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Role of CuO in improving NH$_3$ and SO$_2$ capture on nanoporous Fe$_2$O$_3$ sorbents

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GRAPHICAL ABSTRACT
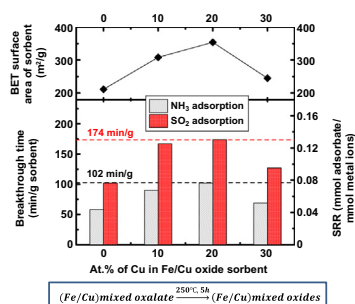
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ABSTRACT

In this work, mixed Fe/Cu oxides as sorbents for SO$_2$ and NH$_3$ removal were investigated. Nanoporous iron oxide mixed with 10, 20 and 30 at.% CuO were prepared by thermal decomposition of the corresponding oxalates at 250 °C for 5 h in air. The mixed Fe/Cu oxalates were obtained from the co-precipitation of iron/copper sulfate and ammonium oxalate during ultrasonication. The physical properties of the oxalate precursors and the resulting mixed Fe/Cu oxides were characterized with SEM, TGA-DSC, FTIR, powder XRD and Mössbauer spectroscopy. The porosity was studied by N$_2$ adsorption-desorption isotherms and small angle X-ray scattering. Evenly dispersed CuO hindered the crystallization of Fe$_2$O$_3$, which significantly increased the specific BET surface area from 211 m^2/g for Fe$_2$O$_3$ to 354 m^2/g for Fe$_{0.8}$Cu$_{0.2}$O$_x$. As a result, SO$_2$ and NH$_3$ adsorption on Fe$_{0.8}$Cu$_{0.2}$O$_x$ were enhanced by about 70% compared to Fe$_2$O$_3$. Compared to Fe$_2$O$_3$-impregnated activated carbons, nanoporous Fe$_{0.8}$Cu$_{0.2}$O$_x$ could capture five times more SO$_2$ per unit weight, which will be attractive for applications in respirators with lower weight and smaller size.

1. Introduction

Activated carbons (ACs) have used in respiratory protective equipment for a long time. The vast number of pores in ACs not only enables good physical adsorption of organic vapors [1–3], but provides large surface areas for the deposition of inorganic compounds. Impregnating ACs with selected salts followed by thermal treatment generally forms well-dispersed nanosized particles or a nm-thin layer of inorganic compounds on the surface of the ACs, which is beneficial for the chemisorption of polar toxic gases like SO$_2$, NH$_3$, HCN, H$_2$S, etc. [4–11]. Previous studies revealed that impregnated ACs treated with a variety of inorganic

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species including Cu, Zn, Co, Ni, Mn, Fe and Al compounds exhibited much higher SO_2 and NH_3 adsorption capacities than the original ACs [12–17]. Nevertheless, one issue regarding impregnated ACs is that carbon accounts for 75–90% of the total weight and is ineffective for adsorbing the above-mentioned inorganic toxic gases. There is always a need to reduce the size and weight of respirators to the user experience. Thus, using nanoporous metal oxides directly as the adsorbents in the absence of ACs may bring benefits. As a prerequisite, the oxides must inherently have high specific surface area to produce enough active sites per unit mass.

Iron oxides, as abundant and environmentally benign compounds, have been of much interest as adsorbents for toxic gases or for wastewater treatment [18–22]. Unfortunately, a very low adsorption capacity for SO_2 was reported [18,19]. Adding a secondary metal component to form Fe-M mixed oxides by doping or forming a solid solution can enhance the properties compared to the individual metal oxides, and some typical examples are $Fe_xCe_{1-x}O_2$, $Mn_{2-x}Fe_xO_3$, TiO_2-Fe_2O_3 and $Fe_{3-x}Cr_xO_4$ [23–25]. Raman et al. [26] reviewed a series of transition metal-substituted iron oxides (Cr, Ti, Mn, Co, Ni, V, Al, Nb) as heterogeneous catalysts for the degradation of recalcitrant organic contaminants. In general, partial substitution of iron by a second metal can generate oxygen vacancies in the case of unequal charge replacement and the particle size and/or pore diameter may be reduced significantly as in $Fe_{3-x}Cr_xO_4$ and $Fe_{2-x}Nb_xO_3$ [27,28].

In recent years, Fe/Cu mixed oxides have been explored as catalysts to treat certain toxic gases such as CO and ammonia perchlorate [29–31]. Compared to the individual iron or copper oxide, the mixture of Fe and Cu in the oxide was able to significantly improve the catalytic activity likely due to the presence of certain synergistic interactions. Large specific surface areas generally mean more active sites, which is key for catalysts or sorbents. Fe/Cu oxides were commonly obtained by heating Fe/Cu mixed hydroxide [29–31]. One issue with this route is that the hydroxide precursors are generally prepared in a very basic environment. Additionally, the prepared Fe/Cu oxides often have low specific surface areas.

Herein nanoporous Fe/Cu binary oxides were synthesized through calcination of the corresponding Fe/Cu oxalate precursors. The physical properties of Fe/Cu oxides and oxalates were characterized by SEM, TGA, FTIR, powder XRD and Mössbauer spectroscopy. The porosities of Fe/Cu oxides were studied by small angle X-ray scattering and N_2 gas adsorption microporosimetry. SO_2 and NH_3 adsorption capacities of Fe/Cu oxide particles were investigated using dynamic flow tests. It demonstrated that adding 20% Cu to form $Fe_{0.8}Cu_{0.2}O_x$ significantly improved SO_2 and NH_3 capacity due to highly increased surface area of the sorbent.

2. Experimental section

2.1. Synthesis of mixed Fe/Cu oxalate hydrate and Fe/Cu oxide

Mixed Fe/Cu oxalate hydrate precursors were prepared from the co-precipitation of $(NH_4)_2C_2O_4$ and a mixture of $FeSO_4$ and $CuSO_4$. Five $(Fe_{1-m}Cu_m)SO_4$ aqueous solutions (m = 0, 10, 20, 30 and 100 at.%) were prepared by mixing $FeSO_4·7H_2O$ powder (Alfa Aesar, 99+%) and $CuSO_4·5H_2O$ powder (Anachemia, 98%) in 400 mL of nano-purified deionized (DI) water (18 MΩ). The concentration of $(Fe_{1-m}Cu_m)SO_4$ was kept at 0.25 M. $(NH_4)_2C_2O_4·2H_2O$ powder (BDH Chemicals, 99.9%) was used as-received to make an $(NH_4)_2C_2O_4$ aqueous solution (0.25 M, 400 mL). Before the reaction, a couple of drops of ~10% ammonia (diluted from 28% to 30% ammonia, 99.9%) were added to adjust the pH of the $(NH_4)_2C_2O_4$ solution to between 7 and 8. Subsequently, 400 mL of the $(NH_4)_2C_2O_4$ solution was added slowly, using a Masterflex peristaltic pump, into the 400 mL $(Fe_{1-m}Cu_m)SO_4$ solution over a

period of 2 h while mild sonication (Branson Sonifier 450, 20 W) was applied. The oxalate precipitates started to form in 10 min. Once the addition of $(NH_4)_2C_2O_4$ was finished, the precipitated Fe/Cu oxalates were centrifuged and washed with DI water three times until the pH reached ~7. Then the samples were dried for 24 h in an oven in air at 60 °C. As a result, five $(Fe_{1-m}Cu_m)$ oxalate precursors (m = 0, 10, 20, 30 and 100 at.%) were prepared.

The as-prepared $(Fe_{0.8}Cu_{0.2})C_2O_4$ precursor was first heated at 250 °C for 3, 4, 5, 6 or 18 h in air in a muffle furnace. The powder XRD patterns of the resulting oxides were compared to ensure the complete decomposition of the precursor. Powder XRD indicated that the strong diffraction peak at 23° (Cu K_α) corresponding to $CuC_2O_4·yH_2O$ was absent after calcination for 5 h. Therefore, all precursors were heated at 250 °C for 5 h respectively to obtain Fe/Cu mixed oxides. Five products α-Fe_2O_3, $Fe_{0.9}Cu_{0.1}O_x$, $Fe_{0.8}Cu_{0.2}O_x$, $Fe_{0.7}Cu_{0.3}O_x$ and CuO were designated as A, B, C, D and E, respectively (see Table 1).

2.2. Sample characterization

SEM images were obtained with a Hitachi S-4700 field emission SEM. Typical imaging conditions include a working distance of 12.5 mm, an accelerating voltage of 5 kV and a beam extraction current of 15 μA. A small amount of oxide powder was dispersed on double-sided carbon tape attached on an aluminum sample puck.

Powder X-ray diffraction patterns of the oxalate precursors and the oxides were collected using a Phillips PW 1720 X-ray generator operated at a voltage of 40 kV and a current of 30 mA. The system is equipped with a Cu Kα radiation source (wavelength = 1.54178 Å) and a diffracted beam monochromator. Typical conditions were a scan rate of 0.05°/step and a dwell time of 40 s/step. The samples were ground into fine powder and put on an aluminum sample holder. Measurements on samples that had adsorbed SO_2 or NH_3 gas were performed immediately after the flow tests finished.

The actual content of Cu in mixed Fe/Cu oxides was determined with a Perkin Elmer Optima 8000 inductively coupled plasma optical emission spectrometer (ICP-OES). ~10 mg of each sample was dissolved in 2 mL of aqua regia solution and waited overnight to dissolve completely. Each solution was then diluted again with 2% HNO_3 to ~1 ppm for ICP-OES measurement. The results are listed in Table 1. It indicates that the experimental results are close to the ideal values.

Small-angle X-ray scattering (SAXS) data were collected using a Bruker-AXS NanoSTAR equipped with a 30 W microfocus Cu K_α source and a Vantec-2000 area detector. The generator operated at a voltage of 45 kV and a current of 650 μA. A 400 μm diameter beam was selected using a series of pinhole collimators and a set of Göbel mirrors. Each oxide sample was ground and packed into a hole (3 mm diameter) on a 0.1 mm thick brass holder, and both sides of the hole were sealed using tape (Scotch® Magic™ 3M Co.). Data were collected for 3600 s per sample and scattering angles ranged from 0.23° to 5.0° (approximately the scattering vector q = 0.016–0.355 $Å^{-1}$). The scattering intensity caused by blank tape was measured using the same holder with tape applied, but no sample.

The experimental SAXS data was fit using a model for spherical pores following Porod's law and the Raleigh equation:

$$I(q) = \frac{A}{q^n} + \frac{B(\sin(qR) - qR\cos(qR))^2}{q^6} + C \tag{1}$$

where the first term determines the scattering from macropores and the second term is related to the mesopores and micropores. A constant background, C, was added to account for background scattering. In Eq. (1), R is the average radius of spherical pores; A and B