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Mössbauer spectroscopy and X-ray diffraction studies of Mg–Al–Fe–O mixed spinel sulphur transfer catalysts

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Mössbauer spectroscopy with X-ray diffraction technique was used to characterize the chemical valences and coordination environments of iron ions in Mg–Fe–Al–O mixed spinel catalysts under different treatments. It was found that the values of quadrupole splitting gradually altered with the calcining temperature, which was connected with the crystalline size of the catalysts. During the thermal treatment, a probable electron density transfer from the oxygen ion to the iron ion in the Fe–O bond resulted in the values of isomer shift decreasing linearly with calcining temperature. The absorption lines were fitted when the atomic fraction of magnesium increased from 1 to 2 in the Mg–Al–Fe–O sample, indicating that a multiphase coexisted in this sample and iron ions had different chemical valences and different coordinated environments. When a sulphated $MgFe_{0.2}Al_{1.8}O_4$ sample was reduced by hydrogen at 500 °C, various iron species with different chemical valences were identified. Fe_3O_4 phase with an anion defect, created in when the sulphated sample was reduced, was proposed as an active species during O_2 and SO_2 simultaneous adsorption on the reduced sulphated sample. © *1998 Kluwer Academic Publishers*

1. Introduction

Sulphur-transfer catalysts, employed for removing SO_x(SO_2 and SO_3) emissions in FCC units, have received a great deal of attention in recent years. In earlier works, Al_2O_3 and MgO were used as an additives to FCC catalysts for SO_x reduction [1, 2]. However, because of the low SO_2-capturing ability of aluminium oxide and the poor reducibility of magnesium sulphate formed on the magnesium oxide during the SO_2 and O_2 adsorption process, they were replaced by magnesium–alumina spinel catalysts in the mid 1980s [3, 4]. Recently, the rare-earth metal oxide, CeO_2 serving as a promoter to enhance the ability of SO_2 oxidation adsorption, has been found to exhibit an excellent improvement action for SO_x adsorption when it is supported on the $MgAl_2O_4$ catalyst [5, 6]. More recently, it has been found that part of the Al^{3+} which is substituted by Fe^{3+} or other transition metal ions in the magnesium–alumina spinel structure, can enhance both the capacity of SO_2 oxidative adsorption and the ability of sulphate reductive decomposition [7–9]. Until now, Mg–Fe–Al–O mixed spinel catalyst has been believed to be an excellent sulphur-transfer catalyst.

In our previous work, the mechanism of the cycle between SO_2 oxidative adsorption and sulphate reductive decomposition on Mg–Fe–Al–O catalyst was studied [10]; the relationship between the basicity, De–SO_2 activity and sulphate reducibility of Mg–Fe–Al–O catalyst was established [11]. Also the surface segregation action, surface and bulk compositions in Mg–Fe–Al–O catalyst were studied using atomic absorption spectroscopy (AES) technique [12]. All of these studies show that iron ions play an important role in simultaneously improving the abilities of oxidative adsorption of SO_2 and reductive decomposition of the sulphate. However, during the cycle of SO_2 oxidative adsorption and sulphate reductive decomposition, the changes in chemical valences and coordination environments of iron ions are not clear. As part of a series of investigations, in the present paper, we report the results of iron ion chemical valences and coordination, and crystal composition in Mg–Fe–Al–O catalysts under different

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treatments using Mössbauer spectroscopy and X-ray diffraction techniques.

2. Experimental procedure

$MgAl_{2-x}Fe_xO_4$ catalysts were prepared by the coprecipitation method. The precursors were magnesium nitrate, sodium aluminate and ferric nitrate. Three different solutions were prepared by adding 51.80 g $Mg(NO_3)_2 \cdot 6H_2O$, 16.48 g $Fe(NO_3)_3 \cdot 9H_2O$ and 40.80 g $NaAlO_2$ into three difference containers which hold 300 ml deionized water, respectively. At the same rate, these solutions were added into a 2000 ml container that holds 500 ml deionized water. The addition was controlled for about an hour. During the addition, the slurry was stirred and the pH value was set at 8–9 using concentrated nitric acid or 2N NaOH. After the addition was finished, the slurry was continuously stirred for an hour and then aged at ambient temperature overnight. The aged slurry was filtered and washed with 10 L deionized water. The filtered cake was dried at 120 °C for 10 h and then heated in a furnace at different temperatures for 4 h. The product was ground and 80–160 mesh powder was used in the experiments.

In the case of SO_2 oxidation adsorption, 3 g catalyst were exposed to the adsorption mixture gases of 1.5% SO_2, 20% O_2 which was balanced by nitrogen. At 700 °C, the sample was allowed to adsorb SO_2 for 30 min. In the case of reduction by hydrogen, a fresh sample or a sulphated sample was reduced in a stream of 30% H_2 in N_2 at 500 °C for 20 min.

The Mössbauer spectra were recorded at room temperature on the AME-50 spectrometer with the ^{57}Co in palladium base as radioactive source. Debye–Waller factors were used to correct all the data. The isomer shifts and the velocities relative to the α-Fe foil standard were reported. The theoretical spectrum was made up of quadrupole doublets, magnetic sexlets or both. All the spectra were computer-fitted assuming Lorentzian line shapes. The accuracy was $\pm 0.01\,mm\,s^{-1}$.

X-ray diffraction (XRD) analysis was carried out on Rigaku-D/max-III diffractometer with CuK_α radiation and a secondary beam monochromator. The Experimental conditions were scan speed 1 deg min^{-1}; scan step 0.02°; voltage and current: 35 kV and 25 mA. The Debye–Scherrer equation was used to determine the crystalline size of the different samples.

Using the liquid nitrogen adsorption method, BET surface specific area, pore volume and the pore-size distribution of the samples calcined at different temperatures were obtained on an ASAP-2400 apparatus. All the data of BET and crystalline size are shown in Table I.

TABLE I Surface specific area, pore volume, pore-size distribution and crystalline size of the $MgAl_{1.8}Fe_{0.2}O_4$ sample calcined at different temperatures

Calcination temperature (°C)	Surface specific area ($m^2\,g^{-1}$)	Pore volume ($ml\,g^{-1}$)	Pore size (nm)	Crystalline size (nm)
300	121	0.4798	1.3	16.8
500	135	0.8724	0.6	9.7
700	129	0.7742	1.2	16.7
800	117	0.5127	1.3	17.4
1000	87	0.3796	4.5	24.8

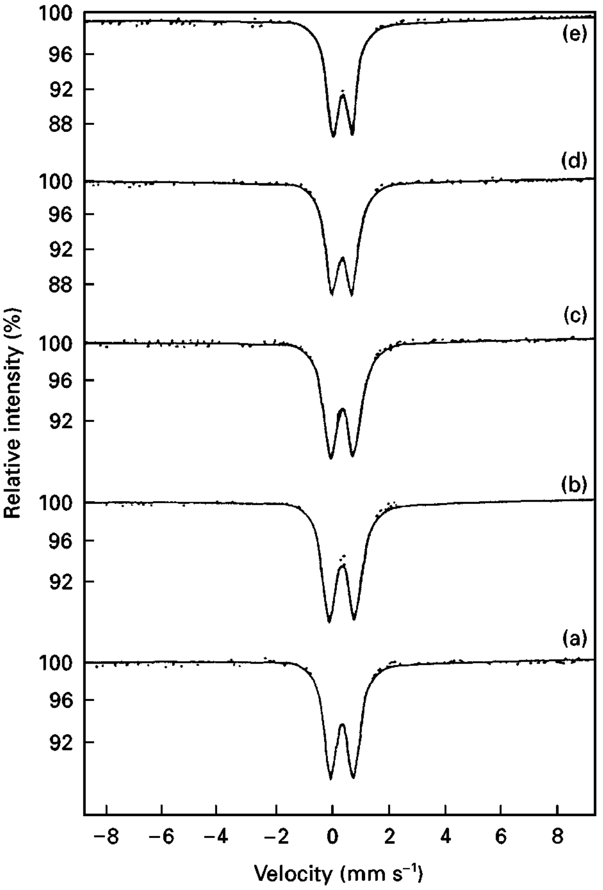

Figure 1 The Mössbauer spectra of the $MgAl_{1.8}Fe_{0.2}O_4$ sample under different calcining temperatures: (a) 300 °C, (b) 500 °C, (c) 700 °C, (d) 800 °C, (e) 1000 °C.

3. Results and discussion

3.1. Effect of the calcination temperature

Mössbauer spectra of $MgAl_{1.8}Fe_{0.2}O_4$ calcined at different temperatures are shown in Fig. 1. On analysing these spectra and the Mössbauer parameters presented in Table II, the following information can be obtained.

1. Under different thermal treatments, all the absorption lines were shown in doublet form. No magnetic signals appeared at high velocities. The absorption intensities of these doublets were slightly reduced when the calcination temperature increased.

2. In the calcination-temperature range between 300 and 500 °C, the widths of the absorption peaks increased. Also, the values of quadrupole splitting (QS) increased from $0.83\,mm\,s^{-1}$ to $0.92\,mm\,s^{-1}$. However, in the temperature range between 500 and 1000 °C, the absorption line widths gradually became narrower, and the values of QS decreased from $0.92\,mm\,s^{-1}$ to $0.69\,mm\,s^{-1}$.

TABLE II Mössbauer parameters of different samples under various treatments

Sample: atomic ratio (Mg:Fe:Al)	Pretreatment condition (°C)	(h)	Spectrum type	Mössbauer parameters IS ($mm\,s^{-1}$)	QS ($mm\,s^{-1}$)
1:0.2:1.8	300	4	Doublet	0.33	0.83
	500	4	Doublet	0.32	0.92
	700	4	Doublet	0.31	0.83
	800	4	Doublet	0.29	0.72
	1000	4	Doublet	0.28	0.69

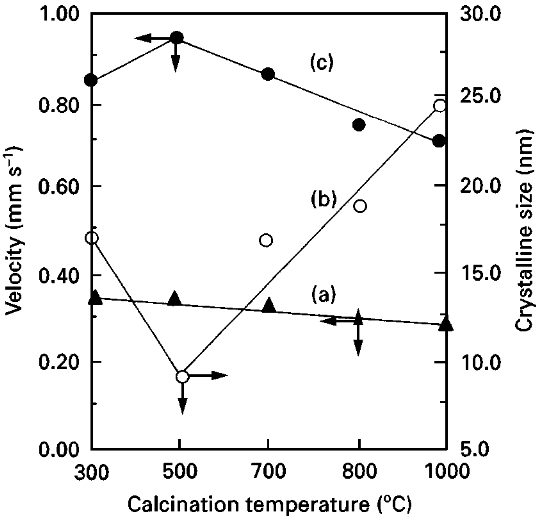

Figure 2 Isomer shift and quadrupole splitting and crystalline size of the samples as a function of calcining temperature. (a) Isomer shift, (b) crystalline size, (c) quadrupole splitting.

3. As the calcination temperature increased from 300 °C to 1000 °C, the isomer shift (IS) value decreased linearly from $0.33\,mm\,s^{-1}$ to $0.28\,mm\,s^{-1}$.

Generally, the magnetic ordering of the structure can cause the Mössbauer spectrum to split into six lines. However, because the magnetic ordering is volume and temperature dependent, when the crystalline size is small enough to be in the superparamagnetic state, the six-line spectrum collapses into a doublet. This is a result of thermal energy overcoming the energy barrier of the crystal field [13–16]. According to this postulation, the estimated particle size is about 2–20 nm [17, 18]. In the present study, the crystalline size of the sample heated at different temperatures was in the range between 9.7 and 24.8 nm. We here attributed these central doublets to the superparamagnetic iron species. These assignments must be considered only as a rough estimate, because the relation between the crystalline size and the Mössbauer parameters is not accurate. The results from Fig. 1 also indicated that all the iron ions occupy the octahedral positions in the crystals. These results can be explained by analysing the crystalline structures of these samples. In the normal spinel structure of $MgAl_2O_4$, aluminium ions generally occupy octahedral sites. When iron ions were introduced into the framework of the magnesium–alumina catalyst, by substituting some aluminium ions, these iron ions occupy the octahedral positions, forming the mixed spinel structure.

At the calcination temperatures between 300 and 500 °C, the broadening in width of the absorption line with temperature was probably a result of the Fe^{3+} ion in a coordinately unsaturated state, which is possibly due to the imperfect crystalline structure in this temperature range.

Fig. 2 shows the isomer shift, quadrupole splitting and the crystalline size as functions of calcination temperature of the samples. These samples were heated at 300, 500, 700, and 800 °C for 4 h but at 1000 °C for 0.5 h. When the calcination temperature increased from 300 °C to 500 °C, the crystalline size decreased from 16.8 nm to 9.7 nm. However, when the calcination temperature increased from 500 °C to 700, 800 and 1000 °C, the crystalline size increased from 9.7 nm to 16.7, 17.4 and 24.8 nm (Fig. 2b and Table I). The variation of the crystalline size is generally related to the phase transformation during the thermal treatment process. When the sample was calcined at 300 °C, the decompositions of the precursors were incomplete; in this case, largely affected by the precursors, the average crystalline size was large. However, when the sample was heated at 500 °C, all the precursors were thermally broken into many small crystals. These small crystals reacted to produce many very fine cores of spinel material because the solid-state reaction for spinel crystal formation occurred at this temperature, as supported by X-ray diffraction analysis [19]. Therefore, at 500 °C, the crystalline size of the sample was very small. In addition, at 500 °C, the sample had the largest surface area and pore volume with the smallest pore size. When the sample was calcined above 500 °C, owing to the growth of the crystal at higher calcining temperature, the crystalline size gradually increased with calcining temperature. At 1000 °C, the crystalline size increased to 24.8 nm accompanied by a decrease in its surface area and pore volume.

Fig. 2c shows that the value of QS increased when the calcining temperature increased from 300 °C to 500 °C and it decreased when the calcining temperature increased from 500 °C to 1000 °C. The change in trend of the QS value with calcining temperature showed the inverse relationship between the crystalline size and the calcining temperature. Therefore, the value of QS, as suggested by other studies [14, 20], was largely related to the crystalline size in this study.

The isomer shift is generally affected by the distribution of electron density around the nucleus of the iron ions. Because isomer shift decreases almost linearly when the calcination temperature increased (Fig. 2a), the s-electron density at the nucleus of the Fe^{3+} therefore seems to increase with the calcination temperature. This was probably caused by electron transfer between the iron and oxygen ions at the Fe–O bond in the structures of these samples [21, 22]. When these samples were heated at different temperatures, electron transfer from oxygen ions to Fe^{3+} ions is different. At the higher calcining temperature, the greater electron density transfer resulted in a larger value of the isomer shift.

3.2. Effect of composition of the sample

When the atomic fraction of iron increased from 0.2 to 0.6, in all samples, only one central doublet in the Mössbauer spectra was observed (Fig. 3). The slight reduction of the QS value indicated that the crystallite size increased slightly as the iron content increased. However, when the atomic fraction of the magnesium atom was raised from 1 to 2, surprisingly, a significant change in the spectrum, as shown in Fig. 3c, was found. This spectrum was fitted with 20 absorption lines: three sets of sextets and a couple of doublet absorption lines near the central sextets. The Mössbauer parameters are summarized in Table III.

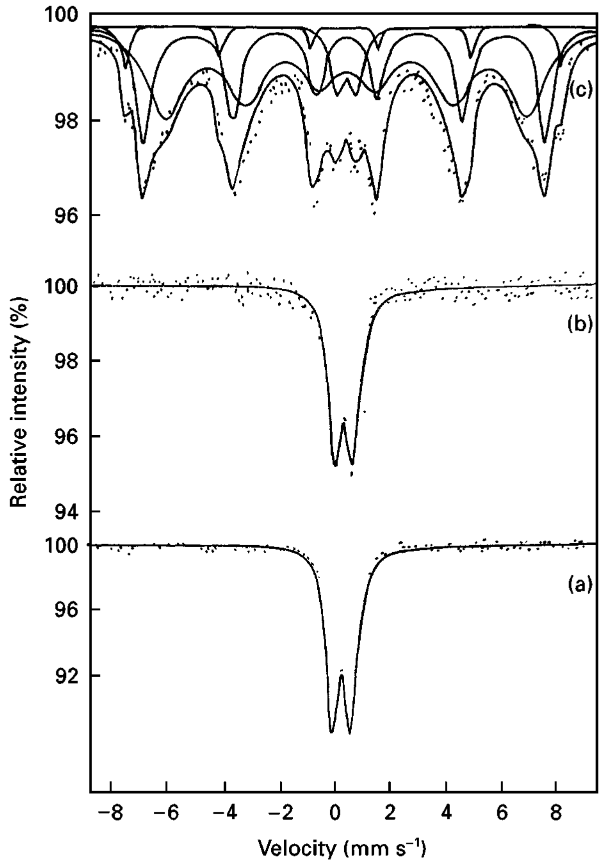

Figure 3 The Mössbauer spectra of the samples with different composition. Ma : Al : Fe (a) 1.0 : 1.8 : 0.2, (b) 1.0 : 1.4 : 0.6, (c) 2.0 : 1.8 : 0.2.

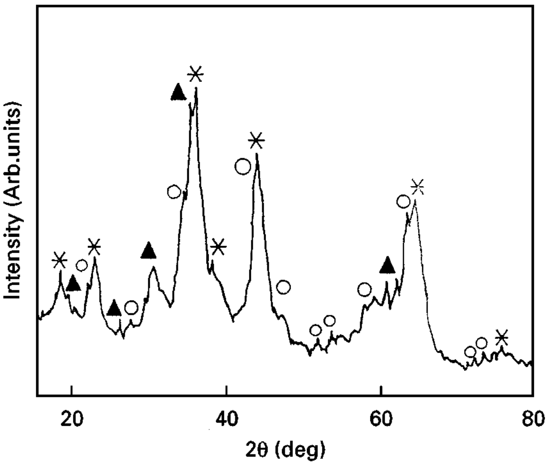

Figure 4 X-ray diffraction spectrum of the $Mg_2Al_{1.8}Fe_{0.2}O_4$ sample calcined at 800 °C. (○) $Mg(FeAl)O_4$, (∗) $MgAl_2O_4$, (▲) $MgFe_2O_4$.

This complex spectrum suggested that the sample of $Mg_2Al_{1.8}Fe_{0.2}O_4$ had complex crystalline structures and iron ions had different coordinate environments.

To analyse the phase composition in the sample of $Mg_2Al_{1.8}Fe_{0.2}O_4$, XRD analysis was performed (Fig. 4). Different phases, $MgFe_2O_4$, $Mg(FeAl)\,O_4$ and $MgAl_2O_4$, were identified in this sample. This revealed that multiphases coexisted and iron ions had different coordinate environments, which were in good agreement with the results from Mössbauer spectroscopy. This sample is magnesium-rich. Because magnesium has a high reactivity with aluminium and iron ions to produce different spinel phases, in the case of magnesium-rich samples, these different solid reactions occurred simultaneously, causing different crystals to be formed.

The central doublet in Fig. 3 is indicative of some superparamagnetic Fe^{3+} species existing in this sample. The three sextets suggest that Fe^{3+} ions had different coordinated environments, which are consistent with the results of XRD (Fig. 3). Sextet 1, corresponding to the larger value of hyperfine field energy ($H = 487.73$ kOe), was responsible for about 5.8% of the Fe^{3+} in the tetrahedral sites. This result indicated that this sample had, to some extent, an inversion in its spinel structures, which was also supported by the results of the ion distribution obtained from the Furuhashi method [23]. Sextets 2 and 3 were ascribed

TABLE III Mössbauer parameters of different samples with different compositions

Samples: atomic ratio (Mg : Fe : Al)	Pretreatment condition		Spectrum type	Mössbauer parameters			Area (%)
	(°C)	(h)		IS (mm s^{-1})	QS (mm s^{-1})	*H* (kOe)	
1 : 0.6 : 1.4	800	4	Doublet	0.29	0.68		100
1 : 0.2 : 1.8	800	4	Doublet	0.29	0.68		100
2 : 0.2 : 1.8	800	4	Doublet	0.27	0.69		6.6
			Sextet 1	0.19	0.03	487.73	5.8
			Sextet 2	0.26	0.01	448.97	31.7
			Sextet 3	0.26	0.03	403.17	56.0

to the characterization of 87.7% of the Fe^{3+} in the octahedral sites. However, the coordinate environments of these two groups of Fe^{3+} ions differed from each other. We attributed sextet 2, which had hyperfine field energy ($H = 448.97$ kOe) with $QS = 0.01\ mm\,s^{-1}$ and $IS = 0.26\ mm\,s^{-1}$, to Fe^{3+} at site B in the $MgFe_2O_4$, and sextet 3, corresponding to the hyperfine field energy $H = 403.17$ kOe with $QS = 0.03\ mm\,s^{-1}$ and $IS = 0.26\ mm\,s^{-1}$ to Fe^{3+} ions at site B in the $Mg(AlFe)O_4$ structure.

3.3. Effect of the reduction by hydrogen

Fig. 5 shows the Mössbauer spectra of the samples treated under different conditions. The Mössbauer parameters and assignments are summarized in Table IV. Fig. 5a is the spectrum of the $Mg_2Al_{1.8}Fe_{0.2}O_4$ sample calcined at 500 °C. The Mössbauer spectrum of the sample that was first treated with 1.5% SO_2 and 20% O_2 at 700 °C for half an hour and then reduced by 30% H_2 at 500 °C for 20 min, is shown in Fig. 5b. Fig. 5c is the spectrum of the sample treated with 30% H_2 at 500 °C for 20 min. Similar to Fig. 1, the central doublet 1 is due to Fe^{3+} species in a superparamagnetic state. Doublet 2, however, is assigned to Fe^{2+} ions in tetrahedrally coordinated sites. The different sextet absorption lines imply that iron ions in a high chemical valence state were reduced to a lower chemical valence. Sextet 1 originated from Fe^{3+} ions occupying tetrahedral sites and sextet 2 was characteristic of $Fe^{2.5+}$ ions, which was a consequence of the existence of Fe_3O_4, because in Fe_3O_4 phase, Fe^{3+} and Fe^{2+} ions in an octahedral environment cannot be distinguished due to the fast electron hopping above the Verway temperature (116k) [24]. Here, Fe_3O_4 seems to be in a non-stoichiometric state due to the broadening of its absorption lines in comparison with the standard spectrum. It can be easily understood that during the reduction process, some lattice oxygen ions were reduced, this would lead to some oxygen deficits appearing in both surface and bulk of the sample. Magnetite with an anion deficit can be described as $Fe_A^{3+}\ [Fe_y^{2+}Fe_x^{3+}]_B O_{4-\theta}$ (θ denotes vacancies) [25]. The existence of 7.2% α-Fe phase is responsible for sextets 3. Based on the above analysis, different iron species, Fe^{3+}, $Fe^{2.5+}$, Fe^{2+} and α-Fe^0, were produced after the sample was reduced by hydrogen.

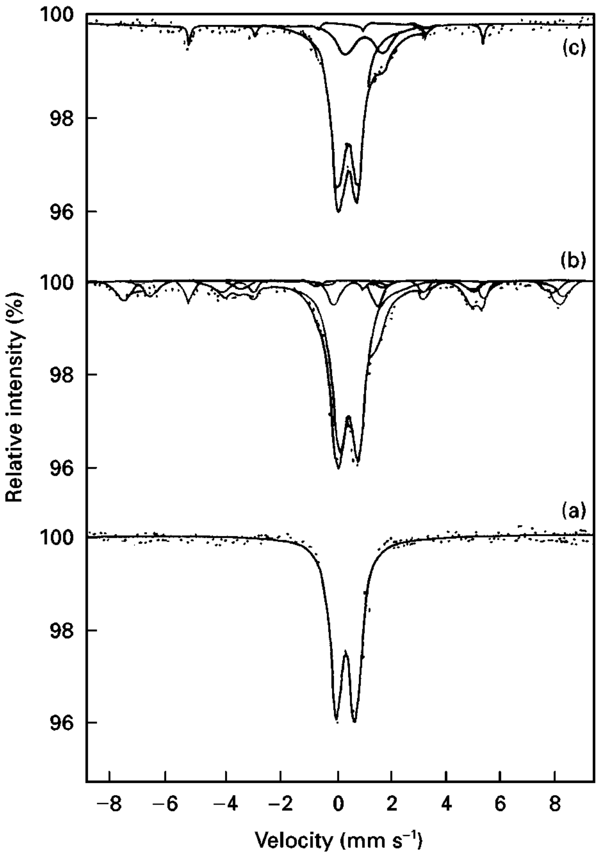

Figure 5 The Mössbauer spectra of the $MgAl_{1.8}Fe_{0.2}O_4$ sample before and after being reduced with hydrogen. (a) Before reduction (sample A). (b) Sample A was first sulphated with SO_2 and oxygen at 700 °C for 30 min; then it was reduced with 30% hydrogen in nitrogen for 20 min at 500 °C. The Mössbauer spectrum was recorded at room temperature after these pretreatments. (c) Sample A was first reduced with 30% hydrogen in nitrogen for 20 min at 500 °C, then the Mössbauer spectrum was recorded at room temperature.

In comparison with the Mössbauer spectra between the reduced sulphated sample (Fig. 5b) and the reduced unsulphated-sample (Fig. 5c), a significant difference was that the Fe_3O_4 phase was formed in the sulphated sample, instead of the unsulphated sample. In addition, the Fe^{3+} ion in a superparamagnetic state and the Fe^{2+} ion in the tetrahedrally coordinated sites increased from 62.35% and 7.6%, to 74.8% and 19.8%, respectively (Fig. 5c). These results indicate that when the sample without sulphate is reduced by hydrogen, many Fe^{3+} ions were reduced to Fe^{2+}

TABLE IV Mössbauer parameters of the sample reduced by hydrogen

Samples: atomic ratio (Mg : Fe : Al)	Pretreatment condition	Spectrum type	Mössbauer parameters			Area (%)
			IS ($mm\,s^{-1}$)	QS ($mm\,s^{-1}$)	H (kOe)	
1 : 0.2 : 1.8	800 °C, 4 h; sulphated at 700° C for 30 min and then reduced at 500 °C for 20 min	Doublet 1	0.36	0.71		62.3
		Doublet 2	0.59	1.64		7.6
		Sextet 1	0.35	0.09	486.49	12.8
		Sextet 2	0.65	0.06	449.69	10.0
		Sextet 3	0.02	0.03	327.60	7.2
1 : 0.2 : 1.8	800 °C, 4 h, and then reduced with H_2 at 500 °C for 20 min	Doublet 1	0.28	0.72		74.8
		Doublet 2	0.87	1.44		19.8
		Sextet	0.04	0.08	328.5	5.4

species and its crystals could easily be broken into small particles due to the reduction by hydrogen. The sextet absorption spectrum exhibited by the 5.4% α-Fe phase was also found. Electrical conduction measurements show that oxygen vacancies are the oxygen adsorption sites in this catalyst [26]. When oxygen molecules are adsorbed on these vacancies, active oxygen species are produced. Active oxygen species can easily react with adsorbed SO_2 to yield sulphate. Therefore, it appears that the Fe_3O_4 phase with an oxygen deficit is one of the active phases for oxygen adsorption on the reduced sulphated-sample. Probably Fe_3O_4 phase has positive effect on SO_2 oxidative adsorption on this catalyst.

4. Conclusion

In the present study, different chemical valences of iron ions and different phases in the Mg–Fe–Al–O mixed spinel solid catalysts in the treatment process were identified by Mössbauer spectroscopy and XRD techniques. A dependence of quadrupole splitting on the calcination temperatures was found, which was associated with the crystalline size. The linear decrease of the isomer shift with calcination temperature indicated that an electron density transfer from the oxygen ion to the iron ion in the Fe–O bond occurred during the thermal treatment process.

The Mössbauer spectrum was not evidently altered when the atomic fraction of iron in the spinel structure increased from 0.2 to 0.6. However, when the atomic fraction of magnesium increased from 1 to 2, some remarkable changes in the Mössbauer spectrum, from only one centred doublet to 20 absorption lines (two doublets and three sextets), were observed. This was a consequence of a multiphase coexisting in this sample, which was also confirmed by XRD analysis.

Fe_3O_4 phase with oxygen vacancies, as evidence of the difference between the reduced sulphated sample and the reduced unsulphated sample, was proposed to be an active phase for oxygen adsorption on the reduced sulphated sample.

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