



Cobalt impregnated porous catalyst promoting ammonium sulfate recovery in an ammonia-based desulfurization process

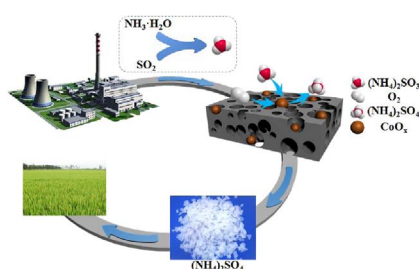


Lidong Wang^{a,*}, Siyu Wu^a, Shuang Liu^a, Shuai Cui^a, Jie Liu^a, Shihan Zhang^{b,*}

^a Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China

^b Key Laboratory of Microbial Technology for Industrial Pollution Control of Zhejiang Province, College of Environment, Zhejiang University of Technology, Hangzhou 310014, China

GRAPHICAL ABSTRACT



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ABSTRACT

Oxidation of ammonium sulfite plays an important role in the ammonia-based wet flue gas desulfurization. In this work, a porous molecular sieve (4A type) supported cobalt catalyst, named as Co-MS-4A, was developed to expedite the oxidation of ammonium sulfite. The experimental results revealed that the oxidation rate was increased by 1.7 to 6.0 times in comparison with the uncatalyzed scenario. The Co-MS-4A catalyst with a nominal Co loading of 1.2 wt% exhibited the highest oxidation rate of $(\text{NH}_4)_2\text{SO}_3$ among the tested catalysts. It was characterized by Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and Energy Dispersive Spectrometer (EDS). The BET data showed that the support retained its mesoporous structure after the cobalt impregnation. Due to the low cobalt loading in the catalyst, no obvious Co diffraction peaks was observed by the XRD. The presence of the cobalt species including Co^{2+} and Co^{3+} in the catalyst was confirmed as depicted by the XPS spectra. The TEM-EDS spectra indicated that cobalt particles distributed uniformly in the tunnels of MS-4A support. Furthermore, the effects of operation parameters, such as ammonium sulfite concentration, catalyst concentration, pH, oxygen partial pressure, and temperature, on the oxidation rate of ammonium sulfite were investigated in a bubbling tank. The apparent activation energy of the ammonium sulfite oxidation catalyzed by Co-MS-4A was $17.67 \text{ kJ} \cdot \text{mol}^{-1}$. The kinetic analysis implied that the catalyzed oxidation of ammonium sulfite is rapid with a Hatta number higher than ~ 4.15 , and that the overall reaction was controlled by the mass transfer of oxygen. The work provides a new approach for recycle of byproduct in ammonia desulfurization without transition metal consumption and pollution.

* Corresponding authors.

E-mail addresses: halburtwang@163.com (L. Wang), shihanzhang@zjut.edu.cn (S. Zhang).

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Nomenclature

a	specific surface area, m^{-1}
c_{O_2}	oxygen concentration at the interfere between liquid phase and solid catalyst, $\text{mol}\cdot\text{L}^{-1}$
c_{cat}	catalyst concentration at the interfere between liquid phase and solid catalyst, $\text{mol}\cdot\text{L}^{-1}$
$c_{\text{S(IV)}}$	sulfite concentration at the interfere between liquid phase and solid catalyst, $\text{mol}\cdot\text{L}^{-1}$
D	diffusion coefficient of oxygen, $\text{m}^2\cdot\text{s}^{-1}$
E	enhancement factor

k_{in}	coefficient of intrinsic reaction rate
k_{L}	mass transfer coefficient of liquid film, $\text{m}\cdot\text{s}^{-1}$
N	mass transfer flux of oxygen, $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
R_{in}	intrinsic reaction rate of sulfite oxidation, $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
R_{obs}	observed reaction rate of sulfite oxidation, $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
T	reaction temperature, K
ν	stirring speed, rpm
α	reaction order of oxygen in the intrinsic reaction
β	reaction order of catalyst in the intrinsic reaction
γ	reaction order of sulfite in the intrinsic reaction

1. Introduction

SO_2 emission imposed serious environmental issues such as acid rain and haze in the past several decades [1–3]. Currently, the wet limestone-gypsum flue gas desulfurization process has been intensively used for SO_2 removal from the flue gas [4,5]. However, it encounters the issues of clogging, insufficient reclamation rate, and low inventory of lime source in China. The ammonia-based desulfurization process is regarded as an excellent solution to the clogging issue [6]. Furthermore, owing to the high reaction rate between the SO_2 and ammonia, the size of the absorber is smaller than that with the conventional gypsum-based process. However, due to the relatively slow oxidation rate of the ammonium sulfite, the reclamation of the desulfurization byproduct as a potential fertilizer is insufficient; it might even re-emit SO_2 and consume the dissolved oxygen in the effluent, so that the secondary environmental pollution is engendered. Hence promoting the oxidation efficiency of ammonium sulfite is a key technical problem for the wide application of ammonia desulfurization.

To address this issue, various transition metal ions, such as Co^{2+} , Mn^{2+} , Fe^{2+} , Cu^{+} , and Ni^{2+} , have been used to promote the oxidation rate of ammonium sulfite. Amongst them, Co^{2+} ion is the most efficient catalyst to enhance the oxidation rate of ammonium sulfite. Literature data [7–10] showed that the rate constant respect to the Co^{2+} varied from 0 to 1.0 depending upon the operation conditions. It should be noted that the dosage of the Co^{2+} ion into the solution can arouse serious contamination on the byproduct and discharge solution as it is difficult to recover the Co^{2+} ion from the spent solution. Furthermore, the dumping of the spent Co^{2+} also increases the cost of the desulfurization process.

Heterogeneous solid catalyst can be a good alternative to the ionic catalyst because it is easy to be recovered from the spent solution. Consequently, a number of porous materials with high specific surface area, such as molecular sieve [11–14], activated carbon [15,16], silicone [17,18], and graphene [19] etc., have been explored and reached a wide application to be served as a support of a catalyst. Currently, our group is developing heterogeneous solid catalyst to promote the magnesium sulfite oxidation. The developed solid supported cobalt catalyst exhibited an excellent ability to promote the oxidation of magnesium sulfite. For example, the oxidation rate of magnesium sulfite increased by 4–6 times with the Co-CNTs and Co-SBA-15 [20,21]. The developed solid catalyst also retained a high catalytic activity after multiple recycling [21]. However, limited information is available on the promotion of ammonium sulfite oxidation. It should be noted that in the magnesium-based process, the primary composition of the sulfite was presented in the form of slurry; however, in the ammonia-based process, the majority of sulfite exists in aqueous solutions. Therefore, the kinetics and reaction mechanisms of sulfite oxidation in the ammonia-based process can be totally different from that in the magnesium-based process.

This work intended to develop a novel solid cobalt-loaded catalyst with a molecular sieve in 4A type (MS-4A) as the support to enhance the ammonium sulfite oxidation. The developed catalyst was

characterized to figure out the active site and species for the catalytic oxidation in the solid catalyst. The kinetics of ammonium sulfite oxidation in presence of this solid catalyst was investigated. Furthermore, the mechanism of heterogeneous catalytic oxidation was revealed. This work can advance the application of heterogeneous solid catalyst for the ammonium-based desulfurization process.

2. Experiment

2.1. Chemicals

The reagents used in this work were as follows: cobalt nitrate hexahydrate (Tianjin Kermel Chemical Reagent, AR, purity $\geq 99.0\%$), hydrochloric acid (Tianjin chemical reagent three factory, hydrogen chloride content of 36%), sodium chloride (Tianjin Beichen Founder Reagent, AR, purity $\geq 99.5\%$), ammonium sulfite (Alfa Aesar Chemical Co., Ltd. AR, purity $\geq 94.0\%$), barium chloride (Tianjin Damao Chemical Reagent, AR, purity $\geq 99.5\%$), sodium hydroxide (Tianjin chemical reagent three factory, AR, purity $\geq 96\%$), glycerol (Tianjin East China Reagent, AR, purity $\geq 99.0\%$), and anhydrous ethanol (TianjinJin Feng Chemical Co., Ltd. AR, purity $\geq 99.7\%$).

The MS-4A is purchased from Tianjin Guangfu Fine Chemical Research Institute as a commercial product. The chemical composition of MS-4A can be expressed as $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 9/2\text{H}_2\text{O}$ with a Si/Al ratio of ~ 2.0 , implying that Al_2O_3 and SiO_2 are two main components in this commercial MS-4A support. Its particle sizes range from 3.0 to 5.0 mm, and the bulk density is $\sim 0.70\text{ g}\cdot\text{cm}^{-3}$.

2.2. Preparation of the Co-MS-4A catalyst

The cobalt-loaded solid catalyst with a nominal cobalt loading of 1.2 wt% was prepared by the impregnation method. 10.0 g MS-4A was immersed in 200 ml $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ solution (2.96 g/L) with a stirring rate of 180 rpm at 25°C for 6 h. The mixtures of MS-4A and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ solution were then settled for another 24 h at room temperature. After that, the obtained MS-4A was dried at 110°C for 12 h, baked at 250°C for 2 h, and calcinated at 400°C for 3 h in the muffle furnace. The prepared cobalt based catalyst, Co-MS-4A, was acquired and stored for use.

2.3. Catalyst characterization

The specific surface area and pore distribution of the prepared catalysts were determined by the N_2 adsorption-desorption method under a temperature of 77 K with the Micromeritics ASAP 2460 analyzer. The specific surface area and pore size distribution of the catalyst were calculated using the Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda method, respectively. The crystalline phases of the prepared catalyst were characterized by X-ray diffraction (XRD, Bruker D8 advance) under the wide-angle (10° – 90°) scanning with a step size of 0.02° . X-ray photoelectron spectroscopy (XPS) was conducted by the ESCALAB 250Xi model energy spectrum under the

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