A fiber optics system for monitoring utilization of ZnO adsorbent beds during desulfurization for logistic fuel cell applications

Achintya Sujan¹, Hongyun Yang², Paul Dimick² and Bruce J. Tatarchuk^{1*}

¹*Department of Chemical Engineering, Auburn University, Auburn, AL 36849 (USA)*

²*IntraMicron Inc., 368 Industry Drive, Auburn, AL 36832*

*brucet@auburn.edu, Tel: +1-334-524-8270, Fax: +1-334-844-2063

Abstract

An in-situ fiber optic based technique for direct measurement of capacity utilization of ZnO adsorbent beds by monitoring bed color changes during desulfurization for fuel cell systems is presented. Adsorbents composed of bulk metal oxides (ZnO) and supported metal oxides (ZnO/SiO₂ and Cu-ZnO/SiO₂) for H₂S removal at 22 °C are examined. Adsorbent bed utilization at breakthrough is determined by the optical sensor as the maximum derivative of area under UV-vis spectrum from 250-800 nm observed as a function of service time. Since the response time of the sensor due to bed color change is close to bed breakthrough time, a series of probes along the bed predicts utilization of the portion of bed prior to H₂S breakthrough. The efficacy of the optical sensor is evaluated as a function of inlet H₂S concentration, H₂S flow rate and desulfurization in presence of CO, CO₂ and moisture in feed. A 6 mm optical probe is employed to measure utilization of a 3/16 inch ZnO extrudate bed for H₂S removal. It is envisioned that with the application of the optical sensor, desulfurization can be carried out at high adsorbent utilization and low operational costs during on-board miniaturized fuel processing for logistic fuel cell power systems.

Keywords:

PEM fuel cells; Desulfurization; ZnO adsorbents; Fiber optic probe; UV-vis Diffuse Reflectance Spectroscopy

1. Introduction

Sulfur impurities such as H_2S and mercaptans widely exist in most hydrogen rich gaseous fuels including natural gas, associated gas, landfill gas and biogas. These impurities are known to severely corrode equipment, pipelines, and poison downstream fuel processor catalysts in fuel cell applications. For instance, 1 ppmv H_2S in the feed stream can cause a reduction in the cell voltage of a fuel cell from 0.675 V to 0.625 V [1]. Adsorptive desulfurization is a relatively low cost alternative compared to conventional hydro-desulfurization which demands stable catalyst performance, high H_2 partial pressures and elevated temperature. Prior to reformation, desulfurization of hydrocarbon fuels is carried out to remove high molecular weight sulfur compounds such as Tetra-hydro Thiophene (THT), T-butyl Mercaptans (TBM) and Dimethyl Sulfide (DMS) etc. However, when these fuels are reformed, the product (mainly syngas) still contains low molecular weight sulfur compounds such as H_2S and trace quantities of COS. To protect high value membrane electrode assemblies in fuel cells, especially PEM fuel cells, post reformat desulfurization is a common step employing metal oxides composed of ZnO , CuO , TiO_2 , Al_2O_3 etc. that serve as polishing adsorbents to remove any residual H_2S downstream of the reformer [2]. COS is commonly converted to H_2S via hydrolysis on pure oxides such as $\gamma\text{-Al}_2\text{O}_3$, TiO_2 [3] or mixed oxide catalysts like $\text{CeO}_2\text{-Al}_2\text{O}_3$ [4], $\text{TiO}_2\text{-ZrO}_2$ [5], $\text{Al}_2\text{O}_3\text{-ZrO}_2$ [6] etc. then removed by aforementioned adsorbents.

In fuel cell systems, the desulfurizer unit experiences temperature variations ranging from ambient temperature to several hundred Celsius during cold startup or transient operations [7]. To overcome the limitation of gas phase mass transport and solid state diffusion resistance during H_2S removal at lower temperatures, ZnO may be deposited on porous supports [8-10]. Recent work in our laboratory involving ZnO dispersed on inert SiO_2 support prepared by

incipient wetness impregnation showed enhanced H_2S adsorption capacity at 400 °C with regenerable performance of up to 10 cycles compared to bulk ZnO [11]. ZnO/SiO₂ can be promoted by various transition metals during room temperature desulfurization. At a Zinc to transition metal molar ratio of 19:1, promoted ZnO/SiO₂ demonstrated a sulfur saturation capacity of 0.213 g_{sulfur}·g_{ZnO}⁻¹ (54% of theoretical value) at room temperature [7].

Currently, sulfur concentration in the outlet stream of a desulfurizer is measured using inline chromatography, detector tubes or portable electrochemical sensors. However, the measured concentration at the outlet cannot directly represent the utilization of an entire adsorbent bed. Moreover, the costs of these methodologies are relatively high and it is not economically practical to integrate such methods for continuous analyses of sulfur compounds for small-scale applications such as miniaturized fuel processors in logistic applications. Several methodologies and techniques are commercially available to directly monitor the utilization of adsorbent beds [12-15]. Such methods are based on probing one or more physical properties of the adsorbent material such as color, density, magnetism, temperature etc. However, a few challenges exist such as (i) a separate unit in the desulfurization process was required in case of on-line detection of sulfur concentration downstream of adsorbent beds (ii) detection based on temperature difference required a fuel pre-heater with accurate temperature measurements at multiple points in the process (iii) detection based on color change of adsorbents using cameras had limitations while monitoring adsorbents with little or no color change such as SiO₂ supported ZnO [16]. Thus, there is a need for a technique to determine the degree of utilization and capacity of adsorbent or catalyst beds that does not require two or more sensors and the accuracy of which does not rely on the measurement of concentration of one or more contaminants.

In-situ fiber optic spectroscopy provides a solution to this challenge. It is gaining attention in the field of heterogeneous catalysis [17-25], continuous process analyses [26-30], batch process analyses [31, 32] and clinical applications [33, 34]. For example, a fiber optic based UV-vis CCD spectrometer was employed for the determination of nickel breakthrough in an ion-exchange column [26]. The non-invasive and inert properties of the optical fibers make them attractive choices for studying chemical processes in-situ without disturbing the integrity of the process. The flexibility of fibers and stainless steel construction of the probe enables high temperature measurements in presence of corrosive gases (H_2S and COS) and moisture. The tip of the probe can be configured in a manner compatible with plug flow conditions in a packed bed. The desulfurization of various sulfur containing gas streams at high temperature is also carried out using metal oxide and zeolite based adsorbents. These adsorbents contain one or more metal oxide components that are optically active in the UV-vis wavelength region and are known to undergo an apparent color change upon adsorption of sulfur compounds at high temperature. For example, during H_2S removal on $ZnFe_2O_4$ (Zinc Ferrite) adsorbent pellets in the temperature range of 300-500°C, a color change from orange, in fresh state to gray or black was observed [35]. Another study involving metal oxides supported on mesoporous silica, $MeOx/SBA-15$ ($Me=Zn, Fe$) during H_2S removal at 300°C exhibited a pale brass-yellow color appearance in the sulfided specimen enriched with FeS [36]. To our knowledge, in-situ reflectance spectroscopy via fiber optics has never been implemented to probe the electronic effects occurring on the metal oxides during adsorptive desulfurization for logistic fuel cell applications.

In the current study, a fiber optic based UV-vis diffuse reflectance spectroscopic system was implemented as an embedded sensor in the desulfurizer assembly to measure the utilization of

adsorbent beds during H₂S removal at 22 °C for logistic fuel cell applications. The efficacy of the embedded fiber optic sensor is evaluated as a function of (i) H₂S concentration (ii) H₂S contact time (iii) Presence of CO, CO₂ and moisture in feed stream and (iv) H₂S adsorption on 3/16 inch extrudates using a 6mm optical probe.

2. Experimental

2.1. Preparation and characterization of Adsorbents

ZnO/SiO₂ and Cu-promoted ZnO/SiO₂ adsorbents are prepared via incipient wetness impregnation followed by drying and calcination in static air as described elsewhere [37, 38]. In short, metal nitrate (Zinc and Copper) solutions of desired molarity are prepared by dissolving metal salts in de-ionized water. The metal nitrate solutions are then impregnated on 100 µm SiO₂ support (Grace Division Inc., pore volume 1 cm³g⁻¹, BET surface area 460 m²g⁻¹) at room temperature. The impregnated samples are then dried overnight for 12h at 110 °C followed by calcination in air for 3h at 400 °C. Commercial ZnO is obtained from BASF (SG-901) in the form of 3/16 inch extrudates. These are used in the form of extrudates as well as crushed and sieved into 100-200 µm.

Nitrogen adsorption-desorption isotherms of adsorbents and SiO₂ support are generated at 77 K (-196 °C) on Autosorb-1C (Quantachrome Instruments). The samples are outgassed at 150 °C for 6h in vacuum (3×10^{-10} mm Hg) prior to analyses. BET surface area of samples is calculated using the Brunauer-Emmett-Teller (BET) equation. The average pore size and pore-size distribution is obtained the adsorption curve of N₂ isotherm and calculated using Barrett-Joyner-Halenda (BJH) method.

2.2. Desulfurization experiments

2.2.1. Fiber optic system

Adsorption experiments were conducted on a Cu-ZnO/SiO₂ adsorbent bed with a fiber optic probe in direct contact with adsorbent particles and simultaneous on-line GC analysis downstream of the bed. Utilization of adsorbent beds was determined by observing the sensor response and H₂S breakthrough curve. A schematic of the probe configuration for plug flow conditions is shown in Fig. 1(a). Fig 1(b) depicts the comparison between a 1.5 mm probe and a 6 mm probe embedded at the bottom of packed beds.

The 6mm probe was not suitable for monitoring the utilization of beds containing micron size adsorbent particles since it disturbs the integrity and uniformity of the bed as shown. Thus, the 1.5 mm probe embedded horizontally at the bottom of 0.1-2 mL packed beds containing $<200 \mu$ adsorbent particles was chosen for the remaining experiments in this study. If not mentioned otherwise, the dimensions of the packed bed (4 mm diameter $\times$ 25.4 mm length), reflectance probe (1.5 mm dia.) and adsorbent particle size (100-200 μ m) were chosen to avoid

gas flow channeling through the bed. An experiment was carried at same operating conditions using the 1.5 mm probe embedded in a bed of dimension (12 mm dia. $\times$ 25.4 mm length) used similarly in an earlier study based on desulfurization for fuel cells [6]. These results are summarized in supplementary Fig. S(10) and Table S(2). In-situ diffuse reflectance spectroscopy of adsorbents was carried out on a spectrometer (Avaspec-2048 by Avantes Inc.) based on a symmetrical Czerny-Turner design with an optical bench and a focal length of 75 mm suitable for analysis in 245-800 nm wavelength range. The spectrometer was equipped with a standard SMA (Sub Miniature version A) connector for incorporating the fiber optic cables. Diffusely reflected light from adsorbent particles was received by a CCD detector array with a sensitivity of 5000 counts μW^{-1} per millisecond of integration time. A 12 volt DC USB powered interface between the spectrometer and spectrum analyzer (or computer) enabled data transfer speeds in the range of 14-31 milliseconds scan^{-1} with an onboard sample averaging speed of 17 milliseconds scan^{-1} . The dimensions of the spectrometer used in this study were 175 mm (length) $\times$ 110 mm (height) $\times$ 44 mm (width) and weighed approximately 716 g.

A stainless steel fiber optic reflectance probe (FCR-7UV200-2-1.5x100) with dimensions 1.5 mm (diameter) $\times$ 100 mm (length) specifically designed for powders was used. The fiber bundle consisted of six emitter fibers and one read fiber. Fluorine-doped SiO_2 with a numerical aperture of 0.22 facilitated the light guiding effect. UV-vis light from a xenon pulsed light source (Avalight-Xe) was conveyed through emitter fibers directly onto the adsorbent bed. The fibers were protected by a Kevlar reinforced PTFE (Polytetrafluoroethylene) jacket with 3.8 mm outer diameter PVC (Polyvinyl chloride) sleeves. The maximum operating temperature of the probe was 65°C. For experiments involving ZnO extrudates, a probe (FCR-7UV200-2-45x140) of dimensions 6 mm (diameter) $\times$ 140 mm (length), also containing six emitter fibers and one read

fiber was used. The minimum bend radius ranged from 20 mm - 60 mm depending on the time at which these fibers are subjected to bending. The maximum operating temperature of the larger probe was 500 °C. The fibers in the large probe were protected by a 5 mm outer diameter flexible chrome plated brass outer tubing for stress relief.

In this study, data was acquired in the reflectance mode because the percentage of diffusely reflected light is independent of the color of sample. H₂S adsorption experiments were also carried out when the spectrometer was operated in scope mode (supplementary Fig. S(1)-S(3)) and absorbance mode (supplementary Fig. S(4)-S(6)). However, since these modes of operation are highly sensitive to degree of color change, they exhibit only a minor change signal response during H₂S adsorption on ZnO and ZnO/SiO₂ materials. The percentage of diffusely reflected light is given as,

$$\text{Diffusely reflected UV-Vis light, } R [\%] = 100 \times \left(\frac{\text{sample} - \text{dark}}{\text{reference} - \text{dark}} \right) \quad (1)$$

In Eq. (1), the term ‘sample’ indicates percent diffusely reflected light from adsorbent particles, ‘dark’ indicates percent reflectance with light source turned off and ‘reference’ indicates the reflectance of a white standard[39], in our case BaSO₄ (Puratronic, 99.9% Alfa Aesar) of 150 μm particle size. To obtain a desired signal-to-noise ratio of 200:1 essential for probing the spectral changes occurring on the adsorbent surface, the scan rate was set to 5s scan⁻¹ with an integration time of 10 ms scan⁻¹. The time between the start of spectral data acquisition and GC injection was recorded to be less than three seconds during adsorption experiments. This time was considered to be time zero during analyses. It is important to mention, in experiments throughout the study, UV-vis light through the fiber optic probe did not cause any photo-induced effects on H₂S gas when passed through an empty quartz tube. Furthermore, the region of the bed

probed by the optical sensor did not cause any change in the H₂S adsorption capacity due to UV-vis light illumination. Spectral data was processed using Origin 2016 software.

2.2.2. H₂S breakthrough curves using on-line GC measurements

H₂S gas with desired concentration at inlet (C_0) was fed using mass flow controllers (Alicat Inc.). H₂S at outlet from adsorption experiments was collected every 2 minutes using an automated six-port gas sampling valve (Valco Instruments) of 250 μ L sampling volume and injected onto a thermal conductivity detector (TCD) equipped with a packed column (Hayesep Q100) using H₂ carrier gas on a gas chromatograph (Varian CP 3800). Depending on the application, detection of lower sulfur concentration may be important. However, in this study, the breakthrough curves are generated based on H₂S concentration analysed by the TCD with a detection limit of 200 ± 50 ppmv of H₂S. The error in values of breakthrough time ' t_{BT} ' and time to reach 50% saturation ' $t_{1/2}$ ' obtained from breakthrough experiments was ± 1.0 min and ± 0.5 min respectively.

3. Results and discussion

H₂S saturation capacities of bulk ZnO, 21% ZnO/SiO₂ and 21% Cu-ZnO/SiO₂ (Cu:Zn molar ratio = 20:80) adsorbents at room temperature (22 °C) are 19 mgS·g_{adsorbent}⁻¹, 53 mgS·g_{adsorbent}⁻¹ and 78 mgS·g_{adsorbent}⁻¹ respectively [40].

3.1. UV-vis diffuse reflectance (R) spectroscopy of adsorbents

The electronic effects occurring on the surface of ZnO and Cu-ZnO adsorbents during H₂S adsorption can be probed using UV-Vis diffuse reflectance spectroscopy [41]. H₂S adsorption on ZnO and Cu-ZnO adsorbents can be treated as a chemical reaction between H₂S in gas phase and metal oxides (CuO and/or ZnO) in solid phase to form corresponding metal sulfides and moisture. The UV-vis diffuse reflectance spectra of fresh and spent adsorbents after sulfidation with 20000 ppmv H₂S in H₂ at 22 °C are shown in Fig. 2(a), (b) and (c).

At first, we examine the electronic effects during H₂S adsorption on ZnO and ZnO/SiO₂ adsorbents as follows,

Eq. (2) is an oxygen to sulfur exchange reaction with no charge transfer since oxidation state of Zn is 2+ in ZnO as well as ZnS. ZnO in its pure crystalline form is excited around 380 nm by UV radiation [42]. The commercial ZnO used in this study is composed of 90% ZnO by weight and 10% by binders or stabilizers that are added to maintain structural integrity during high temperature (>300 °C) operation. These binders also impart a characteristic color to commercial ZnO as shown in Fig. 2(a). The spectrum of spent adsorbent indicates a slight

change in the UV-region of spectrum since ZnS is excited in the same wavelength (380-400 nm) as ZnO [43]. This reduction in area under UV-vis reflectance spectrum of bulk ZnO is accompanied by a color change from light brown to dark brown as shown in Fig. 2(a).

The UV-vis spectrum of ZnO/SiO₂ shown in Fig. 2(b) can be distinguished from that of bulk ZnO in terms of electronic structure dependent size effects such as quantum confinement effects [44], nano-dispersion [45] etc. The absorbance of ZnO/SiO₂ is influenced by absorbance of SiO₂ which is present in majority (80 percent by weight) compared to ZnO that exists at 20 percent loading by weight on SiO₂ support. This can be understood by observing the spectrum of SiO₂ blank as shown in Fig. 2(b) – inset. The sharp peak around 250 nm is indicative of SiO₂ support [46]. The intensity of this peak reduces at higher ZnO loadings and suggests that ZnO may be dispersed not only in pores but also on the surface of SiO₂ support. The spectrum of spent adsorbent in Fig. 2(b) shows the reduction of SiO₂ peak at 250 nm. However, at 22 °C, SiO₂ support offers practically negligible capacity. The SiO₂ signal in the spent adsorbent disappears since the majority of surface and nano-size pores of SiO₂ support will be covered with sulfur that exist majorly as ZnS and also as H₂S dissolved in H₂O from the ZnO sulfidation reaction. In the spectrum of spent adsorbent, the shift in the ZnO peak at 325 nm to higher wavelength (~340 nm) is due to ZnS/SiO₂ formation [47]. The resultant color change is from white (fresh state) to beige (spent state) along with an apparent increase in reflectance as shown in Fig. 2(b). Similar behavior is observed at higher ZnO loadings and suggests that color change is independent of ZnO content on ZnO/SiO₂, thus enabling the technique to analyze samples with ZnO loadings as low as 1% by weight (data not shown).

The spectrum of Cu-ZnO/SiO₂ is shown in Fig. 2(c). The reflectance maxima observed around 500-550 nm is assigned to the Cu-O-Cu bridged structures [48, 49]. However, the ZnO

reflectance edge is attenuated in the spectrum of Cu-ZnO/SiO₂ at a Cu:Zn molar ratio of 20:80. This phenomenon was observed in Cu-Zn mixed oxides [50] prepared by thermal decomposition of co-precipitated Cu and Zn nitrate solutions and was assigned to the presence of electron traps in the ZnO band gap as a result of Cu⁺² ion dissolved in the ZnO matrix. The reflectance spectrum with maximum intensity around 500 nm is reduced to a flat plateau upon H₂S adsorption. The resultant color change is from bluish green to pale green. XPS and ESR characterization experiments reported earlier [40] suggest that a reduction of Cu²⁺ to Cu¹⁺ ion took place during H₂S adsorption on Cu-ZnO/SiO₂ at room temperature. Cu-ZnO/SiO₂ sorbents contain Cu²⁺ and Zn²⁺ sites, thus although Zn exists in an oxidation state of 2+ in sulfided adsorbents, sulfidation of Cu-ZnO/SiO₂ adsorbents involves a chemical reaction with charge transfer. This can be conceptualized based on previous findings [41, 45, 51],

The total percentage of diffusely reflected light from surface of adsorbents depends on the degree of darkness of samples. For example, white substances are perfect reflectors of light (UV and visible) when compared to black substances. ZnO/SiO₂ adsorbents containing dispersed ZnO show only a minor color change upon H₂S adsorption when compared to blank SiO₂ support. The introduction of Cu promoter ion induces a blue color to Cu-ZnO/SiO₂ adsorbents. The degree of diffuse reflectance in case of Cu-ZnO/SiO₂ adsorbents with varying mole percent Copper is shown in supplementary Fig. S(7). The percent reflectance in the plot is taken as the value at which maximum peak intensity is observed which corresponds to a wavelength of 380 nm in case of ZnO/SiO₂ and 500 nm for Cu-ZnO/SiO₂ samples. The CuO concentration on the surface will be higher than ZnO with increasing mole percent Cu as seen from the SEM-EDX analysis of these adsorbents [16]. Fig. S(7) indicates a dramatic decrease in the percentage of

diffuse reflected UV-vis light from surface of adsorbents with increasing Cu mole percent (x) in $\text{Cu}_x\text{-Zn}_{1-x}\text{O/SiO}_2$. Furthermore, there is no apparent difference in color between fresh and spent adsorbents when $x > 0.4$ in $\text{Cu}_x\text{-Zn}_{1-x}\text{O/SiO}_2$.

3.2. Optical technique for monitoring capacity utilization of adsorbent beds

Contaminant breakthrough curves are used to obtain the important parameters such as breakthrough time, saturation time or time to reach 50% breakthrough. Upon reaching the breakthrough time, the flow of contaminant may be stopped or diverted to a fresh bed. This timely operation is important for fuel cells that allow low sulfur threshold concentrations (0.1 ppmv and less) downstream of the desulfurizer. It is impractical to switch flows after sulfur breakthrough has occurred and thus most of the adsorbent must be utilized at breakthrough point.

The utilization of adsorbents at breakthrough can be understood by observing the sharpness of breakthrough curve. In this study, we have defined bed utilization at breakthrough using the $t_{1/2}$ concept (or time at which $C/C_0 = 0.5$) as shown in Fig 3(a).

According to McCabe [52], the fraction of bed capacity unutilized at breakthrough can be rearranged and expressed as a function of breakthrough time and saturation time as follows,

$$\text{Bed capacity unutilized from breakthrough curves, } \frac{\text{LUB}}{L} [\%] = \left(1 - \frac{t_{\text{BT}}}{t_{1/2}}\right) \times 100 \quad (4)$$

Where, LUB is an equivalent length of unused bed, which is held constant and L is total length of adsorbent bed. Let the bed capacity unutilized from breakthrough curves be denoted as U_{IBT} .

Adsorption capacity is usually calculated by numerical integration of the area under breakthrough curve starting from breakthrough time to saturation time. For a fixed bed containing Cu-ZnO/SiO₂ adsorbent, it is known from section 3.1 that the intensity of the diffuse reflectance spectrum reduces to a constant plateau upon H₂S saturation. The combined in-situ spectroscopic response of ZnO and CuO is recorded and the area under each spectrum (Fig. 3(b)) every 0.083 minutes (or 5 seconds) by numerical integration between 250-800 nm of wavelength range is calculated. In Fig. 3(b), R_0 and R_n denote percent UV-vis diffuse reflectance of fresh and spent adsorbent respectively. Thus,

$$\text{Area under each spectrum, } A_t [\text{nm}] = \int_{250\text{nm}}^{800\text{nm}} R_t d\lambda \quad (5)$$

Where, subscript t denotes time on stream (or service time). A plot of Eq. (5) versus time is highlighted by data points in red shown in Fig. 3(c). The reduction in area (A_t) is due to the reduction in percentage of UV-vis light reflected from the surface of adsorbent and is similar to the conversion profile of a solid reactant in a gas-solid reaction, such as H₂S adsorption involving a metal oxide.

In order to determine the precise time at which the portion of the adsorbent bed probed by the optical sensor is utilized at breakthrough, mathematical treatment of in-situ spectral data is necessary. It is important to note that the UV-vis light conveyed via fiber optic from a pulsed Xenon light source is similar in phenomenon to experiments involving pulsed Xe injections into a process. For example, the output profile of pulsed Xe injections into a carbon molecular sieve

column was described by an exponential Gaussian distribution profile [53]. A Gaussian or Lorentzian distribution profile versus time shows a point of maximum intensity. This point can be treated as the time at which there is a sudden change in the behavior of the probed specimen in a process. In the current study, the rate of change of integrated area under the reflectance spectrum (A_t) can be observed for elucidating the time at which sudden change in probed surface of the adsorbent. Thus, the absolute time derivative of numerical values of integrated area (A_t) is calculated as follows,

$$\text{Sensor response, } A_{dt} [\text{nm min}^{-1}] = \left| \frac{d}{dt} (A_t) \right| \quad (6)$$

Where, subscripts t and d denote time and first order derivative respectively. A_{d0} indicates first order time derivative area under spectrum at $t=0$ min or fresh adsorbent. As sulfidation proceeds, A_t values decrease with time. The corresponding A_{dt} values increase up to maximum point which coincides with the midpoint of the A_t versus time curve. As in the case of $t_{1/2}$ that occurs at $C/C_0 = 0.5$ on breakthrough curve, the $t_{\max}$ occurs at point at which $A_t/A_0 = 0.5$. The plot of A_{dt} in Eq. (6) versus time as shown in Fig. 3(c) indicates a maximum value $A_{dt\max}$ corresponding to the time $t_{\max}$. This point indicates the portion of the bed probed by the optical sensor is spent. Beyond time, $t_{\max}$, the $A_{dt\max}$ values decrease until a constant value indicating completely saturated adsorbent surface.

Depending on the probe location, the $t_{\max}$ value can then be compared to the breakthrough time and $t_{1/2}$ values which are obtained from breakthrough curve. Since $t_{\max}$ also represents the breakthrough of portion of the bed between the top of the bed and the location of the probe t_{BT} in Eq. (4) can be replaced with $t_{\max}$ when probe is placed at the bottom of the bed. Thus at H_2S breakthrough point,

$$\text{Bed capacity unutilized determined by optical sensor, } U_{t_{\max}}[\%] = 100 \times \left(1 - \frac{t_{\max}}{t_{1/2}} \right) \quad (7)$$

Eq. (7) describes an optical technique for determining the degree of adsorbent bed utilized at breakthrough.

In a similar way, the technique may be extended to measuring utilization of ZnO and ZnO/SiO₂ adsorbent beds during H₂S removal by processing in-situ diffuse reflectance data of these materials respectively. The in-situ UV-vis spectrum of ZnO and ZnO/SiO₂ during H₂S adsorption at 22 °C is shown in supplementary Fig. S(8) and Fig. S(9) respectively.

3.2.1. Effect of H₂S concentration at inlet

In this section, the effect of inlet H₂S concentration is investigated at 22 °C. Adsorption experiments are conducted on a bed containing 0.22 g of Cu-ZnO/SiO₂ using inlet H₂S concentrations of 2500 ppmv, 5000 ppmv, 10000 ppmv and 15000 ppmv at a constant bed length of 2.54 cm and an inlet flowrate of 100 mLmin⁻¹. The experimental results are shown in Fig. 4(a-d). With increasing H₂S concentration, the treated moles of H₂S per unit time per unit bed length will be higher. According to the mass transfer theory of adsorption, the adsorption wave front will be narrow as compared to the bed length and as a result, the time to reach saturation will be shorter at higher inlet concentration. The $t_{1/2}$ and breakthrough time values from breakthrough curves decrease with an increase in H₂S concentration.

A similar trend is observed with $t_{\max}$ values. However, since the fiber optic probe is located at least a few microns above the final layer of randomly distributed adsorbent particles $t_{\max}$ values are obtained before bed breakthrough time. Indeed, the purpose of the optical sensor is to detect the saturation of adsorbent beds before breakthrough occurs and serve to protect downstream processes from exposure to sulfur contaminants. Although, no apparent difference in color of the adsorbent is observed at different H_2S concentrations, the intensity of the UV-vis signal varied proportionately with the H_2S concentration in the following order $2500 \text{ ppmv} < 5000 \text{ ppmv} < 10000 \text{ ppmv} < 15000 \text{ ppmv}$ H_2S . Although the sensitivity of the optical technique depends on the rate of change of surface chemical reactions on the ZnO based adsorbents, the

global adsorption kinetics that is influenced by bulk properties of the adsorbents such as porosity, surface area etc. is expected to be slow at lower H₂S concentration [54]. Thus, at a fixed scan rate of 12 scans per min, the first order time derivative of area plot as shown by Fig. 4 appeared sharper at higher H₂S concentrations and most of the adsorbent is utilized at breakthrough.

3.2.2. Effect of H₂S flowrate at inlet

At high operating feed flowrates, the adsorbent is charged with higher H₂S molar rate per unit bed cross section per unit time and as a result breakthrough occurs earlier. At low flowrates, H₂S adsorption can become external mass controlled [54] leading to breakthrough curves with a high slope and slow saturation of contaminant. In this section, the performance of the embedded sensor is examined as a function of H₂S flowrate (residence time) through the Cu-ZnO/SiO₂ adsorbent bed at 22 °C. The flowrate is varied from 10 mL min⁻¹ to 100 mL min⁻¹ at constant bed length of 2.54 cm and inlet concentration of 20000 H₂S. Fig. 5(b-d) shows that most of the adsorbent is utilized at breakthrough when H₂S flowrate is varied from 25 mL min⁻¹ to 100 mL min⁻¹. The intensity of the first order time derivative of area plot did not vary proportionately with H₂S flowrate. At a fixed scan rate, the values of $t_{\max}$ are closer to $t_{1/2}$ values at higher flowrate because the portion of the adsorbent bed where the probe is located has less capacity at high H₂S flux.

In the next set of experiments the residence time in the bed is varied by reducing the length of a 2.54 cm bed by 50 percent of its value to 1.3 cm and lastly by doubling the bed length to 5.1 cm while keeping total inlet flowrate and H₂S concentration constant.

For example for a bed length of 5.1 cm, the $t_{\max}$, breakthrough time and $t_{1/2}$ values obtained are 11.3 min, 12 min and 11 min respectively. For the test with bed length of 1.3 cm, which is above the critical bed length (or the minimum bed length to avoid instantaneous breakthrough) a sharp breakthrough curve is obtained (data not shown) and the $t_{\max}$, bed breakthrough time and $t_{1/2}$ values are 2.8 min, 4 min and 3 min respectively. The embedded fiber optic sensor can thus be used for measuring utilization of thin catalyst (or adsorbent) beds, for example during high throughput testing in micro-reactors [55].

3.2.3. Bed capacity unutilized as a function of probe position

In section 3.2.1 and 3.2.2, a linear variation of $t_{\max}$, breakthrough time and $t_{1/2}$ values with H_2S concentrations and contact time through the bed is observed. The physical properties of Cu-ZnO/SiO₂ and ZnO/SiO₂ adsorbents such as pore volume and pore size as well as the physicochemical properties such as bed voidage and bed density are close in values as enlisted in Table 1. However, these properties differ from those of bulk ZnO adsorbent of same particle size. Nevertheless, H_2S adsorption is known to occur on the surface as well as in the pores of bulk ZnO, ZnO/SiO₂ and Cu-ZnO/SiO₂ adsorbents. Since the diameter of the fiber optic probe is 1.5 cm which is almost 100 order of magnitude higher than the average diameter of a single porous adsorbent particle of 0.015 cm diameter (assuming spherical particles) and pore size (4.1 ± 0.1 nm), the optical response from samples will be composed of reflected light from the surface as well as the pores of these adsorbent particles. Thus, assuming (i) absence of any channeling or dispersion effects through the bed (ii) uniform composition of adsorbent bed and (iii) compact plug flow conditions in the bed, the propagation of the color wave front with time can provide a visual indication of the impending sulfur breakthrough through the bed. However, in absence of any visible color change, the optical sensor can be used to monitor the extent of bed capacity unused.

In the next set of experiments, the percent bed capacity unutilized or bed life is determined by placing the fiber optic probe at various points (L_p) along the axial length of a 2.54 cm bed tested with 90 mLmin⁻¹ of 20000 ppmv H_2S as shown in Fig. 6(a). Fig. 6(b) shows a linear dependence of $t_{\max}$ values with distance of probe measured from top most layer of the packed bed.

For each experiment, a $t_{1/2}$ value of $5.5 (\pm 0.01)$ min is obtained from the H_2S breakthrough curve. For example, when the probe is located at probe position L_{p1} (or 0.2 cm) from top, the optical sensor provides a t_{max} value of 0.17 min since it captures the color wave front that propagates through the initial part of the Cu-ZnO/SiO₂ adsorbent bed. The bed utilization measured at this point is approximately 3% using Eq. (7) since only 0.2 cm of bed is saturated with H_2S . Similarly, t_{max} values are obtained by embedding the probe at axial locations of probe L_{p2} (0.8 cm) and L_{p3} (2.3 cm) respectively. A plot of the percent bed capacity unutilized versus t_{max} values results in a linear correlation with slope and intercept values of 39.55 and

103.39 respectively. If $t_{\max}$ is substituted with probe distance from top and $t_{1/2}$ values substituted with total bed length (L_b), the plot of bed capacity unutilized ($UL_{t_{\max}}$) yields a slope and intercept value of 39.37 and 100 respectively as shown in Fig. 6. These values are almost equal to values calculated using $t_{\max}$ and $t_{1/2}$ and Eq. (7) can be rewritten as follows,

$$\text{Bed capacity unutilized, } UL_{t_{\max}} [\%] = 100 \times \left(1 - \frac{L_p}{L_b} \right) \quad (8)$$

For example, when the 1.5 mm fiber optic probe is positioned at approximately 0.3cm below the top most layer of the packed bed containing 100-200 μ particles, the bed capacity unused or fresh will be approximately 88% of total capacity according to Eq. (8). Thus, operating in a regime under which the above mentioned assumptions are valid, the percent bed capacity unutilized can be determined by the optical sensor regardless of variations in H_2S concentration and contact time. It is possible to incorporate one or more probes along the length of the packed bed to simultaneously measure bed utilization at breakthrough and initiate adsorbent replacement or regeneration operation in a timely manner. In this way, the optical sensor facilitates continuous and accurate monitoring of adsorbent beds during desulfurization of feed stocks with varying H_2S concentration or flowrate, thus reducing the cost and need for prior testing of variables to minimize the unutilized portion of the bed.

3.2.4. Presence of moisture, CO and CO₂ in feed

The stainless steel construction of the probe and inert nature of the optical fibers enables the study of H_2S adsorption in presence of feed containing mixture of CO, CO₂ and H₂O at 22 °C. Presence of carbon monoxide, carbon dioxide and moisture can have strong influence on the desulfurization performance of adsorbents due to carbonyl sulfide (COS) formation, water gas

shift reaction and reduction in H₂S capacity as result of competitive adsorption in presence of moisture etc. For example, COS formation is observed at temperature of 200 °C or higher on Cu-ZnO/SiO₂ [56] and ZnO/SiO₂ adsorbents [57] while desulfurization of H₂S stream containing CO and CO₂. However at 22 °C, no COS is detected at the outlet and a CO mole balance across the bed indicates absence of water gas shift reaction. The effects of CO, CO₂ and H₂O is studied individually by adding 30 vol% CO, 30 vol% CO₂ and 0.5 vol% H₂O in a feed stream containing 0.5% H₂S. Table 2 shows that the adsorbent utilization is on average $84 \pm 4\%$ determined by the optical sensor and H₂S breakthrough curves. However, the adsorbent utilization reduced to 79% when 5000 ppmv H₂O is added in the feed containing H₂S, CO and CO₂. Thus, in order to investigate the effect of moisture content, a series of H₂S adsorption experiments are conducted separately in absence of CO or CO₂ in feed. Based on the vapor pressure of H₂O at 22 °C, the moisture content at the inlet is varied by adjusting the flowrate of high purity H₂ through a saturator containing de-ionized water. H₂S breakthrough curves of Cu-ZnO/SiO₂ adsorbent when tested at different moisture contents are shown in Fig. 7. The steps involved during H₂S adsorption in presence of moisture can be known to proceed as follows: (i) H₂S and H₂O from bulk feed are adsorbed on surface of adsorbent (ii) The adsorbed H₂O forms a liquid film inside the 4 nm pores of adsorbent due to capillary condensation (iii) H₂S is readily soluble in water [4 g H₂S L_{H₂O}⁻¹] at 25 °C [58] (iv) The dissolved H₂S then dissociates into HS⁻ and H⁺ ions followed by reaction of HS⁻ species with Cu-ZnO/SiO₂ to form corresponding metal sulfides. A similar observation is reported earlier [59] while studying the effect of moisture, CO₂ and O₂ on H₂S breakthrough behavior of activated carbon adsorbent at 30 °C.

When the surface and pores of the adsorbent are saturated with the adsorbed H₂S and H₂S dissolved in H₂O, additional H₂S flow through bed will result in breakthrough. Under dry feed conditions, the breakthrough curves reflect the mass transfer governed reaction between H₂S and metal oxides. However, broader breakthrough curves shown in Fig. 7(b) and Fig. 7(c) obtained during adsorption in presence of moisture means H₂O decelerates the reaction between H₂S and metal oxides. A slow reduction in area under spectrum 'A₁' was observed that corresponds to the

slow H₂S saturation and breakthrough behaviour in presence of moisture. This is confirmed by Fig S(11-a) and Fig S(11-b) of supporting material. The optical response ' A_{dt} ', however, appears degraded when examined separately as shown in Fig 7(e-f). When the time scale of the optical response is matched to the time scale of the breakthrough curve, a peak maximum can still be identified in case of 0.5% and 1% moisture content. Although, a delayed response is obtained in case of 1% moisture content, it is evident that the onset of response begins to occur at approximately the same time as the bed breakthrough time ' t_{BT} ' as shown in Fig. 7(c). In these experiments, it assumed however that UV-vis irradiation between 250-800 nm via the fiber optic probe did not cause any photo-dissociation of water on the surface of adsorbent, even though photo-dissociation of liquid water is reported at a wavelength of less than 200 nm [60].

3.2.5. Monitoring utilization of ZnO extrudate beds

During high throughput operation, the size of the packed bed and adsorbent particles are typically higher to minimize pressure drop. In this section, the efficacy of the embedded sensor to measure utilization of large size adsorbent particles during H₂S removal is examined by using ZnO extrudates, SG-901 (BASF). The average dimensions of these adsorbent particles are 1 cm (length) by 0.41 cm (diameter). Properties of extrudates are enlisted in Table 1. For this test, however, the 1.5 mm diameter probe cannot accurately determine bed utilization upon H₂S breakthrough due to its relatively small sampling volume compared to the extrudates.

For this purpose, a 6 mm diameter stainless steel fiber optic probe suited for millimeter size particles is used. Fig. 8(a) shows a stainless steel tubular reactor construction of nominal dimensions 22 mm dia. $\times$ 550 mm length with a welded 1 inch hollow stainless side arm equipped with an ultra torr fitting with a gas tight O-ring seal to secure the probe. This type of fitting enabled optimal sensor orientation along the radial geometry of the reactor. The probe is positioned at the bottom of the bed of ZnO extrudates (weight = 15 g, bed volume = 14.3 mL). A feed stream containing 6000 ppmv H_2S is passed over adsorbent bed at 22 $^{\circ}\text{C}$ at 250 mLmin^{-1} . The same signal processing method is followed as discussed in section 3.2 and the outlet H_2S concentration is measured using an on-line GC TCD. Fig. 8(b) shows the optical sensor response and H_2S breakthrough curve of extrudates. The in-situ UV-vis diffuse reflectance spectrum of ZnO extrudates obtained from spectral measurements using the 6 mm probe is the same as the

spectrum for 100-200 μ bulk ZnO particles measured by the 1.5 mm probe. In this case, the H₂S breakthrough time is 41 min and a $t_{\max}$ value is 40.7 ± 0.3 min obtained. However, the $t_{1/2}$ value is 77 min suggesting an adsorbent utilization of only 53%. The low utilization of extrudate beds as seen from broad H₂S breakthrough curves is attributed to the severe diffusion resistance of H₂S through the ZnO lattice [38]. This effect will potentially be worse at lower temperatures.

4. Conclusions

A fast sensing technique using fiber optic based UV-vis diffuse reflectance spectroscopy was developed to accurately measure utilization of packed beds containing metal oxide adsorbents during H₂S removal at room temperature. The area under UV-vis diffuse reflectance spectrum either decreased or increased upon interaction with H₂S depending upon the light reflecting behavior of fresh and spent adsorbents. During H₂S adsorption, a sharp response with maxima, $t_{\max}$ was obtained when the first order derivative of integrated area under in-situ reflectance spectra from 250-800 nm was plotted as a function of service time and compared to the time to reach 50% saturation or breakthrough time of adsorbents. The accuracy of the technique was examined at varying H₂S concentrations and H₂S residence time across the adsorbent bed. The average uncertainty in terms of standard error in $t_{\max}$ measurements throughout the study was ± 0.2 min. In the current study, presence of 30 vol% CO or CO₂ in the feed did not impact the efficacy of the technique to measure the adsorbent utilization during H₂S adsorption. However, presence of 0.5-1 vol% moisture in the feed resulted in slow saturation of H₂S with a broad breakthrough curve and corresponding slow and delayed optical response. The capacity depletion of a 15 mL packed bed 3/16 inch ZnO extrudates during H₂S adsorption was monitored using a 6 mm fiber optic probe. Adsorbent bed utilization determined from in-situ optical measurements

over wide range of operating parameters is expected to provide significant savings in cost of adsorbent materials and avoid the need for over design of adsorption units during compact and small volume desulfurization operation.

Acknowledgements

The authors would like to thank the U.S. army (TARDEC Contract No. W56HZV-05-R-0684) for financial support of this work. The authors also thank Mr. Dwight Cahela from Auburn University for assistance with the experimental setup, Dr. Wenhua Zhu with writing assistance and Shantanu Pradhan for proof reading the article.

REFERENCES

- [1] S. Satokawa, Y. Kobayashi, H. Fujiki, Appl. Catal. B Environ. 56 (2005) 51-56.
- [2] D. Shekhawat, J. Spivey, Fuel Cells: Technologies for Fuel Processing, Elsevier B.V, 2011.
- [3] S. Tong, I.G.D. Lana, K.T. Chuang, Can. J. Chem. Eng. 71 (1993) 392-400.
- [4] A. Sujan, B. Tatarchuk, Proceedings of the 24th North American Catalysis Society Meeting, Pittsburgh, PA, 2015
- [5] J. Bachelier, A. Aboulayt, J.C. Lavalley, O. Legendre, F. Luck, Catal. Today, 17 (1993) 55-62.
- [6] C. Lahousse, A. Aboulayt, F. Mauge, J. Bachelier, J.C. Lavalley, J. Mol. Catal. 84 (1993)

283-297.

- [7] H. Yang, B. Tatarchuk, *AIChE J.* 56 (2010) 2898-2904.
- [8] M. Mureddu, I. Ferino, E. Rombi, M.G. Cutrufello, P. Deiana, A. Ardu, A. Musinu, G. Piccaluga, C. Cannas, *Fuel*, 102 (2012) 691-700.
- [9] X. Wang, T. Sun, J. Yang, L. Zhao, J. Jia, *Chem. Eng. J.* 142 (2008) 48-55.
- [10] G. Liu, Z.-H. Huang, F. Kang, *J. Haz. Mater.* 215 (2012) 166-172.
- [11] H. Yang, Gas Phase Desulfurization Using Regenerable Microfibrous Entrapped Metal Oxide based Sorbents for Logistic PEM Fuel Cell Applications., Auburn University, 2007.
- [12] S. Katikaneni, J. Daly, US Patent No. 8,999,590 (2015).
- [13] J. Daly, US Patent No. 8,697,451 (2014).
- [14] K.J. Myung., S. Yoon, US Patent No. 8,062,597 (2011).
- [15] B. Tatarchuk, H. Yang, P. Dimick, US Patent App. 14/374,606 (2013).
- [16] A. Sujan, B. Tatarchuk, Proceedings of 64th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Philadelphia, PA, 2013.
- [17] A. Bensalem, B.M. Weckhuysen, R.A. Schoonheydt, *J. Phys. Chem. B* 101 (1997) 2824-2829.
- [18] M.H. Groothaert, K. Lievens, H. Leeman, B.M. Weckhuysen, R.A. Schoonheydt, *J. Catal.* 220 (2003) 500-512.
- [19] D. Mores, E. Stavitski, B.M. Weckhuysen, *Chem. Euro. J.* 14 (2008) 11320-11327.
- [20] R.L. Puurunen, B.G. Beheydt, B.M. Weckhuysen, *J. Catal.* 204 (2001) 253-257.
- [21] B.M. Weckhuysen, P.V.D. Voort, G. Catana, *Spectroscopy of Transition Metal Ions on Surfaces*, Leuven University Press, Netherlands, 2000.
- [22] B.M. Weckhuysen, *Chem. Commun.* (2002) 97-110.
- [23] B.M. Weckhuysen, *Phys. Chem. Chem. Phys.* 5 (2003) 4351-4360.
- [24] B.M. Weckhuysen, *In-situ Spectroscopy of Catalysts.*, American Scientific Publishers, USA, 2004.
- [25] F. Benito-Lopez, W. Verboom, M. Kakuta, J.G.E. Gardeniers, R.J.M. Egberink, E.R. Oosterbroek, A. van den Berg, D.N. Reinhoudt, *Chem. Commun.* (2005) 2857-2859.
- [26] M.A. Liauw, L.C. Baylor, O'Rourke, *UV-visible Spectroscopy for On-line Analysis*, Wiley, UK, 2010.
- [27] D.J.W. Ng, M. Assirelli, *Chem. Eng. Res. Des.* 85 (2007) 1348-1354.
- [28] W.H. Shen, X.Q. Chen, *Ind. Eng. Chem. Res.* 48 (2009) 4872-4876.
- [29] S.G. Mueller, J.R. Werber, M.H. Al-Dahhan, M.P. Dudukovic, *Ind. Eng. Chem. Res.* 46 (2007) 4330-4334.
- [30] P. Ege, A. Grislingas, H.I. deLasa, *Chem. Eng. J.* 61 (1996) 179-190.
- [31] S.P. Gurden, J.A. Westerhuis, A.K. Smilde, *AIChE J.* 48 (2002) 2283-2297.
- [32] J. Gabrielsson, H. Jonsson, J. Trygg, C. Airiau, B. Schmidt, R. Escott, *AIChE J.* 52 (2006) 3164-3172.
- [33] J.Q. Brown, K. Vishwanath, G.M. Palmer, N. Ramanujam, *Curr. Op. Biotech.* 20 (2009) 119-131.
- [34] M.D. Keller, S.K. Majumder, M.C. Kelley, I.M. Meszoely, F.I. Boulos, G.M. Olivares, A. Mahadevan-Jansen, *Las. Surg. Med.* 42 (2010) 15-23.
- [35] G.D. Focht, P.V. Ranade, D.P. Harrison, *Chem. Eng. Sci.* 43 (1988) 3005-3013.
- [36] M. Mureddu, I. Ferino, A. Musinu, A. Ardu, E. Rombi, M.G. Cutrufello, P. Deiana, M. Fantauzzi, C. Cannas, *J. Mater. Chem. A* 2 (2014) 19396-19406.
- [37] B. Tatarchuk, H. Yang, P. Dhage, US Patent No. 7,833,316 (2010).

- [38] H. Yang, Y. Lu, B.J. Tatarchuk, *J. Power Sources* 174 (2007) 302-311.
- [39] AvaSpec Operating manual, in: Avantes (Ed.), April 2009, pp. 73.
- [40] P. Dhage, A. Samokhvalov, D. Repala, E.C. Duin, M. Bowman, B.J. Tatarchuk, *Ind. Eng. Chem. Res.* 49 (2010) 8388-8396.
- [41] T. Baird, P.J. Denny, R. Hoyle, F. McMonagle, D. Stirling, J. Tweedy, *J. Chem. Soc. Far.Trans.* 88 (1992) 3375-3382.
- [42] P.R. Potti, V.C. Srivastava, *Ind. Eng. Chem. Res.* 51 (2012) 7948-7956.
- [43] E.S. Agorku, M.A. Mamo, B.B. Mamba, A.C. Pandey, A.K. Mishra, *J. Por. Mater.* 22 (2015) 47-56.
- [44] L.E. Brus, *J. Luminescence*, 31-2 (1984) 381-384.
- [45] P. Dhage, A. Samokhvalov, M.L. McKee, E.C. Duin, B.J. Tatarchuk, *Surf. Interface Anal.* 45 (2013) 865-872.
- [46] H. Yoshida, T. Shimizu, C. Murata, T. Hattori, *J. Catal.* 220 (2003) 226-232.
- [47] M. Tan, W.P. Cai, L.D. Zhang, *Appl. Phys. Letters*, 71 (1997) 3697-3699.
- [48] V.F. Anufrienko, T.M. Yurieva, F.S. Hadzhieva, T.P. Minyukova, S.Y. Burylin, *Reac. Kinet. Catal. Letters*, 27 (1985) 201-205.
- [49] M. Amara, L. Gengembre, D. Olivier, *Appl. Catal.* 41 (1988) 147-164.
- [50] G. Sengupta, A. Chakraborty, S. Banerjee, D.P. Das, R.P. Choudhury, R.K. Banerjee, R.M. Sanyal, *Appl. Catal.* 68 (1991) 1-9.
- [51] C. Corrado, Y. Jiang, F. Oba, M. Kozina, F. Bridges, J.Z. Zhang, *J. Phys. Chem. A* 113 (2009) 3830-3839.
- [52] W.L. McCabe, J.C. Smith, P. Harriott, *Unit Operations of Chemical Engineering*, 4th ed., McGraw-Hill 1985.
- [53] S.-j. Liu, Z.-y. Chen, Y.-z. Chang, S.-l. Wang, Q. Li, Y.-q. Fan, H.-m. Jia, X.-j. Zhang, Y.-g. Zhao, *Analyst* 140 (2015) 428-433.
- [54] H. Yang, D.R. Cahela, B.J. Tatarchuk, *Chem. Eng. Sci.* 63 (2008) 2707-2716.
- [55] S. Senkan, e. al., High throughput testing of heterogeneous catalyst libraries using array micro reactors and mass spectrometry, *Angew. Chem.* 38 (1999) 2794-2799.
- [56] A. Sujan, B. Tatarchuk, *Proceedings of the 249th American Chemical Society National Meeting*, Denver, CO, 2015.
- [57] H.Y. Yang, R. Sothen, D.R. Cahela, B.J. Tatarchuk, *Ind. Eng. Chem. Res.* 47 (2008) 10064-10070.
- [58] www.nist.gov.
- [59] R. Sitthikhankaew, D. Chadwick, S. Assabumrungrat, N. Laosiripojana, *Fuel Proc. Tech.* 124 (2014) 249-257.
- [60] V.e.a. Engel, *J. Phys. Chem.* 96 (1992) 3201-3213.

Table 1

Physical characterization of adsorbents and adsorbent bed properties.

Physical property	Bulk oxides			Supported oxide	Supported binary oxides
	SiO ₂	ZnO		ZnO/SiO ₂	Cu-ZnO/SiO ₂
		Particles	Extrudates		
BET surface area [m ² g ⁻¹]	460.0	35.4	35.4	261.0	257.0
Average pore size [nm]	3.80	-	-	4.23	4.00

Average pore volume [cm ³ g ⁻¹]	0.90	0.04	0.04	0.55	0.51
Weight % loading [L]	-	90.0	90.0	21.0	21.0 (CuO+ZnO)
Bulk density [g mL ⁻¹]	2.65	5.61	5.61	-	-
Packed bed density [g mL ⁻¹]	0.50	1.15	1.05	0.68	0.67
Packed bed voidage [-] [§]	0.31	0.70	0.77	0.41	0.45
H ₂ S saturation capacity [mgS g _{adsorbent} ⁻¹] [‡]	-	19	19	53	78

§ Calculated as per formulae shown in supplementary information

‡ Data reproduced from Tatarchuk et al [37]

Table 2
Adsorbent utilization determined by optical sensor and from H₂S breakthrough curves for different feed compositions.

Feed composition	t _{1/2} [min]	t _{BT} [min]	t _{max} [min]	Utilization at H ₂ S breakthrough [†] [%]	Utilization at bed color change [‡] [%]
0.5% H ₂ S	30.0 ± 0.5	25.0 ± 1.0	23.9 ± 0.2	83.3 ± 2.0	80.1 ± 1.3

0.5% + 30% CO	32.0 ± 0.5	27.0 ± 1.0	26.5 ± 0.2	84.3 ± 2.0	82.8 ± 1.3
0.5%+ 30% CO ₂	26.0 ± 0.5	23.0 ± 1.0	22.9 ± 0.2	88.5 ± 2.0	88.5 ± 1.3
0.5%+ 30% CO + 30% CO ₂	29.0 ± 0.5	25.0 ± 1.0	23.9 ± 0.2	86.2 ± 2.0	82.7 ± 1.3
0.5%+ 30% CO + 30% CO ₂ + 0.5% H ₂ O	49.0 ± 0.5	39.0 ± 1.0	38.9 ± 0.2	79.6 ± 2.0	79.4 ± 1.3

† Bed utilization from breakthrough curves, $1-U_{iBT} [\%] = 100 \times [t_{BT}/t_{1/2}]$

‡ Bed utilization determined by optical sensor, $1-U_{tmax} [\%] = 100 \times [t_{max}/t_{1/2}]$