Preparation of Modified Semi-Coke-Supported ZnFe_2O_4 Sorbent with the Assistance of Ultrasonic Irradiation

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Abstract

Modified semi-coke (MSC) supported ZnFe_2O_4 was prepared under the condition of ultrasonic irradiation. Performance of the sorbents was tested using a fixed-bed reactor as a hot gas desulfurizer. The MSC support, the mass ratio of zinc ferrites to the support, calcination temperature, and the ultrasonic conditions of power and time all had influences on the structure and the breakthrough behavior of the sorbent. Ultrasonic irradiation can help to make ZnFe_2O_4 highly dispersed on MSC. ZnFe_2O_4 /MSC had increased porosity and a larger specific surface area compared to unsupported ZnFe_2O_4 . The sorbent exhibited a higher sulfur capacity at the optimum preparing conditions, where the mass ratio of ZnFe_2O_4 to MSC was 8:10, calcinated at 500°C , and the ultrasonic power and time was 900 W and 1.5 h, respectively.

Key words: hydrogen sulfide; modified semi-coke; ultrasonic; zinc ferrites

Introduction

REMOVAL OF SULFUR-CONTAINING SPECIES is currently a strategic issue (EPA, 1999; Stirling, 2000), which is grounded in environmental regulations combined searchers for new clean sources of energy, such as hot coal gas. For hot coal gas application, sulfide products need to be removed to below several parts per million by volume (ppmv) to protect the equipment used later in the coal gasification process. Among various methods used to remove hydrogen sulfide, dry hot coal gas clean is considered as a very efficient and cost effective approach because this method reduces H_2S down to several ppmv as well as prevents heat loss (Westmoreland, 1996; Jothimurugesan and Gangwal, 1998; Pineda *et al.*, 2000).

Hot gas cleaning has been conducted by using various inorganic sorbents, such as activated carbon (Bandosz, 1999; Cal *et al.*, 2000a, 2000b), ZnO , Fe_2O_3 , CuO , and Mn_2O_3 (Sasaoka *et al.*, 1993, 1994; Ben-Slimane and Hepworth, 1995; Ben-Slimane and Abbasian, 2000). The loss of zinc by vaporization at a high temperature (Bu *et al.*, 2008), the decrease of H_2S adsorption capacity, and the adsorption rate due to fast reduction of Fe_2O_3 and CuO sorbents in the presence of hydrogen gas are some drawbacks of zinc, iron, and copper oxides in high temperature H_2S removal (Yasyerli, 2008). A number of mixed metal oxide sorbents were tried, to achieve better performance in H_2S removal, including ZnFe_2O_4 (Ahmed *et al.*, 2000) and

Zn_2TiO_4 (Lew and Sarofim, 1992a). Lew and Sarofim (1992b) reported that Zn-Ti-O sorbent exhibited a high activity for hydrogen sulfide removal via a mechanism of desulfurization similar with that on ZnO . However, there are still some disadvantages for mixed metal oxide. For ZnFe_2O_4 , several limitations are related to the reduction of iron oxides, zinc losses above 600°C , and carbon deposition in a carbon-rich atmosphere at lower temperatures (Ohtsuka *et al.*, 2009). Many researchers have been trying to develop a higher performance sorbent for hydrogen sulfide removal, such as zinc ferrites doped with different metals (V, Ti, and Cu) (Akyurtlu and Akyurtlu, 1995; Pineda *et al.*, 1997). The addition of TiO_2 or CuO can apparently enhance the overall sulfidation reactivity by inducing substantial structural changes in zinc ferrites.

Recently, researchers have being engaged in reforming the microstructure of sorbents, such as crystal size, pore volume, and surface area, to obtain a higher sulfur capacity, as well as higher resistance and intensity, by selecting appropriate additives and binders and by improving preparation methods. Ultrasonic irradiation can improve the performance of catalysts by increasing the dispersion of active components of catalysts, and increasing the surface area (Jin, 1999; Mikkola and Salmi, 2001). Support materials can also disperse the active components and increase the surface area of sorbents. Some support materials (such as carbon material) may also play roles in converting sulfur species. Presently, the support materials of the sorbent applied for hot coal gas desulfurization are composed primarily of Al_2O_3 , SiO_2 , activated carbon, or other materials whose main chemical compositions are silicon, aluminum, carbon, *etc.* (Xu *et al.*, 2004; Nguyen-Thanh and Bandosz, 2005; Yu *et al.*, 2006; Xie *et al.*, 2007). The quantity of support materials is large in industry scale systems, therefore

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TABLE 1. EQUATIONS FOR CALCULATING SULFUR CAPACITY AND DESULFURIZATION EFFICIENCY

$$\text{Sulfur capacity} = \frac{\text{mass of adsorbed sulfur on sorbent}}{\text{mass of sorbent}} \times 100\%$$

$$\text{Desulfurization efficiency} = \frac{\text{sulfur concentration in inlet gas} - \text{sulfur concentration in exit gas}}{\text{sulfur concentration in inlet gas}} \times 100\%$$

the support materials must be economic and easily available. The Kansai University's research group prepared ZnFe_2O_4 using activated carbon, activated carbon fiber, and brown coal as the support materials. They observed that these carbon-supported ferrites exhibit much larger desulfurization ability than the corresponding unsupported ferrites. ZnFe_2O_4 reduced the H_2S concentration to below 1 ppmv at temperatures of $\geq 400^\circ\text{C}$, and the desulfurization capacity was 100–120% for the ZnFe_2O_4 at the optimal temperatures, roughly twice that of the unsupported ferrites (Ikenaga *et al.*, 2002, 2004). Since semi-coke is similar to active carbon in properties, but much cheaper than the latter, it is feasible to use semi-coke-supported mixed metal oxides in hot coal gas desulfurization.

This article deals with the preparation of modified semi-coke (MSC)-supported zinc ferrites with the assistance of ultrasonic irradiation for obtaining a high-surface-area zinc ferrites sorbent. Effects of support, ultrasonic condition, and calcination temperature on physical properties were examined as well as on the sulfur capacity of sorbent.

Experimental

Materials

Semi-coke (75.86% C, 1.31% H, 8.33% O, 0.45% N, 0.27% S) was used as the support after modified. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and aqueous ammonia ($\sim 26\%$) were used to prepare sorbent.

Modified semi-coke

Semi-coke was oxidized with nitric acid. Typically, 40 mL of semi-coke (6–8-mesh pass) was added into 200 mL HNO_3 (45%), heated at $80\text{--}90^\circ\text{C}$ for 2.5 h, then filtered, washed to pH 7.0, and dried at 110°C for 2–4 h. At last, MSC was obtained after steam activated at 700°C under the atmosphere of 85% N_2 , 5% O_2 , and 10% H_2O (steam).

Preparation of sorbent for H_2S

The sorbent was prepared by the coprecipitation method with the assistance of ultrasonic irradiation (JXD-09, 20 kHz, 900 W, adjustable, home-made). MSC (100-mesh pass) was put into a mixed solution of $\text{Zn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$, and aqueous ammonia was added into this suspension until the pH reached 10 with stirring under ultrasonic irradiation. The coprecipitation solution was dumped into a beaker and followed by boiling, aging, filtrating, and drying at 120°C for 4 h, and then calcined at $400\text{--}700^\circ\text{C}$ in N_2 flow for 4 h to form spinel structure of $\text{ZnFe}_2\text{O}_4/\text{MSC}$. The precursors were mixed with kaolin, crushed and grounded to powder of 100-mesh pass by a ball mill. Distilled water was added into the powder mixture to obtain a paste

with suitable viscosity, and the paste was extruded into a cylindrical shape in an extruder. The cylindrical sorbent extrudates were approximately 3 mm in diameter and 3 mm in height. Then, the sorbent was calcined at 500°C in a muffle furnace for 4 h to obtain high reactivity and mechanical strength.

Characterization of sorbents

The sorbents freshly prepared before adsorption and those after adsorption of H_2S were analyzed by powder X-ray diffraction (XRD) using an X-ray diffractometer (D/max-2500) with monochromatized Cu K α radiation. Surface areas of sorbents were measured by the Brunauer–Emmett–Teller (BET) method using a Micromeritics TriStar-3000, applying adsorption isotherms of nitrogen at -196°C .

Adsorption of H_2S

Simulated coal gas with the following composition (by volume): H_2S 0.2–0.3%, CO 27%, H_2 39%, CO_2 12%, H_2O 10%, and N_2 11.7–11.8% was used in the sulfidation experiments. The exit gases from the reactor were analyzed using a GC equipped with a thermal conductivity detector and a flame photometric detector. Two thermocouples were used to measure the furnace temperature and sorbent bed temperature, respectively. Sulfidation experiments were carried out in the apparatus with a fixed-bed quartz reactor (19 mm in diameter, about 650 mm in length) at 500°C at a space velocity 2000 h^{-1} at pressure of 1 bar. A volume of about 20 mL sorbents was charged into the reactor in each experiment. The H_2S breakthrough time was reported in this study when its concentration exceeds 560 ppmv in the exit gas.

The parameters of sulfur capacity and desulfurization efficiency are defined in Table 1.

Results and Discussion

Physical parameters of different kinds of semi-coke

An excellent support should have a large surface area, appropriate pore volume and size, which have great influence on the dispersion of active component. The effect of modification on the physical properties of semi-coke is shown in Table 2. It can be seen that MSC treated by HNO_3 had a much larger surface area ($142.6\text{ m}^2/\text{g}$) than raw semi-coke ($44.6\text{ m}^2/\text{g}$). The method of combining nitric acid oxidation and activation at a high temperature with vapor almost quadrupled the surface area of semi-coke from 44.6 to $217.2\text{ m}^2/\text{g}$, and also the pore volume from 0.043 to $0.173\text{ cm}^3/\text{g}$. This is clearly due to the reaction of vapor, O_2 , and carbon (Shangguan *et al.*, 2005). The results prove that MSC with a larger surface area, a bigger pore volume and size could be an ideal support.

TABLE 2. PHYSICAL PARAMETERS OF MODIFIED SEMI-COKE

Samples	Pore volume (cm ³ /g)	Surface area (m ² /g)	Pore size (10 ⁻¹⁰ m)
RSC	0.043	44.6	38.1
XSC	0.082	142.6	35.3
MSC	0.173	217.2	31.7

RSC, raw semi-coke; XSC, semi-coke oxidized with aqueous nitric acid treatment; MSC, modified semi-coke.

Effects of different supports on the physical properties of sorbent

The pore volume and surface area of sorbents with different supports are listed in Table 3. The XRD patterns of ZnFe₂O₄/MSC and unsupported ZnFe₂O₄ are shown in Fig. 1. Table 2 shows that the support can increase the surface area of sorbents. Surface areas of zinc ferrites prepared in the presence of semi-coke (Samples A, B, and C; mass ratio of zinc ferrites and support 8:10, calcined at 500°C) were much higher compared with zinc ferrites prepared without using carbon materials. Raw semi-coke has little effect on the surface area of sorbent, from 24.1 to 27.5 m²/g. The surface area of ZnFe₂O₄/MSC (Sample C) reached 44.3 m²/g, which is obviously larger than that of Sample B. This is closely related to the larger surface area and pore volume of the support.

Figure 1 shows that the intensity of the XRD peaks of unsupported zinc ferrites was considerably higher than these of supported zinc ferrites. The results indicate that by supporting zinc ferrites were highly dispersed in smaller crystallite size (Xie *et al.*, 2010), which is consistent with the results of BET.

Effects of ultrasonic irradiation conditions on zinc ZnFe₂O₄/MSC sorbent

Effects of ultrasonic irradiation on the crystal structure of ZnFe₂O₄/MSC precursors were studied. Figure 2 shows the XRD patterns of the samples prepared at the same calcination condition (500°C, N₂ flow), but different ultrasonic irradiation conditions. It can be seen that though the spinel structure of zinc ferrites was formed for all cases, it is obvious that along with the peaks of Fe₂O₃ and ZnO, the ZnFe₂O₄ peak with a lower intensity were observed for ultrasonic power of 450 W and 700 W. The ultrasonic irradiation of 900 W for 1.5 h gave almost no miscellaneous phase. The results prove that high purity and small grain of ZnFe₂O₄ was formed and more evenly dispersed on the support at increased ultrasonic power

TABLE 3. PARAMETERS OF THE PHYSICAL PROPERTIES OF SORBENTS SUPPORTED ON DIFFERENT MODIFIED SEMI-COKES AND UNSUPPORTED ZnFe₂O₄ SORBENT

Sorbent	Support	Pore Volume (cm ³ /g)	Surface Area (m ² /g)
ZnFe ₂ O ₄ /RSC	Raw semi-coke	0.129	27.5
ZnFe ₂ O ₄ /XSC	XSC	0.143	31.6
ZnFe ₂ O ₄ /MSC	MSC	0.164	44.3
ZnFe ₂ O ₄	—	0.117	24.1

FIG. 1. X-ray diffraction (XRD) spectra of ZnFe₂O₄/modified semi-coke (MSC) and ZnFe₂O₄ fresh sorbent.

and time. Clearly, the effect of cavitation during coprecipitation was responsible for the highly dispersed catalysts with high activity (Yan *et al.*, 2007).

Effects of calcination temperature on the active component in ZnFe₂O₄/MSC

To elucidate the effects of calcination temperature on the structure of the active component, ZnFe₂O₄/MSC prepared under the optimum condition of ultrasonic irradiation (900 W 1.5 h) was calcined at 400–700°C under N₂ flow. XRD patterns of ZnFe₂O₄/MSC calcined at different temperatures are shown in Fig. 3. It shows that the spinel structure of ZnFe₂O₄ in the ZnFe₂O₄/MSC sorbent prepared by coprecipitation with the assistance of ultrasonic irradiation was formed after calcination at 400–700°C. The characteristic peaks of ZnFe₂O₄ sorbent calcined at a lower temperature (400°C) had a broader width, but became narrower in width and higher in intensity as the calcination temperature increased. This explains the larger crystallite size at increased calcination temperatures.

FIG. 2. XRD spectra of different ultrasonic power and time on ZnFe₂O₄ forming.

FIG. 3. XRD spectra of $\text{ZnFe}_2\text{O}_4/\text{MSC}$ precursors calcined at different temperature.

Effect of support on sulfur capacity of sorbent

The effect of support on the sulfur capacity of sorbent was investigated at 500°C and is shown in Fig. 4. The sulfur capacity of unsupported FeZn_2O_4 was lower compared with other sorbents. Sulfur capacity of supported sorbent increased with the increasing surface area and pore volume of support, because zinc ferrites were better dispersed on the support with the larger surface area. The phenomena may be explained by the fact that more porosity and a larger specific surface area could make H_2S more easily diffused to active sites, which consequently gave $\text{ZnFe}_2\text{O}_4/\text{MSC}$ sorbent a higher adsorption rate and speed (Ikenaga *et al.*, 2005).

Effects of ultrasonic irradiation condition on the breakthrough time of sorbent

To evaluate the effects of ultrasonic irradiation on the breakthrough time of sorbent, Sample 1 (700 W, 0.5 h) and Sample 2 (900 W, 1.5 h) were sulfided at 500°C by 2800 ppmv of H_2S in inlet gas. As shown in Fig. 5, the breakthrough curves of different sorbents prepared under different ultrasonic irradiations during coprecipitation. The breakthrough curves of Sample 1 (700 W, 0.5 h) and Sample 2 (900 W, 1.5 h) were all kept horizontal at first 8 h. Following that H_2S was

FIG. 4. Comparison of the sulfur capacity of ZnFe_2O_4 supported with different MSC and unsupported sorbent.

FIG. 5. Breakthrough curves of sorbents prepared under different ultrasonic irradiation condition.

detected at the exit gas for Sample 1, and Sample 1 was quickly penetrated through at about 14 to 16 h. On the other hand, 145 ppmv H_2S was detected at the exit gas for Sample 2 after 15 h and the sample was penetrated through gradually, giving a much longer breakthrough time. With the increase of power and time of ultrasonic irradiation, the active component grains became smaller and more evenly dispersed on the surface of support (Yan *et al.*, 2007). Therefore, the optimum ultrasonic irradiation condition is power 900 W, time 1.5 h.

Effects of calcination temperature on the breakthrough time of sorbents

As mentioned earlier, zinc ferrites crystallize size increased with increasing calcinations temperature. To elucidate the effects of calcination temperature on the breakthrough time of sorbents, the breakthrough curves of MSC-supported zinc ferrites (mass ratio of zinc ferrites to support 8:10, ultrasonic 900 W, 1.5 h; calcined at 400–700°C) were obtained at 500°C. As shown in Fig. 6, the sorbent calcined at 500°C had the

FIG. 6. Effects of calcination temperature on the breakthrough time of sorbents.

FIG. 7. Breakthrough curves of sorbents containing a different mass ratio of ZnFe_2O_4 to MSC.

longest breakthrough time, almost 20 h. The sorbent calcined at 400°C had the shorter breakthrough time because the spinel structure of zinc ferrites were not formed completely at a calcinations temperature lower than 500°C . With the calcinations temperature increased from 500 to 700°C , the breakthrough time declined. The results clearly indicate that smaller crystallite and higher surface area seem to be important for the high adsorption of hydrogen sulfide (Ikenaga *et al.*, 2002).

Effects of mass ratio of MSC to zinc ferrites on the adsorption of H_2S

To examine the effects of the mass ratio of zinc ferrites to MSC on the breakthrough time of sorbent prepared with the assistance of ultrasonic irradiation (900 W, 1.5 h), the mass ratio was selected at six levels (4:10, 6:10, 7:10, 8:10, 9:10, 1:1, marked B4, B6, B7, B8, B9, and B10, respectively), and the temperature of sulfidation was 500°C . As shown in Fig. 7, the breakthrough curves of all sorbents kept horizontal in the first 8 h. Then, Sample B4 was the first to be penetrated through in the following 2 h. Sorbents B6, B9, and B10 were penetrated through gradually during the following 5 h. The breakthrough time of samples B7 and B8 reached 16 h, and B8 had the largest sulfur capacity (16.79%). The results show that the optimum mass ratio of zinc ferrite to MSC was 8:10. If too much zinc ferrite was supported on semi-coke, the pore volume and pore size of sorbent became so small that the surface area for effective reaction decreased and the ability of sulfur removal thus declined. Consequently, the dispersion of zinc ferrite on support was remarkably decreased for too big a ratio of zinc ferrites to MSC, which in turn lowered sorbent utilization. Therefore, there is an optimum ratio between the active component and support (Jian *et al.*, 2008).

Summary

An MSC, which was prepared from raw semi-coke by combining nitric acid oxidation and steam activation at a high temperature, was an ideal support because of its much larger BET surface area, pore volume, and size.

Prepared by coprecipitation with the assistance of ultrasonic irradiation and calcined at 500°C , $\text{ZnFe}_2\text{O}_4/\text{MSC}$ was

provided with the spinel structure. As the power and time of ultrasonic irradiation increased, the crystal grain of zinc ferrites was better dispersed on MSC and the spinel structure of zinc ferrites was much more easily formed at a lower temperature.

The optimum mass ratio between zinc ferrites to MSC was 8:10; as the loading increased, the pore size of support became smaller, and the effective surface area declined, which reduced the adsorption capacity of $\text{ZnFe}_2\text{O}_4/\text{MSC}$ sorbent.

The optimum calcination temperature of $\text{ZnFe}_2\text{O}_4/\text{MSC}$ prepared by coprecipitation with the assistance of ultrasonic irradiation was 500°C . With the increase of calcination temperature, the crystallize size of ZnFe_2O_4 became larger and the effective contact area between H_2S and area declined.

The $\text{ZnFe}_2\text{O}_4/\text{MSC}$ prepared by coprecipitation with the assistance of ultrasonic irradiation is an efficient sorbent for hydrogen sulfide removal. The sorbent $\text{ZnFe}_2\text{O}_4/\text{MSC}$ under optimum conditions (mass ratio 8:10, power 900 W, time 1.5 h calcined at 500°C), gave a sulfur capacity of 16.79%. Compared with ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4/\text{MSC}$ made H_2S diffuse easily to sorbent because of a more abundant pore structure and a larger BET surface area.

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Author Disclosure Statement

No competing financial interests exist.

References

- Ahmed, M.A., Alonso, L., Palacios, J.M., Cilleruelo, C., and Abanades, J.C. (2000). Structural changes in zinc ferrites as regenerable sorbents for hot coal gas desulfurization. *Solid State Ionics* 138, 51.
- Akyurtlu, J.F., and Akyurtlu, A. (1995). Hot gas desulfurization with vanadium-promoted zinc ferrite sorbents. *Gas. Sep. Purif.* 9, 17.
- Bandos, T.J. (1999). Effect of pore structure and surface chemistry of virgin activated carbons on removal of hydrogen sulfide. *Carbon* 37, 483.
- Ben-Slimane, R., and Abbasian, J. (2000). Regenerable mixed metal oxide sorbents for coal gas desulfurization at moderate temperatures. *Adv. Env. Res.* 4, 147.
- Ben-Slimane, R., and Hepworth, M.T. (1995). Desulfurization of hot coal-derived fuel gases with manganese-based regenerable sorbents. 3. Fixed-bed testing. *Energy Fuels* 9, 372.
- Bu, X.P., Ying, Y.J., Zhang, C.Q., and Peng, W.W. (2008). Research improvement in Zn-based sorbent for hot gas desulfurization. *Powder Technol.* 180, 253.
- Cal, M.P., Strickler B.W., and Lizzio A.A. (2000a). High temperature hydrogen sulfide adsorption on activated carbon. I. Effects of gas composition and metal addition. *Carbon* 38, 1757.
- Cal, M.P., Strickler B.W., and Lizzio A.A. (2000b). High temperature hydrogen sulfide adsorption on activated carbon. II. Effects of gas temperature, gas pressure and sorbent regeneration. *Carbon* 38, 1767.

- U.S. Environmental Protection Agency (EPA). (1999). Control of air pollution from new motor vehicles: Proposed tier 2 motor vehicle emissions standards and gasoline sulfur control requirements. EPA, 40CFR, Parts 80, 85 and 86, AMSFRL: 6337-3, RIN 2060-A123; Federal Register/Vol. 64, No.92/Thursday, 13 May 1999.
- Ikenaga, N., Chiyoda, N., Matsushima, H., and Suzuki, T. (2002). Preparation of activated carbon-supported ferrite for absorbent of hydrogen sulfide at a low temperature. *Fuel* 81, 1569.
- Ikenaga, N., Chiyoda, N., Matsushima, H., and Suzuki, T. (2004). Preparation of zinc ferrite in the presence of carbon material and its application to hot-gas cleaning. *Fuel* 83, 661.
- Ikenaga, N., Ohgaito, Y., and Suzuki, T. (2005). H_2S absorption behavior of calcium ferrites prepared in the presence of coal. *Energy Fuels* 19, 170.
- Jiang, L.Y., Zhou, S.X., and Wang, W.C. (2008). Adsorption of formaldehyde by activated carbon loaded with manganese oxides. *Acta Sci. Circum.* 28, 337.
- Jin, Q.H. (1999). *Microwave Chemistry*. Beijing: Science Press.
- Jothimurugesan, K., and Gangwal S.K. (1998). Regeneration of zinc titanate H_2S sorbents. *Ind. Eng. Chem. Res.* 37, 1929.
- Lew, S., Sarofim, A.F., and Flytzani-Stephanopoulos, M. (1992a). Modeling of the sulfidation of zinc-titanium oxide sorbents with hydrogen sulfide. *AIChE J.* 38, 1161.
- Lew, S., Sarofim, A.F., and Flytzani-Stephanopoulos, M. (1992b). The reduction of zinc titanate and zinc oxide solids. *Chem. Eng. Sci.* 47, 1421.
- Mikkola, J.P., and Salmi, T. (2001). Three-phase catalytic hydrogenation of xylose to xylitol—Prolonging the catalyst activity by means of on-line ultrasonic treatment. *Catal. Today* 64, 271.
- Nguyen-Thanh, D., and Bandosz, T.J. (2005). Activated carbons with metal containing bentonite binders as adsorbents of hydrogen sulfide. *Carbon* 43, 359.
- Ohtsuka, Y., Tsubouchi, N., Kikuchi T., and Hashimoto, H. (2009). Recent progress in Japan on hot gas cleanup of hydrogen chloride, hydrogen sulfide and ammonia in coal-derived fuel gas. *Powder Technol.* 190, 340.
- Pineda, M., Fierro, J.G., Palaciso, J., Cilleruelo, C., Garcia, E., and Ibarra, J. (1997). Characterization of zinc oxide and zinc ferrite doped with Ti or Cu as sorbents for hot gas desulphurization. *Appl. Surf. Sci.* 119, 1.
- Pineda, M., Palacios, J.M., Alonso, L., Garcia, E., and Moliner, R. (2000). Performance of zinc oxide based sorbents for hot coal gas desulfurization in multicycle tests in a fixed-bed reactor. *Fuel* 79, 885.
- Sasaoka, E., Hirano, S., Kasaoka, S., and Sakata, Y. (1994). Stability of zinc oxide high-temperature desulfurization sorbents for reduction. *Energy Fuels* 8, 763.
- Sasaoka, E., Sakamoto, M., Ichio, T., Kasaoka, S., and Sakata, Y. (1993). Reactivity and durability of iron oxide high temperature desulfurization sorbents. *Energy Fuels* 7, 632.
- Shangguan, J. Li, Z.L., Yang, Z., Fan, H.L., Shen, F., and Miao, M.Q. (2005). The effect of heating semi-coke at high temperature on its SO_2 removal capacity. *Taiyuan Univ. Tech.* 36, 134.
- Stirling, D. (2000). *The Sulfur Problem: Cleaning Up Industrial Feed-Stocks*. Cambridge, United Kingdom: Royal Society of Chemistry.
- Westmoreland, P.R., and Harrison, D.P. (1976). Evaluation of candidate solids for high-temperature desulfurization of low-BTU gases. *Environ. Sci. Technol.* 10, 659.
- Xie, W., Chang, L.P., Wang, D.H., Xie, K.C., Terry, W., and Yu, J.L. (2010). Removal of sulfur at high temperatures using iron-based sorbents supported on fine coal ash. *Fuel* 89, 868.
- Xie, W., Chang, L., Xie, K., Terry, W., and Yu, J. (2007) Two-step hot coal gas desulphurization process integrated with direct production of elemental sulfur using iron-based sorbents: A preliminary study. Presented at the 24th International Pittsburgh Coal Conference, Johannesburg, South Africa, September 10–14.
- Xu, H., Liang, M., Li, C., and Wang, Y. (2004). Sulfidation and regeneration performance of sorbents for hot coal gas desulphurization. *Proc. Chinese Soc. Electr. Eng.* 24, 198.
- Yan, G., Huo, C., and Liu, H.Z. (2007). Application of ultrasonic technologies in catalytic chemistry. *Ind. Catal.* 15, 1.
- Yasyerli, S. (2008). Cerium–manganese mixed oxides for high temperature H_2S removal and activity comparisons with V–Mn, Zn–Mn, Fe–Mn sorbents. *Chem. Eng. Process.* 47, 577.
- Yu, J., Chang, L., Xie, W., Song, H., and Xie, K. (2006). A study on the ash from coal gangue fired power plant—characteristics and application. Presented at the 23rd Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 25–28.