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DEVELOPMENT OF CuO SORBENT MATERIALS SUPPORTED ON METAL OXIDES AND CLAYS APPLIED TO FLUE GAS DESULFURIZATION

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ABSTRACT

In the present work, CuO-based sorbent materials supported on tonsil and bentonite were prepared and evaluated for flue gas desulfurization using thermogravimetry. Results were compared to sorbents supported on commercial alumina, zirconia and titania. Application of ultrasonic energy during preparation of sorbent materials was evaluated, and their sorption capacity, as well as their activation energy, were improved. Sorbent materials supported on tonsil have similar SO_2 retention than those supported on alumina, and the latter is the most commercial sorbent material for dry flue gas desulfurization. A modified shrinking core model was adapted to simulate the experimental results, and the kinetics parameters were estimated by performing a non-linear regression analysis. All sorbent materials were active at 300-500 °C for flue gas desulfurization.

KEYWORDS: Cupric oxide, tonsil, bentonite, flue gas desulfurization, ultrasonic energy, kinetics parameter estimation.

1. INTRODUCTION

In Mexico, the largest part of the electrical energy is produced by burning fossil fuels. The most common fuel employed during the last decade was heavy fuel oil, and then, it has been gradually switched to natural gas according to the Secretary of Energy (SENER, 2016). Another fossil fuel that is intensely used is coal, and it is intended that its burning will augment in the next years. On the other hand, the contribution of diesel and petcoke to the production of energy is minimal. From these fuels, heavy fuel oil, coal, and petcoke contain high amount of sulfur in their chemical structures, so their SO_X emission factors are quite high, around 73.4 kg/m^3 for heavy fuel oil, and 38 kg/ton for coal and petcoke. On the other hand, natural gas is cleaner, and its SO_X emission factor is only 0.0096 kg/Mm^3. Based on that, since natural gas is being more employed every year, the total SO_X emissions have been decreasing recently. Nevertheless, the emissions coming from power plants that burn heavy fuel oil, coal and petcoke, are and will be still high, and the potential risks (acid rain, human health, visibility, and so on) associated with these emissions will be latent. For that, a great environmental challenge in these plants is to decrease the SO_X emissions in the flue gases. Some studies have been done in order to determine the most economical way of decreasing the SO_X emissions (Islas and Grande, 2008). One of the re-emerging technologies is the use of selective sorbent-materials based on copper oxide (CuO) supported on metallic oxides, and sometimes doped with magnesia, ceria, and chromia (Chen and Zhang, 2018; Dorge et al., 2016; Liu et al., 2010; Rezaei et al., 2015; Sun et al., 2016; Yuono et al., 2015). These materials are able to adsorb the SO_X, and once saturated, they can be regenerated either by thermal or reduction-oxidation processes. In this way, the solid waste would be minimal, avoiding the problem of waste disposal. Unfortunately, there are some limitations due to the thermomechanical stability of the support, low surface area, and low dispersion of the active phase. Therefore, new materials, or preparation methods, must be developed to overcome these constraints. Another important issue is the cost of the raw material, and a cheap support must be found and applied. In order to be considered a low-cost raw material, this must be abundant in nature, require little processing, or be a byproduct of waste material from waste industry. Clays, such as bentonite, tonsil and kaolin are abundant in Mexico; therefore, they can be considered a local low- cost raw material. Bentonite is an aluminiumhydrosilicate, in which the proportion of silicic acid to alumina is about 4:1. On the other hand, tonsil is created from bentonite by acid activation. During the acid activation, the individual layers are attacked by the acid, and aluminum, iron, calcium and magnesium ions are released from the lattice. The acid penetrates from the surface of the crystal into its structure of the individual layers, which causes the inner surface of these crystal platelets to increase in size, and the formation of active acid centers.

Furthermore, to increase the activity of the materials, innovative techniques must be used. Recently, ultrasonic energy has been applied for activating clays. The purpose is to improve their surface characteristics by reducing the particle size due to a delamination effect and breaking of layers in other directions, while the crystalline character is retained. In this way, to morphology of the clays is altered, and since the reduction of particle size increases the specific surface area, more active sites would be available. Also, when supported materials are prepared, the application of ultrasonic energy causes the precursor salt crystallites be cracked reducing its crystal size. This originates more active sites on the final material (Allahyari et al, 2014; Parvas et al., 2014; Poli et al., 2008; Rahmani et al., 2016; Sadeghi et al., 2015; Yang and Chen, 2017; Xiao et al., 2014).

In the present work, the effect of support, application of ultrasonic energy during the impregnation step, and temperature for flue gas desulfurization is analyzed in the performance of sorbent-materials. The study is based on the thermogravimetrical behavior of CuO based materials supported on commercial alumina, titania, zirconia, bentonite and tonsil.

2. MATERIALS AND METHODS

Sorbent-materials were prepared using the classical wet impregnation method by adding a known amount of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) solution to Al_2O_3 (alumina), bentonite, TiO_2 (titania), tonsil, and ZrO_2 (zirconia). The surface area of the supports was determined according to the one-point BET method. During impregnation, mechanical stirring, at 300 rpm, was employed to ensure homogeneous dispersion. After the impregnation, the solids were dried at 110°C for 12 h and calcined at 450°C during 4 h under a continuous air flow. Additionally, materials were prepared on the same supports, but during the impregnation step, ultrasonic energy at 20 kHz was applied during 1 h. After calcination, samples of the sorbent-materials were analyzed by Atomic Absorption Spectroscopy to determine the actual composition of CuO in the sorbent materials. Table 1 presents the composition of the different materials.

The sulfation of the materials was carried out in a thermogravimetric balance (TA Instruments 2050) by passing a stream of certified 3600 ppm_v SO_2/N_2 through 0.020 g of sorbent material. The gas flow rate was 100 mL/min, which is the maximum flow of the thermobalance. The gain of weight in the material was assigned to the sorption of SO_2 on the active sites.

3. RESULTS AND DISCUSSION

3.1. Effect of temperature

The sulfation of the different materials was analyzed using a temperature program from 100 up to 750°C with a heating rate of 10°C/min in the TGA instrument in order to determine the temperature interval where the SO_2 adsorption process is preferred. Experimental results are shown in Figure 1. It can be noticed that SO_2 adsorption begins around 300°C producing an increase in the weight of the sorbent materials. This is clearly observed when alumina, titania and zirconia are used as support. On the other hand, when bentonite and tonsil are employed, it is uncertain at which temperature the SO_2 adsorption begins because there is a loss of weight up to 450°C. This is attributed to the elimination of humidity retained inside the pores of the clays, and the possible rearrangement of the crystalline structure; however, it can be assumed that the SO_2 adsorption would begin at the same temperature. The chemisorption process continues in all the materials up to certain temperature, over 500-650°C depending on the support. After this temperature, the SO_2 is thermally desorbed from the active sites.

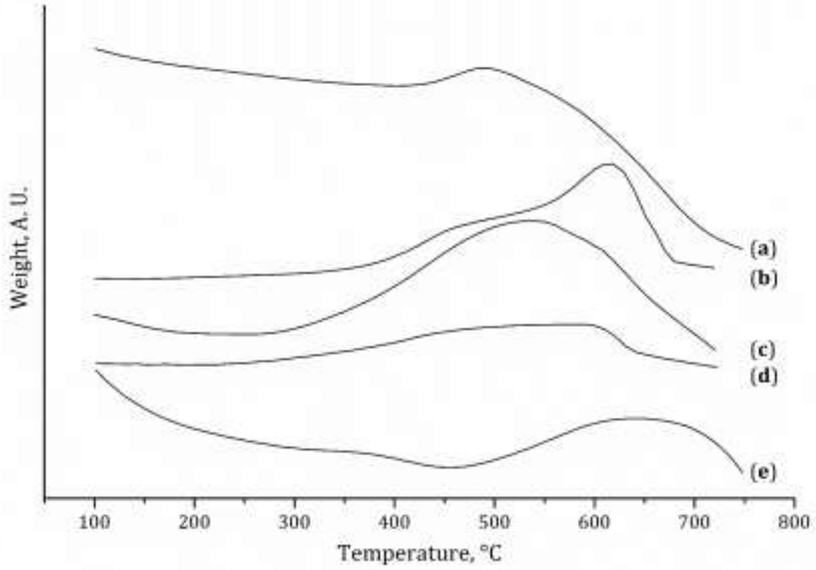

Figure 1: Thermogravimetrics profiles of the CuO based materials in the SO_2 sorption process ($m_{sorbent}$ = 0.020 g; gas mixture: 3600 ppm_v SO_2/N_2 at 100 mL/min; heating rate of 10 °C/min). (a) Bentonite; (b) Titania; (c) Alumina; (d) Zirconia; (e) Tonsil.

3.2. Effect of support

The effect of support on the sorption capacity of the different materials was studied at 300 and 400°C, and the results are presented in Figure 2. It is observed that materials prepared on alumina have the greatest sorption capacity at the different temperatures and preparation methods. On the other hand, materials prepared on zirconia were less active for SO_2 adsorption. Among the studies clays, materials supported on tonsil were more active than those prepared on bentonite, and their reactivity were close to the materials prepared on alumina. The higher sorption capacity was attributed to the surface area of the support since the alumina and the clays have higher surface area compared to titania and zirconia, as it is noticed in Table 1. Higher surface area may lead to better dispersion of the CuO, and therefore, more available active sites. On the other hand, from an economical point of view, alumina is more expensive than bentonite and tonsil (U.S. Geological Survey, 2018). The price of alumina (in USD per ton) is 450, whereas, the price of bentonite and tonsil are 75, and 160, respectively. Therefore, bentonite and tonsil were selected as support for further studies presented in this work, considering that lower efficiency of these materials compared to alumina may be overcome by the production cost.

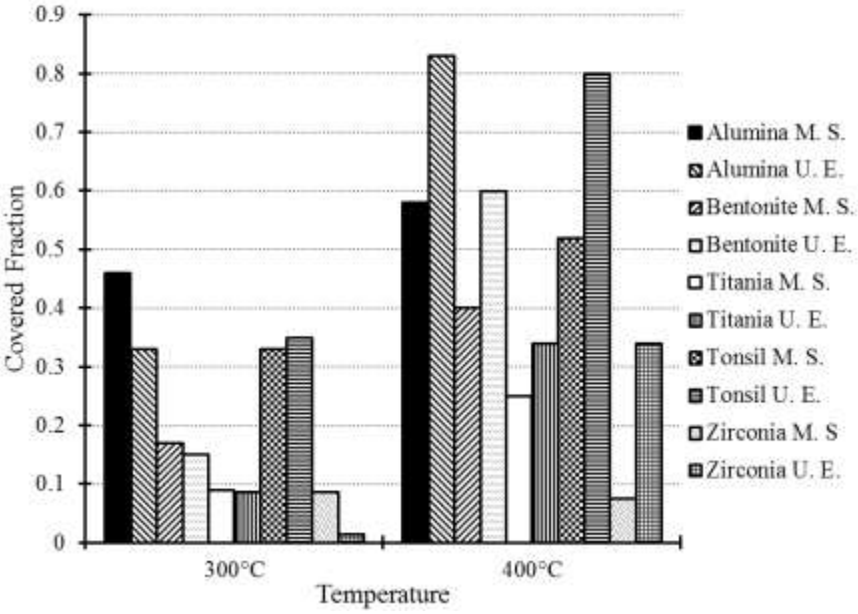

Figure 2: Performance of CuO based materials at 300 and 400 °C with respect to the support (alumina, bentonite, titania, tonsil, and zirconia) and preparation method (M.S.: mechanical stirring; U.E.: ultrasonic energy) in the SO_2 sorption process for 90 min ($m_{sorbent}$ = 0.020 g; gas mixture: 3600 ppm_v SO_2/N_2 at 100 mL/min).

Table 1: CuO load in the supported materials.

Sorbent Material	Support surface area (m^2/g)	CuO Load (wt%)
CuO/Al_2O_3 M. S.	100 - 120	6.94 ± 0.02
CuO/TiO_2 M. S.	5 - 10	6.25 ± 0.04
CuO/ZrO_2 M. S.	10 - 20	6.07 ± 0.02
CuO/Bentonite M. S.	70 - 90	6.03 ± 0.12
CuO/Tonsil M. S.	170 - 200	5.68 ± 0.08
CuO/Al_2O_3 U. E.	100 - 120	5.68 ± 0.03
CuO/TiO_2 U. E.	5 - 10	4.96 ± 0.01
CuO/ZrO_2 U. E.	10 - 20	5.15 ± 0.02
CuO/Bentonite U. E.	70 - 90	4.16 ± 0.15
CuO/Tonsil U. E.	170 - 200	5.34 ± 0.16

M. S.: Mechanical Stirring

U. E.: Ultrasonic Energy

3.3. Effect of ultrasonic energy

Sorbent materials were prepared by the wet impregnation method, but in some cases, the materials were mechanically stirred during impregnation, and in other cases ultrasonic energy at 20 kHz was applied in this step during 1 h. As it can be seen in Figure 2, materials prepared with ultrasonic energy were more active than those prepared by the classical method. This is assigned to a reduction of the particle size of the materials, and a modification in the crystal structure of the support provoked by cavitation, as it has been probed by others (Perez-Maqueda et al., 2005; Allahyari et al, 2014; Rahmani et al., 2016; Sadeghi et al., 2015; Parvas et al., 2014; Yang and Chen, 2017; Poli et al., 2008). When ultrasonic energy is applied to a suspension, microbubbles are formed, and they may implode in the surroundings of a suspended particle leading to microjet and shock-wave impacts on the surface, as well as interparticle collisions, which can produce a particle-size reduction, and other mechanochemical processes, such as disaggregation and delamination. The reduction of the particle size increases the number of available active sites, and the modification of the crystalline structure may produce a synergic effect between the support and the CuO leading to a greater activity for SO_2 adsorption.

3.4. Kinetics parameters estimation

Several models have been developed to represent the heterogeneous non-catalytic solid-gas reaction; however, the most popular used to describe the sulfation of solid sorbents are based on the shrinking core process (Amiri et al., 2015; Djedouani et al., 2016, Jeong et al., 2015; Tomanović et al., 2015). This model considers that a first-order chemical reaction between the SO_2 and the unreacted core of a spherical particle happens first in the outside surface of the particle. Then, the reaction zone moves to the inside of the sorbent, leaving behind a converted material and inert solid called "ash". In this way, there is an unreacted core of the material without reacting that is being shrunk during the chemical reaction. The relationship between the time and the covered fraction depends on the rate-limiting step, as is shown in Table 2.

Table 2: Relationship between the time and the covered fraction depending on the rate-determining step for the shrinking core process.

Rate-limiting step	**Function**
Chemical reaction	$\frac{t}{\tau} = \left[1 - (1-\theta)^{1/3}\right]$ $\tau = \frac{\rho_B \cdot R}{b \cdot k \cdot C_g}$
Diffusion through the product layer	$\frac{t}{\tau} = \left[3 - 3(1-\theta)^{2/3} - 2(1-\theta)\right]$ $\tau = \frac{\rho_B \cdot R^2}{6 \cdot b \cdot \mathcal{D}_e \cdot C_g}$
Mass transfer through gas film	$\frac{t}{\tau} = \theta$ $\tau = \frac{\rho_B \cdot R}{3 \cdot b \cdot k_g \cdot C_g}$

Where: $\boldsymbol{\theta}$ is the covered fraction, $\boldsymbol{\rho_B}$ is the molar density of the active sites in the solid, ***b*** is the molar ratio of solid reactant to gas reactant (ratio of stoichiometric coefficient), ***R*** is the radius of unreacted core, ***k*** is the kinetics constant for the surface reaction, $\boldsymbol{C_g}$ is the SO_2 concentration in the flue gas, $\boldsymbol{D_e}$ is the effective diffusion coefficient of SO_2 through the "ash", $\boldsymbol{k_g}$ is the mass transfer coefficient of the fluid through the particle.

Non-linear regression analysis was performed using Polymath^{TM}. Nevertheless, none of the original equations for shrinking unreacted core model were able to represent the whole sulfurization reaction of the sorbent material. The closest was the model that considers the diffusion through the product layer as the rate-limiting step. For this reason, it was assumed that the SO_2 effective diffusion coefficient, $\mathbf{D_e}$, depends on the conversion using a semi-empirical equation as has been done by others (Amiri at el., 2015; Lee and Koon, 2009; Sun et al., 2017).

$$\mathcal{D}_e = \mathcal{D}_{e0} \cdot \left[1 + \alpha_1 e^{(-\alpha_2 \cdot \theta)}\right]$$

Kinetics parameters were again estimated with Polymath^{TM}, and the results are shown in Table 3. According to these results, a good fit was obtained since the $\boldsymbol{R_{adj}}$ was high, and, with the exception of the material supported on bentonite and prepared with mechanical stirring, it was greater than 0.99. Figures 3 and 4 present the fit between the experimental data and the proposed model.

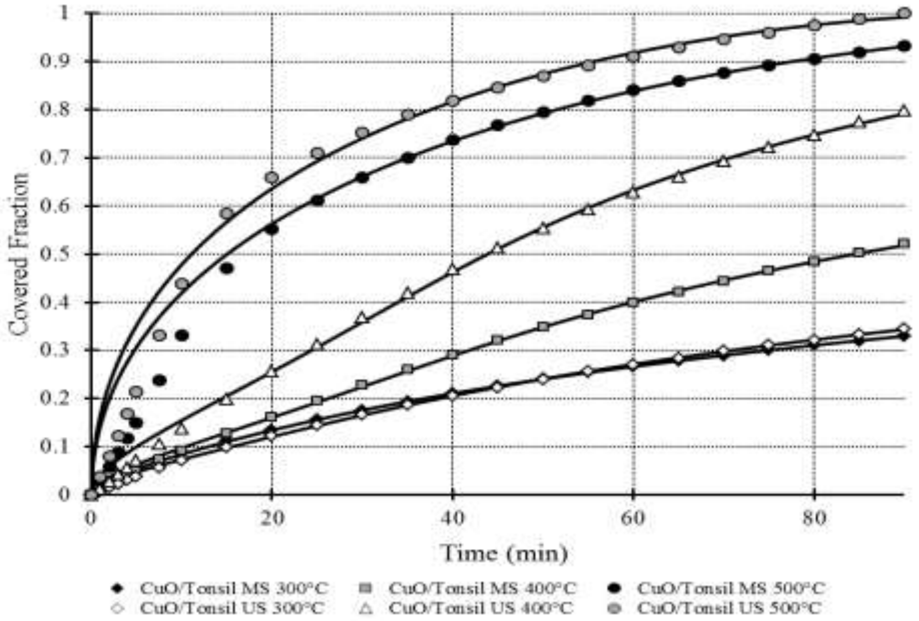

Figure 3: Mathematical adjustment of the experimental SO_2 sorption data to the proposed kinetics model for materials supported on tonsil at 300, 400, and 500 °C ($m_{sorbent}$ = 0.020 g; gas mixture: 3600 ppm_v SO_2/N_2 at 100 mL/min); (solid line represents the tendency of the mathematical kinetics model).

Table 3: Parameter estimation results for the proposed model in the CuO based materials supported on clays.

Material	T [°C]	τ	α_1	α_2	R^2_{adj}
CuO/Bentonite MS	300	6870.629 ± 87.2165	6.292 ± 0.0625	17.644 ± 0.2696	0.997
	400	716.851 ± 93.3026	0.016 ± 0.0159	-9.863 ± 1.9729	0.954
	500	24.187 ± 6.0108	0.051 ± 0.0174	-8.148 ± 0.3614	0.972
CuO/Bentonite US	300	5768.763 ± 818.8243	6.465 ± 0.7811	12.849 ± 1.1008	0.998
	400	503.697 ± 0.0006	22.910 ± 0.0002	12.0794 ±0.0000	0.998
	500	58.45004 ± 6.1756	0.001 ± 0.0002	-13.235 ± 0.4977	0.995
CuO/Tonsil MS	300	1991.505 ± 7.2779	2.883 ± 0.0868	12.059 ± 0.2446	0.999
	400	629.302 ± 2.3050	7.599 ± 0.0800	7.098 ± 0.0371	0.999
	500	136.462 ± 1.3297	$5.159\times10^{-6} \pm 2.11\times10^{-7}$	-12.018 ± 4.2922	0.997
CuO/Tonsil US	300	1739.502 ± 0.0759	4.784 ± 0.0010	11.194 ± 0.0009	0.999
	400	193.438 ± 0.0150	10.106 ± 0.0021	4.513 ± 0.0004	0.998
	500	73.271 ± 8.059	0.382 ± 0.0186	0.042 ± 0.0064	0.994

The diffusion coefficient, $\boldsymbol{D_{e0}}$, cannot be directly determined since other parameters that make up τ, such as ρ_B and $\boldsymbol{R}$, are unknown. Nevertheless, tendencies with respect to temperature and preparation method can be observed. First, it is important to assert that a decrease in the τ value implies that $\boldsymbol{D_{e0}}$ increases since the other parameters are constant, and vice versa. An increase in τ value means a reduction in the diffusion coefficient. Based on this statement, it is noted that the application of ultrasonic energy enhances the diffusion coefficient at any temperature in both bentonite and tonsil supported materials, and for that reason, the activity of these materials are higher. This is in agreement with previous works, in which ultrasonic energy is applied to clays to improve their characteristics for different applications, as it was previously explained (Allahyari et al, 2014; Parvas et al., 2014; Poli et al., 2008; Rahmani et al., 2016; Sadeghi et al., 2015; Yang and Chen, 2017; Xiao et al., 2014).

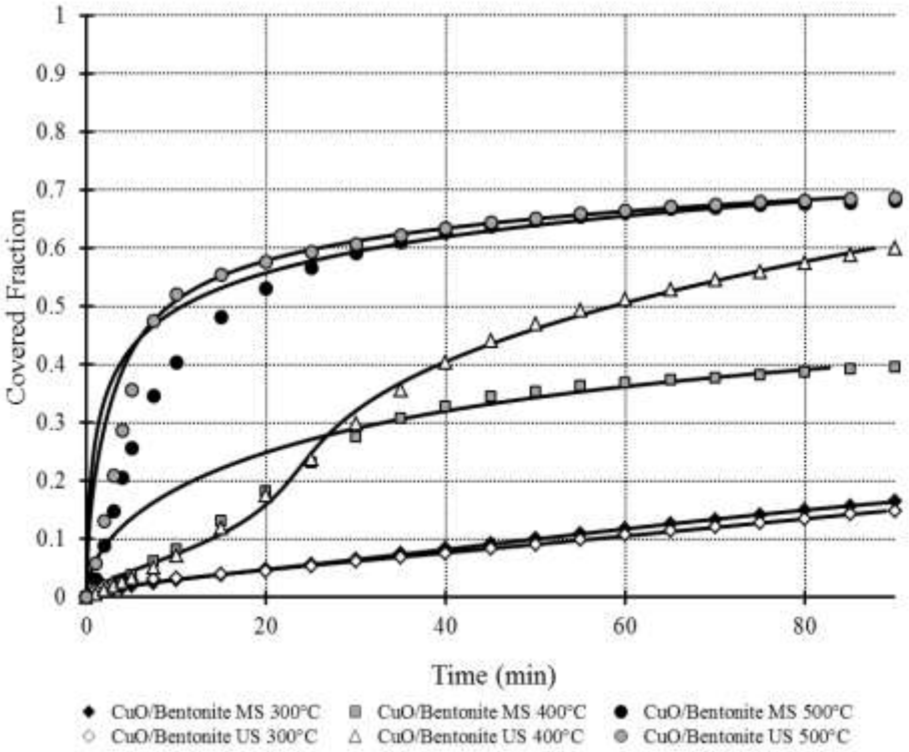

Figure 4: Mathematical adjustment of the experimental SO_2 sorption data to the proposed kinetics model for materials supported on bentonite at 300, 400, and 500 °C ($m_{sorbent}$ = 0.020 g; gas mixture: 3600 ppm_v SO_2/N_2 at 100 mL/min); (solid line represents the tendency of the mathematical kinetics model).

On the other hand, it is noted that as the temperature increases also does the diffusion coefficient, so the activation energy can be estimated. The obtained results are displayed in Table 4. The activation energy is smaller for sorbent materials prepared with ultrasonic energy compared to those made with only mechanical stirring. Therefore, the application of ultrasonic energy during preparation of sorbent materials facilitates the subsequent activation of the materials by temperature. On the other hand, sorbent materials supported on tonsil have smaller activation energy than those prepared on bentonite. The effect of temperature is more remarkable in materials supported in tonsil, so they are more active.

Table 4: Activation energy for the proposed kinetics model for the CuO based materials supported on clays.

Material	**E_A/R**
CuO/Bentonite MS	11,380 ± 231.8
CuO/Bentonite US	11,190 ± 2032.9
CuO/Tonsil MS	7,677 ± 615.6
CuO/Tonsil US	5,440 ± 107.9

4. CONCLUSIONS

The effects of ultrasonic energy during preparation, type of support and adsorption temperature on CuO based sorbent materials were evaluated for SO_2 adsorption using thermogravimetry. The shrinking core model was used to represent the adsorption process. According to the obtained results, the application of ultrasonic energy during the impregnation procedure of sorbent materials supported on bentonite and tonsil improves their sorption capacity and decreases the activation energy for SO_2 adsorption compared to those sorbent materials prepared by mechanical stirring. CuO supported on tonsil had similar SO_2 uptake performance than CuO supported on alumina (with or without ultrasonic energy assistance), and the latter is the most popular and commercial sorbent material for dry flue gas desulfurization. However, regeneration cycles must be carried on to evaluate the potential use of this cheaper sorbent material. Low SO_2 uptake in CuO based sorbents supported on bentonite could be attributed to a possible rearrangement of their crystalline structure. All sorbent materials can be applied in the temperature range from 300 up to 550°C which is the common temperature of flue gases in Mexican power plants.

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