

Preparation and Characterization of CuO/ γ -Al₂O₃ for Adsorption of SO₂ in Flue Gas

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Abstract

Adsorbent CuO/ γ -Al₂O₃ was successfully prepared by the dry impregnation using Cu(NO₃)₂·3H₂O solution on commercial γ -Al₂O₃. Impregnation and calcination process was be done repeatedly to get a desired CuO content on the support. The impregnations were done at 50°C for 8 hours or 120°C for 5 hours. Calcinations were carried out at a temperature of 400°C for 8 hours. Adsorbent obtained from this preparation contained Cu: 7.93% (named 8Cu), 14.76% (15Cu) and 28.98% (30Cu). Pore characteristic indicated that the surface area decreased with the increase in Cu content in the adsorbent (from 207 in original support to 124 m²/g in 8Cu). Similar tendency was found for the pore volume (from 0.47 to 0.28 mL/g).

In batch adsorption test, the amount of adsorbed SO₂ was calculated from the increase in mass of adsorbent. Adsorbent 8Cu had the best adsorption capacity in term of mol ratio, ie. 0.78 SO₂/CuO (close to stoichiometry). Original support of γ -Al₂O₃ was found to be inert to SO₂. In semi-continue test, the adsorption was carried under a flow of gas containing 2.5% SO₂. The amount of adsorbed SO₂ was calculated from the different of SO₂ content between influent to effluent. It was found again that the best adsorbent was 8Cu with the adsorption capacity of 0.97 mol/mol CuO.

Keywords: dry impregnation, adsorbent characterization, adsorption capacity, SO₂ reactive adsorption

1. Introduction

The use of coal as fuel for power plants has been increasing, and there is also a tendency in increasing the use of low quality coal with a high impurity particularly sulfur. In the other hand, this condition brings about an increase in SO₂ emission which is very harmful for human health, environment and process equipments. A simple mass balance for combustion in a steam power plant operated with a coal having a sulfur content of 0.44% (dry basis) and 5% excess air (a condition in a pulverized burner) produces a flue gas with a SO₂ emission exceeding the environmental standard of 750 mg/Nm³ in Indonesia. Meanwhile, the coal consumption for steam power plants in Indonesia may increase from 80 to 250 million ton in 2012 to 2030, with a sulfur content in the range of 0.1% to those above 1%.

There are two basic methods of elimination of SO₂ from the flue gas of a coal-fired power plant: wet and dry methods. The dry method has been considered to have some advantages, especially against a potential emission of waste water in the wet methods (Dehghani and Bridjianian, 2010). In the dry method, an adsorbent has an ability to absorb SO₂ and hopefully it can be regenerated without changing the adsorption capacity. CuO/ γ -Al₂O₃ is one of a promising adsorbent in eliminating SO₂ from flue gas and resuling CuSO₄ ((Xie et al., 2004; Wittayakun et. al, 2002). Moreover, adsorption of SO₂ by CuO takes place at a temperature in the range of flue gas temperature, 300- 450°C (Mathieu, et al, 2013; Xie et al, 2003). The use of γ -Al₂O₃ as support for CuO offers advantages a large specific surface area (150-300 m²/ g), and heat resistance of up to 700-900°C.

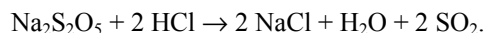
Based on the above mentioned advantages, we considered that CuO/ γ -Al₂O₃ may be a prospective adsorbent for a flue gas desulfurization in coal-fired power plants. Regeneration spent adsorbent or decomposition of CuSO₄ at a temperature of about 700°C produced SO₃ which an intermediate of saleable sulfuric acid (McCrea et al., 1970; and Himmelblau, 1989). Our experimental works on preparation, particle characterization and measurement of capacity of adsorbent CuO/ γ Al₂O₃ are presented in this paper. An adsorption-regeneration cycle was also conducted as a preliminary exploration.

2. Method

Adsorbent CuO may be prepared using the impregnation method on a support in order to get a large surface area. In our study, we used γ -Al₂O₃ having a surface area in the range of 200-300 m²/g. Adsorbent was then characterized for its particles properties and also tested for its adsorption capacity of SO₂ in its mixture with N₂.

2.1 Preparation of Adsorbent

Basically the procedure for preparation of SO₂ may be found in any standard textbook of chemistry, based on reaction:



Gaseous SO₂ obtained from the above reaction was injected into a storage tank and mixed with air to get a desired composition. The mixture was allowed for at least 12 hours (overnight) to be homogeneous.

2.2 Preparation of Adsorbent

A commercial γ -Al₂O₃ support has been used. This support was firstly subject to calcination at 550°C. This support had originally a specific surface area of 207 m²/g. Solution of Cu(NO₃)₂.3H₂O was impregnated on support. The impregnated support was then dried in two steps: at a temperature of 50°C for 8 hour and at 120°C for 5 hour. Finally the dried particles was calcined at a temperature of 400°C for 8 hour. It was intended to get adsorption with Cu contents of 8%, 15% and 30% by weight (in accordance with Xie et al., 2003).

Adsorbent CuO/ γ -Al₂O₃ having various Cu contents was obtained using the following procedures.

- a. Adsorbent 8Cu intended to have a Cu content of 8% was prepared as follows:
 - i. impregnation using solution of 8% Cu(NO₃)₂
 - ii. drying and calcination.
- b. Adsorbent 15Cu for 15% Cu:
 - i. first impregnation using solution of 8% Cu(NO₃)₂
 - ii. second impregnation using solution of 7% Cu(NO₃)₂
 - iii. drying and calcination.
- c. adsorbent 30Cu for 30% Cu:
 - i. first impregnation using solution of 8% Cu(NO₃)₂
 - ii. second impregnation using solution of 8% Cu(NO₃)₂
 - iii. third impregnation using solution of 8% Cu(NO₃)₂
 - iv. forth impregnation using solution of 6% Cu(NO₃)₂
 - v. after each impregnation, particles was dried in two steps: 50°C for 8 h and then 120°C for 5 h
 - vi. finally calcination at 400°C for 8 h.

2.3 Particles Properties

Analysis on the physical properties of adsorbent CuO/ γ -Al₂O₃ were as follows:

- a. AAS for measuring the amount of Cu successfully attached on support
- b. BET for measuring the specific surface area and volume; then followed by pore mean diameter
- c. SEM for observation to surface morphology.

XRD analysis was also applied for examination of crystalline phase of adsorbent after multiple use, ie. adsorption and desorption (Bereketidou, et. al, 2012).

2.4 Adsorption Capacity

Adsorption capacity of adsorbent was tested using an electrically heated adsorption-reaction vessel, with two methods of operation: batch and semi-continue (Figure 1). In the batch method, about one gram of catalyst was put in a reaction vessel having a volume of 40 mL. The vessel was then heated to a desired temperature: 300, 350, 400 or 450°C, under a flowing N₂. When the desired temperature was achieved, a mixture of 50%-mol SO₂ and 50% air was introduced into the vessel. The catalyst and gas were then allowed to contact intimately and react in the vessel for about 6 hours. The progress of adsorption was observed with the following methods:

- a. reaction-1, increasing weight of catalyst: $\text{CuO} + \text{SO}_2 + 0,5 \text{O}_2 \rightarrow \text{CuSO}_4$

b. reaction-2, decreasing pressure inside the vessel: $\text{SO}_2 + 0,5 \text{O}_2 \rightarrow \text{SO}_3$.

The initial pressure inside the vessel was atmospheric, i.e. 700 mmHg. Decreasing pressure inside the reaction vessel was measured using *Extech-Micromanometer type 407910*.

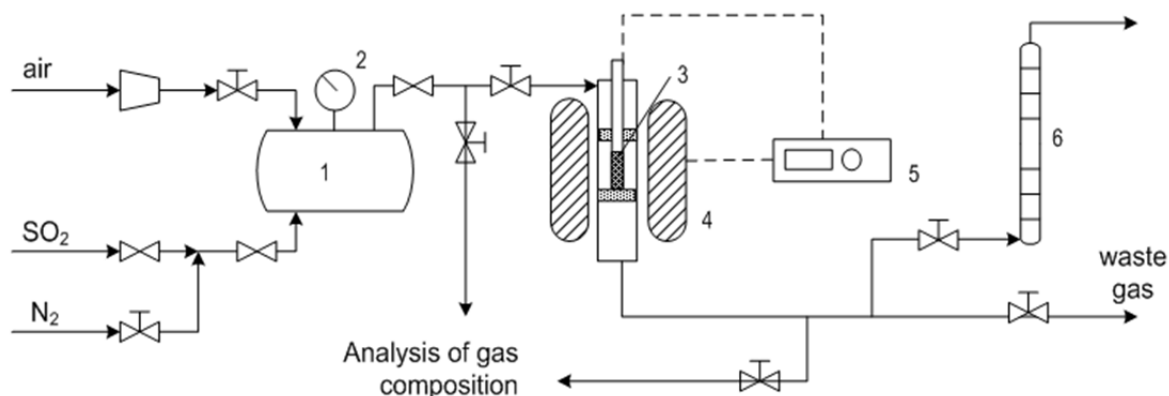


Figure 1. Experimental set up

1. Storage tank; 2. Manometer; 3. Adsorbent; 4. Electric furnace; 5. Temperature controller; 6. Bubble soap meter.

The adsorption condition in semi-continuous test was similar with the batch adsorption in terms of varying temperature and types of catalyst. A mixture of 2.5%-mol SO_2 and air was allowed to flow continuously with a rate in the range of 1.6 – 2.0 mL/min (as measured at the ambient condition: 30°C and 700 mmHg). The pressure in the reactor was kept atmospheric, and experiments on adsorption were carried out for about 1 hour. The progress in adsorption was observed by the decrease in SO_2 concentration between influent and effluent of the reaction vessel. In this measurement, SO_2 in the influent were measured at the beginning and end of experiment, and was assumed constant. The concentrations of SO_2 in the effluent were measured every 5 min, using titrimetry i.e.: (i) absorption of SO_2 in the flowing gas into a solution of 20% H_2O_2 and followed by titration with solution of NaOH 0.1 M to calculate the formation of H_2SO_4 :

c. reaction-3, chemical absorption: $\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{SO}_3 + \text{H}_2\text{O}$ and $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

a. reaction-4: $\text{H}_2\text{SO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

Increasing the weight of catalyst before and after each experiment was also used as a re-check to the mass balance (see reaction-1).

3. Results and Discussion

3.1 Characterizations of Adsorbent

Using the above experimental procedure, the desired Cu contents in adsorbent were successfully obtained (see Table 1). Unfortunately, the specific surface area and the specific volume of adsorbent were found to decrease with increasing the Cu content. As an example, our adsorbent 8Cu had a specific surface area of 190.49 m^2/g , while the original $\gamma\text{-Al}_2\text{O}_3$ support has 207.39 m^2/g , thus a decrease of 16 m^2/g . This phenomenon was also reported by (Xie, et. al, 2003) as they found a decrease in surface area of 35 m^2/g in an adsorbent with Cu content of 8% from the original $\gamma\text{-Al}_2\text{O}_3$ support.

A different result was reported in (Aguila, et. al, 2008), i.e. a more or less constant pore surface area for attachment of CuO on $\gamma\text{-Al}_2\text{O}_3$ (see Table 1, rows 8 and 9). They also mentioned that an attachment of CuO of 4% required a surface area of about 100 m^2/g of support. Thus for a catalyst with a CuO content up to 4%, all CuO might be highly dispersed inside a support having a surface area of about 200 m^2/g . So did our adsorbent with a CuO content of about 7.9%, its had a only slightly lower surface area than the original support. Despite decreasing pore surface area with increasing CuO content, all our catalyst had a more or less same pore characteristic with those reported by many researchers (Mathieu, et. al, 2013, see Table 1, rows 10-17).

Table 1. Pore properties of adsorbent

No	Code	Cu content by mass	Pore properties		
			Surface area, m ² /g	Volume, mL/g	Mean Diameter Å
our experiments					
1	0Cu/ γ -Al ₂ O ₃	0%	207.39	0.4754	91.6915
2	8Cu	7.93%	190.49	0.4356	91.4728
3	8Cu	7.93%	190.21	0.4272	89.8292
4	15Cu	14.76%	160.57	0.3724	92.7558
5	15Cu	14.76%	164.51	0.3633	88.3233
6	30Cu	28.98%	128.62	0.2846	88.5063
7	30Cu	28.98%	124.80	0.2839	91.0001
Aguila, et. al, 2008					
8	γ -Al ₂ O ₃	0%	208	-	-
9	CuO/ γ -Al ₂ O ₃	2.0%	210	-	-
Mathieu, et. al, 2013 (from a variety of literature)					
10	γ -Al ₂ O ₃	0%	100	-	-
11	CuO/ γ -Al ₂ O ₃	4.9%	112	-	-
12	CuO/ γ -Al ₂ O ₃	4.3%	117	-	-
13	CuO/ γ -Al ₂ O ₃	7.0%	113	-	-
14	CuO/ γ -Al ₂ O ₃	9.0%	244	-	-
16	CuO/ γ -Al ₂ O ₃	6.0%	171	-	-
17	CuO/ γ -Al ₂ O ₃	8%	166	-	-

SEM analysis on our adsorbent indicated that the morphology of 8Cu (7,9% CuO) was still more or less similar to the original support (se Figure 2). While for adsorbents 15Cu and 30Cu, pores were blocks or damage.

3.2 Adsorption Capacity

Generally, an adsorbent with a Cu content has a higher activity or/and a higher adsorption capacity. Adsorption capacity is presented in two units:

- mg of SO₂ per g of adsorbent as usually presented as a specification of catalyst
- mol of SO₂ per mol of Cu to evaluate effectively of Cu utilization.

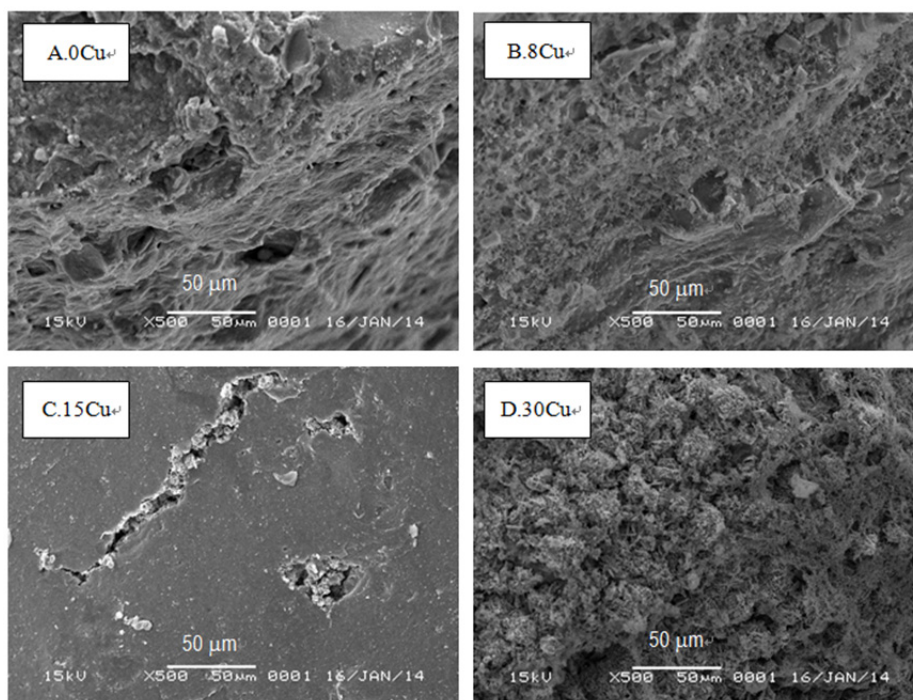


Figure 2. Morphology from SEM analysis

Results in experiments on adsorption capacity are presented in Table 2 for both methods of testing: batch and semi-continue. Indeed the adsorption capacity in term of mg SO₂/g of adsorbent increased in the test using the batch method, but it was not proportional to Cu content. Moreover the adsorption effectively, amount of adsorbed SO₂ decreased in term of mol SO₂/mol Cu. As previously mentioned, adsorbent 15Cu had a relatively low specific surface area then 8Cu and 30Cu (Table 1), which was also confirmed by the observation on their morphology (Figure 2). Probably, this was a reason why the adsorption capacity of 15Cu was lower compared to that of 8Cu.

In the semi-continue method, the best adsorbent was also that with a Cu content of 8% as represented by the progress of adsorption in term of mol SO₂/mol of Cu (Figure 3 and Table 2). Adsorption capacities of our adsorbent were more or less similar to those obtained by (Wittayakun, et. al, 2002), and generally higher than those reported by (Mathieu, et. al, 2013).

From our experiments in the batch method, the original support γ -Al₂O₃ had a very low adsorption capacity of SO₂ of 6 mg/g of catalyst (see Table 2). While in the semi-continuous adsorption test, no-adsorption was found. The adsorption capacity of Al₂O₃ is indeed questionable. Several literature mentioned that there is no-adsorption of SO₂ on Al₂O₃ such as (Wittayakun, et. al, 2002). However as shown by Mathieu, et al, 2013 (see also Table 2), some others showed the ability of Al₂O₃ to adsorb SO₂ and the difficulty in the regeneration of spent adsorbent, Al₂(SO₄)₃.

XRD pattern of used 8Cu catalyst (after adsorption) is presented in Figure 4. Spectrum of CuO was still detected at about 35° and 38°. This indicated, some CuO was not yet utilized. The original γ -Al₂O₃ was still detected in XRD pattern, while pattern of Al₂O₃ was not detected. Thus, there was not any reaction between Al₂O₃ and SO₂ as observed in the adsorption capacity test on the original support using the semi-continuous method (Table 2).

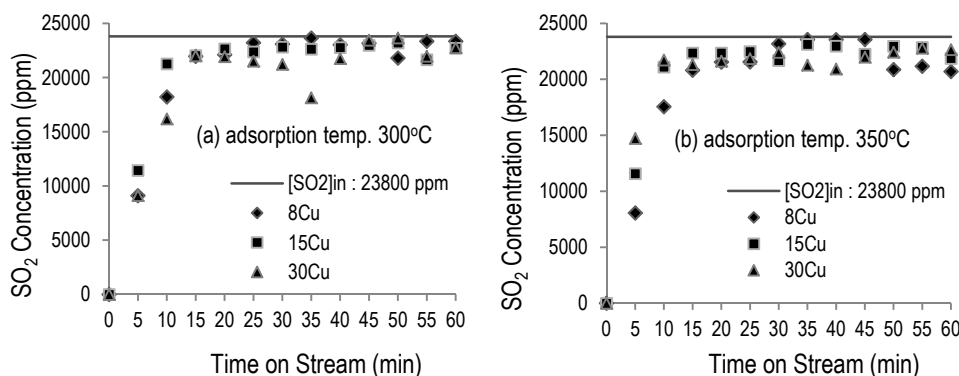


Figure 3. Progress in the semi-continuous adsorption

Table 2. Adsorption capacity

No.	Cu content, by mass	Batch method		Semi-continue method	
		mg SO ₂ /g of adsorbent	mol SO ₂ per mol of Cu	mg SO ₂ /g of adsorbent	mol SO ₂ /mol of Cu
our experiments at adsorption temperature of 300°C					
			50% SO ₂ in gas; adsorption for 6 h	2.5% SO ₂ in gas; gas flow rate 1.6 – 2.0 mL/s	
1	0	6	0	0	0
2	7.93%	63	0.78	58	0.72
3	14.76%	81	0.53	44	0.29
4	28.98%	119	0.39	63	0.21
Wittayakun, et. al, 2002					
5	1%			45	
6	2.3%			64	
Mathieu, et. al, 2013 (from a variety of literature)					
7	0%			~ 30	
8	6.0%			14.2	

9	4.9%		65
10	4.3%	38	
11	7.0%	48 – 61	
12	9.0%		17 – 93
13	6.0%		40
14	8.0%		115
15	25.0%		68

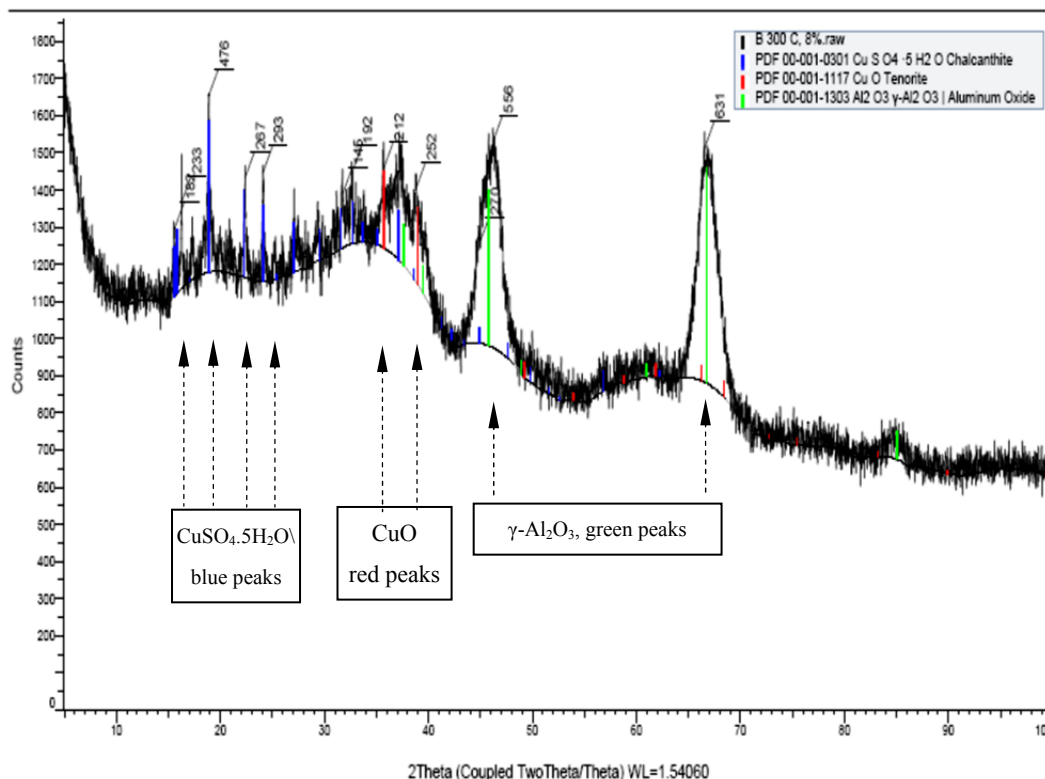


Figure 4. XRD pattern of 8Cu after adsorption

Regeneration of saturated adsorbent or SO₂ desorption was carried out at 600°C for 20 minutes, under the flowing air. As expected, up to four cycles, the regenerated adsorbent performed quite similar to the fresh adsorbent (Figure 5, for adsorbent 8Cu). This result on adsorption-desorption cycle was better than those reported in (Xie, et al, 2004). But, some reseachers mentioned an adsorbent with a CuO content of about 8% could be used (adsorption-desorption) with an adsorption capacity of around 40 g/g for 2 – 750 cycles (Mathieu, et. al, 2013).

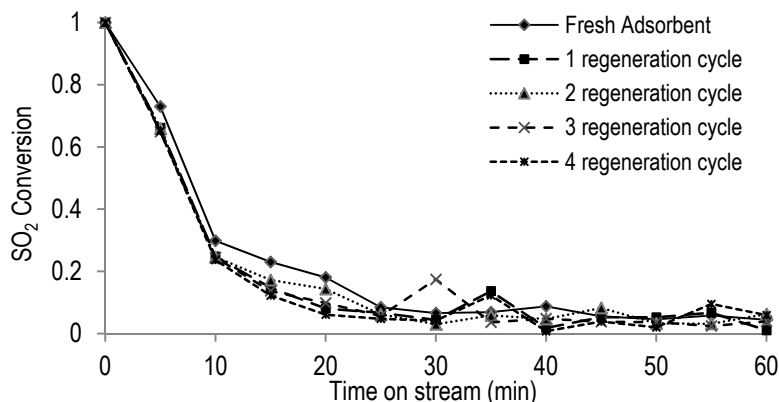


Figure 5. Adsorption-desorption cycles of 8Cu

4. Conclusions

Adsorbent CuO/ γ -Al₂O₃ had successfully been prepared by the dry impregnation method using Cu(NO₃)₂·3H₂O solution on γ -Al₂O₃ as support. Three adsorbents with three different CuO contents of about 8%, 15% and 30% had been characterized and measured its capacity. The best adsorbent was 8Cu (containing 7.93% Cu) with an adsorption capacities of 0.72 and 0.97 mol SO₂/mol of Cu in batch and semi-continuous method of testing respectively. The effective adsorption capacity was found to decrease with increasing Cu content, since the layer of Cu might block the pore of support in adsorbent. Support γ -Al₂O₃ was found to be inert for SO₂. Support of γ -Al₂O₃ was found to be inert for SO₂. Desorption at 600°C did not affect the adsorbent activity up to four adsorption-desorption cycles. With this prospective results, research will be continued further to optimize the Cu content in adsorbent (probably less than 8%) and adsorption test for gas with a SO₂ concentration of about 2500 ppm (flue gas in a coal fired power station).

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