



# Inexpensive metal oxides nanoparticles doped $\text{Na}_2\text{CO}_3$ fibers for highly selective capturing trace HCl from HCl/ $\text{CO}_2$ mixture gas at low temperature



Shuoyang Liang<sup>a</sup>, Zhengyun Fan<sup>b</sup>, Weidong Zhang<sup>b</sup>, Min Guo<sup>a</sup>, Fangqin Cheng<sup>c</sup>, Mei Zhang<sup>a,c,\*</sup>

<sup>a</sup> School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

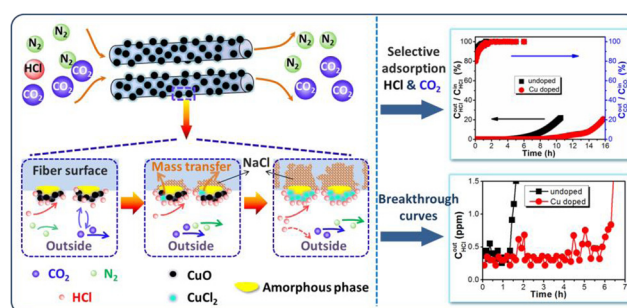
<sup>b</sup> Institute of Technology of Shougang Group, Beijing 100043, China

<sup>c</sup> Shanxi Collaborative Innovation Center of High Value-added Utilization of Coal-related Wastes in Shanxi University, China

## HIGHLIGHTS

- Metals oxides doped  $\text{Na}_2\text{CO}_3$  fibers were prepared via ultrasonic atomization method.
- Breakthrough (< 1ppm) time of the Cu doped sorbent increased from 2 h to 6.5 h.
- Cu doped sorbent showed high HCl selectivity with much low HCl/ $\text{CO}_2$  ratio (1:25 v/v).
- Cu doping strongly promotes the reactivity of  $\text{Na}_2\text{CO}_3$  fibers and HCl at 150 °C.
- The sorbents could maintain stable cyclic performance after three regenerations.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Inexpensive metal doped  
HCl removal  
Selective  
Low temperature

## ABSTRACT

A novel inexpensive metal oxides doped sorbents had been investigated for selective capture of hydrogen chloride (HCl) from HCl/ $\text{CO}_2$  (1:25 v/v) mixture gas at 150 °C. In this work, metals oxides (Fe, Mn, Ce and Cu) grains supported on the  $\text{Na}_2\text{CO}_3$  fibers were firstly prepared via ultrasonic atomization loading method, respectively. The results of HCl removal experiments showed that Cu dopant with optimal content synergistically facilitated HCl capture performance, continuously removing HCl from initial content of 1% to less than 1 ppm as long as 6.5 h. And the HCl capacity reached 3.15 mmol/g, corresponding to the conversion of active component  $\text{Na}_2\text{CO}_3$  was up to 0.89. Meanwhile, the Cu doped sorbent exhibited a strongly selective adsorption of HCl under extreme lower volume ratio HCl/ $\text{CO}_2$  of 1:25. The enhancement of  $\text{Na}_2\text{CO}_3$  reactive activity depended on the highly dispersed copper oxides nanoparticles on the surface of  $\text{Na}_2\text{CO}_3$  fibers. CuO species in copper oxides reacted with HCl to form  $\text{CuCl}_2$ , while the presence of amorphous phase connecting CuO nanoparticles and  $\text{Na}_2\text{CO}_3$  strongly promoted the mass transfer in product layers. The intensification of these two aspects made copper doped adsorbent exhibited significant HCl removal performance. Moreover, during regeneration test, the sorbents could maintain fairly stable cyclic performance within three cycles.

\* Corresponding author at: School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China.

E-mail address: [zhangmei@ustb.edu.cn](mailto:zhangmei@ustb.edu.cn) (M. Zhang).

## 1. Introduction

Blast furnace gas (BFG) is often regarded as a reusable derivative energy source for recycling in the iron and steel industry due to its high calorific value, large heat and high pressure [1,2]. However, it is generally known that trace toxic components are present in BFG based on the complex reaction in the blast furnace [3–5]. In recent years, with the wide application of dry-dusting technology, gas transportation pipelines frequently occurred corrosion, perforation and salt accumulation, which seriously affect the blast furnace gas circulation system [6–9]. As the literature report, the dew point corrosion of stainless steel pipes is mainly attributed to the existence of hydrochloric acid, forming by HCl gas phase dissolving in water drops when the temperature is lower than dew point. Normally, the content of hydrogen chloride (HCl) in BFG is above 300 ppm and the normal temperatures of BFG after dry-dusting process is about 150 °C. Despite trace content in BFG, a large amount of HCl is produced with continuous and efficient operation (0.9 kg HCl per ton of iron), which results in the deactivation of catalysts used for subsequent synthesis and separation processes besides inevitably corrodes the gas transportation pipeline. The existence of carbon dioxide (CO<sub>2</sub>), another acid gas in the BFG with 25% content, frequently causes great difficulty for selectively capturing HCl under extremely lower molecular ratio 0.03: 25 HCl/CO<sub>2</sub>. Hence, it is necessary to develop a dry sorbent, which not only has excellent chlorine capacity, but also overcomes the significant interference effect of CO<sub>2</sub>.

The experiment of solid adsorbents in a fixed bed for acid gas capture is generally accepted among laboratory researches.[10–15] Recently, more chlorination studies are focused on spraying dry adsorbents for HCl removal from hot flue gas (> 400 °C), attributing to quite weak chlorination activity of adsorbents at low temperature [16–21]. Duo et al. [22] discovered Na<sub>2</sub>CO<sub>3</sub> sorbents showed optimal performance of HCl removal at 500 °C, while the reactive activity rapidly decreased when the temperature was decreased. Bhaskar et al. [14] suggested there was a 90% decline of the breakthrough time with Ca-C sorbent for HCl adsorption when the temperature decreased from 350 °C to 200 °C. Besides, the reaction of hydrated lime with HCl, reported by Yan et al. [23], was influenced significantly by the temperature, corresponding with the conversion less than 15% at 170 °C. The reaction and kinetics of calcium hydroxide and HCl at low temperature were systematically studied by Fonseca et al. [24–26] It is pointed out that with the absence of water vapor in simulated gas the utilization rate of active components was almost less than 10%. Therefore, such solid particles as alkali metal or alkaline earth metal oxides are difficult to be employed for HCl adsorption at low temperature.

At present, widely adopted commercial materials for acid gases removal at low temperature include active alumina, mesoporous silica, zeolites, metal–organic frameworks (MOFs) and activated carbon (AC) etc., attributing to their large surface area and easy regeneration [27–30]. By considering capacity and selective, alkali oxides or carbonates supported on porous materials has attracted most attention for adsorbing acid gases at low temperature base on the combination of physical sorption and chemical sorption [31–34]. Micoli et al. [31] demonstrated Na<sub>2</sub>CO<sub>3</sub> supported on AC showed chloride breakthrough capacity of 0.33 mmol/g, which was three times of AC, with atmospheric pressure at 40 °C. However, the chlorine capacity and cost are not satisfactory enough to be widely used in blast furnace industries. Therefore, strongly selective and high capacity of sorbent for HCl removal at low temperature is always challenging but attractive.

Moreover, metal oxides and rare earth oxides attracted much attention on co-adsorption capturing gases [28,35–37]. Balsamo et al. [38,39] reported Cu oxide doped sorbent improved the utilization of ZnO for H<sub>2</sub>S removal at 30 °C, ascribing to its high dispersion and co-adsorption performance of the nanoparticles. Skrzypski et al. [40] suggested the desulfuration test of Cu doped nanostructure ZnO sorbent had been extended by six times than ZnO sorbent at 200 °C, due to the

diffusion acceleration for the presence of Cu. Jiang et al. [41] studied the MnO<sub>x</sub> doped sorbent for selective catalytic reduction of NO, suggesting amorphous Mn on the surface played an important role. Wang et al. [42] also studied CeO<sub>2</sub> doped catalysts for selectively simultaneous removal of NO and Hg<sup>0</sup> under CO<sub>2</sub>-enriched flue gas. Liu et al. [43] demonstrated that HCl was first adsorbed and dissociated on the surface of α-Fe<sub>2</sub>O<sub>3</sub>, enhancing the Hg<sup>0</sup> adsorption reactivity. The pristine CuO-ZnO composite showed more strongly selectivity responding to H<sub>2</sub>S gas than to other gases at 225 °C, mainly due to the formation of CuS, thereby leading to enhanced conductivity reactivity, pointed by Park et al. [44]. In addition, copper oxide supported on AC showed a high efficiency (greater than 90%) of simultaneous adsorption trace HCl and H<sub>2</sub>S at 485 °C, reported by Tseng et al. [45].

Regeneration performance of renewable adsorbents based on acid-base neutralization mechanism has attracted much attention in the gas–solid adsorption process. Among the impregnation process, the surface morphology of supported active components can be controllable in the first preparation process, in which the chemical reaction between substrate and alkali oxide can't be ignored. The pore structure of the support may suffer irreversible destruction during cycling, resulting in a decrease in the adsorption activity of regenerated sample prepared by dissociation and re-impregnation with respect to the fresh one [32,46,47]. Therefore, poor renewable performance, associated with higher economic costs, is not what industrial applications would like to see.

In general, there is a lack of articles on HCl removal from BFG for its extreme condition, namely, selective capturing trace HCl (300 ppm) with the interference of CO<sub>2</sub> (25%) at low temperature (150 °C). Based on these reports on metal oxides as co-adsorption for acid gas capture, we conjecture that the active metal oxides evenly distributed on the adsorbent surface may also enhance its capture performance of HCl. In previous study, we have confirmed that Na<sub>2</sub>CO<sub>3</sub> fibers supported on alumina exhibited favorable adsorption performance of HCl from HCl/N<sub>2</sub> mixture gas at low temperature [48]. In this study, four kinds of metal oxides were successfully loaded to the surface of Na<sub>2</sub>CO<sub>3</sub> fibers sorbents prepared by ultrasonic atomization loading method. Furthermore, the dynamic HCl adsorption tests of these adsorbents were studied in a fixed bed from simulated gas (HCl 1%, CO<sub>2</sub> 25%, N<sub>2</sub> balanced) atmosphere at 150 °C.

## 2. Experimental

### 2.1. Materials

Commercial activated alumina balls (AAB), diameter of 3–5 mm, were produced in Shandong province (China). Ferric nitrate, copper nitrate, manganese nitrate, cerium nitrate and sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>), were all analytical reagents, produced by Sinopharm Chemical Reagent Co., Ltd., China without further purification, respectively.

### 2.2. Preparation of sorbents

The Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> support (NaAAB), namely, Na<sub>2</sub>CO<sub>3</sub> fibers were uniformly covered on the surface of activated alumina balls (AAB), was prepared by wetness impregnation method [48]. Then four species of nitrate (Fe, Cu, Mn, Ce) were dissolved into deionized water to prepare 0.2 mol/L corresponding precursor solution, respectively. The precursor solution was covering on the surface of NaAAB by ultrasonic humidification atomization method. Each 5 g NaAAB were humidified by ultrasonic atomization for 3 min, atomization rate was 30 mL/min. Afterward, the samples were placed in a muffle furnace, controlling the calcination temperature from 30 °C to 500 °C, with the rate of 6 °C/min, and calcined at 500 °C in air for 5 h. The obtained sorbents were named MX-NaAAB, M represents the metal species, and X represents the concentration of the precursor (mol/L). The real loading content of metal

Download English Version:

<https://daneshyari.com/en/article/6578085>

Download Persian Version:

<https://daneshyari.com/article/6578085>

[Daneshyari.com](https://daneshyari.com)