FT-IR study of the interaction of magnesium ferrite with SO_2

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The interaction of SO_2 with the inverted spinel $MgFe_2O_4$ in the presence and in the absence of oxygen has been studied by FT-IR spectroscopy in the temperature range 300–773 K. SO_2 adsorbs in the form of sulfito complexes that transform to sulfato complexes both in the presence and in the absence of oxygen. Evidence is found for a catalytic effect of the ferric oxide component in the oxidation of SO_2. Sulfate species are stable up to 773 K. Pyridine adsorption experiments show that sulfated magnesium ferrite is a Lewis acidic solid and does not present Brønsted acidity.

Keywords: Magnesium ferrite; FT-IR spectroscopy; SO_2 adsorption; surface acidity

1. Introduction

The emissions of SO_x (SO_2 and SO_3) from waste gases represent a paramount environmental problem. To limit such emissions different sorption and catalytic technologies have been developed for the desulphurization of fuel gases and liquids or waste gases. Iron-based oxides (like Fe_2O_3 and ferrite spinels) are used industrially to remove H_2S from coal gas using absorption–oxidation cycles [1,2]. In this case H_2S is absorbed on metal oxides (forming metal sulphides) that are regenerated by oxidation giving back the metal oxide and SO_2. Ce-containing $MgAl_2O_4$ [3] have been proposed as sorbants/catalysts to remove SO_2 from fluid catalytic cracking flue gases. In these cases SO_2 is oxidized to SO_3 by the CeO_2 component, adsorbed on the $MgAl_2O_4$ in the form of sulphate species and released as H_2S after reduction in the cracking reactor. Iron oxide based materials are reported to be also very efficient for this purpose, although they interfere with the cracking reaction [3].

On the other hand, iron oxide is an active catalyst for the oxidation of SO_2 to SO_3 even at high temperature [4], and, in the past, it has also been used industrially for sulphuric acid production [5].

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In order to evaluate possible alternatives of adsorbants and catalysts for SO_2 abatement and/or conversion, we investigated the interaction of SO_2 with $MgFe_2O_4$ powders prepared via the aerogel method.

2. Experimental

The production of $MgFe_2O_4$ aerogels (100 m^2/g) has been described previously [6]. This material is constituted by the inverted spinel structure of magnesioferrite. Bulk and surface characterization of this catalyst has also been reported [7,8].

The FT-IR spectra have been recorded by a Nicolet 5ZDX Fourier transform instrument, using pressed disks of the pure catalyst powders. Conventional IR cells with gas manipulation and evacuation apparatus have been used. Before the adsorption experiments, the $MgFe_2O_4$ pressed disks were activated by calcination in air at 773 K for 1 h and by outgassing at 640 K for 15 min.

SO_2 has been taken from cylinders produced by SIO (Milan, Italy) and used without further purification. No contaminants were detected by IR analysis.

3. Results and discussion

The spectrum of a $MgFe_2O_4$ pressed disk after the activation procedure presents a complex absorption in the region 3800–3300 cm^{-1}, due to residual surface hydroxy-groups, some broad absorptions in the region 1600–1300 cm^{-1} due to residual carbonate species, and a cut-off limit, just below 800 cm^{-1}, due to the higher frequency side of the skeletal absorptions. The nature of the surface hydroxy-groups, bonded both to Mg and Fe ions, has been discussed in detail in ref. [8]. Outgassing procedure has been limited to 15 min in order to avoid partial reduction of the sample, as discussed previously [6], in spite of allowing small amounts of carbonate species to remain adsorbed on the surface.

The contact with SO_2 at room temperature immediately causes the formation of a strong and broad absorption in the region 1100–800 cm^{-1}, with a main maximum at 930 cm^{-1} and shoulders near 1030 and 800 cm^{-1} (fig. 1, curve a). These bands indefinitely resist outgassing at r.t., being certainly due to strongly bonded species. The most likely assignment for these bands, taking into account both chemical and spectroscopic considerations, is to S-bonded sulfito complexes. In fact, the free sulfite ion is pyramidal with C_{3v} symmetry, with four fundamental vibrational modes, all both IR and Raman active. The symmetric stretching ν_1 (A_1 symmetry) and the asymmetric stretching ν_3 (E symmetry) have been detected by Raman spectroscopy at 967 and 933 cm^{-1}, respectively, for the free ion in solution [9] and unsplit at 970 cm^{-1} (broad) in the IR spectrum of crystalline Na_2SO_3 [10]. According to Newman and Powell [10] when the sulfite ion is S-bonded to a metal, so retaining nearly a C_{3v} symmetry, ν_3 shifts toward 1100 cm^{-1}. However, follow-

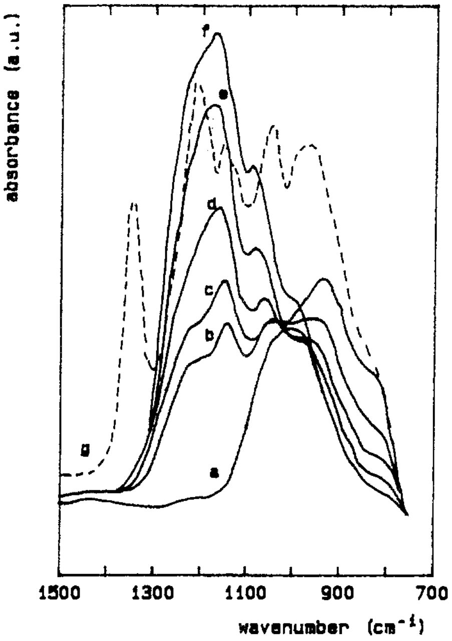
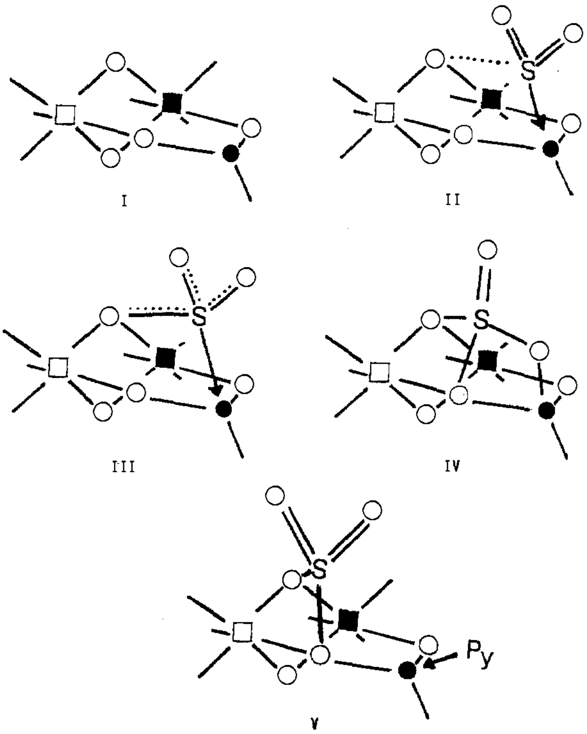


Fig. 1. FT-IR spectra of the surface species arising from contact of an activated $MgFe_2O_4$ sample with SO_2 gas (45 Torr) for 5 min and outgassing at room temperature (a), and after heating in oxygen (85 Torr) at 373 K (b), 473 K (c), 573 K (d), 673 K (e) and 773 K (f). (g) is after (f) and outgassing at 673 K. The spectrum of the activated $MgFe_2O_4$ catalyst has been subtracted.

ing Nyberg and Larsson [11] the detection of ν_1 below 960 cm^{-1} should be an indication of O-bonded sulfito complexes. On the other hand the lowering of the symmetry with respect to C_{3v} will cause the splitting of the doubly degenerate ν_3 with the consequent appearance of three stretching modes, as in our case.

On surfaces, it is possible to propose the existence of sulfito complexes that are both S- and O-bonded, and this is likely our case. In scheme 1 we propose, on pure speculative bases, the structure of an active site for SO_2 adsorption (I), thought to occur on the 110 face of the inverse spinel structure. In the drawing, full symbols are iron ions (square: octahedrally coordinated; circle: tetrahedrally coordinated), open square is a Mg ion (octahedrally coordinated) and open circles are oxide ions. The formation of sulphite species (drawings II and III) occurs through a primary interaction of the sulphur atom with iron cation, but the successive reaction with an oxide ion leads to sulphite species that are S-bonded to Fe ions and O-bonded bridging Mg and Fe ions.

The spectrum remains unchanged if such surface sulfite species are left in contact with oxygen at r.t. However, if this contact is carried out at higher temperatures (fig. 1, b–f) the bands of sulfite species progressively decrease in intensity, while bands grow at higher frequencies, with a main maximum at 1150 cm^{-1} and shoulders at 1230, 1050 and, possibly, near 1000 cm^{-1}. The presence of an isosbes-



Scheme 1.

tic point near 1025 cm^{-1} indicates that sulphites are converted into a new species without formation of any intermediate species.

The new bands fall in the typical absorption region of sulfate ions. The free sulfate ion is tetrahedral (T_d symmetry) and is characterized by four fundamental vibrational modes, all Raman active, even though only two of them are IR active. The IR active modes are the asymmetric stretching ν_3, quoted at 1105 cm^{-1}, and the asymmetric deformation ν_4, quoted at 611 cm^{-1} (both F_2 symmetry) [11].

When a complex is formed the symmetry is lowered and this can cause the splitting of the degenerate vibrational modes and the activation in IR of Raman active modes. In the region above 800 cm^{-1} one can expect up to three modes arising from the triply degenerate ν_3, and a fourth band due to the activation in IR of the Raman active symmetric stretching mode ν_1, quoted at 983 cm^{-1} for the free ion [9]. The spectrum we observe, with four components, agrees either with a C_{2v} symmetry for the sulfate ion, like in bidentate and bridging complexes, or with an even lower symmetry.

Upon completion of the oxidation treatment (fig. 1, f), the spectrum is slightly modified, the maximum shifting towards 1180 cm^{-1} and the higher frequency component being no more resolved. This could indicate that other types of sulfate ions are also formed.

The symmetry of the surface sulfato complexes clearly depends also on successive outgassing of the samples. After outgassing at 473 K the spectrum of the sulfato complexes is significantly modified (fig. 1, g). In particular, a sharp band appears at 1350 cm^{-1}, and the main maximum is now sharper near 1200 cm^{-1}, with several components at lower frequencies. The same spectrum is observed if the sample after contact with SO_2 (so containing sulfite species) is outgassed at increasing temperatures (fig. 2). This indicates that sulfites can be oxidized to sulfates also in the absence of gas-phase oxygen, at the expense of Mg ferrite where Fe^{3+} is partially reduced to Fe^{2+}. However, oxidation of sulfites to sulfates already occurs at 373 K in the presence of gas-phase oxygen while it needs at least 473 K in the absence of oxygen. It is worth mentioning that the oxidation of SO_2 into sulfate species in the presence of oxygen occurs on $MgFe_2O_4$ at much lower temperatures than those reported on MgO (773 K [12]) or on $MgAl_2O_4$ (720 K [13]), showing the role of the reducible component ferric oxide. The bands of sulfate species decrease in intensity very slowly by outgassing at 773 K, showing that below this temperature they are definitely stable.

The sharp band at 1350 cm^{-1} reminds of those observed in the region 1360–1380 cm^{-1} on several metal oxides doped with sulfate species, like Fe_2O_3 [14], Al_2O_3 [15] and TiO_2 [15–17]. Saur et al. [15] elegantly demonstrated that this band is due to the S=O double bond stretching of a tricoordinated sulfate species with

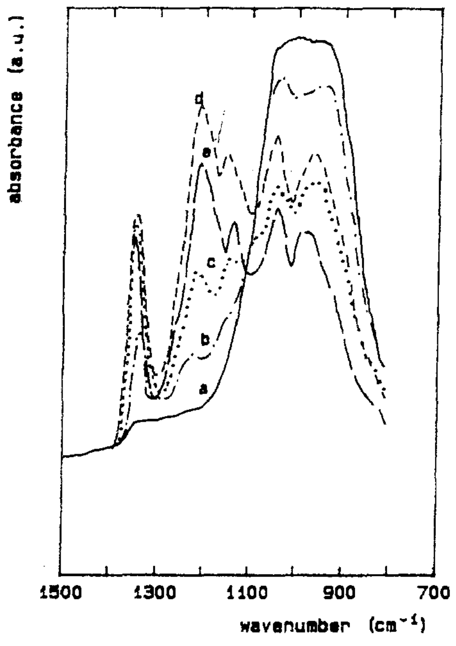


Fig. 2. FT-IR spectra of the surface species arising from contact of an activated $MgFe_2O_4$ sample with SO_2 gas (45 Torr) for 5 min and outgassing at 373 K (a), 473 K (b), 573 K (c), 673 K (d) and 773 K (e). The spectrum of the activated $MgFe_2O_4$ catalyst has been subtracted.

three long S–O bonds and one short S=O bond standing up on the surface. This species is likely formed, probably together with other ones, by outgassing sulfated $MgFe_2O_4$ too. In scheme 1 (drawing IV) we propose a structure for such a species. The slightly lower S=O stretching in the present case is likely due to the inductive effect relative to the presence of Mg^{2+} ions.

The identification of such a species is also supported by the behaviour of the band at 1350 cm^{-1} upon adsorption/desorption of water and other bases like pyridine (fig. 3). This behaviour is definitely the same as reported on other metal oxides [14–17]. The band at 1350 cm^{-1} clearly shifts strongly to lower frequencies after adsorption of pyridine, but is progressively restored upon pyridine desorption. This is likely due to the interconversion of triply-bonded sulfate species (drawing IV) with a doubly bonded one (drawing V) having nearly a C_{2v} symmetry.

The spectrum of adsorbed pyridine on sulfated $MgFe_2O_4$ is the same as observed on the sulfur-free $MgFe_2O_4$ [6,8]. In both cases, the presence of Lewis acid sites is evidenced by the detection of coordinated pyridine. In particular, the most sensitive 8a vibrational mode of adsorbed pyridine is observed at 1608 cm^{-1}, significantly shifted upward with respect to the liquid-phase value (1583 cm^{-1}), so indicating the presence of medium-strong Lewis sites, constituted by coordinatively unsaturated Fe^{3+} ions. On the contrary, the lack of detection of the bands typical of pyridinium ions (broad bands near 1640 cm^{-1}, split, and near 1550 cm^{-1}) clearly indicate that Brønsted acid sites are absent. This behaviour differs from what is

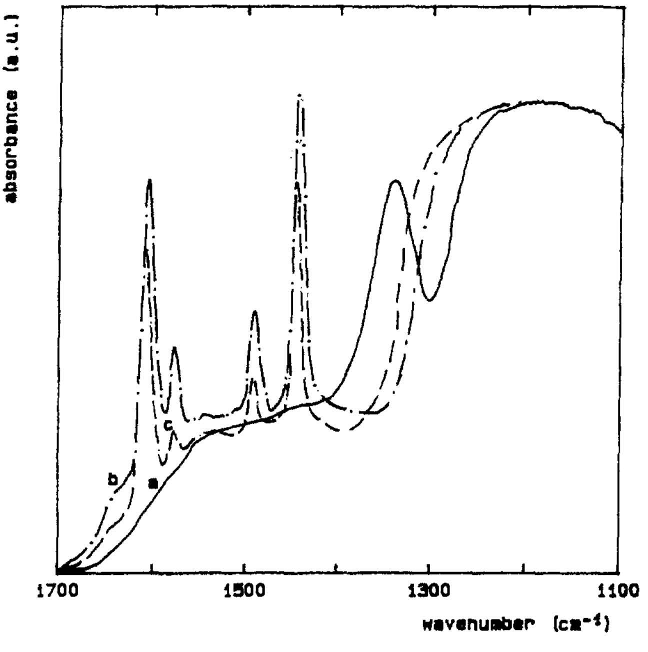


Fig. 3. Spectra of a sulfated $MgFe_2O_4$ sample after outgassing at 640 K (a), after contact with pyridine vapour and outgassing at room temperature (b) and at 373 K (c).

observed on several pure metal oxides, like Fe_2O_3, TiO_2, Al_2O_3 and ZrO_2 [14–18] where sulfation causes the formation of strong Brønsted acid sites that allow these materials to become "solid superacids". In the present case the basic component arising from MgO probably neutralizes the acidity arising from the presence of sulfate ions.

4. Conclusions

The main conclusions from the present work can be summarized as follows:

(1) SO_2 adsorbs at room temperature on the inverted spinel $MgFe_2O_4$ giving rise to sulfito complexes probably both S- and O-bonded.

(2) Sulfites are converted into sulfates by heating both in the presence and in the absence of oxygen, although the presence of gas-phase oxygen speeds up the oxidation process.

(3) The oxidation of SO_2 into sulfates is observed at much lower temperatures than in the case of MgO and $MgAl_2O_4$, so providing evidence for the catalytic effect of the ferric oxide component.

(4) Sulfate species can in part take a tricoordinated form when outgassed, but they convert into a C_{2v}-like species when water or pyridine are coadsorbed.

(5) Sulfation of $MgFe_2O_4$, unlike that of several pure oxides, does not cause the formation of Brønsted acid sites.

(6) Sulfate species on $MgFe_2O_4$ are stable up to near 773 K.

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