FT-IR study of the interaction of magnesium ferrite with SO₂

Ermanno Astorino a, Guido Busca b,1, Gianguido Ramis b
and Ronald J. Willey a

a Department of Chemical Engineering, Northeastern University, Boston, MA 02115, USA
b Istituto di Chimica, Facoltà di Ingegneria, Università, P. le Kennedy, I-16129 Genoa, Italy

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The interaction of SO₂ with the inverted spinel MgFe₂O₄ in the presence and in the absence of oxygen has been studied by FT-IR spectroscopy in the temperature range 300-773 K. SO₂ 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 SO₂. 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 Bronsted acidity.

Keywords: Magnesium ferrite; FT-IR spectroscopy; SO₂ adsorption; surface acidity

1. Introduction

The emissions of SOₓ (SO₂ and SO₃) 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 Fe₂O₃ and ferrite spinels) are used industrially to remove H₂S from coal gas using absorption–oxidation cycles [1,2]. In this case H₂S is absorbed on metal oxides (forming metal sulphides) that are regenerated by oxidation giving back the metal oxide and SO₂. Ce-containing MgAl₂O₄ [3] have been proposed as sorbants/catalysts to remove SO₂ from fluid catalytic cracking flue gases. In these cases SO₂ is oxidized to SO₃ by the CeO₂ component, adsorbed on the MgAl₂O₄ in the form of sulphate species and released as H₂S 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 SO₂ to SO₃ even at high temperature [4], and, in the past, it has also been used industrially for sulphuric acid production [5].

1 To whom correspondence should be addressed.
In order to evaluate possible alternatives of adsorbants and catalysts for SO₂ abatement and/or conversion, we investigated the interaction of SO₂ with MgFe₂O₄ powders prepared via the aerogel method.

2. Experimental

The production of MgFe₂O₄ aerogels (100 m²/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 MgFe₂O₄ pressed disks were activated by calcination in air at 773 K for 1 h and by outgassing at 640 K for 15 min.

SO₂ 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 MgFe₂O₄ 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 SO₂ 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 C₃ᵥ symmetry, with four fundamental vibrational modes, all both IR and Raman active. The symmetric stretching ν₁ (A₁ symmetry) and the asymmetric stretching ν₃ (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 Na₂SO₃ [10]. According to Newman and Powell [10] when the sulfite ion is S-bonded to a metal, so retaining nearly a C₃ᵥ symmetry, ν₃ shifts toward 1100 cm⁻¹. However, follow-