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Article

Mössbauer spectroscopic characterization of ferrites as adsorbents for reactive adsorption desulfurization

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ABSTRACT

Sulfur in transportation fuels is a major source of air pollution. New strategies for the desulfurization of fuels have been explored to meet the urgent need to produce cleaner gasoline. Adsorptive desulfurization (ADS) is one of the most promising complementary and alternative methods. Herein, nanocrystalline ferrite adsorbents were synthesized from metal nitrates and urea using a microwave assisted combustion method. A series of ADS experiments were performed using a fixed-bed reactor to evaluate the ADS reactivity over the ferrites, which was found to have the order $\text{MgFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CuZnFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$. This effect is explained by the fact that the low degree of alloying of Mg-Fe and the doped Mg increased the interaction between Fe and S compounds, leading to a significant improvement in the desulfurization capability of the adsorbent. Additionally, Mg can dramatically promote the decomposition of thiophene. X-ray diffraction and Mössbauer spectroscopy were used to characterize the fresh, regenerated, and sulfided adsorbents. Although the ferrite adsorbents were partially sulfided to bimetallic sulfides during the adsorption process, they were successfully regenerated after calcining at 500 °C in air.

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1. Introduction

Sulfur in transportation fuels such as diesel, gasoline, and jet fuel remains a major source of air pollution [1]. More stringent environmental regulations for the oil refining industry have been enacted worldwide, and the Euro V emission standards require the sulfur content in gasoline to be less than 10 ppm. However, it is difficult to reduce the sulfur of liquid fuels to a very low level with conventional hydro desulfurization methods without a decrease in octane number. Therefore, new

strategies for desulfurization have been explored to meet the urgent need to produce cleaner gasoline [2].

Adsorptive desulfurization (ADS) is one of the most promising complementary and alternative desulfurization techniques. Reactive adsorption refers to processes using metal-based adsorbents to capture sulfur to form metal sulfides in the presence of hydrogen [3]. The sulfur atom is retained on the adsorbent, while the hydrocarbon portion of the fuel molecule is released back into the process stream. This process can achieve ultra-deep desulfurization with low octane number

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loss. During the past decade, several reports have been published on fuel desulfurization by reactive adsorption [4–6]. The Conoco Phillips Petroleum Company developed what is known as a S-Zorb process using Ni/ZnO as an effective reactive adsorbent for the production of low sulfur gasoline [4,5]. In this adsorbent, Ni functions as a hydro desulfurization site, while ZnO takes up the produced H₂S and is simultaneously converted into ZnS. Gao's group [6] studied the use of Ni/ZnO-SiO₂-Al₂O₃ as an adsorbent for the ADS of fluid catalytic cracking (FCC) gasoline in a fixed-fluidized bed reactor at low pressures in the presence of hydrogen. Their results indicated that high temperature, high pressure, high hydrogen-to-oil molar ratio, and low weight hourly space velocity (LHSV) are favorable for improving the desulfurization ability of the adsorbent but are not conducive to maintaining the octane number of FCC gasoline.

Additionally, kinetic experiments in a thermobalance and performance tests in different types of reactors have shown that ferrites can be used as regenerable adsorbents for hot coal gas desulfurization in integrated gasification combined cycle (IGCC) technologies for clean and efficient power generation [7]. The H₂S concentration in the outlet gas from a fixed-bed reactor can be as low as a few ppm and the ferrite adsorbent conversion at breakthrough may be above 70%, indicating a high adsorbent reactivity for the sulfidation process [8,9]. However, these features are frequently associated with structural changes occurring both in the fresh or regenerated and the sulfided adsorbents, and, unfortunately, these changes are not easy to detect with the usual characterization techniques.

In this study, nanocrystalline ferrite adsorbents were synthesized from stoichiometric metal nitrate and urea mixtures using a microwave assisted combustion method. To evaluate the ADS reactivity over the ferrites, a series of ADS experiments with a model gasoline feedstock (*n*-heptane containing thiophene) were performed using a fixed-bed reactor. The structural changes occurring in the ferrites during calcination at high temperature or regeneration in oxidizing atmosphere and the metallic sulfides formed during the sulfidation process were investigated in detail by powder X-ray diffraction (XRD) and ⁵⁷Fe Mössbauer spectroscopy.

2. Experimental

2.1. Preparation of AFe₂O₄ adsorbents

Nanocrystalline ferrites AFe₂O₄ (A = Mg, Co, Ni, Zn, and CuZn) were prepared by the exothermic reaction of mixtures of metallic nitrates (metallic A and Fe) and urea (CO(NH₂)₂) (as reducing agent) [10,11]. Stoichiometric ratios of metallic nitrate (A(NO₃)₂·*n*H₂O), ferric nitrate (Fe(NO₃)₃·9H₂O), and urea were dissolved in a small amount of doubly distilled water. The molar ratios in the mixture were 1.7(U):1(M):16.65(W), where U, M, and W denote the molar ratios of urea, metal nitrates, and water, respectively. The vessel containing the solution was placed in a microwave oven that was then operated at a maximum power of 800 W for 20 min. The solution boiled and underwent dehydration followed by decomposition with the evo-

lution of large amounts of gas. After the solution reached the point of spontaneous combustion, it instantly became a solid powder accompanied by the release of large amounts of heat and vapor.

2.2. Characterization of adsorbents

XRD analyses of the samples were carried out using a Rigaku D/Max-RB diffractometer with a Cu K_α monochromatized radiation source operated at 40 kV and 100 mA. The XRD patterns were compared with the calculated patterns obtained from the Inorganic Crystal Structure Database (ICSD) using Jade 6.0 software. The crystallite sizes of the prepared and annealed samples were estimated using the Scherrer equation.

⁵⁷Fe Mössbauer spectra were recorded on a Topologic 500 A spectrometer with a proportional counter at room temperature. ⁵⁷Co (Rh) moving in constant acceleration mode was used as the radioactive source. All spectral analyses were conducted assuming a Lorentzian line shape for computer fitting. The Doppler velocity of the spectrometer was calibrated with respect to α-Fe foil.

2.3. Evaluation of ADS performance of ferrites

The adsorption experiments were performed in a fixed-bed reactor at 500 °C under the following operating conditions: 0.3 g catalyst diluted to 3 mL with SiO₂, H₂ partial pressure of 1.0 MPa, LHSV of 2 h⁻¹, and H₂/oil of 600. The model gasoline feedstock was *n*-heptane containing thiophene, with a total sulfur concentration of 3000 mg/L. All of the sulfur contents reported in this work were determined by gas chromatography (GC) analysis. The sulfur removal was expressed as the equation [12]: Sulfur removal = (1 - C_t/C₀) × 100%, where C₀ is the sulfur concentration in the feedstock (mg/L) and C_t is the transient effluent sulfur concentration (mg/L) at any time *t* (min). Additionally, a regeneration experiment for the ferrite adsorbents was conducted at 500 °C in air and was considered to be complete when SO₂ was undetectable in the outlet gas.

3. Results and discussion

Figure 1 shows the XRD patterns of representative samples of ferrites synthesized by the microwave combustion method using various metallic nitrates. The pattern of the MgFe₂O₄ sample indicated a low crystallinity, with two broad peaks (around 2θ = 35° and 63°) corresponding to the position of the two main peaks of spinel ferrite. The diffraction peaks of the Co, Ni, and Zn ferrite samples were perfectly indexed to a single phase with cubic spinel structure of space group *Fd-3m* (standard JCPDS Card Nos. 22-1086 of cubic CoFe₂O₄, 10-0325 of cubic trevorite NiFe₂O₄, and 22-1012 of cubic ZnFe₂O₄), and no secondary phases were detected in the XRD patterns. This confirmed the phase purity of the final products. The broadening of the peaks for these samples indicates the fine particle nature of the ferrite powder [13]. Additionally, all the peaks of the CuZnFe₂O₄ sample matched well with those of standard JCPDS Card No. 22-1012 for the cubic ZnFe₂O₄ phase. The positions of the

Fig. 1. Powder XRD patterns of AFe₂O₄ ferrites obtained by the microwave combustion method. (1) MgFe₂O₄; (2) CoFe₂O₄; (3) NiFe₂O₄; (4) ZnFe₂O₄; (5) CuZnFe₂O₄.

XRD peaks were shifted to higher 2θ owing to the doping of Cu in the zinc ferrite. This shift can be explained by the fact that the doping cation Cu²⁺ (0.073 nm) has a smaller ionic radius than that of Zn²⁺ (0.083 nm) and by a possible redistribution of Zn²⁺ and Fe³⁺ ions caused by Cu²⁺ ions in the tetrahedral/octahedral ionic sites [11]. Furthermore, using the Scherrer equation, the particle size of the ferrites was calculated 5.0, 27.6, 44.6, 72.3, and 92.0 nm for the MgFe₂O₄, CoFe₂O₄, NiFe₂O₄, ZnFe₂O₄, and CuZnFe₂O₄ samples, respectively. A small particle size may be expected to reduce the diffusion path and promote the adsorption desulfurization performance of the ferrites to some extent. The doping of Cu in the zinc ferrite resulted in a measurable progressive increase in the degree of crystallinity of the produced cubic phase. The formation of Cu-doped zinc ferrites is more endothermic than the formation of pure Zn-ferrite. When Cu was introduced into the system, less heat would have been liberated, thereby increasing the molecular concentration of Cu at the crystal surface and degree of crystallinity of the product.

The desulfurization reactivity over the AFe₂O₄ adsorbents was compared under the reaction conditions with model gasoline (*n*-heptane containing thiophene to a total sulfur concentration of 3000 mg/L). The breakthrough curves of sulfur over the adsorbents are shown in Fig. 2. Generally, there are two basic components in a reaction ADS adsorbent: the reactive part (Ni, Cu, Co, Pt, and Pd), which has a relatively high affinity for sulfur compounds, and the adsorptive part (ZnO, MnO₂, FeO, and CaO) that accepts the sulfur and regenerates the reactive part [14]. However, there have only been a few studies of ferrites as ADS adsorbents until now. In our study, the ferrites may have been partially reduced in the H₂ atmosphere during the ADS process, forming metal or alloy and metallic oxide composites to serve as the adsorptive and reactive part, respectively. In a blank experiment, the sulfur removal reached 27%, which indicated that the thiophene was partially thermally-decomposed at the chosen reaction temperature (500 °C). The MgFe₂O₄ adsorbent initially gave a high sulfur removal of 95%, but was partially deactivated to 75% by 40 h, while the

ZnFe₂O₄ adsorbent also exhibited a high initial sulfur removal of 100% but was deactivated by 50% within the same period. This indicated that structural change of the ferrites and the formation of iron sulfides occurred during the desulfurization process.

The results in Fig. 2 show that the desulfurization capability of the ferrite adsorbents during the 40 h continuous ADS process had the following sequence: MgFe₂O₄ > NiFe₂O₄ > CuZnFe₂O₄ > ZnFe₂O₄ > CoFe₂O₄, which may have been caused by the different types of ferrite with probable site migration and/or change in oxidation state. MgFe₂O₄ exhibited the highest ADS properties, which may have been because its spinel structure was not destroyed in the reducing atmosphere used and because the doped Mg increased the interaction between Fe and S compounds, leading to a significant improvement in the desulfurization capability of the adsorbent. Additionally, basic/acid sites provided by adsorbents may promote the decomposition of thiophene [15,16]. Mg is a generally basic element which can dramatically promote the decomposition of thiophene, which may also have given MgFe₂O₄ the best desulfurization performance. Furthermore, doping with Cu can substantially increase the overall sulfidation rate of zinc ferrite, because Cu increases the amount of reactive part and thereby the desulfurization performance. This result is similar to those observed for Cu-doped zinc ferrites used as regenerable adsorbents for hot coal gas desulfurization [9].

To understand the relationship between the structures of the ferrites and their desulfurization properties in depth, a detailed characterization of the ferrites was carried out. The structure of the ferrites was found to have changed significantly after the ADS experiments, as shown in Fig. 3. These structural changes were observed through the formation of different types of metallic sulfides during the sulfidation process. Typical diffraction peaks at $2\theta = 29.9^\circ$, 33.8° , 43.6° , and 53.1° corresponding to those of Fe_{1-x}S (JCPDS No. 29-0725) were detected in the XRD pattern of the MgFe₂O₄ sample. Trace amounts of FeS were also found. The crystalline phases of the AFe₂O₄ ($A =$

Fig. 2. Breakthrough curves for adsorptive desulfurization of model gasoline on AFe₂O₄ adsorbents at 500 °C, H₂ partial pressure = 1.0 MPa, LHSV = 2 h⁻¹, and H₂/oil = 600. (1) Blank; (2) CoFe₂O₄; (3) ZnFe₂O₄; (4) CuZnFe₂O₄; (5) NiFe₂O₄; (6) MgFe₂O₄.

Fig. 3. Powder XRD patterns of AFe₂O₄ ferrite adsorbents after ADS experiments. (1) MgFe₂O₄; (2) CoFe₂O₄; (3) NiFe₂O₄; (4) ZnFe₂O₄; (5) CuZnFe₂O₄.

Ni, Zn, and CuZn) adsorbents were identified by comparison with standard iron sulfide JCPDS files (hexagonal FeS, No. 37-0477 and cubic FeS, No. 23-1123), which confirmed that the ferrite adsorbents had been sulfided during the ADS process. Especially, the presence of ZnS phase was found in the pattern of the ZnFe₂O₄ sample, which means that ZnO in the ZnFe₂O₄ system acted as a sulfur acceptor via diffused H₂S from the thiophene [17]. Additionally, crystalline Co₃Fe₇ (JCPD No. 48-1816) or CoFe (JCPD No. 44-1433) phase was detected in the CoFe₂O₄ sample, and Fe_{0.64}Ni_{0.36} phase (JCPD No. 47-1405) was detected in the NiFe₂O₄ sample. The formation of Fe-base alloy may have protected the metallic phase from agglomeration during the subsequent reduction treatment and desulfurization process [12]. However, the formation of Fe-base alloy may weaken the Fe–S bond and adversely affect reactive ADS. Combined with the structural changes and the ADS properties, it can be speculated that the formation of Fe-base alloy works against desulfurization, suppressing the metal to metallic sulfide transformation.

In spinel ferrites AFe₂O₄ (A = Mg²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, etc.), there are twice as many octahedral B cationic sites as tetrahedral cationic A sites. In normal spinel, A divalent ions occupy the tetrahedral sites and only Fe³⁺ ions occupy the octahedral sites. In contrast, in the inverse spinel, A divalent ions occupy the octahedral sites and Fe³⁺ ions are equally distributed in octahedral and tetrahedral sites [18]. ⁵⁷Fe Mössbauer spectroscopy is a tool for clarifying the chemical state and relative amount of iron species in a material, which can assist in understanding the structural changes of ferrites during the ADS process.

Room temperature Mössbauer spectra of representative ferrite samples are shown in Fig. 4. The spectral parameters such as isomer shift (IS, δ), quadrupole splitting (QS, Δ) and hyperfine field (H) were computed and are summarized in Table 1. As shown in Fig. 4, the spectrum of fresh MgFe₂O₄ was fitted well by two doublets with IS = 0.16 mm/s, QS = 0.63 mm/s and IS = 0.34 mm/s, QS = 0.66 mm/s, which can be ascribed to tetrahedrally and octahedrally oxygen-coordinated

Fig. 4. ⁵⁷Fe Mössbauer spectra of (a) fresh, (b) spent, and (c) regenerated MgFe₂O₄ adsorbent.

Fe³⁺ ions in (Mg²⁺_{1-x}Fe³⁺_x)_A[Mg²⁺_xFe³⁺_{2-x}]_BO₄ magnesium ferrite, where round and square brackets denote tetrahedral (A) and octahedral [B] coordination sites, respectively, and where x represents the degree of inversion [19]. Based on the Mössbauer parameters of the doublets for MgFe₂O₄, it was concluded that spinel MgFe₂O₄ had been successfully synthesized by

Table 1

⁵⁷Fe Mössbauer parameters of MgFe₂O₄ samples.

Sample	A (%)	δ^a (mm/s)	H (T)	Δ (mm/s)	2 Γ (mm/s)	Site ^b
Fresh	68.6	0.16	—	0.63	0.47	A-site in MgFe ₂ O ₄
	31.4	0.34	—	0.66	0.37	B-site in MgFe ₂ O ₄
Spent	25.9	0.05	19.5	-0.07	0.22	C-site in Fe _{1-x} S
	27.8	0.61	29.7	0.00	0.32	A-site in Fe _{1-x} S
	32.6	0.41	—	0.94	1.29	MgFeS
	13.6	0.11	21.8	0.08	0.30	B-site in Fe _{1-x} S
Regenerated	9.2	0.58	—	0.80	0.46	A-site in MgFe ₂ O ₄
	43.0	0.38	51.0	-0.21	0.46	α -Fe ₂ O ₃
	39.9	0.27	—	0.75	0.58	B-site in MgFe ₂ O ₄
	7.9	0.46	—	2.40	0.58	MgFe ₂ O ₄ with oxygen vacancies

^a Relative to α -Fe at room temperature.

^b Site identification considered to be the most probable case.

the microwave assisted combustion method. The structural change of the MgFe_2O_4 during the ADS process was determined from measurements of the chemical state of Fe in the spent adsorbent, as shown in Fig. 4(b) and Table 1. The Mössbauer spectrum could be fitted with one doublet and three sextets. The doublet with $\text{IS} = 0.41 \text{ mm/s}$ and $\text{QS} = 0.94 \text{ mm/s}$ associated with the MgFe bimetallic sulfide (MgFeS) accounted for 32.6% of the total spectral area. The sextets with $\text{IS} = 0.61 \text{ mm/s}$, $\text{QS} = 0.00 \text{ mm/s}$, and $H = 29.7 \text{ T}$ could be ascribed to A sites in Fe_{1-x}S pyrrhotite. The other two sextets, which had $\text{IS} = 0.11 \text{ mm/s}$, $\text{QS} = 0.08 \text{ mm/s}$, and $H = 21.8 \text{ T}$ and $\text{IS} = 0.05 \text{ mm/s}$, $\text{QS} = -0.07 \text{ mm/s}$, and $H = 19.5 \text{ T}$ were attributed to B-sites and C-sites in Fe_{1-x}S pyrrhotite, respectively. The A-, B-, and C-sites in Fe_{1-x}S were assigned according to the hyperfine field distribution. The high ratio of Fe_{1-x}S phase in the spent MgFe_2O_4 sample (ca. 67.4% of the total spectral area) was not sulfurized completely, which explained why the MgFe_2O_4 maintained a high sulfur removal activity after 40 h continuous ADS. Combined with the XRD data for spent MgFe_2O_4 , it can be speculated that the MgFe_2O_4 was decomposed and reduced by H_2 during the ADS process, leading to its structural distortion. The sulfur content on the surface of the MgFe_2O_4 increased significantly with elapsed ADS time, which led to it taking on the general formula of ferrous sulfide, Fe_{1-x}S . This result is similar to the thermodynamic behavior and phase transformation of transition metal-sulfur systems, especially in the Fe-S system [20].

For the ADS process, it is crucial to regenerate the adsorbent. In this work, the regeneration of sulfurized MgFe_2O_4 was conducted at 500°C in air and was considered to be complete when SO_2 was undetectable in the outlet gas. As shown in Fig. 4(c), the Mössbauer spectrum of regenerated MgFe_2O_4 could be fitted with a sextet and three doublets. The sextet associated with $\alpha\text{-Fe}_2\text{O}_3$ accounted for 43.0% of the total spectral area. The doublet having Mössbauer parameters of $\text{IS} = 0.46 \text{ mm/s}$ and $\text{QS} = 2.40 \text{ mm/s}$ accounted for about 7.9% and was attributed to MgFe_2O_4 with oxygen vacancies, which means that the sulfurized MgFe_2O_4 was re-oxidized after treatment at 500°C for 3 h in air. Moreover, about 50% of the MgFe_2O_4 was regenerated completely. As shown in Table 1, the two doublets with $\text{IS} = 0.27 \text{ mm/s}$, $\text{QS} = 0.75 \text{ mm/s}$ and $\text{IS} = 0.58 \text{ mm/s}$, $\text{QS} = 0.80 \text{ mm/s}$ were assigned to the A-sites and B-sites in MgFe_2O_4 , respectively, and were similar to those detected in fresh MgFe_2O_4 . Therefore, the regeneration process was effective in eliminating all traces of iron sulfides in the MgFe_2O_4 adsorbent.

The Mössbauer spectra and parameters of fresh, spent, and regenerated NiFe_2O_4 adsorbent are shown in Fig. 5 and Table 2, respectively. The spectrum of NiFe_2O_4 consisted of two clearly split Zeeman sextets. The isomer shifts of the sextets were in the range of $0.27\text{--}0.37 \text{ mm/s}$, which is typical of that for Fe^{3+} ions. Bulk NiFe_2O_4 has an inverse spinel structure in which Ni^{2+} occupies B-sites totally while the Fe^{3+} ions are distributed between A- and B-sites as $(\text{Fe}^{3+})_A[\text{Fe}^{3+}, \text{Ni}^{2+}]_B\text{O}_4$ [21]. As shown in Table 2, the fraction of iron ions in (A) and (B) sites in the NiFe_2O_4 sample were 59% and 39%, respectively, which indicated that spinel NiFe_2O_4 had been successfully synthesized by the microwave assisted combustion method.

Fig. 5. ^{57}Fe Mössbauer spectra of (a) fresh, (b) spent, and (c) regenerated NiFe_2O_4 adsorbent.

The Mössbauer spectrum of the spent NiFe_2O_4 sample showed three sextets and two doublets. The sextet with the Mössbauer parameters of $\text{IS} = 0.03 \text{ mm/s}$, $\text{QS} = 0.03 \text{ mm/s}$, and $H = 30.7 \text{ T}$ was attributed to A-sites in Fe_{1-x}S . The other two sextets, which had $\text{IS} = 0.18 \text{ mm/s}$, $H = 21.0 \text{ T}$, and $\text{IS} = 0.17 \text{ mm/s}$, $H = 19.5 \text{ T}$, were attributed to Fe atoms at nonequivalent lattice sites B and C of Fe_{1-x}S , respectively. The two doublets,

Table 2
 ^{57}Fe Mössbauer parameters of NiFe_2O_4 samples.

Sample	A (%)	δ^a (mm/s)	H (T)	Δ (mm/s)	2Γ (mm/s)	Site ^b
Fresh	61.2	0.26	49.6	0.00	0.38	A-site in NiFe_2O_4
	38.8	0.37	52.7	-0.01	0.29	B-site in NiFe_2O_4
Spent	36.0	0.03	30.7	0.03	0.67	A-site in Fe_{1-x}S
	9.8	0.18	21.0	0.06	0.21	B-site in Fe_{1-x}S
	23.6	0.17	19.5	0.08	0.44	C-site in Fe_{1-x}S
	7.40	0.30	—	0.68	0.48	Fe^{3+} in Fe_2S_3
	23.2	0.75	—	-0.18	0.32	Fe^{2+} in NiFeS
Regenerated	33.0	0.29	49.5	-0.03	0.39	A-site in NiFe_2O_4
	45.3	0.37	51.9	-0.14	0.32	B-site in NiFe_2O_4
	21.7	0.62	46.1	0.02	0.38	$\alpha\text{-Fe}_2\text{O}_3$

^a Relative to $\alpha\text{-Fe}$ at room temperature.

^b Site identification considered to be the most probable case.

which had $IS = 0.30$ mm/s, $QS = 0.68$ mm/s and $IS = 0.75$ mm/s, $QS = -0.18$ mm/s, were attributed to Fe^{3+} in Fe_2S_3 and Fe^{2+} in $NiFeS$ violarite, respectively [22,23]. According to the above analysis, the spinel $NiFe_2O_4$ adsorbent was almost completely transformed into iron sulfides during the 40-h ADS process. In the dynamic balance of ADS, iron sulfide was reduced by the H_2 to form non-stoichiometric $Fe_{1-x}S$ phase. Additionally, nickel ferrites have excellent reaction ADS performance, which may be attributed to Ni functioning as a hydrodesulfurization site [6].

The spent $NiFe_2O_4$ adsorbent was regenerated at 500 °C for 3 h in air. The Mössbauer spectrum of regenerated $NiFe_2O_4$ showed three sextets. The two sextets having the Mössbauer parameters of $IS = 0.29$ mm/s, $H = 49.5$ T and $IS = 0.37$ mm/s, $H = 51.9$ T were attributed to the Fe^{3+} ions distributed between the A- and B-sites of $NiFe_2O_4$, respectively. The other sextet was attributed to $\alpha-Fe_2O_3$. Comparison of the Mössbauer spectra of fresh $NiFe_2O_4$ and regenerated $NiFe_2O_4$ indicates that the nickel ferrite adsorbent was also successfully regenerated.

As shown in Fig. 6 and Table 3, the Mössbauer spectrum of fresh $ZnFe_2O_4$ adsorbent showed a doublet with $IS = 0.35$ mm/s, $QS = 0.40$ mm/s, which corresponded to Fe^{3+} ions occupying octahedral sites in the normal spinel phase $ZnFe_2O_4$. The

Table 3⁵⁷Fe Mössbauer parameters of $ZnFe_2O_4$ samples.

Sample	A (%)	δ^a (mm/s)	H (T)	Δ (mm/s)	2Γ (mm/s)	Site ^b
Fresh	100	0.35	—	0.40	0.37	$Fe^{3+}[O]$
Spent	26.2	0.25	21.5	0.08	0.32	B-site in $Fe_{1-x}S$
	28.4	0.17	18.5	0.08	0.38	C-site in $Fe_{1-x}S$
	8.6	0.80	31.4	-0.23	0.28	A-site in $Fe_{1-x}S$
	24.3	0.60	—	0.65	0.65	Fe^{2+} in $FeZnS$
	12.5	0.22	11.0	0.13	0.24	D-site in $Fe_{1-x}S$
Regenerated	50.2	0.38	51.5	-0.21	0.38	$\alpha-Fe_2O_3$
	49.8	0.34	—	0.46	0.45	$Fe^{3+}[O]$

^a Relative to $\alpha-Fe$ at room temperature.^b Site identification considered to be the most probable case.

structure of the $ZnFe_2O_4$ also changed significantly during the ADS process. The appearance of one doublet and four sextets for spent $ZnFe_2O_4$ may be reasonably assigned to $FeZnS$ sphalerite and $Fe_{1-x}S$, respectively. There were four nonequivalent iron sites, A, B, C, and D, in the $Fe_{1-x}S$. Under the reducing atmosphere well as the presence of thiophene, the zinc ferrite adsorbent was unstable and readily decomposed into the single oxides ZnO and Fe_2O_3 . The ferric oxide was further reduced to metallic iron, which led to the formation of a $Fe_{1-x}S$ structure mixed with sphalerite during the sulfidation process. However, when the sulfided adsorbent was regenerated at 500 °C for 3 h in air, its Mössbauer spectrum (Fig. 6(c)) showed a well-defined doublet and a sextet. The Mössbauer parameters shown in Table 3 enabled these sites to be assigned to the presence of $ZnFe_2O_4$ and $\alpha-Fe_2O_3$. Consequently, these Mössbauer results indicate that the regeneration process was effective in eliminating all traces of iron sulfides, although the regenerated adsorbent was incompletely converted to the spinel phase owing to apparent diffusional limitations in the solid-state reaction [8].

4. Conclusions

Nanocrystalline AFe_2O_4 ferrite adsorbents ($A = Mg, Zn, Ni, Co$, and $CuZn$) were successfully synthesized from stoichiometric metal nitrate and urea mixtures using a microwave assisted combustion method. The as-prepared AFe_2O_4 were effective adsorbents for the reactive ADS of model gasoline. The ADS reactivity over the ferrites was found to have the following order: $MgFe_2O_4 > NiFe_2O_4 > CuZnFe_2O_4 > ZnFe_2O_4 > CoFe_2O_4$. This effect is explained by the fact that the low degree of alloying of $Mg-Fe$ and the doped Mg increased the interaction between Fe and S compounds, leading to a significant improvement in the desulfurization capability of the adsorbent. Additionally, Mg is a typical basic element which can dramatically promote the decomposition of thiophene. XRD and Mössbauer spectroscopy were used to characterize the fresh, regenerated and sulfided adsorbents in detail. The obtained results indicated a change in oxidation state of the adsorbents. During the adsorption process, the ferrites were partially sulfided to the monometallic and/or bimetallic sulfides. However, the ferrite adsorbents were found to be successfully regenerated under oxidizing conditions.

Fig. 6. ⁵⁷Fe Mössbauer spectra of (a) fresh, (b) spent, and (c) regenerated $ZnFe_2O_4$ adsorbent.

Graphical Abstract

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Mössbauer spectroscopic characterization of ferrites as adsorbents for reactive adsorption desulfurization

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Ferrite adsorbents can be synthesized using a microwave assisted combustion method, yielding a high desulfurization capability. Mössbauer spectroscopy was used to characterize the ferrites. The adsorbents were successfully regenerated under oxidizing conditions.

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铁氧体吸附剂的穆斯堡尔谱解析及其反应吸附脱硫性能

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摘要: 运输燃料中的含硫化合物依然是空气污染的主要源头. 随着人们环保意识日益增强, 世界各国对燃料油标准特别是硫含量提出了越来越严格的要求. 为了应对燃料油的无硫化趋势, 探索新型脱硫技术去除油品中的含硫化合物成为研究热点. 吸附脱硫技术 (ADS) 能够选择性地脱除汽油中的含硫化合物, 而不影响其中的烯烃含量, 从而避免了加氢精制过程

中烯烃饱和导致的辛烷值降低问题,成为目前成熟的清洁油品生产技术。

本文采用微波辅助燃烧技术,将一定化学计量比的金属硝酸盐和尿素混合物快速燃烧反应,成功合成一系列铁氧体吸附剂 (MgFe_2O_4 , NiFe_2O_4 , $\text{CuZnFe}_2\text{O}_4$, ZnFe_2O_4 , CoFe_2O_4)。以含有噻吩的正庚烷 (总含硫量 3000 mg/L) 为汽油模型,在固定床反应器中 500 °C 反应条件下探索了所合成铁氧体吸附剂的吸附脱硫性能。结果表明,铁氧体吸附脱硫活性大小为: $\text{MgFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CuZnFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$ 。其中 MgFe_2O_4 较其他铁氧体具有更高的吸附脱硫性能。这是由于 Mg-Fe 合金化程度低,而且掺杂的 Mg 降低了 Fe 与 S 之间的相互作用,从而显著提高了吸附脱硫性能。此外, Mg 作为一种典型的碱金属可在一定程度上显著促进噻吩分解。

X 射线衍射和穆斯堡尔谱作为敏感的结构和组成检测手段,广泛用于解析铁氧体吸附剂在吸附脱硫过程中的结构和相态变化。通过穆斯堡尔谱成功解析了铁氧体中 Fe 的存在形式及其化合态。对新鲜铁氧体吸附剂、吸附脱硫后的吸附剂以及氧化再生的吸附剂进行监测对比,发现在吸附过程中铁氧体被部分硫化成 Fe_{1-x}S 和双金属硫化物。在空气中经高温 (500 °C) 处理可成功实现铁氧体吸附剂再生。本文通过对铁氧体吸附剂的结构解析和性能测试,为新型吸附脱硫剂开发提供了理论依据。

关键词: 铁氧体; 吸附脱硫; 穆斯堡尔谱; 再生

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