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Kinetic and reaction mechanisms of calcium bisulfite catalytic oxidation

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Abstract

In this paper, the oxidation of calcium bisulfite in the presence of ferrous ions as a catalyst is studied in a laboratory scale apparatus at a fixed oxygen partial pressure (21.3 kPa) and at a temperature of 45 °C. The analysis of the experimental results, carried out by using the theory of mass transfer with chemical reaction, indicates that the slow reaction regime has been explored, and the transition from the kinetic to the diffusional subregime identified. A kinetic analysis allows to develop a reaction rate equation, assuming that the bisulfite oxidation in the presence of ferrous ions follows a parallel reaction mechanism; the resulting overall reaction rate has been found to be of first order with respect to ferrous ion concentration and of three halves with respect to bisulfite concentration. Moreover, the catalytic effect of ferrous ions has been compared with that of manganese ions previously studied, showing that ferrous is a catalyst more active than manganese.
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1. Introduction

Calcium bisulfite oxidation is considered to be an important issue in limestone–gypsum flue gas desulfurization processes, since the achievement of a byproduct with a low adverse impact on the environment depends on its proper management. In particular, a precipitate mostly made of gypsum ($CaSO_4 \cdot 2H_2O$) can be obtained which, in comparison with the solid mixture of $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4$ usually produced, is characterized by an inferior chemical oxygen demand (COD) and a less-expensive sludge disposal (Lancia et al., 1999). Numerous studies have been undertaken on the calcium bisulfite oxidation reaction, both in the presence and in the absence of catalyst; several authors have devoted their researches to the comprehension of oxidation reaction path, in particular when the occurrence of a chemical reaction is accompanied by diffusional phenomena (i.e., the diffusion of oxygen in the liquid phase), which cause complex

interactions rather difficult to enlighten, hindering the achievement of coherent conclusions (see Lancia et al., 1999). This circumstance is encountered when the oxidation reaction takes place in the so-called *heterogeneous conditions*, achieved by contacting a sulfurous solution with an oxygen containing gas phase, that is the operating condition in flue gas desulfurization (FGD) processes. On the other hand, the study of sulfite oxidation in *homogeneous conditions* (by contacting a sulfite solution with an oxygen saturated solution) led to relatively consistent results: in a previous work Lancia and coworkers (1996) showed how the following equation appears to be the most appropriate to describe the kinetics of the oxidation reaction for a pH range of 7.5–9 in homogeneous conditions

$$r = k c_M^{1/2} c_{S(IV)}^{3/2}, \tag{1}$$

where r is the reaction rate expressed as moles of SO_4^{2-} produced per unit time and volume, k is the kinetic constant, c_M the catalyst concentration and $c_{S(IV)}$ the total sulfite concentration. A partial agreement exists only on the value of

kinetic constant at 25 °C, which ranges between 2×10^6 and $36 \times 10^6 \, \text{m}^3/\text{mol s}$, while the activation energy ranges from 50 to 150 kJ/mol. Eq. (1) can be interpreted by assuming that the reaction takes place via a free radical mechanism, with a chain initiated by the catalyst autoxidation or by the action of UV light (Bäckstrom, 1927; Dogliotti and Hayon, 1968).

However, independently on homogeneous or heterogeneous oxidation, a well-known result is that the reaction is highly sensitive to operative conditions, such as the liquid phase composition (sulfite concentration, dissolved oxygen, pH), and the presence, even in traces, of catalysts (Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}) and inhibitors (alcohols, phenols, hydroquinone).

This research group has experimentally studied bisulfite oxidation reaction in heterogeneous conditions with and without catalyst, specifically in the presence of manganese (Astarita, 1967; Lancia and Musmarra, 1999; Lancia et al., 1999). More precisely, as for the uncatalyzed reaction, the kinetics of the calcium bisulfite oxidation was found to follow a kinetic equation of zero order in oxygen and three halves in HSO_3^- ions, that is (Lancia et al., 1996)

$$r = k_u c_{HSO_3^-}^{3/2}, \tag{2}$$

where K_u is the uncatalyzed kinetic constant and $c_{HSO_3^-}$ the bisulfite ion concentration, with $k_u = 1.19 \times 10^{-4} \, \text{m}^{3/2}/\text{mol}^{1/2}\text{s}$ at $T = 45\,°C$.

Afterwards, the reaction was carried out in the presence of a catalyst, in a laboratory-scale well-mixed reactor, where the gas phase was a mixture of oxygen and nitrogen, while the liquid phase was obtained by mixing two aqueous solutions, one obtained by dissolving $Ca(OH)_2$ into a SO_2 solution and the other containing manganous sulfate. The results have been interpreted following the approach indicated by Astarita et al. (1983), that is with increasing catalyst concentration, three different reaction regimes were identified, namely the slow kinetic, the slow diffusional and eventually the fast reaction regime, together with the transition from one regime to another. In particular, a parallel reaction mechanism was developed, according to which the overall reaction rate can be calculated as the sum of the uncatalyzed (Eq. (2)) and catalyzed reaction rate, the last being of first order in manganous ion, as expressed by the following equation (Lancia and Musmarra, 1999; Lancia et al., 1999):

$$r = k_u c_{HSO_3^-}^{3/2} + k_c c_{Mn^{2+}}, \tag{3}$$

where k_c is the catalyzed kinetic constant and $c_{Mn^{2+}}$ the bisulfite ion concentration, with $k_c = 0.193 \, \text{s}^{-1}$ at $T = 45\,°C$.

The purpose of the present paper is to study the oxidation reaction in the presence of a different catalyst, namely the ferrous ion added as $FeSO_4$, and to compare the performances of the two catalysts (Fe^{2+} and Mn^{2+}). The choice of the new catalytic species has been effectuated considering the natural presence of iron as Fe_2O_3 in dolomite particles, which are widely used, together with limestone, as sorbents in FGD processes (Al-Shawabkeh et al., 1997; Huss et al., 1982).

2. Experimental apparatus and procedure

A sketch of the laboratory scale apparatus is reported in Fig. 1. The apparatus consists of a thermostated stirred reactor with lines for continuous feeding and discharging of both gas and liquid phase. The reactor is a Pyrex 0.088 m i.d. cylinder with a hemispherical bottom, with two vertical baffles and a liquid overflow, allowing a liquid head of about 100 mm. A two flat blade axial stirrer, located about 70 mm below the liquid overflow, was used to provide through mixing in the liquid phase, with stirrer speed variable in the range $0–13.3 \, \text{s}^{-1}$. The vessel is jacketed, and the temperature was set in all experiments at 45 °C. The gas phase was a mixture of oxygen and nitrogen with oxygen concentrations of 21%; it was taken from cylinders and bubbled in the reactor through a glass tube submerged of about 80 mm below the liquid-free surface. The volumetric flow rate of the gas fed to the reactor, measured by a rotameter (ASA), was kept constant at $1.39 \times 10^{-4} \, \text{m}^3/\text{s}$. Such gas flow rate, in conjunction with the stirrer speed of $6.7 \, \text{s}^{-1}$, gave a liquid hold up of $4.2 \times 10^{-4} \, \text{m}^3$. As concerns the liquid solution, particular attention was paid to its preparation, taking care of setting up two distinct feed solutions, in order to avoid the reaction initiation by catalyst in the tank itself. Thus one tank was filled with a clear solution prepared by dissolving analytical grade calcium hydroxide into analytical grade sulfur dioxide in solution and by diluting with bidistilled water. A second tank was instead filled with a solution of $FeSO_4 \cdot 7H_2O$ in bidistilled water. Referring concentrations to the reactor volume, the Ca^{2+} concentration ranged from 0.5 to $30 \, \text{mol/m}^3$, while the total S(IV) concentration ranged from 0.6 to $64 \, \text{mol/m}^3$, with a pH in the range of 2.0–4.0. The concentration of ferrous sulfate was varied in the range $5 \times 10^{-3}–1 \times 10^{-1} \, \text{mol/m}^3$. The total liquid flow rate was kept constant at the value $9.53 \times 10^{-7} \, \text{m}^3/\text{s}$, corresponding to a mean residence time into the reactor τ of about 440 s.

At the beginning of each experiment, as soon as the liquid in the reactor reached the overflow, agitation was started and the gas stream was introduced. It was assumed that steady state was reached after a time longer than 6τ had elapsed. The oxidation rate at steady state was evaluated by measuring the inlet and outlet liquid streams of the total sulfate concentration; specifically, total sulfate concentration was measured by means of a turbidimeter (Hach DR/2010) at 450 nm wavelengths. Furthermore, in both streams the concentration of total sulfite and Ca^{2+} ion were measured. Total sulfite concentration was measured by iodometric titration using starch as an indicator, while the Ca^{2+} ion concentration was measured by EDTA titration using muresside as an indicator. It is to be noted that each experiment was repeated at least twice, in order to be sure of the obtained results.