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Research article

Breakthrough studies of Co_3O_4 supported activated carbon monolith for simultaneous SO_2/NO_x removal from flue gas

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ABSTRACT

This work investigates the deposition precipitation, pore volume impregnation and hydrothermal methods of synthesizing activated carbon monolith supported metal oxide adsorbent (Co_3O_4/ACM). The hydrothermally synthesized Co_3O_4 activated carbon monolith adsorbent (Hm-Co_3O_4/ACM) demonstrate better adsorption capacity (SO_2 is 123.1, NOx is 130.2 mg/g) than the adsorbents synthesized by the other methods. The adsorbent displayed high affinity to NO_x adsorption where this influence was associated to operation conditions, physical and chemical properties of the adsorbent which were expressed in the plot of the breakthrough curve. Moreover, the surface properties (BET), thermal decomposition (TGA), functional groups (FTIR), chemical composition (XRD) and surface morphology (FESEM) of the adsorbent were investigated. The Langmuir adsorption isotherm fitted the experimental results meanwhile, the thermal regeneration of the adsorbent over two cycles showed an average regeneration efficiency of 94.4% for SO_2 and 94.8% for NOx. Finally, the post regeneration characterization analyses were discussed.

1. Introduction

Greenhouse effects, acid rain, smog and other environmental problems are caused by the emission of gases such as carbon dioxide (CO_2), sulfur dioxide (SO_2) and nitrogen oxides (NO_x) [1,2]. The most widely used pollutants emission control technologies for SO_2 removal is the wet flue gas desulfurization (WFGD) and the selective catalytic reduction (SCR) or the selective non-catalytic reduction (SNCR) for NO_x removal. The ammonia-based WFGD compared with the other WFGD processes has the advantages of higher desulfurization efficiency, lower investment, useful byproducts and does not produce secondary pollution however, the ammonia-based WFGD technology is immature in large scale in industries such as sintering plants while ammonia escape and aerosol phenomena are major concerns [3]. The SCR system has the drawback of poor catalyst durability (coverage of the catalyst by very fine dust particles), ammonia slip, low NO_x reduction and high temperature requirement [2]. Except the control technologies commonly applied in SO_2 and NOx emission control, the simultaneous removal of multi-pollutant has received more attention [4,5].

Adsorption is a simple and cost effective dry process method for removing process gases and vapors from air in a dry process [6]. Comparatively, the dry process is preferred over the wet process in terms of cost and environmental considerations. In the wet process, wastewater is produced and there is reheating energy required for pollutant removal [7]. The dry adsorption option has the advantage of minimum secondary pollution production, low operational cost, regenerable and applicable at lower pollutant concentrations [8,9]. There are several types of solid adsorbent that are used in dry adsorption, but monolith is single out due to its high void fraction, uniform flow distribution, large geometric surface area, resistance to thermal shock, low pressure drop at a high flow rate and high dust tolerance [6,10]. The detailed advantages on the monolith adsorbent are available in the literature [11–13].

The limitations of pressure drop, mass transfer, deactivation and regeneration can be address by systematic studies of adsorbent structures and the impregnation of MOs on the adsorbent. The dispersion of metal oxide (MO) on adsorbents was demonstrated by many researchers [14,15]. The metal oxide, tricobalt tetraoxide (Co_3O_4) has a unique low-temperature activity and its oxidation state changes between Co_3O_4, Co_2O_3, CoO and Co [16]. More detailed information regarding the Co_3O_4 catalyst can be found elsewhere [17,18]. Another aspect of research that is attracting interest is in the improvement, regeneration

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and reusability of adsorbent for eco-friendly disposal with reduction of cost by several cyclic adsorption processes.

Simulated gases in place of flue gas are used in the laboratory in conducting catalytic activity test for simultaneous SO_2 and NO_x removal [19]. In this work, Co_3O_4 active phase was dispersed on activated carbon monolith (Co_3O_4/ACM) by the deposition precipitation, pore volume impregnation and the hydrothermal synthesis methods. Coal was burnt to generate flue gas and was used in the catalytic activity test for the simultaneous SO_2/NO_x removal. The breakthrough curve studies were performed, and adsorption isotherms based on Langmuir and Freundlich were used for the description of adsorption of the SO_2 and NO_x over Co_3O_4/ACM adsorbents. Finally, two cycles of regenerations with FTIR, BET, TGA, FESEM and XRD characterization were used in investigating the adsorbent with adsorption capacity.

2. Materials and methods

2.1. Chemicals

Nitric acid (HNO_3, 65%), Furfuryl alcohol (FA, $C_5H_6O_2$, 98%), urea (CH_4N_2O) and cobalt nitrate hexahydrates ($Co(NO_3)_2.6H_2O$) were purchased from Sigma-Aldrich, Malaysia. All the chemicals and reagents used were of analytical reagent (AR) grade.

2.1.1. Adsorbent

The ceramic monoliths were purchased from Beihai Huihuang Chemical Packing Co. Ltd., China. Table 1 presents the specifications of the monolith structure used.

2.2. Catalyst preparation

2.2.1. Adsorbent carbonization and activation

The monolith was immersed in furfuryl alcohol as the carbon precursor for 20 min and the excess coating solution was with-drawn from the monolith channels by blowing pressurized air followed by drying at 100 °C for 24 h. The monolith was carbonized in a vertical furnace at 800 °C for 4 h and at a heating rate of 5 °C min^{-1} under N_2 flow until it cooled. Activation was carried out by heating the substrate in presence of CO_2 at a heating rate of 5 °C min^{-1} to 350 °C for 2 h. The adsorbent Activated Carbon Monolith was obtained (ACM).

2.2.2. Acid surface modification

ACM was oxidized by complete immersion in HNO_3 for 24 h followed by filtration and washing with deionized water several times and then drying in an oven at 70 °C for 24 h. Finally, the oxidized ACM was obtained.

2.2.3. Pore volume wetness impregnation method

The ACM was impregnated with an appropriate aqueous solution containing single cobalt nitrate hexahydrates ($Co(NO_3)_2.6H_2O$) precursor. The mixture was heated with constant stirring at 70 °C and 300 rpm until the entire liquid evaporated then it was dried at 110 °C for 24 h. Finally, the substrate was heat treated under nitrogen flow at a heating rate of 5 °C min^{-1} up to 500 °C and for 4 h.

Table 1
Specifications of bare monolith.

Monolith	Cells	Chemical compositions
Cross section circular Surface area 1cm^2/g Length 2.50 ± 0.02 mm Diameter 2.50 ± 0.02 mm	Channel square Wall thickness 0.25 ± 0.02 mm Width 1.02 ± 0.02 mm Cells 400 (cpsi)	SiO_2 50.9 ± 1.0% Al_2O_3 35.2 ± 1.0% MgO 13.9 ± 0.5% others < 1%

Table 2
ACM developed by three methods of synthesis.

Metal precursor	Pore impregnation method	Deposition precipitation method	Hydrothermal method
$Co(NO_3)_2.6H_2O$	Im-Co_3O_4/ACM	Dp-Co_3O_4/ACM	Hm-Co_3O_4/ACM

2.2.4. Deposition precipitation method

A closed 350 mL reactor vessel equipped with pH meter, thermometer and magnetic stirrer was loaded with the mixture of 250 mL deionized water, ACM substrate and $Co(NO_3)_2.6H_2O$ precursor. The pH of the solution was adjusted to 3.5 by adding few drops of diluted HNO_3. The mixture was heated to 90 °C and then a solution of urea in 3 mL of water was added. After 18 h, the slurry was cooled to room temperature and filtered. The coated support was thoroughly washed with deionized water and dried at 120 °C for 24 h. After cooling to room temperature, subsequent gradual heat treatment under nitrogen flow at a heating rate of 5 °C min^{-1} to 500 °C and for 4 h was performed.

2.2.5. Hydrothermal method

The metal precursor ($Co(NO_3)_2.6H_2O$) and urea were dissolved in 80 mL deionized water then transferred into a 100 mL Teflon lined stainless steel autoclave, a disc of ACM was added as a growth substrate. Afterwards, the autoclave was sealed and heated to 100 °C for 5 h. The system was cooled to ambient temperature, washed and ultrasonicated for 2 min, the coated substrate and the precursor were annealed under an inert condition at a heating rate of 3 °C min^{-1} up to 300 °C and for 2 h. Table 2 summarizes the developed adsorbents.

2.3. Characterization

The surface functional groups on the adsorbent were examined using Thermo Nicolet AES0200682 Fourier transform infrared (FTIR) spectroscopy which consisted of liquid nitrogen cooled mercury-cadmium-telluride detector and a spectra tech diffuse reflectance accessory. The morphology of the adsorbent was observed through a field emission scanning electron microscope (FESEM, Nova NanoSEM 230, FEI, USA). The specific surface area (S_{BET}) and total pore volume (Vp) were determined by the adsorption and desorption of N_2 at 77 K using (Micrometrics ASAP2020) on powders previously outgassed at 200 °C for 4 h under inert gas flow to remove water and other atmospheric contaminants; S_{BET} was determined according to the Brunauer-Emmett-Teller (BET) method. The TGA experiments were performed using a thermogravimetric analyzer (NetzschSTA409), the system was washed from temperature to 700 °C at a rate of 10 °C/min under flow in air. The X-ray diffraction (XRD) method to analyze the chemical composition of adsorbent was used with an X'Pert Philips PW3040 diffractometer using Cu Kα radiation (2θ range = 20°–80°; step = 0.05° 2θ; time per step = 0.2 s).

2.4. Activity test

A fixed bed reactor made of stainless steel reactor was used to prevent corrosion by the corrosive gases such as SO_2. The schematic diagram of the experimental setup is shown in Fig. 1. Prior to the catalyst activity, the adsorbent was crashed in accordance with the work of Gaudillere et al. [20] and about 1 g of Co_3O_4/ACM adsorbent was placed in the center of the reactor. The adsorbent was sealed by quartz wool and preheated with N_2 at 120 °C for 30 min to remove any adsorbed water and impure gaseous molecules that may be coated on the surface of the adsorbent. The N_2 stream connection was then changed to the flue gas stream for the simultaneous SO_2/NOx removal in atmospheric pressure, a similar work can be found in the literature [21]. A stream of flue gas was produced by burning coal in a vertical tubular