



Kinetics and mechanism of magnesium sulphite oxidation promoted by a novel cobalt-based molecular sieve catalyst



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ABSTRACT

The oxidation of magnesium sulphite is crucial in recycling the byproduct of magnesium desulphurisation. In this study, a novel cobalt-based catalyst was prepared using a wet impregnation method by loading cobalt species on a molecular sieve carrier. The catalyst was characterised using scanning electron microscopy, X-ray fluorescence, Brunauer–Emmett–Teller analysis, X-ray diffraction, and energy dispersive X-ray spectroscopy. The catalyst was confirmed to be a mesoporous material. The macroscopic kinetics of magnesium sulphite oxidation catalysed by this cobalt-based catalyst was investigated in a stirred tank reactor. The results showed that reaction orders with respect to catalyst, magnesium sulphite, and oxygen concentrations were 0.39, 0, and 0.41, respectively. The apparent activation energy was 35.2 kJ mol⁻¹. In addition, a comparison of the rates of external diffusion, internal diffusion, and intrinsic reaction revealed that the internal diffusion of oxygen might be the rate-controlling step of magnesium sulphite oxidation. The results provide a new approach for recycling the magnesium desulphurisation byproduct.

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1. Introduction

As the main precursor of acid rain and haze, sulfur dioxide (SO₂) has become an important environmental issue for several decades. In China, the prominent source of SO₂ emissions is from the scattering industrial boilers, which is estimated to be no less than 500,000 units in total amounts before 2014 [1]. Magnesium desulphurisation is a promising technique for flue gas cleaning [2] and has been widely used in industrial boilers [3]. Magnesium hydrate, used as the absorbent, reacts with SO₂ and forms insoluble magnesium sulphite, which is then oxidised to form soluble magnesium sulphate [4], a potential fertiliser [5]. However, the oxidation rate of magnesium sulphite, as a pollutant that might release SO₂ and consume dissolved oxygen in the water [6], is comparatively low, thus resulting in poor utilisation of the desulphurisation byproduct. The byproduct therefore comprises of both sulphite and sulphate from industrial boilers and must be discarded, which results in wasteful magnesium sulphate consumption and secondary sulphite pollution.

Enhancing sulphite oxidation in the presence of a catalyst is reliable and effective and is considered a free radical reaction [7].

Transition metals have been reported to show excellent catalytic performance in accelerating sulphite oxidation [8,9]. Cobalt is the most widely used catalyst for increasing the oxidation rate of sulphite [10–14]. Lancia et al. [15–20] investigated the catalytic effect of manganese ions on sulphite oxidation and calculated the kinetic parameters. Karatza et al. [21] demonstrated the catalytic effect of cuprous ions on sulphite oxidation. Yuegang et al. [22] reported the photochemical oxidation kinetics of sulphite catalysed by ferric ions. Furthermore, Semler et al. [23] studied the catalytic effect of the combination of ferrous and manganese ions on sulphite oxidation. However, these studies focused on the homogeneous catalytic behaviour of transition metal ions in aqueous solutions, which causes critical transition metal ion pollution during the process of sulphite oxidation. Moreover, the consumption (i.e., no recycling) of transition metal ions is financially inviable. Therefore, realizing a recyclable transition metal catalyst is essential for flue gas desulphurisation.

Compared with conventional transition metal ion catalysts for sulphite oxidation, solid catalysts deserve more attention because of their ease of recycling, which reduces consumption and secondary pollution. Several methods are available for preparing solid catalysts, such as impregnation, co-precipitation, deposition–precipitation, hydrothermal treatment, urea–nitrate combustion, and sol–gel methods [24]. Using supported catalysts with active ions on the carrier of porous materials, such as

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Nomenclature

c_i	reactant concentration at the interface between liquid and solid catalyst
c_A	concentration of reactants on the catalyst surface in general
c_b	reactant concentration in the aqueous bulk
c_{Co}	concentration of cobalt at the phase interfere
c_{O_2}	equilibrium concentration of oxygen at the phase interfere
$c_{S(VI)}$	concentration of sulphate at the phase interfere
D_{ed}	external diffusion coefficient
D_{id}	internal diffusion coefficient
k_{in}	coefficient of intrinsic reaction rate
L	pore length which depends on the diameter of catalyst particles
mL	Thiele modules
n	reaction orders of oxygen in the intrinsic reaction
p	reaction orders of sulphite in the intrinsic reaction
q	reaction orders of cobalt catalyst in the intrinsic reaction
r_{ed}	external diffusion rate of the reactants which includes oxygen and sulphite
r_{id}	internal diffusion rate of the reactants which includes oxygen and sulphite
r_{in}	intrinsic reaction rate of sulphite oxidation

molecular sieves [25–28], activated carbons [29,30], and silicone [31,32], is a promising approach that combines the advantages of homogeneous and heterogeneous catalysts. Few studies have reported on preparing solid catalysts for increasing sulphite oxidation rates, which confines the recycling of desulphurisation byproducts to coal-fired industrial boilers.

For increased byproduct utilisation in magnesium-based desulphurisation, in this study, a novel solid catalyst was prepared to increase the magnesium sulphite oxidation rate. Based on the catalytic performance of transition metal ions, cobalt was selected as the active component and loaded on a molecular sieve carrier through wet impregnation. The oxidation kinetics of magnesium sulphite was investigated in the presence of the supported catalyst, clarifying the oxidation system operation in wet magnesium desulphurisation.

2. Experimental

2.1. Preparation and characterisation of the cobalt-based molecular sieve catalyst

The cobalt-based molecular sieve catalyst was prepared through wet impregnation. Molecular sieves (4A) were added to an aqueous solution containing the desired concentration of $Co(NO_3)_2 \cdot 6H_2O$, and the mixture was rotated in a thermostatic shaker for 4 h. After 24 h, the mixture was filtered, washed with deionized water, thoroughly oven-dried at 110 °C for 8 h, calcined at 250 °C for 2 h, and subsequently calcined at 400 °C in a muffle furnace for 3 h. The obtained catalyst was ready for use.

The surface and cross-sectional morphologies of the catalyst were observed using scanning electron microscopy (SEM; S4800, Hitachi, Japan). The specific surface area and pore size were evaluated using Brunauer–Emmett–Teller analysis (Tristar 3020, Micromeritics, USA). The components of the catalyst were analysed using wavelength-scanning X-ray fluorescence (XRF; XRF 1700, S4, Bruker, Germany; Table 1). The cobalt species on the catalyst surface were identified using X-ray diffraction (XRD, D8

Advance, Bruker, Germany). Surface elemental analysis was performed using energy dispersive X-ray spectroscopy (EDS, System 7, Thermo Noran, USA).

2.2. Preparation and analysis of magnesium sulphite samples

The magnesium sulphite samples were prepared by precipitation of concentrated sodium sulphite and magnesium chloride with vigorous agitation and separation. This precipitate of magnesium sulphite was then washed and placed in a vacuum rotary evaporator (R201L, SENCO, China). The purity of hydrate magnesium sulphite product was 99% which was confirmed by wavelength-scanning X-ray fluorescence (type XRF-1700), EDTA titration, and barium sulphate spectrophotometry [33].

2.3. Experimental method and apparatus

A bubbling apparatus was used to study the catalysed oxidation kinetics of magnesium sulphite [13]. The reaction temperature was kept constant by a water bath (type AMO-C). After supplying 200 mL of deionized water, the prepared solid catalyst was added to the reactor. Pure nitrogen, oxygen, and air were blended in a specific ratio through flow adjustment and injected into the reactor as the oxidation gas. The oxygen partial pressure varied from 0.10 to 0.80 atm, and the total gas flow rate was kept $60 Lh^{-1}$. Simultaneously, the reaction was initiated by adding magnesium sulphite ($0.085\text{--}0.343 \text{ mol L}^{-1}$) which was dissolved within 30 s. A solution of hydrochloric acid and sodium hydroxide was used to adjust the pH. A trace amount of the reaction solution was pipetted at regular intervals, dissolved in hydrochloric acid, and diluted; the solution volume reduced by approximately 1–2%, which slightly influenced the experimental results. The sulphate concentration at various time points t was determined using barium sulphate spectrophotometry. The results indicated that the sulphate concentration increased linearly with increasing reaction time. Because the overall reaction rate was defined as $r = \frac{dc}{dt} = \frac{d[SO_4^{2-}]}{dt}$, it was calculated based on the slope of the curve which represented the relationship between sulphate concentration and reaction time [13].

3. Results and discussions

3.1. Characterisation of the supported catalyst

The SEM images of the molecular sieve before and after cobalt species loading were compared (Fig. 1). The surface of fresh molecular sieve was microporous and relatively smooth (Fig. 1(A)). After loading of the cobalt species, a bunch of irregular clusters of spicules grew unevenly on the carrier surface (Fig. 1(B)). These clusters might be a mixture of cobalt monoxide (CoO) and cobalt trioxide (Co_2O_3). The diameter of a single cluster was approximately 0.1–0.3 μm .

Fig. 2 shows that the N_2 adsorption–desorption isotherm of the supported catalyst was a type III isotherm [34], indicating that the catalyst exhibited a low adsorption capacity at low pressures and that the adsorption capacity increased with increasing pressure. Moreover, the prepared catalyst was confirmed to be a mesoporous material with uniform pore size because well-developed H3 type hysteresis loops were observed [34] on the isotherm; the specific

Table 1
Detection of the components of catalyst samples by XRF.

Component	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	Fe ₂ O ₃	CoO	CaO	K ₂ O	TiO ₂	Cl
(wt%)	46.49	25.42	11.19	2.69	1.50	1.27	0.49	0.44	0.17	0.17

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