

## REMOVAL OF SO<sub>2</sub> AND NO OVER RICE HUSK ASH (RHA)/CaO-SUPPORTED METAL OXIDES

IRVAN DAHLAN, GUI MEEI MEI, AZLINA HARUN KAMARUDDIN,  
ABDUL RAHMAN MOHAMED, KEAT TEONG LEE\*

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,  
Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

\*Corresponding Author: chktlee@eng.usm.my

### Abstract

The activity of rice husk ash (RHA)/CaO-based sorbent supported with various metal oxides for the removal of SO<sub>2</sub> and NO from simulated flue gas of combustion process has been studied. In this study, RHA/CaO-based sorbents were impregnated with an appropriate metal nitrates solution followed by drying and calcinations, which resulted in the sorbent having the following active phases; MgO, MnO, CoO, ZnO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>. The sorbent-catalysts were tested in a fixed bed reactor by passing mixture gas consisting of SO<sub>2</sub> (2000 ppm), NO (500 ppm), O<sub>2</sub> (10 %), water vapor (50%) and N<sub>2</sub> as a balance at a total flow rate of 150 mL/min and reaction temperature of 87°C. The results showed that RHA/CaO sorbents impregnated with CeO<sub>2</sub> displayed the highest sorption capacity among other impregnated metal oxides for the simultaneous removal of SO<sub>2</sub> and NO. Infrared spectroscopic results indicate the formation of both sulfate (SO<sub>4</sub><sup>2-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) species due to a catalytic role played by CeO<sub>2</sub>.

Keywords: Rice husk ash (RHA), Metal oxides, Sorbent-catalysts, SO<sub>2</sub>, NO.

### 1. Introduction

It is well known that acid rain is one of the most serious environmental issues related to large-scale fossil fuel combustion, especially in urban areas. Sulfur oxides (SO<sub>x</sub>) and nitric oxides (NO<sub>x</sub>) are the main anthropogenic acid gases that not only lead to formation of acid precipitation, but also impose adverse effects on human health, aquatic ecosystems, crops and manmade materials. Typically, SO<sub>x</sub> and NO<sub>x</sub> in flue gases consist of more than 98% of sulfur dioxide (SO<sub>2</sub>) [1]

and over 90-95% of nitric oxide (NO) [2]. Therefore, considerable attention has been given to remove SO<sub>2</sub> and NO from flue gas combustion system. Nevertheless, the most common technology used today is still using two separated systems to remove these pollutants. For example, the SNOX process of Haldor Topsoe combines the wet-gas sulfuric acid process for SO<sub>2</sub> removal and the selective catalytic reduction (SCR) process for the removal of NO [3, 4].

Thus, particular efforts have been directly made to find a suitable method of simultaneous removal of SO<sub>2</sub> and NO. The dry sorption method is now considered to be the most attractive way to treat waste gases containing SO<sub>2</sub> and NO. These methods have the advantages of being simple with less equipment, lower capital and operating costs, and limited secondary waste generation [5, 6]. Unfortunately, only few works have been reported to remove NO and SO<sub>2</sub> simultaneously by the dry method [7, 8], especially using siliceous materials such as rice husk ash (RHA). RHA is an agricultural waste material that available abundantly in rice-producing countries such as Malaysia.

Previously, we have reported the sorption characteristics of SO<sub>2</sub> over the RHA/CaO sorbent [9, 10]. However, this sorbent was unable to remove NO gases. Currently, a wide range of metals/metal oxides [11, 12] and activated carbon-supported metal oxides [13, 14] have been reported to have good activities for NO removal from waste gases. In this current work, RHA/CaO sorbent was prepared by employing impregnation method with various metal oxides. This sorbent was then tested for SO<sub>2</sub> and NO removal activity and characterized by X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared (FTIR).

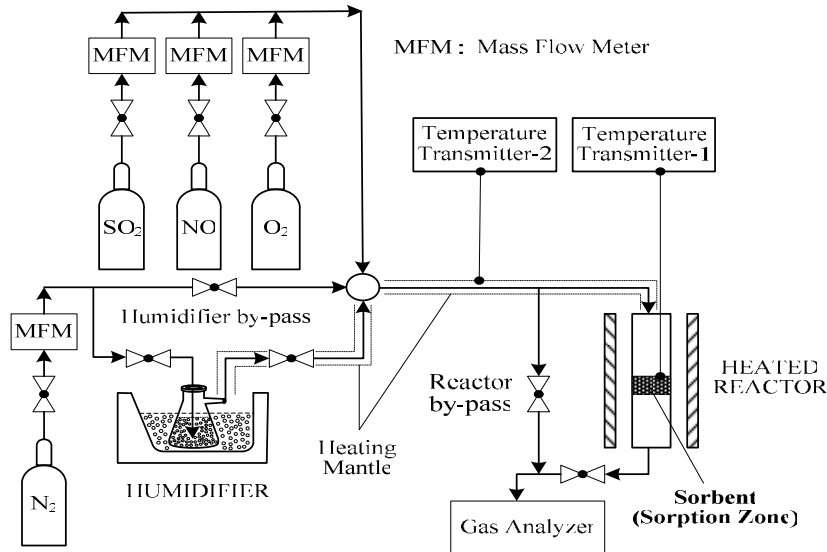
## **2. Materials and Methods**

### **2.1. Materials and preparation of RHA-based sorbent**

The raw rice hush ash (RHA) used in this work is collected directly without any pretreatment from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Nibong Tebal, Malaysia and the CaO was obtained from BDH Laboratories, England. Prior to use, the RHA was sieved to produce less than 200 µm particle size. The chemical composition of raw RHA is 68.0% SiO<sub>2</sub>, 2.30% K<sub>2</sub>O, 1.20% P<sub>2</sub>O<sub>5</sub>, 0.71% MgO, 0.59% CaO, 0.32% SO<sub>3</sub>, 0.32% Cl<sub>2</sub>O, 0.16% Al<sub>2</sub>O<sub>3</sub>, 0.40% others and 26.0% LOI. The preparation of the sorbent proceeded in two steps. Water hydration method [6] was used to prepared RHA/CaO sorbent based on the optimum hydration conditions reported in our previous studies [9]. Then, pore volume impregnation method [13] was separately employed to obtain various RHA/CaO-supported metal oxides (5 wt.%), which were prepared by thermal decomposition of the metal nitrates, i.e: Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Acros, 99%); Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Acros, 99%); Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (Fluka, 98%); Mn(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O (Fluka, 97%); Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Fluka, 99%); Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (Fluka, 97%); and Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (Fluka, 98%). The sorbent obtained in the powder form was then pelletized, crushed and sieved in order to achieve the required particle size (250–300 µm) for the sorption capacity/activity test toward SO<sub>2</sub>/NO by subjecting it to simulated flue gas.

## 2.2. Activity test

The activity of the sorbent toward SO<sub>2</sub> or NO is expressed here as SO<sub>2</sub> or NO sorption capacity and is defined by the weight of SO<sub>2</sub> or NO captured from the flue gas per gram sorbent [15]. The sorption capacity experiments were conducted in a fixed bed reactor attached to an experimental rig as shown in Fig. 1.



**Fig. 1. Schematic Diagram of the Experimental Set-up for Simultaneous Removal of SO<sub>2</sub> and NO.**

The sorbent (0.5 g) was dispersed on the borosilicate glass wool (0.05 g) in the center of the reactor. The simulated flue gas with flow rate 150 mL/min was normally composed of 2000 ppm SO<sub>2</sub>, 500 ppm NO, 10% O<sub>2</sub>, 50 % H<sub>2</sub>O and N<sub>2</sub> as a balance was subsequently passed through the sorbent at a reaction temperature of 87°C. Prior to each run, the sorbent bed was humidified for 15 min by passing N<sub>2</sub> gas through the humidification system with 50% relative humidity. The concentration of the flue gas was measured using a Portable Flue Gas Analyzer IMR 2800P before and after the sorption process. The concentrations of SO<sub>2</sub>/NO were recorded continuously for every minute until 60 min. The amount of SO<sub>2</sub>/NO captured by the sorbent was evaluated from the time the sorbent could maintain 100% removal of SO<sub>2</sub>/NO until it shows negligible activity (the outlet SO<sub>2</sub>/NO concentration becomes the same as the inlet concentration) or until 60 min operation.

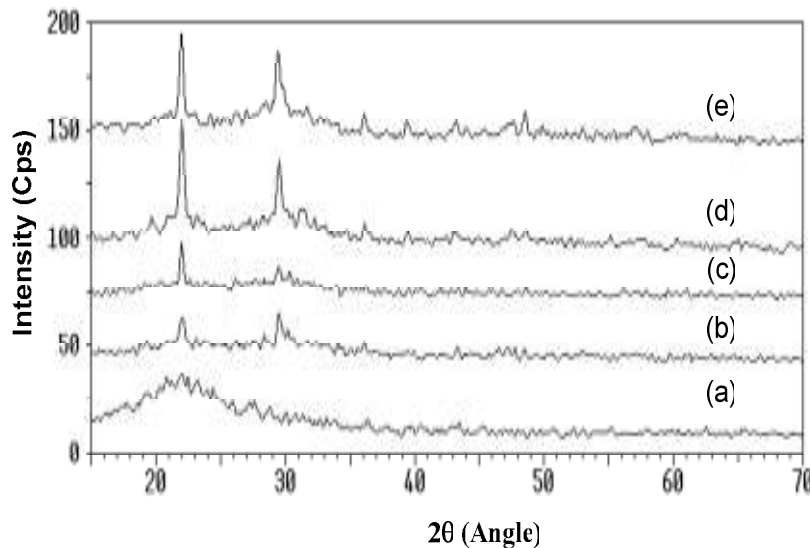
## 2.3. Sorbent characterization

The chemical composition of raw RHA and metal loading of the RHA-based sorbent were analyzed using Rigaku RIX 3000 X-ray Fluorescence (XRF)

spectrometer. X-ray diffraction (XRD) spectrum was recorded on a Siemens D5000 X-ray diffractometer to determine the phases present in the sorbent in the range of diffraction angle ( $2\theta$ )  $10^\circ$ – $70^\circ$  at a sweep rate of  $1^\circ/\text{min}$ . The Fourier transform infrared (FTIR) spectrum was carried out on a Perkin-Elmer FTIR 2000 spectrometer over the frequency range of  $4000$  to  $400\text{ cm}^{-1}$ .

### 3. Results and Discussion

The X-ray diffraction patterns of the raw RHA and as well as prepared RHA/CaO sorbent supported with ZnO, MnO, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, respectively, are shown in Fig. 2. The X-ray reflections of amorphous silica from raw RHA are observed with a broad peak around  $2\theta \sim 22^\circ$  diffraction angle [16, 17]. Whereas, the prepared RHA/CaO sorbents supported with various metal oxides displayed poor crystallinity with the diffraction lines due to only silica ( $2\theta \sim 22^\circ$ ) and calcite ( $2\theta \sim 29.4^\circ$ ) [18] are visible. No diffraction lines attributed to ZnO, MnO, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> crystal phases obviously appeared in the prepared RHA/CaO sorbents, indicating that these metal oxides were highly dispersed on the RHA/CaO surface.



**Fig. 2. X-ray Diffraction Patterns for: (a) Raw RHA and RHA/CaO Sorbent Supported with (b) ZnO, (c) MnO, (d) Fe<sub>2</sub>O<sub>3</sub>, (e) CeO<sub>2</sub>.**

In order to compare the performance of these prepared sorbents, activity tests were carried out. Table 1 shows the sorption capacity for simultaneous removal of SO<sub>2</sub> and NO for RHA/CaO-supported metal oxide sorbents in terms of the time for sorbent can maintain 100% removal and the amount of SO<sub>2</sub> and NO being absorbed. It was observed that sorption capacity of each sorbent in removal of SO<sub>2</sub> and NO are different. The longer the time of the sorbent can maintain 100% removal of SO<sub>2</sub> and NO, the higher the amount of SO<sub>2</sub> and NO were removed

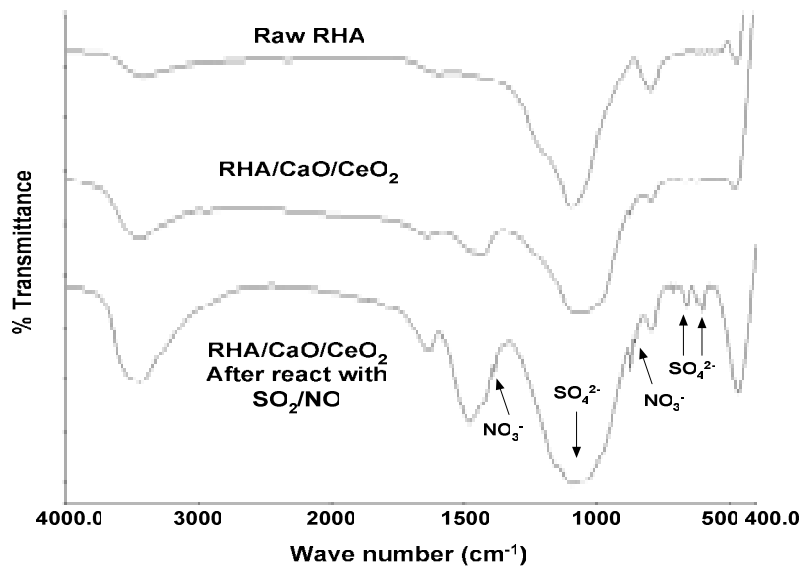
from simulated flue gas. It was found that most of the supported metal oxides exhibit good result in simultaneous removal of SO<sub>2</sub>/NO. However, there were no significant differences in the sorption capacity during 100% SO<sub>2</sub> removal over RHA/CaO sorbent-supported with MgO, CoO, ZnO and Al<sub>2</sub>O<sub>3</sub> indicating that reaction rate for SO<sub>2</sub> removal was almost similar under the operating conditions used. A significant improvement in the SO<sub>2</sub> sorption capacity was achieved when RHA/CaO sorbent were impregnated with MnO, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. On the other hand, RHA/CaO sorbent supported with ZnO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, shows maximum NO removal during 60 min operation time. Nevertheless, only a small amount of NO was removed when MgO was impregnated to RHA/CaO sorbent. The difference of SO<sub>2</sub>/NO sorption capacities between the active phases may be due to the characteristic nature and the reaction mechanism of these sorbents. RHA/CaO-supported CeO<sub>2</sub> exhibits a higher sorption capacity than other supported metal oxides for removing SO<sub>2</sub> and NO simultaneously.

**Table 1. Sorption Capacity of Different RHA/CaO-Supported Metal Oxide Sorbents for Simultaneous Removal of SO<sub>2</sub> and NO.**

RHA/CaO-supported metal oxide	Time during 100% removal (min)		Sorption capacity (mg pollutant/g sorbent)	
	SO <sub>2</sub>	NO	SO <sub>2</sub>	NO
MgO	13	3	10.218	0.138
MnO	20	16	15.720	0.736
CoO	16	35	12.576	1.610
ZnO	9	60	7.074	2.761
Al <sub>2</sub> O <sub>3</sub>	11	60	8.646	2.761
Fe <sub>2</sub> O <sub>3</sub>	23	60	18.078	2.761
CeO <sub>2</sub>	36	60	28.296	2.761

The RHA/CaO-supported CeO<sub>2</sub> sorbent was further subjected to FTIR analysis to characterize specific functional group. The corresponding FTIR spectrums of raw RHA, RHA/CaO-supported CeO<sub>2</sub> sorbent before and after subjected to SO<sub>2</sub>/NO are plotted in Fig. 3. The spectrums showed the raw RHA and prepared sorbents were mainly composed of amorphous silica due to a band situated around 460-470 cm<sup>-1</sup> (Si-O-Si band), 795 cm<sup>-1</sup> (Si-O-Si symmetric) and 1100 cm<sup>-1</sup> (Si-O-Si asymmetric) [19-22]. Moreover, the band around 3450 cm<sup>-1</sup> is typically caused by hydroxyl groups or adsorbed water due to O-H stretches. Since the sorbent was prepared from RHA, this also can be caused by silanol groups [20, 22]. On the other hand, after RHA/CaO-supported CeO<sub>2</sub> sorbent was subjected to SO<sub>2</sub>/NO gases, the products of the reaction were detected, mainly sulfate (SO<sub>4</sub><sup>2-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) species. These species are characterized by S-O bending near 600 cm<sup>-1</sup>, a single peak close to 657 cm<sup>-1</sup> and a broad band due to S-O stretching at around 1050-1100 cm<sup>-1</sup>. Furthermore, a single peak close to 1640 cm<sup>-1</sup> related to hydroxyl groups (O-H bending) was

also appeared [20, 23]. Additionally, a slight/weak band around  $853\text{ cm}^{-1}$  and  $1384\text{ cm}^{-1}$  are detected for nitrate ( $\text{NO}_3^-$ ) species [23, 24].



**Fig. 3. FTIR Spectra of the Raw RHA, RHA/CaO-Supported with  $\text{CeO}_2$  and after React with Simulated Flue Gas.**

As many authors have shown that the presence of  $\text{NO}$  together with  $\text{SO}_2$  can enhance the sorption capacity of calcium-based sorbents [8, 25-27], whereby the existence of  $\text{SO}_2$  and  $\text{NO}$  accelerated the removal of each other, respectively. In this study, it was also assumed that metal oxide, particularly  $\text{CeO}_2$  plays a catalytic role in simultaneous removal of  $\text{SO}_2$  and  $\text{NO}$ .  $\text{CeO}_2$  has been reported to have sufficient oxidation activity at active centers to promote oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  and allow the sorption of  $\text{SO}_2/\text{SO}_3$  (at basic sites) with formation of sulfates [28]. At the same time, oxidation and sorption of  $\text{NO}$  to form nitrates would also take place. Apart from that, catalytic activity of the RHA/CaO-supported  $\text{CeO}_2$  is closely related to their surface area and the degree of crystallinity, and this needs further study.

#### 4. Conclusions

In this study, RHA/CaO supported with various metal oxides has been prepared to investigate the removal of  $\text{SO}_2$  and  $\text{NO}$  from simulated flue gas. It was found that RHA/CaO-supported  $\text{CeO}_2$  shows higher sorption capacity among other supported metal oxides and it also exhibits good result in simultaneous removal of  $\text{SO}_2/\text{NO}$ . The presence of  $\text{CeO}_2$  in the RHA/CaO sorbent plays a catalytic role in simultaneous removal of  $\text{SO}_2$  and  $\text{NO}$  which results in the formation of sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) species. Although the mechanism of simultaneous removal of  $\text{NO}$  and  $\text{SO}_2$  is still under investigation in the laboratory, this indicates

that RHA/CaO-supported CeO<sub>2</sub> sorbent could be a promising sorbent to be used in commercial processes.

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