



Rice husk ash sorbent doped with copper for simultaneous removal of SO₂ and NO: Optimization study

Lee Chung Lau, Keat Teong Lee*, Abdul Rahman Mohamed

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

ARTICLE INFO

Article history:

Received 13 April 2010

Received in revised form 2 July 2010

Accepted 21 July 2010

Available online 30 July 2010

Keywords:

Rice husk ash
Desulfurization
Denitrification

ABSTRACT

In order to reduce the negative impact of coal utilization for energy generation, the pollutants present in the flue gas of coal combustion such as sulfur dioxide (SO₂) and nitrogen oxide (NO) must be effectively removed before releasing to the atmosphere. Thus in this study, sorbent prepared from rice husk ash that is impregnated with copper is tested for simultaneous removal of SO₂ and NO from simulated flue gas. The effect of various sorbent preparation parameters; copper loading, RHA/CaO ratio, hydration period and NaOH concentration on the sorbent desulfurization/denitrification capacity was studied using Design-Expert Version 6.0.6 software. Specifically, Central Composite Design (CCD) coupled with Response Surface Method (RSM) was used. Significant individual parameters that affect the sorbent capacity are copper loading and NaOH concentration. Apart from that, interaction between the following parameters was also found to have significant effect; copper loading, RHA/CaO ratio and NaOH concentration. The optimum sorbent preparation condition for this study was found to be 3.06% CuO loading, RHA/CaO ratio of 1.41, 8.05 h of hydration period and NaOH concentration of 0.80 M. Sorbent characterization using SEM, XRD and surface area analysis were used to describe the effect of sorbent preparation parameters on the desulfurization/denitrification activity.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Increasing world population and rapid economic development has caused the worlds' energy consumption to increase annually. In tandem with this, the quantity of power plants worldwide has also been increasing rapidly especially in developing countries like China and India to ensure adequate supply of energy. The thought of renewable energy such as biomass, solar, hydroelectric, geothermal and wind energy being an alternative is not forthcoming considering their uncertainty and instability in ensuring long term energy security. Therefore, renewable energies could not be treated as significant sources of energies yet, at least for the time being. The main sources of fuel used for energy production in power plants are fossil fuels like petroleum, natural gas and coal. Coal, which is relatively cheaper and in abundance as compared to other fossil fuels is widely used over the world and its consumption rate has been increasing due to the volatility of oil and natural gas prices. Nevertheless, the combustion of coal in power plants emit pollutants to the atmosphere, causing severe air pollution which affects the ecosystems including human beings; namely global warming and acid rain.

Two of the main air pollutants produced are sulfur oxides (SO_x) and nitrogen oxides (NO_x). SO_x is produced when sulfur compound in coal reacts with oxygen in the air during combustion and 98% is released as sulfur dioxide (SO₂) [1]. SO₂ with the existence of oxygen in the atmosphere would form sulfur trioxide (SO₃) which would subsequently be hydrated by water in the air to produce sulfuric acid and finally drop to earth as acid rain. On the other hand, NO_x is formed due to the oxidation of molecular nitrogen in the combustion air at high temperature, with 90–95% consisting of nitrogen oxide (NO) [2]. NO could form photochemical smog after reacting with ozone which can damage human respiratory system [3]. In addition, nitrogen oxide is also recognized as an acid rain precursor and one of the greenhouse gases with high global warming potential. Therefore, there are necessities to develop technologies to abate the release of these air pollutants to the atmosphere.

For SO₂ emission control, wet type flue gas desulfurization (FGD) technology using calcium based sorbents such as calcium oxide and calcium hydroxide are commonly adopted in large scale coal-fired power plants and industrial boilers [4]. However, this wet type method requires extensive investment cost due to high equipment cost and requirement to handle corrosive liquid. As an alternative, dry type FGD which is cheaper and simpler with lower capital cost would be a better option for developing countries like China and India which has high energy consumption growth rate but lower investment ability when it comes to environmental abatement system. In addition, dry type FGD generates solid waste that avoids

* Corresponding author. Tel.: +60 4 5996467; fax: +60 4 5941013.
E-mail address: chktlee@eng.usm.my (K.T. Lee).

Table 1
Range and levels of sorbent preparation parameters.

Parameters	Coding	Units	Levels				
			$-\alpha$	-1	0	1	α
Copper loading	x_1	%	0	3.04	7.50	11.96	15.00
RHA/CaO ratio	x_2	–	0.50	1.41	2.75	4.09	5.00
Hydration period	x_3	h	4.00	8.05	14.00	19.95	24.00
NaOH concentration	x_4	mol/dm ³	0	0.20	0.50	0.80	1.00

the requirement to handle corrosive liquid that is generated in wet type FGD. The solid waste generated could also be utilized as fertilizer in order to avoid waste generation [5]. Nevertheless, SO₂ removal efficiency and sorption capacity for sorbents used in dry type FGD is not high enough for commercial application. Thus, more research is required to develop sorbents with higher SO₂ removal efficiency and sorption capacity. Recently, research interests are concentrated at siliceous calcium based sorbents extracted from waste material. For instance, Lee et al. and Shi and Xu reported the use of coal fly ash while Dahlan et al. utilized rice husk ash [1,4–6]. In another study, oil palm ash was also used to synthesize the sorbent [7]. On the other hand, for denitrification process (NO removal), selective catalytic reduction (SCR) is the more popular choice using catalyst-support type sorbent. Some of the sorbents under research are Cu–Mn–CeO_x/Al₂O₃/Al Alumite catalyst [8], zirconia-supported cobalt catalyst [9], Rh/Al₂O₃ catalyst [10] and Co₃O₄/TiO₂ catalyst [11]. On top of that, some catalysts with activated carbon as support are also investigated by Zhu et al. [12,13]. In that study, copper oxide and vanadium oxide were used as active components to reduce NO by NH₃.

The main research interest in this study lies with the utilization of rice husk ash, a natural waste material which has no market value, by converting it to sorbent capable of absorbing air pollutants. Rice husk ash is mainly composed of amorphous silica which could undergo pozzolanic reaction with calcium hydroxide to give a complex calcium silicate hydrate which is capable of adsorbing sulfur dioxide [14]. However, unlike previous study on the preparation of sorbent prepared from siliceous material which is only used to remove SO₂, the sorbent prepared in this study will be focus on simultaneous removal of SO₂ and NO. The challenge lies in using appropriate additives like sodium hydroxide [15] and metal oxides [16]. The addition of sodium hydroxide could accelerate the hydration process that forms more reactive silicate species that has high surface area and good SO₂ sorption capacity. On the other hand, the addition of metal oxides that are capable to catalyze denitrification reactions will subsequently lead to simultaneous removal of SO₂ and NO. Although Dahlan et al. has reported various metal oxide that can be used for simultaneous removal of NO, however most of the metal oxides used are derived from expensive metal such as cerium, and thus this devoid the purpose of synthesizing low cost sorbent [16]. Thus in this study, a lower cost metal oxide, copper will be used to synthesize sorbent with NaOH/CaO/rice husk ash. In short, the aim of this study is to analyze the effect of sorbent preparation parameters towards the CuO/NaOH/CaO/rice husk ash sorbent for simultaneous removal of SO₂ and NO. The preparation parameters studied are copper loading, the ratio between raw rice husk ash and calcium oxide (RHA/CaO ratio), hydration period and NaOH concentration.

2. Experimental

2.1. Sorbent preparation

Raw rice husk ash (RHA) was collected directly from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Nibong Tebal, Malaysia and utilized without any pretreatment, except it was grinded

to obtain particle size less than 200 μm. Then, RHA was mixed with calcium oxide (CaO, BDH Laboratories, England) at specific ratio and undergoes water hydration process at 70 °C for a specific hydration period in a 250 ml conical flask containing sodium hydroxide (NaOH) (Sigma–Aldrich) solution at specific concentration. The slurry formed was filtered and dried completely at 85 °C. After that, appropriate amount of copper nitrate hemipentahydrate (Cu(NO₃)₂·5/2H₂O, Sigma–Aldrich) was added to the sorbent by wet impregnation method. Resulting sorbent was dried and calcined in static air at 600 °C for 4 h. Finally, the sorbent was pelletized, crushed and sieved to obtain particle size in range of 200–300 μm and stored for experimental use.

2.2. Designs of experiments and statistical analysis

The effect of four sorbent preparation parameters on the resulting sorbent's desulfurization/denitrification activity will be studied using Central Composite Design (CCD) coupled with Response Surface Method (RSM). This was executed using Design-Expert Version 6.0.6 (Stat-Ease, Inc.) software. The CCD consists of a two level full factorial design (2⁴ = 16), eight axial points and six center points. The four parameters are copper loading, RHA/CaO ratio, hydration period and NaOH concentration. The range and levels of the parameters is listed in Table 1. The α -value in this study was fixed at 1.68 (rotatable). A mathematical model was then developed in order to obtain a regression analysis of the experimental data. The polynomial equation that correlates the sorbent denitrification/desulfurization activity to the sorbent preparation parameters by linear, quadratic, cubic and interaction terms is shown in Eq. (1);

$$y = a_0 + \sum_{i=1}^4 a_i x_i + \sum_{i,j=1}^4 a_{ij} x_i x_j + \sum_{i=1}^4 a_{ij} x_i^2 + \sum_{i,j,k=1}^4 a_{ijk} x_i x_j x_k + \sum_{i=1}^4 a_{iii} x_i^3 \quad (1)$$

where y is the predicted sorbent sorption capacity (mg pollutant/g sorbent), a_0 is the offset term, a_i is the linear effect, a_{ij} is the first order interaction effect, a_{ii} is the squared effect, a_{ijk} is the second order interaction effect and a_{iii} is the cubic effect. In addition, every term in the equation was evaluated for its statistical significance. Subsequently, the optimum sorbent preparation conditions were identified using the model developed.

2.3. SO₂ and NO sorption activity study

SO₂ and NO sorption capacity of the sorbent were tested using a fixed bed test rig. 0.5 g of sorbent supported by glass wool was placed in the middle of a heated tubular reactor. Simulated flue gas containing SO₂ (2000 ppm), NO (500 ppm), O₂ (10%) and balance N₂ at a flow rate 150 ml/min was then initiated to flow pass the sorbent. Prior to contact with the sorbent, N₂ was passed through a humidification system which consists of two conical flasks immersed in water bath at specific temperature in order to humidify the flue gas. Reaction temperature was held constant at 150 °C throughout the experiment for isothermal analysis. The outlet gas was analyzed continuously by an IMR 6000 flue gas analyzer to measure the concentration of SO₂ and NO. In this study, only the

Table 2
Experimental design matrix and results.

Sorbent code	Experimental parameters				SO ₂ sorption capacity (mg/g)	NO sorption capacity (mg/g)
	CuO loading, x_1 (%)	RHA/CaO ratio, x_2 (no unit)	Hydration period, x_3 (h)	NaOH concentration, x_4 (mol/dm ³)		
R1	7.50	5.00	14.00	0.50	7.20	1.73
R2	11.96	4.09	19.95	0.20	4.20	0.98
R3	11.96	1.41	19.95	0.80	5.70	1.43
R4	7.50	2.75	14.00	0.50	6.00	1.50
R5	7.50	2.75	14.00	0.50	5.70	1.35
R6	3.04	4.09	19.95	0.80	8.40	2.10
R7	11.96	1.41	8.05	0.80	7.50	1.88
R8	11.96	4.09	8.05	0.20	3.90	0.98
R9	7.50	2.75	24.00	0.50	6.90	1.73
R10	15.00	2.75	14.00	0.50	5.40	1.50
R11	7.50	2.75	14.00	0.50	5.10	1.28
R12	7.50	2.75	14.00	0.50	6.00	1.58
R13	7.50	2.75	4.00	0.50	6.60	1.65
R14	3.04	1.41	19.95	0.20	7.20	1.80
R15	3.04	4.09	8.05	0.80	6.60	1.58
R16	7.50	2.75	14.00	0.00	3.60	0.90
R17	7.50	2.75	14.00	0.50	6.30	1.58
R18	7.50	2.75	14.00	1.00	4.80	1.20
R19	7.50	0.50	14.00	0.50	6.60	1.80
R20	3.04	1.41	8.05	0.20	4.20	0.98
R21	0.00	2.75	14.00	0.50	5.70	1.65
R22	3.04	1.41	19.95	0.80	11.10	3.38
R23	3.04	1.41	8.05	0.80	12.60	3.15
R24	11.96	4.09	8.05	0.80	7.20	1.73
R25	3.04	4.09	8.05	0.20	7.50	1.95
R26	11.96	1.41	19.95	0.20	3.60	0.90
R27	3.04	4.09	19.95	0.20	6.30	1.65
R28	11.96	1.41	8.05	0.20	4.50	1.20
R29	11.96	4.09	19.95	0.80	5.70	1.50
R30	7.50	2.75	14.00	0.50	6.30	1.65

amount of time sustained for 100% removal of SO₂ and NO was recorded for further analysis. Knowing the gas flow rate and concentration, the sorbent sorption capacity was calculated based on the mass balance between the inlet and outlet gas. The schematic diagram of the experimental rig is shown in Fig. 1 [17].

2.4. Characterization of sorbent

Selected sorbents were characterized with scanning electron microscopy (SEM), X-ray diffractometry (XRD) and nitrogen adsorption–desorption analysis. These analyses were conducted to investigate the surface morphology, phases composition and specific surface area (and also average pore size and pore volume) of the sorbents, respectively. SEM was performed on a Leo Supra 35Vp-24-58 at accelerating voltage of 3 kV while a Siemens Diffractometer D5000 was used for XRD at a scan rate of 0.05°/s. On the other hand, Autosorb IC Quantachrome analyzer was used for nitrogen adsorption–desorption analysis.

3. Results and discussion

3.1. Development of regression model

There are two responses taken into consideration in this study which are sorption capacity of sorbents at 100% removal of SO₂ and NO, respectively. The experiment design matrix and results are shown in Table 2. From Table 2, the sorption capacity of SO₂ and NO ranged from 3.60 to 12.60 mg SO₂/g sorbent and 0.90 to 3.38 mg NO/g sorbent. Apart from that, six center points (R4, R5, R11, R12, R17 and R30) are included and scattered in the design matrix to investigate the experimental error. The experimental errors were calculated as 7.0% for SO₂ removal and 8.9% for NO removal. Using Design-Expert 6.0.6 software, the responses of SO₂ and NO removal

are correlated with the sorbent preparation parameters and are shown in Eqs. (2) and (3) respectively.

$$\begin{aligned}
 y_{\text{SO}_2} = & 16.39 - 5.83x_1 - 2.10x_2 - 0.17x_3 + 5.91x_4 + 0.23x_1^2 \\
 & + 1.60x_2^2 + 1.45x_3^2 - 1.13x_4^2 + 1.07x_1x_2 - 1.07x_1x_3 \\
 & - 0.64x_1x_4 + 0.11x_2x_3 - 2.04x_2x_4 - 0.75x_3x_4 + 1.97x_1^3 \\
 & + 0.92x_2^3 - 1.73x_4^3 + 1.93x_1x_2x_4 + 1.18x_2x_3x_4 \quad (2)
 \end{aligned}$$

$$\begin{aligned}
 y_{\text{NO}} = & 1.95 - 0.74x_1 - 0.28x_2 + 0.025x_3 + 0.75x_4 + 0.098x_1^2 \\
 & + 0.19x_2^2 + 0.15x_3^2 - 0.15x_4^2 + 0.15x_1x_2 - 0.19x_1x_3 \\
 & - 0.11x_1x_4 - 0.025x_2x_3 - 0.30x_2x_4 - 0.013x_3x_4 + 0.24x_1^3 \\
 & + 0.087x_2^3 - 0.22x_4^3 + 0.11x_1x_2x_3 + 0.31x_1x_2x_4 + 0.11x_2x_3x_4 \quad (3)
 \end{aligned}$$

where y_{SO_2} and y_{NO} represent predicted SO₂ and NO sorption capacity of sorbent, respectively.

The R^2 values for Eqs. (2) and (3) are 0.9286 and 0.9605, respectively. This indicates that only 7.14% and 3.95% of the total variability is not explained by the regressors in the model for SO₂ and NO sorption capacity, respectively. This result therefore verifies that the developed model could represent and predict the actual simultaneous desulfurization and denitrification activity within the range of parameters studied.

3.2. Analysis of regression model

Analysis of variance (ANOVA) was performed to investigate the significance of the developed model and to study the effect of each

Table 3
ANOVA of regression model for sorbent desulfurization activity.

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	845.92	19	44.52	6.85	0.0018
x_1	167.75	1	167.75	25.80	0.0005
x_2	21.82	1	21.82	3.36	0.0968
x_3	0.63	1	0.63	0.10	0.7615
x_4	172.33	1	172.33	26.50	0.0004
x_1^2	0.90	1	0.90	0.14	0.7175
x_2^2	41.76	1	41.76	6.42	0.0297
x_3^2	34.22	1	34.22	5.26	0.0447
x_4^2	20.83	1	20.83	3.20	0.1038
x_1x_2	18.37	1	18.37	2.82	0.1237
x_1x_3	18.37	1	18.37	2.82	0.1237
x_1x_4	6.61	1	6.61	1.02	0.3370
x_2x_3	0.18	1	0.18	0.03	0.8699
x_2x_4	66.31	1	66.31	10.20	0.0096
x_3x_4	9.00	1	9.00	1.38	0.2666
x_1^3	54.23	1	54.23	8.34	0.0162
x_2^3	11.91	1	11.91	1.83	0.2057
x_3^3	41.71	1	41.71	6.42	0.0297
$x_1x_2x_4$	59.51	1	59.51	9.15	0.0128
$x_2x_3x_4$	22.22	1	22.22	3.42	0.0942
Residual	65.02	10	6.50	–	–

parameter towards the sorbent sorption capacity and is shown in Tables 3 and 4, respectively. From the ANOVA result, Fisher Test value (F -value) for desulfurization regression model is 6.85, larger than theoretical $F_{0.05(19,10)}$ value (2.774), while Fisher Test value (F -value) for denitrification regression model is 10.94, larger than theoretical $F_{0.05(20,9)}$ value (2.936). On top of that, Pareto plots in Figs. 2 and 3 show all the significant terms with corresponding F values for Eqs. (2) and (3), respectively. All these findings indicate that both regression models are statistically significant and reliable to predict the sorbent sorption activity at 95% confidence level.

3.3. Effect of sorbent preparation parameters

The models will then be utilized to study the effect of sorbent preparation parameters on desulfurization and denitrification capacity. In order to identify the individual sorbent preparation parameters or interaction between parameters that significantly affect the sorbent sorption capacity, the F values for each of the term in both regression models are compared against the theoretical F -value. F -value larger than theoretical value indicates significance.

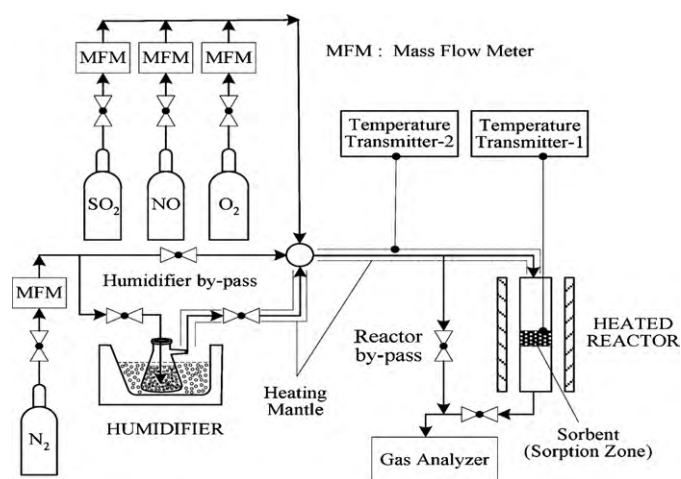


Fig. 1. Schematic diagram of the desulfurization/denitrification test rig.

Table 4
ANOVA of regression model for sorbent denitrification activity.

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	15.23	20	0.76	10.94	0.0004
x_1	2.74	1	2.74	39.33	0.0001
x_2	0.37	1	0.37	5.37	0.0457
x_3	0.02	1	0.02	0.22	0.6530
x_4	2.78	1	2.78	39.98	0.0001
x_1^2	0.16	1	0.16	2.25	0.1681
x_2^2	0.57	1	0.57	8.18	0.0188
x_3^2	0.37	1	0.37	5.36	0.0458
x_4^2	0.37	1	0.37	5.34	0.0462
x_1x_2	0.36	1	0.36	5.22	0.0482
x_1x_3	0.57	1	0.57	8.16	0.0189
x_1x_4	0.20	1	0.20	2.94	0.1207
x_2x_3	0.01	1	0.01	0.15	0.7122
x_2x_4	1.45	1	1.45	20.88	0.0013
x_3x_4	0.00	1	0.00	0.04	0.8532
x_1^3	0.82	1	0.82	11.76	0.0075
x_2^3	0.10	1	0.10	1.51	0.2505
x_3^3	0.70	1	0.70	9.99	0.0115
$x_1x_2x_3$	0.20	1	0.20	2.94	0.1207
$x_1x_2x_4$	1.58	1	1.58	22.66	0.0010
$x_2x_3x_4$	0.20	1	0.20	2.94	0.1207
Residual	0.63	9	0.07	–	–

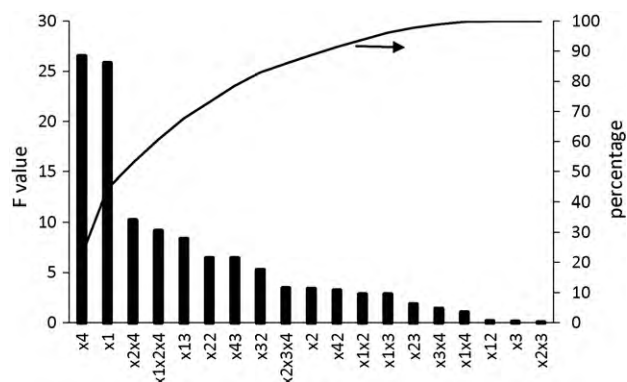


Fig. 2. Pareto plot of every term in Eq. (2) and corresponding F values.

In this study, only the terms with $\text{Prob} > F$ value less than 0.01 will be discussed.

For the desulfurization regression model, significant terms are x_1 , x_4 and x_2x_4 . On the other hand, significant terms for denitrification regression model are x_1 , x_4 , x_2x_4 , x_1^3 and $x_1x_2x_4$. It can be seen in Eqs. (2) and (3) that the significant terms that affect the desulfurization model is almost similar to the denitrification model, with exception of x_1^3 and $x_1x_2x_4$. According to the F -value computed in the analysis, CuO loading (x_1) and NaOH concentration (x_4) have the same level of significance for both desulfurization and denitrification activity. For CuO loading, a minus sign indicates that it has an antagonistic effect on the sorbent sorption capacity. Increasing CuO loading would reduce the sorbent sorption capacity of SO_2 and NO. The main reason for impregnating copper species on the sorbent is to enhance NO sorption by siliceous sorbent. Thus the antagonistic effect of higher copper loading on sorbent denitrification capacity is rather un-expected as copper can easily react with NO to form copper nitrate and facilitate NO removal as shown in the work of Liu et al. [18]. Therefore, one possible explanation for the antagonistic effect of copper loading is due to the agglomeration of copper that subsequently reduced the dispersion of copper on the sorbent surface. Without good dispersion of copper, this will reduced the contact between copper and NO molecules. Furthermore, agglomeration of copper on the sorbent surface would also block the pores and reduces the surface area for reactive species of the sorbent to react with SO_2 . Therefore, effectiveness of SO_2 and NO sorption are reduced with higher copper loading. However, sorption capacity of sorbent could not be directly related to surface area. Referring to Table 5, R16 with highest surface area has the lowest sorption capacity of SO_2 and NO. This result agrees well with the work of Dahlan et al. [4] which stated that desulfurization activity did not correlate well with surface area of the sorbent derived from rice husk ash.

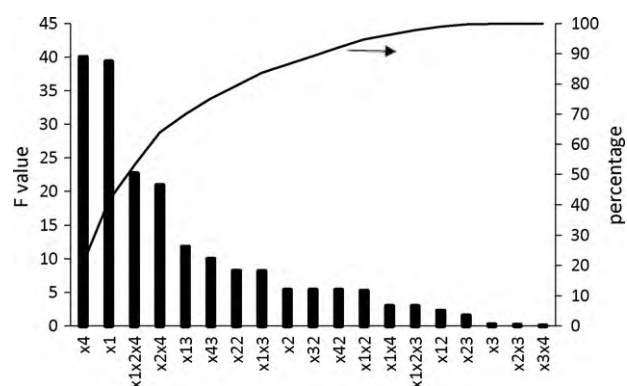


Fig. 3. Pareto plot of every term in Eq. (3) and corresponding F values.

Table 5
BET surface area, average pore size and pore volume of selected sorbents.

Sorbent Code	BET surface area (m^2/g)	Average pore size (\AA)	Pore volume (cm^3/g)
R10	14.12	89.00	0.0314
R16	24.55	174.53	0.1071
R23A (raw R23)	17.31	118.71	0.0514
R23B (spent R23)	7.98	168.61	0.0336

In contrast to copper loading, NaOH concentration used during sorbent preparation process has a synergistic affect towards the desulfurization and denitrification process as seen by the positive sign of term x_4 in the model equation. This can also be easily verified by visually comparing the data obtained in Table 2. When comparing the activity between sorbents R20 and R23, R7 and R28, R8 and R24, R3 and R26, it is clearly seen that increasing NaOH concentration from 0.20 M to 0.80 M significantly increases the desulfurization/denitrification activity. The effect of NaOH found in this study agrees well with Liu et al. [19] that synthesize sorbent with iron blast furnace slag and hydrated lime. However, this finding is not in well agreement with the report of Dahlan et al. [1] in which it was found that addition of NaOH in the range 0–0.25 M improves desulfurization activity but higher NaOH concentration (0.25–0.5 M) in hydration process have adverse effect towards the desulfurization activity for sorbent derived with cerium oxide. In order to explain this, the role of NaOH must first be understood. The main reason for adding NaOH as additive during the sorbent preparation step is to increase the dissolution of silica from the siliceous material so that it can react with CaO to form the reactive species required for good desulfurization/denitrification activity [19]. Thus with higher concentration of NaOH used, this will promote higher dissolution rate of silica to form more reactive species that will further enhances the sorbent activity. In this study, since copper is used instead of cerium, derived sorbent may have larger tolerance towards NaOH concentration, at least in the range of NaOH concentration used in this study.

On the other hand, RHA/CaO ratio and hydration period were found to have insignificant affect on the desulfurization/denitrification. It was well reported in the literature that the preparation of sorbents from siliceous materials is a very slow process due to the slow dissolution rate of silica from siliceous material. Therefore, conventional method of increasing the process is either by using a very long hydration period or increasing the amount of siliceous material used (higher RHA/CaO ratio). However, in this study, it was clearly shown that the slow rate of silica dissolution can be easily overcome by the addition of NaOH up to a point that increasing the hydration period and RHA/CaO ratio no longer affect the desulfurization/denitrification activity. However, at this point although the individual parameters, hydration period and RHA/CaO ratio do not affect the desulfurization/denitrification activity, but it should be noted that RHA/CaO interacts with other parameters to give a significant effect on the sorbent desulfurization/denitrification activity. RHA/CaO gives a first order interaction with NaOH concentration and second order interaction with copper loading and NaOH concentration. The interaction between parameters will be presented in the following section.

Figs. 4 and 5 show the surface plot on the effect of interaction between RHA/CaO ratio and NaOH concentration on desulfurization and denitrification activity, respectively. At low NaOH concentration (0.20 M), increasing RHA/CaO ratio could improve the desulfurization and denitrification activity. However, adverse effect on desulfurization and denitrification activity will occur if RHA/CaO ratio is increased at high NaOH concentration (0.80 M). The following explains this phenomenon. At low NaOH concentration, it is not sufficient to increase the dissolution of silica out

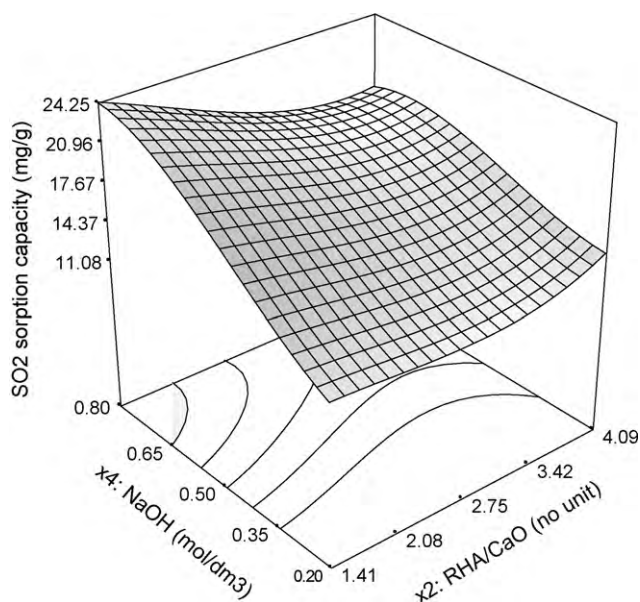


Fig. 4. Surface plot of desulfurization activity: x_2x_4 interaction at $x_1 = 7.5$, $x_3 = 14$.

from the ash material and therefore limits the reaction between silica and CaO to form the reactive species such as calcium silicate hydrates compound. Therefore, higher RHA/CaO ratio would allow more silica to react with CaO which subsequently form more reactive species to increase the desulfurization/denitrification activity. Nevertheless, at higher concentration of NaOH, silica can be easily extracted out from the siliceous compound and therefore, the positive effect of higher RHA/CaO ratio is no longer significant. On the contrary, the high ratio of RHA/CaO could instead interfere with the formation of reactive species reaction due to the presence of too much inert material from the ash.

From the regression model, it was found that interaction between parameters x_1 , x_2 and x_4 is significant for denitrification activity and is shown in Fig. 6. The F value for term $x_1x_2x_4$ is 22.66. From the cubic plot, at low level of copper loading, it was found that the interaction effect toward denitrification activity is similar with term x_2x_4 . However, at high copper loading, varying RHA/CaO

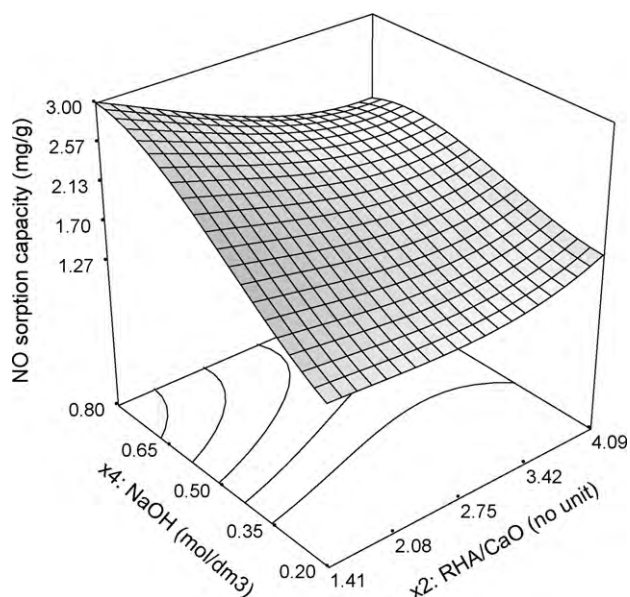


Fig. 5. Surface plot of denitrification activity: x_2x_4 interaction at $x_1 = 7.5$, $x_3 = 14$.

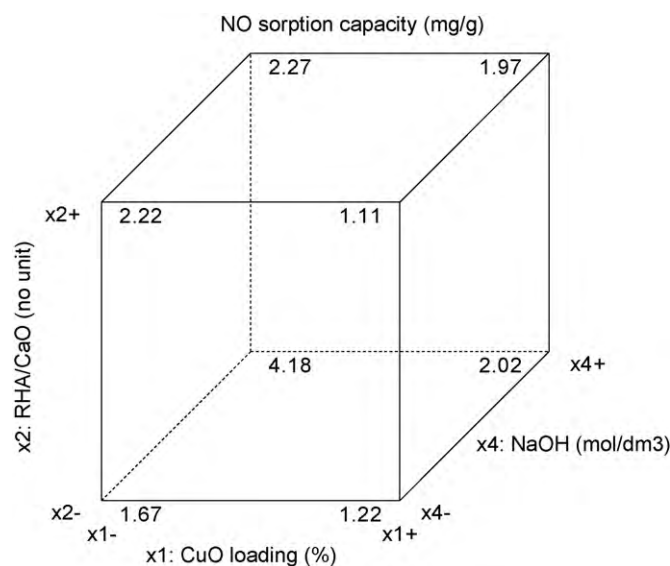


Fig. 6. Cubic plot of denitrification activity: $x_1x_2x_4$ interaction at $x_3 = 14$.

ratio has no significant effect on denitrification activity regardless if NaOH is either fixed at high or low level. This phenomenon is predictable as RHA/CaO was found to have low significance effect on denitrification activity. Agglomeration of copper on sorbent surface and pore blockage at high level of copper loading could be the main reason why interaction of x_2x_4 is insignificant at high level copper loading.

3.4. Sorbent characterization

In order to understand how the chemical and physical properties of the sorbents affect its desulfurization/denitrification activity, selected sorbents were subjected to various characterization analyses.

3.4.1. XRD

XRD analyses were carried out for R10, R16, R23A (sorbent R23 before reaction) and R23B (spent R23 sorbent) as shown in Fig. 7(a–d), respectively. In the XRD pattern of R23A, identified silicate compounds were sodium calcium silicates ($\text{Na}_2\text{CaSiO}_4$, $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ and combeite high ($\text{Na}_5\cdot 27\text{Ca}_3(\text{Si}_6\text{O}_{18}))$) and calcium silicate (Ca_3SiO_5 and CaSi_2O_5). These silicate compounds are believed to be the active species that could reduce SO_2 from flue gas through complex reactions. The identification of silicate compounds agrees well with the result of the activity study in which R23A is the sorbent with highest sorption capacity in this study. Nevertheless, the only copper species detected in low intensity in R23A is tenorite (CuO). This could be due to highly dispersed CuO on the sorbent surface. Therefore, not much crystalline CuO could be detected by the XRD method. From XRD patterns of R10 and R16, CuO in the form of tenorite is identified at high intensity at $2\theta = 36^\circ$ and 39° especially for R10 that was impregnated with highest CuO loading in this study (15%). Apart from tenorite, copper oxide nitrate ($\text{Cu}_8\text{O}_8(\text{NO}_3)$) is also detected as another copper species in R10 and R16. $\text{Cu}_8\text{O}_8(\text{NO}_3)$ could originate from copper nitrate hemipentahydrate ($\text{Cu}(\text{NO}_3)_2\cdot 5/2\text{H}_2\text{O}$) that was impregnated before calcinations of the sorbents and subsequently did not completely reduced to CuO . On the other hand, calcite is detected in all the XRD patterns of the selected sorbents. Calcite is identified as one of the products of pozzolanic reaction as it is also formed in the reaction of coal fly ash and lime [20,21].

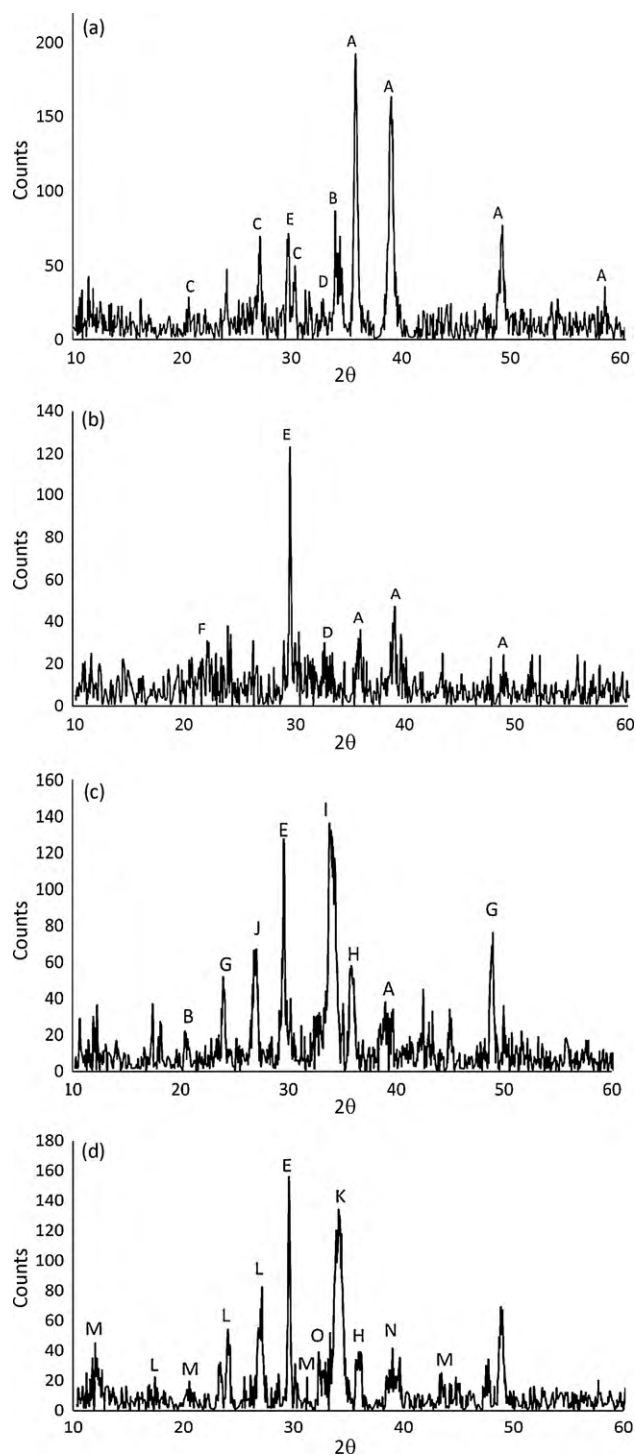


Fig. 7. XRD spectrums: (a) R10, (b) R16, (c) R23A, and (d) R23B. XRD label: (A) CuO tenorite; (B) $\text{Na}_2\text{CaSiO}_4$ sodium calcium silicate; (C) SiO_2 stishovite; (D) $\text{Cu}_8\text{O}_8(\text{NO}_3)$ copper oxide nitrate; (E) CaCO_3 calcite; (F) SiO_2 cristobalite; (G) $\text{Na}_5.27\text{Ca}_3(\text{Si}_6\text{O}_{18})$ combeite high; (H) CaSi_2O_5 calcium silicate; (I) Ca_3SiO_5 calcium silicate; (J) $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ sodium calcium silicate; (K) $\text{Ca}_3(\text{SO}_3)_2 \cdot 12(\text{SO}_4)_{0.88}$ calcium sulfate sulfite; (L) $\text{Na}_2\text{Cu}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ krohnkite; (M) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ gypsum; (N) Na_3NO_3 sodium nitrate; (O) NaNO_2 sodium nitrite.

Apart from that, sodium calcium silicate ($\text{Na}_2\text{CaSiO}_4$) is the only calcium silicate compound detected in R10. By comparing the sorption activity of R10 with R16, which no calcium silicate compound was detected, sorption capacity of R10 is found to be better than R16 but not as good as R23A in which many types of silicate compounds are formed. This further proves that silicate compounds are the key

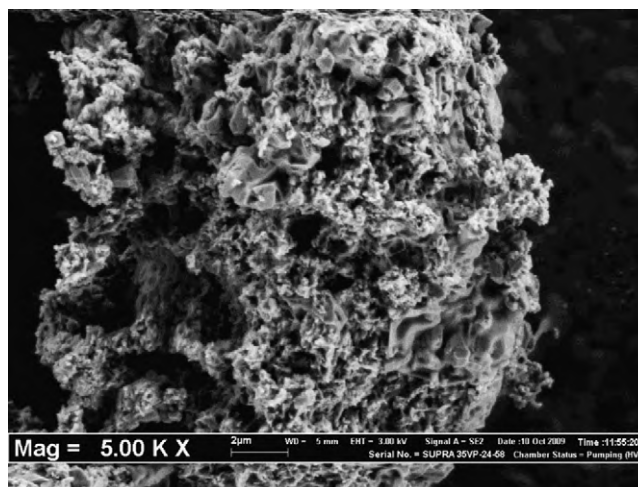


Fig. 8. SEM micrograph of R23A.

components for the formation of sorbent with high sorption capacity of SO_2 and NO . As for R16 which undergoes hydration process without NaOH , cristobalite (SiO_2) was detected. This indicates that the pozzolanic reaction for R16 is incomplete and could be most probably due to the absence of NaOH during hydration process. In addition to that, SiO_2 in the form of stishovite was also detected in R10. Since R10 (15% copper loading) is the only sorbent that stishovite was detected, addition of high amount of copper could be related to the formation of stishovite, a rare form of SiO_2 . In the XRD of R23B which undergoes desulfurization/denitrification process, sulfate compounds such as krohnkite ($\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$), calcium sulfate sulfite ($\text{Ca}_3(\text{SO}_3)_2 \cdot 12(\text{SO}_4)_{0.88}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are detected. On top of that, products of denitrification activity are identified as sodium nitrate (Na_3NO_3) and sodium nitrite (NaNO_2). Formation of sodium based denitrification products shows that addition of sodium hydroxide in the hydration process plays an important role not only in formation of silicate compounds, but also takes part in the denitrification activity. Addition of copper, on the other hand, probably only acted as catalyst instead of the main reactant. Therefore, detection of copper product was not found in the XRD.

3.4.2. SEM

The surface morphology of R23A and R23B is shown in Figs. 8 and 9, respectively. By comparing the micrographs of R23A

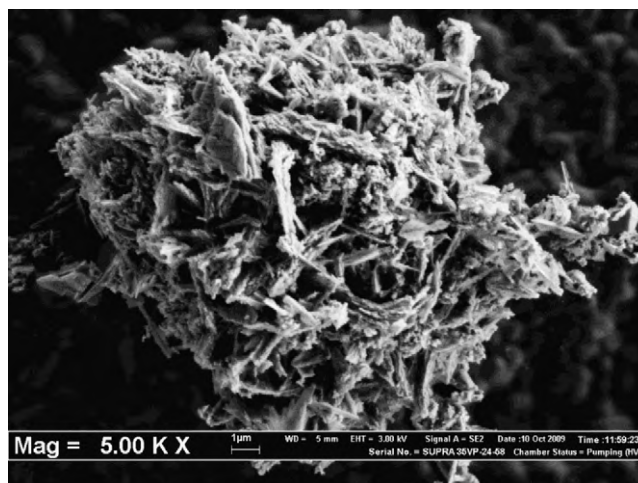


Fig. 9. SEM micrograph of R23B.

and R23B, structure transformation could be seen clearly after the sorbent was subjected to desulfurization/denitrification activity. R23A shows a porous structure with CuO well dispersed on the surface. However, after the activity study, it was found that irregular rod like structure covered the sorbent surface, possibility by the product of desulfurization/denitrification activity. This structure could be caused by the combination of several products detected by XRD such as calcium sulfate sulfite ($\text{Ca}_3(\text{SO}_3)_2 \cdot 12(\text{SO}_4)_{0.88}$), krohnkite ($\text{Na}_2\text{Cu}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sodium nitrate (Na_3NO_3) and sodium nitrite (NaNO_2).

3.5. Optimization

From the developed models for desulfurization and denitrification activity, optimization were carried out over the range of sorbent preparation parameters in this study to obtain sorbent with the optimum sorption capacity and least extreme sorbent preparation process conditions (mild process conditions). By using Design-Expert Version 6.0.6 (Stat-Ease, Inc.), solutions were generated by maximizing SO_2/NO sorption capacity and setting all the sorbent preparation parameters within the range of this study.

The most desirable optimized condition predicted by the software is 3.04% CuO loading, RHA/CaO ratio of 1.43, 19.94 h of hydration period and NaOH concentration of 0.80 M with predicted sorption capacity of 11.27 mg SO_2/g and 3.39 mg NO/g . However, when the solutions were carefully investigated, it was found that another solution gave milder sorbent preparation condition as the hydration period is only 8.05 h compare to 19.94 h. Therefore, the optimum condition was selected as 3.06% CuO loading, RHAraw/CaO ratio of 1.41, 8.05 h of hydration period and NaOH concentration of 0.80 M with predicted sorption capacity of 12.10 mg SO_2/g and 3.06 mg NO/g . In order to validate the selection, three experiments were carried out with sorbent prepared using the optimum conditions. The result shows that the range of SO_2 and NO sorption are 11.10–13.50 mg/g and 2.40–3.08 mg/g, respectively. Thus, it can be concluded that the selected condition is optimum within the range of sorbent preparation conditions investigated in this study.

4. Conclusion

In this study, the sorbent prepared from rice husk ash and impregnated with copper oxide were found effective in removing SO_2 and NO simultaneously. The sorbent preparation parameter that are found to significantly affect both desulfurization and denitrification activity are CuO loading and NaOH concentration. However, RHA/CaO ratio is found to be significant in denitrification activity but not in desulfurization activity. Contrary, effect of hydration period was found to be insignificant for both processes. From the XRD analysis, several types of calcium silicate compounds were detected and believed to play an important role in the high sorption capacity of the sorbent. On top of that, CuO in the form of tenorite was also detected. The conditions to prepare sorbent with optimum desulfurization and denitrification capacity are 3.06% CuO loading, RHA/CaO ratio of 1.41, 8.05 h of hydration period and NaOH concentration of 0.80 M.

Acknowledgements

The authors would like to acknowledge Universiti Sains Malaysia (Research University Waste Management Cluster Grant 1001/PAWAM/814021, Postgraduate Research Grant Scheme 8031005 and USM Fellowship) for the financial support given.

References

- [1] I. Dahlan, M.M. Gui, A.H. Kamaruddin, A.R. Mohamed, K.T. Lee, Removal of SO_2 and NO over rice husk ash (RHA)/CaO-supported metal oxides, *J. Eng. Sci. Technol.* 3 (2008) 109–116.
- [2] H. Bosch, F. Janssen, Catalytic reduction of nitrogen oxides—a review of the fundamentals and technology, *Catal. Today* 2 (1988) 369–531.
- [3] L. Dong, S. Gao, W. Song, G. Xu, Experimental study of NO reduction over biomass char, *Fuel Process. Technol.* 88 (2007) 707–715.
- [4] I. Dahlan, K.T. Lee, A.H. Kamaruddin, A.R. Mohamed, Key factor in the rice husk ash/CaO sorbent for high flue gas desulfurization activity, *Environ. Sci. Technol.* 40 (2006) 6032–6037.
- [5] K.T. Lee, A.R. Mohamed, S. Bhatia, K.H. Chu, Removal of sulfur dioxide by fly ash/CaO/CaSO₄ sorbents, *J. Chem. Eng.* 114 (2005) 171–177.
- [6] L. Shi, X. Xu, Partially sulfated lime-fly ash sorbents activated by water or steam for SO_2 removal at a medium temperature, *Energy Fuels* 19 (2005) 2335–2339.
- [7] N.F. Zainudin, K.T. Lee, A.H. Kamaruddin, S. Bhatia, A.R. Mohamed, Study of adsorbent prepared from oil palm ash (OPA) for flue gas desulfurization, *Sep. Purif. Technol.* 45 (2005) 50–60.
- [8] Y. Guo, M. Sakurai, H. Kameyama, A. Matsuyama, Y. Kudoh, Selective catalytic reduction of nitric oxide by propene over a Cu–Mn–CeO_x/Al₂O₃/Al aluminate catalyst, *J. Chem. Eng. Jpn.* 37 (2004) 406–414.
- [9] B. Tsyntsarski, V. Avreyska, H. Kolev, Ts. Marinova, D. Klissurski, K. Hadjiivanov, FT-IR study of the nature and reactivity of surface NO_x compounds formed after NO adsorption and $\text{NO} + \text{O}_2$ coadsorption on zirconia- and sulfated zirconia-supported cobalt, *J. Mol. Catal. A: Chem.* 193 (2003) 139–149.
- [10] F.Y. Chang, J.C. Chen, M.Y. Wey, Catalytic removal of NO in waste incineration processes over Rh/Al₂O₃ and Rh–Na/Al₂O₃: effects of particulates, heavy metals, SO_2 and HCl , *Fuel Process. Technol.* 90 (2009) 576–582.
- [11] M.F. Irfan, J.H. Goo, S.D. Kim, Co₃O₄ based catalysts for NO oxidation and NO_x reduction in fast SCR process, *Appl. Catal. B: Environ.* 78 (2008) 267–274.
- [12] Z. Zhu, Z. Liu, H. Niu, S. Liu, Promoting effect of SO_2 on activated carbon-supported vanadia catalyst for NO reduction by NH_3 at low temperatures, *J. Catal.* 187 (1999) 245–248.
- [13] Z. Zhu, Z. Liu, S. Liu, H. Niu, T. Hu, T. Liu, Y. Xie, NO reduction with NH_3 over an activated carbon-supported copper oxide catalysts at low temperatures, *Appl. Catal. B: Environ.* 26 (2000) 25–35.
- [14] G.H. Jung, H. Kim, S.G. Kim, Preparation and characterization of lime-silica solids, *Ind. Eng. Chem. Res.* 39 (2000) 1264–1270.
- [15] I. Dahlan, K.T. Lee, A.H. Kamaruddin, A.R. Mohamed, Evaluation of various additives on the preparation of rice husk ash (RHA)/CaO-based sorbent for flue gas desulfurization (FGD) at low temperature, *J. Hazard. Mater.* 161 (2009) 570–574.
- [16] I. Dahlan, K.T. Lee, A.H. Kamaruddin, A.R. Mohamed, Selection of metal oxides in the preparation of rice husk ash (RHA)/CaO sorbent for simultaneous SO_2 and NO removal, *J. Hazard. Mater.* 166 (2009) 1556–1559.
- [17] K.T. Lee, A.M. Mohtar, N.F. Zainudin, S. Bhatia, A.R. Mohamed, Optimum conditions for preparation of flue gas desulfurization absorbent from rice husk ash, *Fuel* 84 (2005) 143–151.
- [18] Q. Liu, Z. Liu, W. Wu, Effect of V_2O_5 additive on simultaneous SO_2 and NO removal from flue gas over a monolithic cordierite-based CuO/Al₂O₃ catalyst, *Catal. Today* 147S (2009) S285–S289.
- [19] C.F. Liu, S.M. Shih, J.H. Yang, Reactivities of NaOH enhanced iron blast furnace slag/hydrated lime sorbents toward SO_2 at low temperatures: effects of the presence of CO_2 , O_2 , and NO_x , *Ind. Eng. Chem. Res.* 49 (2010) 515–519.
- [20] W. Ma, C. Liu, P.W. Brown, S. Komarneni, Pore structures of fly ashes activated by $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, *Cem. Concr. Res.* 25 (1995) 417–425.
- [21] J. Fernandez, J. Renedo, A. Garea, J. Viguri, J.A. Irabien, Preparation and characterization of fly ash/hydrated lime sorbents for SO_2 removal, *Powder Technol.* 94 (1997) 133–139.