped sorbents for efficient removal of H₂S/COS over wide temperature range, while inhibiting formation of COS, so that the desulfurization process is cost-effective and scaleable, and the sorbent is regenerable over higher number of cycles without significant activity loss.

References

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