RAPID COMMUNICATION

Effect of non-steam component of steam-hydrogasifier product gas upon sulfidation of zinc oxide sorbent

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Abstract−Sulfidation of zinc oxide sorbent by desulfurization of steam-hydrogasifier product gas was affected by non-steam components of the reactant gas in a complicated manner. Relative abundance of each component appeared to shift the reaction equilibrium toward ZnO sulfidation, thereby enhancing the extent of sorbent utilization for sulfur removal, while their respective contributions were not simply additive toward the overall increase of sulfur capture capacity of the sorbent. This subtle outcome will have to be further investigated by varying, respectively, the individual abundance of each non-steam component as well as H_2S content of the reactant gas to be desulfurized.

Key words: Sulfidation, Zinc Oxide, Sorbent, Hydrogen Sulfide

Steam-hydrogasification, which is one of the conversion processes for producing fuel gas from carbonaceous species, possesses a unique advantage over dry gasification in that transport of feed is facilitated in its slurry form and enhancement of reaction rate can be obtained in the case of renewable energy resources with high moisture content [1]. The composition of steam-hydrogasifier product gas is also unique, accounting for high contents of methane and steam in addition to hydrogen, carbon monoxide and carbon dioxide which represent the components of fuel gas typically produced from dry gasification [2]. While sulfur impurity contained in the carbonaceous feedstock is readily converted to H_2S and COS or CS_2 in the course of dry gasification, it is predominantly converted to H_2S in steam-hydrogasification due to comparatively high partial pressure of hydrogen and steam [2]. Hydrogen sulfide, which is a poison to the catalysts or a cause of corrosion in the downstream process, can be most favorably removed by ZnO-based sorbent at medium or high temperature; however, the reaction equilibrium is known to be significantly affected by the moisture content of fuel gas to be desulfurized [3-5]:

$$H_2S + ZnO \leftrightarrow ZnS + H_2O \tag{1}$$

A previous study on desulfurization of a process gas consisting of nitrogen and steam with 2,000 ppmv H_2S showed that the equilibrium of ZnO sulfidation is shifted progressively toward the backward reaction as the steam content increases from 0 to 30, then to 45 volume % [6].

As it is very likely that non-steam components of steam-hydrogasifier product gas also affect the reaction equilibrium of ZnO sulfidation, an additional study was performed for desulfurization of reactant gases consisting of methane, hydrogen, carbon monoxide, carbon dioxide, and steam with their composition varying from a typical composition of steam-hydrogasifier product gas: 22.0% methane, 18.7% hydrogen, 8.8% carbon monoxide, 5.5% carbon dioxide, and 45% steam. With 800 ppmv H_2S included as the sulfur impurity in the reactant gas at reactor inlet, H_2S breakthrough profile of the desulfurized gas at reactor outlet was monitored at 636 K and 1 atm using a packed bed reactor, and sulfur capture capacity of the sorbent was evaluated at 8,000 hr^{-1} space velocity and 2 ppmv H_2S breakthrough threshold. Flow rate of the reactant gas was typically 190-200 ml/min. A reactor made from a quartz tube (12 mm o.d. and 9 mm i.d.) was loaded with ZnO sorbent particles in the size of 150 to 250 micrometer, typically in the amount of 1.9-2.0 g. These sorbent particles were obtained by crushing Sud-Chemie ZnO sorbent pellets and then sieving the crushed pellets. The particle size is appropriate for minimizing intraparticle diffusional effects [6]. Physical properties of the ZnO sorbent pellets are listed in Table 1. H_2S concentration of the gas stream was measured by gas chromatograph equipped with a flame photometric detector. Details of the experimental apparatus and procedure are essentially the same as those used in our previous study. The following mass balance equation for sorbent sulfidation was used to evaluate sulfur capture capacity of the sorbent from H_2S breakthrough profile of the reactor effluent:

$$S_{cap} = \frac{FR \times \int_0^{BT}(c_{in} - c_{out})dt \times 32 \times 10^{-4}}{V_{mol}m_{sample}} \tag{2}$$

where S_{cap} denotes the sulfur capture capacity in (gram of sulfur)/ (100 gram of sorbent) [6]. Other symbols shown above are explained in the Nomenclature section.

First, the sorbent particles were sulfided by a reactant gas consisting of 55% nitrogen and 45% steam with 800 ppmv H_2S content (hereafter referred to as reactant gas #1), and 2 ppmv H_2S breakthrough in the reactor effluent was observed when approximately

Table 1. Physical properties of Sud-Chemie ZnO sorbent pellets

ZnO content (wt%)	88-90
Bulk density (g/cm^3)	1.35
Surface area (m^2/g)	50
Pellet size (mm)	4.76

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Fig. 1. 2 ppmv H₂S breakthrough of reactor effluent for reactant gases #1 and #2.
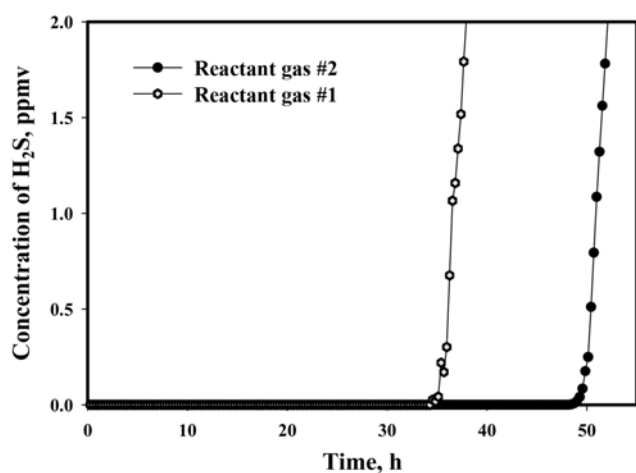

Fig. 2. 2 ppmv H₂S breakthrough of reactor effluent for reactant gases #3 to #6.

37.8 hours elapsed after the start-up of sorbent sulfidation. Next, the sulfided sorbent particles were replaced with a new load of sorbent particles, which were then sulfided by another reactant gas simulating a typical steam-hydrogasifier product gas with 800 ppmv H_2S content (hereafter referred to as reactant gas #2), the composition of which is described above. In this case, 2 ppmv H_2S breakthrough in the reactor effluent was observed when approximately 52.0 hours elapsed after the start-up of sorbent sulfidation. As shown in Fig. 1, comparison of sorbent sulfidation by these two reactant gases indicates that, on the basis of 2 ppmv H_2S breakthrough threshold, the sorbent particles were utilized further, i.e., for approximately 14.2 hours more, as nitrogen in reactant gas #1 was replaced with methane, hydrogen, carbon monoxide and carbon dioxide in reactant gas #2. This enhancement in sorbent utilization for desulfurization may be attributed to the shift of sulfidation equilibrium toward zinc sulfide, in which the non-steam components of reactant gas #2 played a role. To assess the extent of contribution by each non-steam component toward such enhancement, four more reactant gases, i.e., reactant gases #3 to #6, were prepared as shown in Table 2 with 45% steam and 800 ppmv H_2S content commonly included in the gases. As each of the four gases was desulfurized by flowing through each new load of sorbent particles, different H_2S concentration profiles of the reactor effluent versus the time elapsing for sorbent sul-
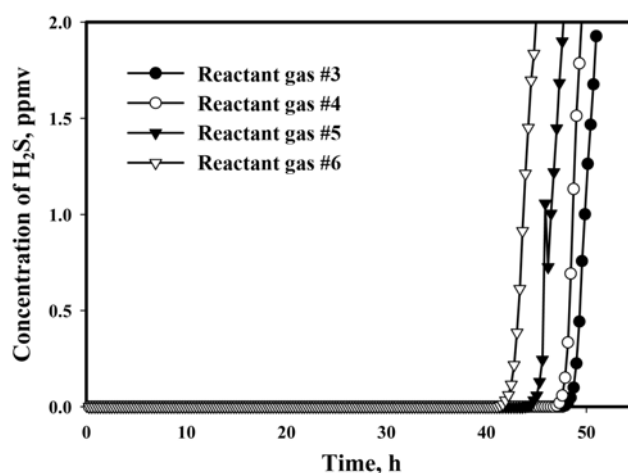
fidation were observed as shown in Fig. 2. As expected intuitively, H_2S breakthrough profiles for these four gases were located between H_2S breakthrough profiles for reactant gas #1 and reactant gas #2. Table 2 also lists the time for 2 ppmv H_2S breakthrough in the reactor effluent from desulfurization of each of these four gases and compares them with those for reactant gases #1 and #2. Fig. 2 and Table 2 provide evidences that, for desulfurization of the steam-hydrogasifier product gas, the extent of contribution from each non-steam component toward enhanced sorbent utilization is in the order (5.5% CO_2)<(8.8% CO)<(18.7% H_2)<(22.0% CH_4). A plausible explanation for this order of contribution may be the relative volumetric abundance of each non-steam component in the reactant gas; however, its relevance will have to be further discussed in comparison with those of other physicochemical properties such as the polarity of each component or its possible interaction with steam in the reactant gas.

For each of the reactant gases tested in this study, sulfur capture capacity of the sorbent, which corresponds to the extent of sorbent utilization for desulfurization of reactant gas, was calculated on the

Table 2. Composition (vol%) of reactant gases and time (hr) for 2 ppmv H₂S breakthrough

Components	Reactant gases*					
	#1	#2	#3	#4	#5	#6
CH_4	-	22.0	22.0	-	-	-
H_2	-	18.7	-	18.7	-	-
CO	-	8.8	-	-	8.8	-
CO_2	-	5.5	-	-	-	5.5
N_2	55.0	0.0	33.0	36.3	46.2	49.5
H_2O	45.0	45.0	45.0	45.0	45.0	45.0
t_{Break}	37.8	52.0	51.0	49.4	47.6	44.9

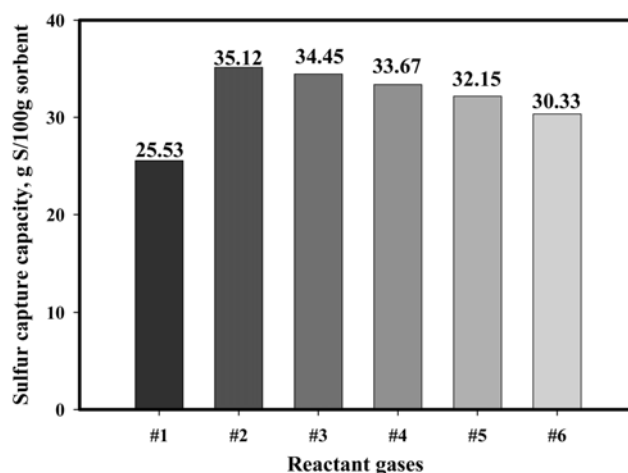*Each of the reactant gases contains H₂S content of 800 ppm

Fig. 3. Sulfur capture capacity of zinc oxide sorbent for desulfurizing reactant gases by 2 ppmv H₂S breakthrough.

basis of 2 ppmv H$_2$S breakthrough threshold and is displayed for comparison in Fig. 3. It is again evident that each non-steam component of reactant gas #2 made its respective contribution toward the enhanced sorbent utilization for desulfurization as discussed above, and it is also noteworthy that these respective contributions are not simply additive toward the overall enhancement of sorbent utilization. That is, with reference to sulfur capture capacity of the sorbent for desulfurization of reactant gas #1, replacing a part of N$_2$ in reactant gas #1 with CO$_2$ by 5.5% resulted in increase of S$_{cap}$ by 18.8%, replacing a part of N$_2$ in reactant gas #1 with CO by 8.8% resulted in increase of S$_{cap}$ by 25.9%, replacing a part of N$_2$ in reactant gas #1 with H$_2$ by 18.7% resulted in increase of S$_{cap}$ by 31.9%, and replacing a part of N$_2$ in reactant gas #1 with CH$_4$ by 22.0% resulted in increase of S$_{cap}$ by 34.9%, respectively. However, replacing all of N$_2$ in reactant gas #1 with CO$_2$, CO, H$_2$ and CH$_4$ altogether by the corresponding volume fractions described above (this is essentially replacing reactant gas #1 with reactant gas #2) resulted in increase of S$_{cap}$ by 37.6%, which is substantially less than the sum of increase of S$_{cap}$ attributed to the respective non-steam component of the steam-hydrogasifier product gas. This result implies that the equilibrium of sulfidation of zinc oxide sorbent by desulfurization of steam-hydrogasifier product gas is affected by its non-steam components in a complicated manner.

To clarify the subtle results presented above, a more comprehensive study will have to be performed by varying, respectively, the individual abundance of each non-steam component as well as H$_2$S content of the reactant gas to be desulfurized. Such a study will help elucidate the individual roles of non-steam gas components and any complication owing to their possible interaction with high-content steam in determining the extent of sorbent utilization for removal of sulfur from steam-hydrogasifier product gas with a comprehensive range of H$_2$S concentration.

NOMENCLATURE

BT : breakthrough time measured in hours
t : time elapsing after the start-up of sorbent sulfidation
FR : gas flow rate in liters/hour at the standard conditions
V$_{mol}$: gas molar volume in liters/mol at the standard conditions
m$_{sample}$: sorbent weight in grams
C$_{in}$: inlet H$_2$S concentration in ppmv
C$_{out}$: outlet H$_2$S concentration in ppmv

REFERENCES

1. S. K. Jeon, C. S. Park, C. E. Hackett and J. M. Norbeck, *Fuel*, **86**, 2817 (2007).
2. J. M. Norbeck, C. S. Park, A. S. K. Raju and C. Vo, California Energy Commission Consultant Report, University of California, Riverside (2008).
3. K. C. Kwon, Y. Park, S. K. Gangwal and K. Das, *Sep. Sci. Technol.*, **38**, 3289 (2003).
4. I. I. Novochinskii, C. Song, X. Ma, X. Liu, L. Shore and J. Lampert, *Energy Fuels*, **18**, 576 (2004).
5. T. J. Lee, I. H. Cho and N.-K. Park, *Korean J. Chem. Eng.*, **26**(2), 582 (2009).
6. K. Kim, S. K. Jeon, C. Vo, C. S. Park and J. M. Norbeck, *Ind. Eng. Chem. Res.*, **46**, 5848 (2007).