

# Adsorption of Sulfur Dioxide by Copper Oxide Supported on Alumina and Mordenite

Paper # 735

(this paper has not been reviewed for technical content)

**Jatuporn Wittayakun**

School of Chemistry, Institute of Science  
Suranaree University of Technology  
Nakhon Ratchasima, 30000, Thailand

**Kampanat Mahachanon and Nurak Grisdanurak**

Department of Chemical Engineering  
Faculty of Engineering, Khon Kaen University  
Khon Kaen, 40002, Thailand

## ABSTRACT

In this study, copper oxide supported on alumina ( $\text{CuO}/\text{Al}_2\text{O}_3$ ) and mordenite ( $\text{CuO}/\text{MOR}$ ), with Si/Al ratio of 15 and 19, were investigated for  $\text{SO}_2$  adsorption. The catalysts were prepared by ion exchange method for 24 hours, washed, and calcined at  $550^\circ\text{C}$  and the copper loading was determined by atomic absorption spectroscopy (AAS). Particles of copper oxide on  $\text{Al}_2\text{O}_3$  could be clearly observed as cylindrical particles by scanning electron microscope (SEM) while those on mordenite possibly resided in the pore structure and could not be clearly seen. The adsorption of  $\text{SO}_2$  (1000 ppm in helium) was carried out in a flow system connected with a thermogravimetric analyzer (TGA) where the studied temperature was between 300 and  $500^\circ\text{C}$ . The  $\text{SO}_2$  adsorption behaviors of freshly calcined and freshly oxidized catalysts were similar and lead to a conclusion that the form of copper was oxide. At constant temperature, adsorption capability increased with copper loading. The highest adsorption was obtained on  $\text{CuO}/\text{Al}_2\text{O}_3$  but it took so much longer adsorption time than  $\text{CuO}/\text{MOR}15$  and  $\text{Cu}/\text{MOR}15$ . Thus,  $\text{Cu}/\text{Al}_2\text{O}_3$  was not considered as a good candidate for  $\text{SO}_2$  adsorption. Both  $\text{Cu}/\text{MOR}15$  and  $\text{Cu}/\text{MOR}19$  were effective for  $\text{SO}_2$  adsorption and they reached adsorption equilibrium in 15 and 10 minutes, respectively, without any sign of deactivation after 3 cycles.

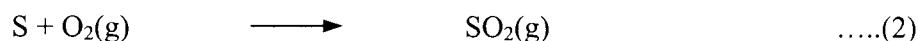
## INTRODUCTION

At the present there is more awareness of air pollution caused by emission of nitrogen oxides ( $\text{NO}_x$ ) and sulfur oxides ( $\text{SO}_x$ ) from industrial combustion. Both  $\text{NO}_x$  and  $\text{SO}_x$  are respiratory irritants and are responsible for acid rain because they can combine with moisture and cause damage to both animals and plants<sup>1</sup>. The emission of  $\text{NO}_x$  can be controlled effectively by selective catalytic reduction (SCR) where  $\text{NO}_x$  is converted into nitrogen gas and water by ammonia over  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst<sup>2</sup>. However,  $\text{V}_2\text{O}_5/\text{TiO}_2$  is not effective for  $\text{SO}_x$  removal.

Sulfur dioxide ( $\text{SO}_2$ ) is a major component of  $\text{SO}_x$ . The amount of  $\text{SO}_2$  can be reduced by an addition of  $\text{SO}_x$  sorbents such as molecular sieve or by use of low sulfur fuel obtained from catalytic hydrodesulfurization (HDS) technique. It was reported that  $\text{Cu}/\text{ZSM}5$  and  $\text{Cu}/\text{MOR}$  were studied for a reduction of  $\text{NO}_x$  and the presence of  $\text{SO}_2$  improved the  $\text{NO}$  decomposition at high temperature.

Catalytic HDS of petroleum feedstock is a process to convert sulfur in petroleum to hydrogen sulfide ( $\text{H}_2\text{S}$ ) as shown in equation 1 by hydrogen gas over catalysts containing transition metal

such as Ni, Co, Mo, or W<sup>3</sup>. However, the remaining sulfur is readily oxidized with oxygen and form SO<sub>2</sub>.<sup>4</sup>



One method to remove SO<sub>2</sub> is wet lime-limestone scrubbing in which SO<sub>2</sub> from flue gas combustion reacts with calcium oxide and calcium carbonate (equation 3 and 4, respectively) to form calcium sulfite (CaSO<sub>3</sub>) which can be oxidized further to calcium sulfate (CaSO<sub>4</sub>)<sup>5</sup>. The drawback of this process is that it produces solid and liquid waste which are hard to manage.



Copper oxide (CuO) is active for SO<sub>2</sub> removal where SO<sub>2</sub> is oxidized to sulfur trioxide (SO<sub>3</sub>) and then to copper sulfate (CuSO<sub>4</sub>).<sup>6,7-9</sup> The interest of this study is to investigate SO<sub>2</sub> removal by adsorption by copper supported on mordenite (Cu/MOR) and copper supported on alumina (Cu/Al<sub>2</sub>O<sub>3</sub>). Mordenite and alumina were selected as catalytic supports because they have high surface area and low capability to adsorb SO<sub>2</sub>. Two types of mordenite were used in this study: one with Si/Al ratio of 15 (MOR15) and another with Si/Al ratio of 19 (MOR19). The SO<sub>2</sub> for all experiments had concentration of 1000 ppm in helium. This concentration was relatively similar to the concentration of SO<sub>2</sub> found in flue gas. All catalysts were prepared by ion exchange technique and the metal loading was determined by atomic absorption spectroscopy (AAS). The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). Finally, the adsorption was performed in a thermogravimetric analyzer (TGA).

## EXPERIMENTAL PROCEDURE

### Catalyst Preparation

The Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/MOR catalysts were prepared by ion-exchange technique. Each support was mixed and stirred in a solution of copper acetate monohydrate (Cu(OAc)<sub>2</sub>·H<sub>2</sub>O) which had a concentration of 0.01, 0.1, and 0.2 molar for 24 hours at room temperature. After the exchange, samples were washed with distilled water, filtered, dried overnight at 110°C, and calcined at 500°C for 3 hours.

### Catalyst Characterization

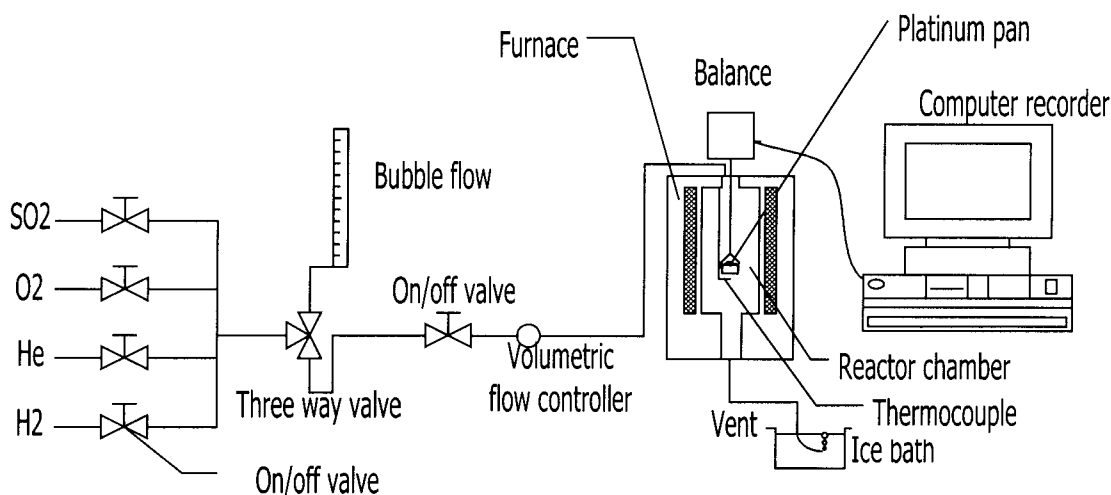
The copper loading of the Cu/MOR and Cu/Al<sub>2</sub>O<sub>3</sub> catalysts was confirmed by atomic absorption spectroscopy (AAS, Perkin-Elmer 3030B). After calcination, the phase of copper in each catalyst was analyzed by powder X-ray diffractometer (Bruker H, model D5005) with Cu K $\alpha$  radiation. The catalyst surface morphology was studied by a JEOL JFC-6400 scanning electron microscope (SEM).

### SO<sub>2</sub> Adsorption of Cu Catalyst after Calcination, Reduction, and Oxidation

The purpose of this study was to confirm whether the active copper species was in metal or oxide form. The catalysts used for this experiment were 1.74%Cu/Al<sub>2</sub>O<sub>3</sub>, 1.35% Cu/MOR15, and 1.73 Cu/MOR19. The SO<sub>2</sub> adsorption behavior of freshly calcined, reduced, and oxidized catalysts on a thermogravimetric analyzer (TGA) (Shimadzu TGA-50) at 500°C were compared. SO<sub>2</sub> 1000 ppm in helium balance was used in all adsorption studies.

### Adsorption of SO<sub>2</sub> on Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/MOR Catalysts and Catalyst Regeneration

The amount of adsorption was studied by TGA where the weight change during the adsorption experiment was detected. The apparatus setting is shown in Figure 1 where the TGA instrument was connected to a three-way valve hooked with inert and reactive gases. In general procedure, approximately 20 mg of a catalyst was loaded in the TGA pan, purged with helium, and heated to 500°C. The gas was then switched to oxygen at a flow rate 50 ml/min and kept for 20 minutes to complete copper oxidation to copper oxide. Then the catalyst was purged with helium flow for 10 minutes and then exposed to SO<sub>2</sub> (1000 ppm in helium) at the flow rate of 50 ml/min for 60 minutes where adsorption saturation was reached. The catalyst was purged again for 10 minutes with helium to remove the unadsorbed SO<sub>2</sub> and, finally, regenerated with hydrogen (flow rate 50 ml/min) for 20 minutes. The regeneration of catalysts was investigated afterward by operating with similar procedure as above for 2 more cycles.



**Figure 1** Reactor scheme for SO<sub>2</sub> adsorption study.

### RESULTS AND DISCUSSION

Supported copper catalysts were prepared by ion-exchange using copper acetate with the concentration of 0.01, 0.1, and 0.2 molar for 24 hours. The metal loading of all catalysts were determined by AAS and shown in Table 1.

Catalysts in Table 1 were characterized by powder XRD to determine the phase and form of active metal. However, neither the peak of copper nor copper oxide was observed. This phenomena could be caused by low metal loading, good metal dispersion on the support, or the migration of metal into the support bulk, or the combination of all those. Thus, we could not yet conclude about the phase of copper metal from XRD results. In fact, the form of copper was

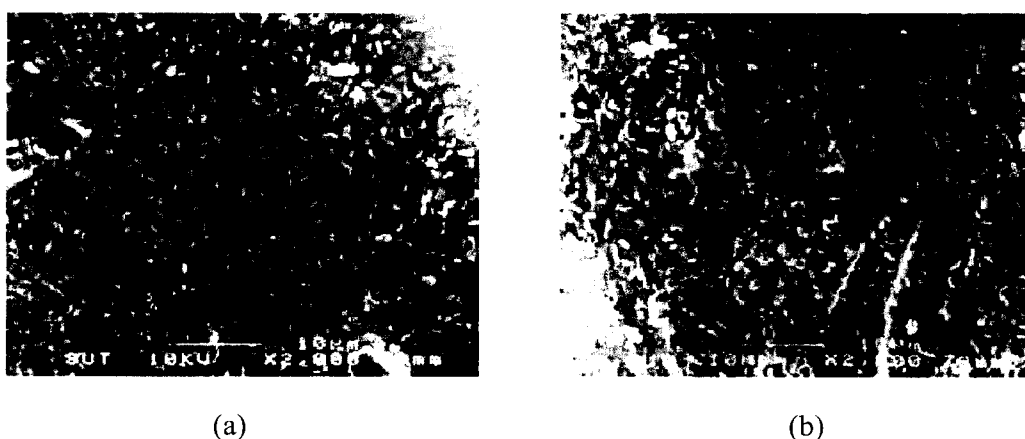
concluded by comparison the adsorption behavior between freshly calcined, reduced, and oxidized catalysts.

**Table 1** Amount of copper loading on alumina and mordenite determined by AAS.

Support	Concentration of Cu(OAc) <sub>2</sub> (molar)	% Cu on catalyst
Al <sub>2</sub> O <sub>3</sub>	0.01	1.00
	0.1	1.74
	0.2	2.30
MOR15	0.01	1.35
	0.1	1.94
	0.2	2.67
MOR19	0.01	1.73
	0.1	2.23
	0.2	2.34

From SO<sub>2</sub> adsorption of freshly calcined, reduced, and oxidized catalysts at similar experimental conditions, it was found (not shown here) that freshly calcined and freshly oxidized catalysts were good adsorbents for SO<sub>2</sub> and they adsorbed in similar fashion while freshly reduced catalysts displayed very low adsorption. Thus, it was concluded that the active form for SO<sub>2</sub> adsorption is copper oxide. As a result, catalysts in the rest of adsorption experiment were oxidized before the SO<sub>2</sub> adsorption.

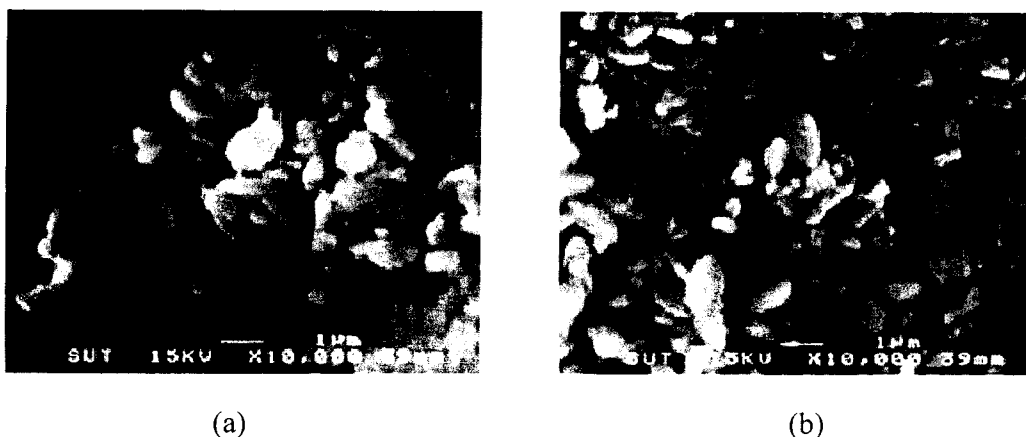
SEM images of CuO/Al<sub>2</sub>O<sub>3</sub> with the magnification of 2,000 (Figure 2) show the cylindrical shape of copper oxide with the approximately 2.2 μm in length on both 1% and 2.3% loading. Even though both cases had similar particle size, the density of CuO particle per area in 2.3% was higher than 1.0% and could be distinguished by SEM. Clustering of small particles to form larger particle were observed in the case of higher loading (i.e., Figure 2 b).



**Figure 2** SEM images of (a) 1.0%Cu/Al<sub>2</sub>O<sub>3</sub> and (b) 2.3%Cu/Al<sub>2</sub>O<sub>3</sub> taken with electron energy of 10 kV at the 2,000 fold magnification.

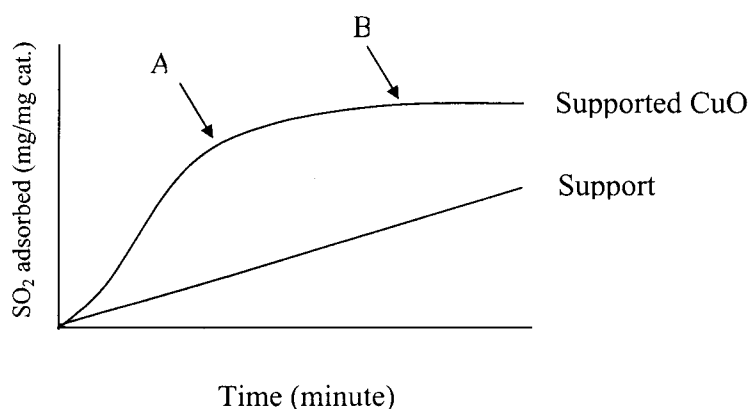
Figure 3 shows SEM images of MOR15 and 1.94%Cu/MOR15 both taken at 10,000 fold magnification. Both images show zeolite particles but not the copper particles because the metal

resides inside the mordenite cavity as a result of ion exchange. Similar images were obtained from MOR19 and Cu/MOR19 and, thus, the same explanation was applied.



**Figure 3** SEM images of (a) MOR15 (b) 1.94%Cu/MOR15 taken with electron energy of 10 kV at the 2,000 fold magnification

Supported CuO catalysts and their supports (alumina, MOR15, and MOR19) were tested for adsorption ability at 500°C compared to the pure supports. Their adsorption characteristic is shown in Figure 4. Alumina and mordenite adsorbed SO<sub>2</sub> slowly and never reached equilibrium during the studied time and the adsorption was strong. By reduction with hydrogen at 500°C, only 20-40% of supports can be regenerated. At this point, it was concluded that alumina and mordenite with Si/Al ratio of 15 and 19 are not good sorbents for SO<sub>2</sub>. In contrast, supported CuO adsorbed SO<sub>2</sub> much faster than their support and reached saturation (point B in Figure 4). All supported catalysts could be regenerated around 90% at 5 minutes and around 100% after 15 minutes. The higher copper loading, the faster the regeneration process was.



**Figure 4** SO<sub>2</sub> adsorption characteristic of support (Al<sub>2</sub>O<sub>3</sub>, MOR15, and MOR19) and supported CuO at 500°C. Point A is where the rate of adsorption slow down and point B is where the adsorption reaches equilibrium.

The details of SO<sub>2</sub> adsorption on support materials and supported CuO are shown in Table 2. As expected, the adsorbed amount in all catalysts increased with metal loading. On CuO/Al<sub>2</sub>O<sub>3</sub>, as the metal loading increased, the amount SO<sub>2</sub> adsorbed per 1%CuO decreased. These phenomena possibly due to the increase in metal particle size from sintering which lowered the surface

area. Clustering of metal particles on alumina were seen from SEM image shown in Figure 2b. Despite the fact that the CuO/Al<sub>2</sub>O<sub>3</sub> catalysts had the highest adsorption ability, they were the slowest to reach the adsorption equilibrium compared to Cu/MOR. Thus, they were not considered to be appropriate for SO<sub>2</sub> adsorption and the rest of this article only mentions results from Cu/MOR15 and Cu/MOR19. In CuO/MOR15, less decrease in adsorption per metal loading was observed. However, the similar behavior was not observed in CuO/MOR19 catalysts indicating better metal dispersion.

**Table 2** Amount SO<sub>2</sub> adsorbed on studied material to reach point A and B; and the time that adsorption equilibrium was reached.

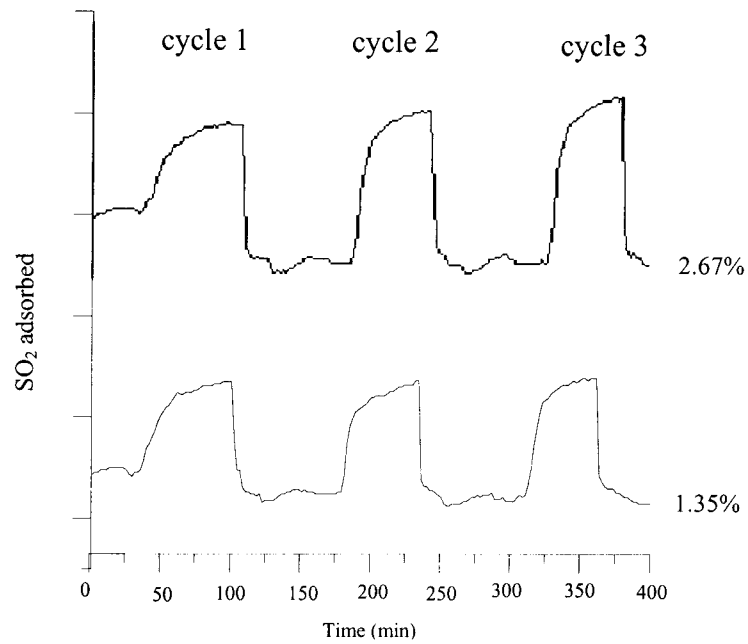
Catalysts	Time to reach point A (minute)	Time to reach point B (minute)	Amount SO <sub>2</sub> adsorbed at B (mg/g catalyst)	Normalized amount SO <sub>2</sub> adsorbed (mg/g 1%CuO)
Al <sub>2</sub> O <sub>3</sub>	> 80	> 80	20.0*	-
1.00% CuO/Al <sub>2</sub> O <sub>3</sub>	44	80	45.5	45.5
1.74% CuO/Al <sub>2</sub> O <sub>3</sub>	44	80	59.9	34.4
2.30% CuO/Al <sub>2</sub> O <sub>3</sub>	44	80	64.0	27.8
MOR15	> 45	> 45	15.1**	-
1.35% CuO/MOR15	15	35	23.0	17.0
1.94% CuO/MOR15	15	35	27.8	14.3
2.67% CuO/MOR15	15	35	34.0	12.7
MOR19	> 40	> 40	22.0***	-
1.73% CuO/MOR19	10	30	23.4	13.5
2.23% CuO/MOR19	10	30	27.0	12.1
2.34% CuO/MOR19	10	30	30.0	12.8

\*at 80 minutes

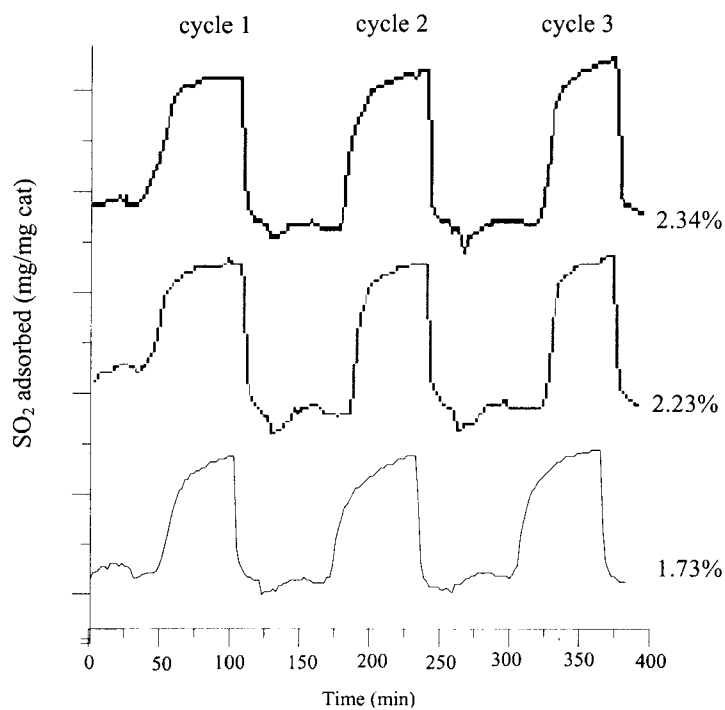
\*\*at 45 minutes

\*\*\*at 40 minutes

The ability of Cu/MOR for SO<sub>2</sub> adsorption was tested for 3 cycles. Prior to the SO<sub>2</sub> adsorption the catalysts were oxidized by oxygen for 20 minutes to ensure the complete CuO formation and purged with helium. The catalysts were then exposed to SO<sub>2</sub> flow until the adsorption more or less reached equilibrium, before regeneration with hydrogen flow for 20 minutes. Similar procedures were repeated for 3 cycles. The results from Cu/MOR15 and Cu/MOR19 are shown in Figure 5 and 6, respectively. Cu/MOR15 and Cu/MOR19 are effective for SO<sub>2</sub> adsorption and the catalysts in all studied loading can be regenerated and reused without any sign of deactivation. It was interesting that the amount of SO<sub>2</sub> adsorbed in the first cycle was slightly lower than the second and third cycle because the weight at the beginning of the cycle was higher. After regeneration in the first cycle, the catalyst weight was lower than at the beginning even though an oxidation was performed before the second cycle. It was possible that at first there was a thick oxide layer on copper particle was removed by reduction. After the re-oxidation, only thin layer of oxide was formed. The other possible explanation is because the re-oxidation step after regeneration by hydrogen was more complete into the bulk of particles than the previous oxidation resulting in more amount of active copper oxide.



**Figure 5** SO<sub>2</sub> adsorption on 1.35% and 2.67% CuO/MOR15. Note that the adsorbed amount on both loadings are in different scale.



**Figure 6** SO<sub>2</sub> adsorption on 1.73%, 2.23%, and 2.34%.Cu/MOR19. Again, the adsorbed amount on three loadings are in different scale.

## CONCLUSIONS

Supported CuO on alumina and mordenite, prepared by ion exchange, could adsorb SO<sub>2</sub> better than the supports. Copper oxide supported on mordenite with Si/Al ratio of 15 and 19 were effective for SO<sub>2</sub> adsorption and show no sign of deactivation after 400 minutes. They reached equilibrium quickly after 15 and 10 minutes, respectively. In contrast, Cu/ Al<sub>2</sub>O<sub>3</sub> was not considered as a good candidate for SO<sub>2</sub> adsorption because it took much longer to reach adsorption equilibrium. At constant temperature, adsorption capability in all catalysts increased with copper loading. Moreover, metal sintering was observed on Cu/Al<sub>2</sub>O<sub>3</sub> but not on CuO/MOR19.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the funding from Shell Centennial Educational Fund.

## REFERENCES

1. Mackenzie, F. T.; Mackenzie, J. A. *Our Changing Planet: An Introduction to Earth System Science and Global Environmental Change*. New Jersey, USA: Prentice Hall, 1995.
2. Farrauto, R. T.; Bartholomew, C. H., *Fundamental of Industrial Catalytic Processes*, Chapman & Hall, 1997.
3. Satterfield, C. N., *Heterogeneous catalysis in industrial practice*, 2<sup>nd</sup> ed., McGraw-Hill, 1991.
4. Schwartz, A. T.; Bunce, D. M.; Silberman, R. G.; Stanitski, C. L.; Stratton, W. J.; Zipp, A. P. *Chemistry in Context*, 2<sup>nd</sup> Edition. American Chemical Society, 1997.
5. Kotz, J. C., Joesten, M. D., Wood, J. L., and Moore, J. W., *The Chemical World: Concepts and Applications*, Florida, USA: Harcourt Brace & Company, 1994.
6. Waqif M.; Saur, O.; Lavalley, C.; Perathoner, S.; Centi, G., *J. Phys. Chem.*, **1991**, 95, 4051-8.
7. Macken, C.; Hodnett, B. K.; Papparatto, G., *Ind. Eng. Chem. Res.*; **2000**; 39(10); 3868-3874.
8. Jeong, S. M. and Kim, S. D., *Ind. Eng. Chem. Res.*, **1997**, **36** (12), 5425 -5431.
9. Jeong, S. M. and Kim, S. D., *Ind. Eng. Chem. Res.*, **2000**, **39** (6), 1911 -1916.