Application of Mesoporous Silica as Catalyst Support in Sulfur Dioxide Removal: Metal and Amine Sorbent Modifications

Muhammad Adli Hanif¹, Naimah Ibrahim¹, Khairuddin Md Isa¹ and Aishah Abdul Jalil²,³

¹School of Environmental Engineering, Kompleks Pusat Pengajian Jejawi 3, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia.
²Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM Johor Bahru, 81310 Skudai, Johor, Malaysia.
³Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, UTM Johor Bahru, 81310 Skudai, Johor, Malaysia.

E-mail: naimah@unimap.edu.my

Abstract. Emission of hazardous SO2 into the atmosphere due to the burning of fossil fuels in various industries is detrimental not only to the environment but also to human beings. Various mitigation techniques have been implemented to overcome this problem, with flue gas desulfurization (FGD) method being the most commonly used. Dry FGD does not typically perform as good as wet method and requires new type of sorbent to be tested. Mesoporous silica (MS), a sorbent with porosity in the range of 2-50 nm is considered as attractive alternative due to its high specific surface area, ordered pore structures and wide array of morphologies. Due to relatively weak interaction between MS and SO2 adsorbate during dry FGD process, additives are introduced to overcome this problem. These MS are modified with basic additives which are deemed more favorable for SO2 adsorption. Metal and amine-based additives are commonly employed where the latter are reported to obtain higher adsorption capacity. Increasing additive loading is beneficial up to an optimal value depending on the types of additives.

1. Introduction

Sulfur dioxide (SO2) is colorless gas commonly persist in the atmosphere, originating from conventional thermal power plant in which electricity is produced by means of fossil fuel combustion. The concentration of SO2 emitted varies, up to 1540 ppm; depending on the sulfur content of the fossil fuel [1]. Depending on meteorological condition, the emitted SO2 may travel much further from the emitting point as the residence time of the gas is between 3 to 5 days. In the presence of other substances such as O2 and H2O, SO2 can easily react to form hazardous compounds such as sulfur trioxide (SO3), sulfurous acid (H2SO3) and various sulfate particles. SO2 acts as precursor of acid rain which consequently induces acidification of water (lake, stream etc.), damage in plantations and forests, and corrosion of buildings. According to WHO, an exposure as short as 10 minutes may cause changes in respiratory functions of an asthmatic person, while longer exposure may lead to damage in lung functionality or even death [2].

Flue gas desulfurization (FGD) is an end-of-pipe treatment method used in removing SO2 before the flue gas is disposed into the atmosphere. Wet FGD using lime or limestone are the most common method used with high SO2 removal, however, the process requires huge amount of water, large area for
installation and sludge production [3–4]. Dry FGD is seen more attractive, as the sorbent has the possibility to be regenerated and less treatment of waste and residue is required. As SO₂ removal efficiency via dry FGD method is considered inferior compared to wet FGD [1], various new sorbents are being synthesized and tested, to overcome shortcomings of the dry method.

Mesoporous silica (MS) is a sorbent with porosity in the range of 2-50 nm [5] and has unique properties such as ordered pore structures and wide array of morphologies. MS also possesses high surface area, thanks to nano-templating approach during the material synthesis. The naming of MS typically follows a particular system, three letters followed by a number depending on the group of researchers who first synthesize the material or the characteristics of the material itself.

| Mesoporous silica | Full name                                      |
|-------------------|------------------------------------------------|
| MCM-41            | Mobil Composition of Matter-41                |
| SBA-15            | Santa Barbara Amorphous-15                    |
| KIT-6             | Korea Institute of Science and Technology-6   |
| HMM-33            | Hiroshima Mesoporous Material-33              |
| TUD-1             | Technische Universiteit Delft-1                |
| KCC-1             | KAUST Catalysis Centre-1                      |
| FSM-16            | Folded sheets mesoporous material-16          |

In this paper, the use of various MS as catalyst support in SO₂ removal will be discussed as a basis for further work on SO₂ removal by KCC-1. The characteristics of each MS will be briefly explained to describe the different properties which may lead to different abilities in removing SO₂ from the flue gas. Finally, modification of MS by additive incorporation will be discussed to give an insight on the method and conditions preferred to obtain an optimum SO₂ removal.

2. Characteristics of MS

All MS are synthesized by reacting tetraethyl orthosilicate, TEOS (Si(OC₂H₅)₄) as the silica source and different various structure/directing template substances depending on the required MS. Recent synthesis of MS also reported the used of low cost siliceous materials such as rice husk ash, oil palm ash and beach sand as a substitute for TEOS [6–8].

Nitrogen (N₂) adsorption-desorption at 77 K shows that MCM-41, SBA-15 and KIT-6 follows Type IV (a) isotherm with H1 hysteresis loop [9–10]. This templated MS underwent capillary condensation during adsorption-desorption and demonstrated narrow spectrum of uniform mesopores. The use of MS in flue gas treatment is deemed attractive due its high surface area which are reported to be in the range of 969-1153 m²/g for MCM-41 [11–12], 525-977 m²/g for SBA-15 [13–14] and 569 m²/g for KIT-6 [10]. Although MS demonstrates high surface area, the interactions between MS and SO₂ molecules are relatively weak [14]. This problem can be overcome by incorporating various kind of additives (or catalysts) on MS, which acts as catalyst support in the reaction system. As SO₂ is an acidic gas, the use of additives which can provide enough basicity is essential to neutralize the acidity caused by adsorbed SO₂ which may limit the performance of the adsorbent. However, the inclusion of additives will contribute to the reduction in surface area and pore volume of MS, which can be ascribed to two reasons [10, 15]: (i) dispersion of the additives on the MS surface and (ii) pore fillings by the additives. Excessive additives may cause pore blocking which subsequently weaken the adsorbent performance.
3. Characteristics of MS

Studies on SO\textsubscript{2} removal were typically conducted via breakthrough experiment with a fixed bed or packed bed reactor made of quartz, glass or stainless steel as shown in Fig. 1. The ability of a sorbent to remove SO\textsubscript{2} from flue gas is determined by (i) SO\textsubscript{2} breakthrough time or (ii) by calculating the adsorption capacity using the value of inlet SO\textsubscript{2} concentration, C\textsubscript{0}; breakthrough concentration of SO\textsubscript{2}, C\textsubscript{A}; gas flow rate, Q\textsubscript{f}; gas molar fraction, y\textsubscript{t}; mass of catalyst, m\textsubscript{c}; and breakthrough time, t; using Eq. 1 [16]:

\[
q = \frac{C_0 Q f y_t}{m_c} \int_0^t \left( 1 - \frac{C_A}{C_0} \right) dt
\]  

As mentioned earlier, incorporation of additives on MS is essential as the interactions between MS and SO\textsubscript{2} are relatively weak. The additives need to be carefully selected, bearing in mind that basic additives are preferable to counter acidity brought about by adsorption of SO\textsubscript{2}. Two types of additives commonly utilized in modification of MS is metal and amine-based additives. Metal salts are incorporated into MS via wet impregnation method followed by oven-drying and calcination. Calcination temperature plays an important role as the average pore diameter of the sorbent increase at higher temperature. This has been observed by Li et al. [17] when the calcination temperature of Al-Cu/MCM-41 was increased from 300 to 500°C. Further increase in calcination temperature is ineffective, which may be attributed to collapsing of pores. Flowing synthetic air during calcination period is also beneficial as it helps to disperse the metal additives [18].

On the other hand, amine-based additives are introduced on MS via wet impregnation followed by drying. Washing step prior to drying may also be included to remove excess organic solvent (e.g. ethanol, methanol) used for dissolving amine-based additives [12]. Amine-modified MSs are not subjected to calcination due to high volatility, nature of amine, which may resulted in excessive loss of amine due to evaporation [11]. Table 2 summarizes previous studies on SO\textsubscript{2} removal using modified mesoporous silica (in terms of the gaseous components, initial SO\textsubscript{2} concentration, reaction temperature and the resulting sorption capacity).

As can be seen in Table 2, all amine-modified MS show better SO\textsubscript{2} removal performance compared to metal-modified MS, with highest removal achieved by MCM-41 modified with polyethylenimine (PEI) (299.8 mg SO\textsubscript{2}/g sorbent) [22]. This may be attributed to the strength of amine, a naturally basic substance; to counter the increase in acidity during adsorption process. However, it must be noted that the study using metal-modified MS was conducted at higher temperature (400°C) and lower inlet SO\textsubscript{2} concentration (250 ppm). As SO\textsubscript{2} adsorption is a thermodynamically controlled process with an exothermic nature, metal-modified MS suffer from low heat of adsorption at high SO\textsubscript{2} uptake caused by
surface heterogeneity [11–12]. According to Eq. 1, the use of lower inlet SO₂ concentration will undoubtedly lead to weaker adsorption capacity, simply due to lack of the SO₂ adsorbate molecules to be adsorbed.

### Table 2. Summary of previous studies on SO₂ removal using modified MS

| Sorbent                  | Gas mixture  | SO₂ concentration (ppm) | Reaction temperature (°C) | Sorption capacity (mg SO₂/g sorbent) | Ref. |
|--------------------------|--------------|--------------------------|---------------------------|--------------------------------------|------|
| Metal-based additives    |              |                          |                           |                                      |      |
| CuO/KIT-6                | SO₂, O₂      | 250                      | 400                       | 8.97                                 | [10] |
| CuO/Ce/KIT-6             | SO₂, O₂      | 250                      | 400                       | 39.71                                |      |
| CuO/SBA-15               | SO₂, O₂      | 250                      | 400                       | 64.06                                | [18] |
| CuO/SBA-15               | SO₂, O₂      | 250                      | 400                       | 110                                  | [19] |
| CuO/SBA-15               | SO₂, O₂      | 250                      | 400                       | 43.1                                 | [20] |
| CuO-Co₂/MCM-41           | SO₂, O₂      | 250                      | 400                       | 15                                   |      |
| CuO-LiCl/MCM-41          | SO₂, O₂      | 250                      | 400                       | 80                                   | [21] |
| Li-doped/MCM-41          |              |                          |                           | 130                                  |      |
| Amine-based additives    |              |                          |                           |                                      |      |
| BHAP/MCM-41              | SO₂, H₂O     | 500                      | 25/50                     | 181.93                               | [11] |
| TER/MCM-41               | SO₂, H₂O     | 700                      | 25/40                     | 140.29                               | [12] |
| TEA/SBA-15               | SO₂, CO₂     | 1340                     | 25                        | 177                                  | [13] |
| TMGL/MCM-41              | SO₂, H₂O     | 2000                     | 30                        | 223                                  | [14] |
| mPEI/MCM-41              | SO₂, H₂O     |                          |                           | 299.8                                |      |
| mG3/MCM-41               | SO₂          | 1000                     | 23/50                     | 278.02                               | [22] |
| mG2/SBA-15               | SO₂          |                          |                           | −153.74                              |      |
| TEA/SBA-15               | SO₂          | 600                      | 100                       | 146.3                                | [23] |

The influence of additive loading on SO₂ removal by modified MS can be seen in table 3. The increase in amine loading resulted in substantial change of the additives into bulk-like properties [14, 24]. However, increment of amine loading is only effective up to a certain optimal point, as excessive loading will lead to complete pore plugging. These optimal loading is highly dependent on the type of amine additives used as these materials interact differently with the MS catalyst support. Previous works by Zhi et al. [13] and Zhang et al. [24] demonstrates that highest SO₂ removal can be achieved by modifying SBA-15 with triethanolamine at 75% loading while the optimal loading for 1,3-bis(3-propylthiopropyl)silane-imidazolium chloride (FIL) on the same MS is only at 10%. Additionally, adsorption pathway (physisorption or chemisorption) also plays a role in determining optimal amine loading as tetramethylguanidinium lactate (TMGL) added onto MCM-41 exhibited two optimal conditions, at 10% due to high physisorption and at 40% due to structure distortion into bulk-like properties [14].

### Table 3: Summary of optimal loading on various MSs towards SO₂ removal

| Additive    | MS   | Loading tested (%) | Optimal loading (%) | Ref.  |
|-------------|------|--------------------|---------------------|-------|
| Triethanolamine | SBA-15 | 20-95              | 75                  | [13]  |
| TMGL        | MCM-41 | 10-60              | 10 and 40           | [14]  |
| FIL         | SBA-15 | 5-20               | 10                  | [24]  |
Studies by Gaudin et al. [10] and Mathieu et al. [21] using modified KIT-6 and MCM-41, respectively; found that the use of single additive may have insignificant effect on SO$_2$ adsorption, however, when combined with another insignificant additive, the resulting synergistic effect could enhance the overall performance of the sorbent. In this case, MS modified with copper-based additive did not perform well due to huge reduction in surface area and possible pore plugging caused by big copper particles, while cerium-based additive simply had oxidizing effect. Combination of the two additives on MS via co-precipitation resulted in higher sorption capacity than the sum of individual sorption capacity of copper and cerium.

4. Conclusions
Mesoporous silica with its unique properties of high specific surface area, ordered pore structures and wide array of morphologies has been proven to be appealing alternative for dry flue gas desulfurization. Mesoporous silica, specifically MCM-41, SBA-15 and KIT-6, act as catalyst support and have been incorporated with various additives ranging from metals, ionic liquid and amine-based additives to improve the adsorption capacity of the sorbent. Reaction parameters such as temperature, SO$_2$ inlet concentration, loading of additives and composition of flue gas need to be considered as each factor significantly affect the performance of a modified MS. Current highest SO$_2$ removal was achieved by MCM-41 modified with polyethylenimine (PEI) which removes 299.8 mg of SO$_2$ per gram of sorbent. However, the use of KCC-1, an MS which reported to have better properties than its predecessors have yet to be tested in SO$_2$ removal. Additionally, as MS can be synthesized in various morphologies with ordered structure, new kind of MS may be developed in the future which bring the possibility of better performance than the reported studies.

Acknowledgements
This study was supported by Collaborative Research Grant (9023-00001) between Universiti Malaysia Perlis, Universiti Teknologi Malaysia, Universiti Tun Hussein Onn Malaysia and Universiti Malaysia Pahang.

References
[1] Flagiello D, Erto A, Lancia A and Di Natale F 2018 Fuel 214 p 254
[2] WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide (2005)
[3] Rosas J M, Ruiz-Rosas R, Rodríguez-Mirasol J and Cordero T 2017 Chem. Eng. J. 307 p 707
[4] Ma Y, Yuan D, Mu B, Gao L, Zhang X and Zhang H 2018 Fuel 219 p 12
[5] Porada S, Zhao R, Van Der Wal A, Presser V and Biesheuvel P M 2013 Prog. Mater. Sci. 58 p 1388
[6] Salazar Hoyos L A, Faroldi B M and Cornaglia L M 2020 Catal. Commun. 135 p 105898
[7] Razak H A, Abdullah N, Setiabudi H D, Yee C S and Ainirazali N 2019 IOP Conf. Ser.Mater. Sci. Eng. 702 p 012024
[8] V Sales R, Moura H O, Câmara A B, Rodriguez-Castellón E, Silva J A, Pergher S B 2019 Catalysts 9 p 651
[9] Thommes M, Kaneko K, Neimark A V, Olivier J P, Rodriguez-Reinoso F, Rouquerol J and Sing K S 2015 Pure Appl. Chem. 87 p 1051-69
[10] Gaudin P, Dorge S, Nouali H, Kehrli D, Michel M, Josien L, Fioux P, Vidal L, Soulard M, Vierling M and Molière M 2015 Appl. Catal. A Gen. 504 p 110-8
[11] Tailor R and Sayari A 2016 Chem. Eng. J. 289 p 142
[12] Tailor R, Ahmadalinezhad A and Sayari A 2014 Chem. Eng. J. 240 p 462
[13] Zhi Y, Zhou Y, Su W, Sun Y and Zhou L 2011 Ind. Eng. Chem. Res. 50 p 8698
[14] Li X, Zhang L, Zheng Y and Zheng C 2015 Energ. Fuel. 29 p 942
[15] Shahul Hamid M Y, Triwahyono S, Jalil A A, Che Jusoh N W, Izan S M and Tuan Abdullah T. A 2018 Inorg. Chem. 57 p 5859
[16] Ahmad N, Md Ali U F, Yong S H, Ibrahim N, Ahmad R and Muhammad Ridwan F 2018 Web of Conferences 34 p 20
[17] Li S, Li K, Hao J, Ning P, Tang L and Wang C 2017 J. Chem. Eng. Japan 50 p 376
[18] Gaudin P, Fioux P, Dorge S, Nouali H, Vierling M, Fiani E, Molière M, Brilhac J F and Patarin 2016 Fuel Process. Technol. 153 p 129-36
[19] Berger M, Brillard A, Dorge S, Habermacher D, Nouali H, Kerendoncuff P, Vierling M, Molière M, Patarin J and Brilhac JF 2020 J. Hazard. Mater. 385 p 121579
[20] Berger M, Fioux P, Dorge S, Nouali H, Habermacher D, Fiani E, Vierling M, Moliere M, Brilhac J F and Patarin J 2017 Catal. Sci. Technol. 7 p 4115-28.
[21] Mathieu Y, Soulard M, Patarin J and M. Molière 2012 Fuel Process. Technol. 99 p 35
[22] Tailor R, Abboud M and Sayari A 2014 Environ. Sci. Technol. 48 p 2025
[23] Wei L, Gao Z and Wang Y 2017 Asia-Pacific J. Chem. Eng. 12 p 660
[24] Zhang L, Xiao L, Zhang Y and France L J 2018 Energ. Fuel. 32 p 678