

## **Fast and Highly Efficient SO<sub>2</sub> Capture by TMG Immobilized on Hierarchical Micro-Meso-Macroporous AlPO-5/ Cordierite Honeycomb Ceramic Materials**

Jin Xu, Xiaoling Zha, Yumei Wu, Qingping Ke\*, Weifang Yu\*

College of Chemistry and Materials Engineering, Wenzhou University, Zhejiang 325035, P. R. China.

### **1 Materials**

Ortho-phosphoric acid, Aluminum isopropoxide (98%) and Tetramethylguanidine (TMG, 99%) and carbon dioxide (CO<sub>2</sub>, ≥99.999%) were obtained from Aladdin Industrial Inc. (China). Nitrogen (N<sub>2</sub>, ≥99.999%) were purchased from Wenzhou Changsheng Gas Co., LTD., China. N<sub>2</sub>/SO<sub>2</sub> mixture gas with 2.60% SO<sub>2</sub> were purchased from Changzhou Jinghua Industrial Gas Co., LTD., China. Cordierite honeycomb ceramic (CHC) were provided by Jiangxi Pingxiang Sanhe Ceramics Co., LTD., China. All agents were used without any further purification.

### **2 Syntheses of AlPO-5 and MeAlPO-5**

AlPO-5 samples were prepared as described in the literature<sup>[1]</sup>, and its composition was 1P<sub>2</sub>O<sub>5</sub>:0.8Al<sub>2</sub>O<sub>3</sub>:0.6TMG:33H<sub>2</sub>O. Typically, aluminum isopropoxide (4.08 g) were added to deionized water (7.9 mL), followed by addition of H<sub>3</sub>PO<sub>4</sub> (1.8 mL) under stirring. TMG (1.1 mL) was then introduced into the gel under stirring. All above operations were run at 15 °C. Finally, this synthesized gel was transferred into an autoclave and hydrothermal crystallization at 150 °C for 6 h. The formed solid was collected by filtrating, dried at 100 °C overnight.

### **3. Characterizations**

Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 surface areas. Before the measurements, the sample was degassed for 4 h at 350 °C (TMG-AlPO-5 was degassed at 60 °C for 4h).

Brumauer-Emmett-Teller (BET) method was used to calculate the specific surface

areas of samples.

X-ray diffraction (XRD) patterns of samples were recorded on a RIGAKU UltimalVdiffractometer with the Cu K $\alpha$  radiation.

Transmission electron microscopy (TEM) images of samples were taken on a FEI Tecnai G2 F30 S-Twin microscope, and the electron beam accelerating voltage was 300 kV.

Scanning electron microscopy (SEM) images were obtained on a high-resolution field emission (JSM6700F, JEOL) and operated at 15 kV. The samples were coated with a thin layer of platinum to prevent charging before scanning.

Thermogravimetric (TG) analyses were performed on a Perkin-Elmer Diamond TG-DTA thermal analyzer under the flow of N<sub>2</sub>.

FT-IR spectra were measured from KBr disks on a Perkin-Elmer spectrometer.

#### 4. Breakthrough experiments

SO<sub>2</sub> breakthrough experiments were carried out on a Modular Microreaction System (OI-MMRS 01.2009, Ehrfeld Mikrotechnik BTS GmbH, Germany). Two mass flow controllers (5850E, Brooks instrument, America), connected to N<sub>2</sub> and SO<sub>2</sub> gas cylinders, respectively, were used to provide the desired feed concentration and flowrate. SO<sub>2</sub> concentration at the outlet was measured by an In-situ FT-IR (Bruker Optik Asia Pacific Limited, Germany).

SO<sub>2</sub> capacity was calculated by

$$q_S = \frac{Q \int_0^\infty (c_{in} - c_{out}) dt}{m_{IL}} \quad (S1)$$

where  $q_S$  is the capacity in mol SO<sub>2</sub>/mol IL,  $Q$  is the flowrate in l/min,  $c$  is SO<sub>2</sub> concentration in mol/l, in for the inlet feed and out for the outlet,  $t$  is time in min,  $m_{IL}$  is total IL loading of the adsorbent sample in mol.

In order to quantify the adsorption rate for easy comparison with previously reported materials<sup>[2]</sup>, the adsorption breakthrough curve was also used to estimate  $t_{0.9}$ , which had been defined as the time required to achieve 90% adsorption capacity under constant partial pressure (or concentration) of the interested adsorbate.<sup>[3]</sup> The calculation is based on the assumptions of linear and fast adsorption, negligible axial dispersion effects, and mass transfer controlled process that can be described by an overall coefficient. The procedure is briefly introduced below.

Breakthrough experiments give a step signal at the inlet. The dimensionless outlet concentration profile corresponds to residence time distribution function,  $F(t) = \frac{c_{out}(t)}{c_{in}}$ . It was first converted to residence time distribution density function,

$E(t)$ , by<sup>[3]</sup>:

$$E(t) = \frac{dF(t)}{dt} \quad (S2)$$

$E(t)$  was used then to calculate average residence time ( $\tau$ ) and theoretical plate number ( $N$ ) using

$$\tau = \int_0^{\infty} tE(t)dt \quad (S3)$$

$$\frac{1}{N} = \frac{\int_0^{\infty} (t - \tau)^2 E(t)dt}{\tau^2} \quad (S4)$$

The calculated  $N$  is  $2.8 \times 10^2$  and  $\tau$  is 28 min, respectively. Noticing the fact that  $\tau$  is much greater than the space time (about 0.04 min), the following concise correlation may be derived based on the above mentioned assumptions<sup>[4]</sup>,

$$k_m = \frac{2N}{\varepsilon\tau} \quad (S5)$$

where  $k_m$  is the overall mass transfer coefficient in  $\text{min}^{-1}$ ,  $\varepsilon$  is the voidage ( $\approx 0.85$ ). Substituting the adsorption data shown in Figure 1 into Eqs. (S2) to (S5) gives  $k_m \approx 23 \text{ min}^{-1}$ . Finally, the equivalent  $t_{0.9}$  can be calculated according to its definition

$$t_{0.9} = \frac{\ln \frac{1}{1-0.9}}{k_m} \quad (\text{S6})$$

The estimated  $t_{0.9}$  of SO<sub>2</sub> adsorption on our TMG-AlPO-5/CHC is about 0.1 min, significantly less than literature reported values of 30-200 min<sup>[5]</sup>.

Cyclic adsorption/desorption experiments were also performed at room temperature (Figure S1). It may be seen from Figure S1 that significant SO<sub>2</sub> capacity can be retained for cycles.

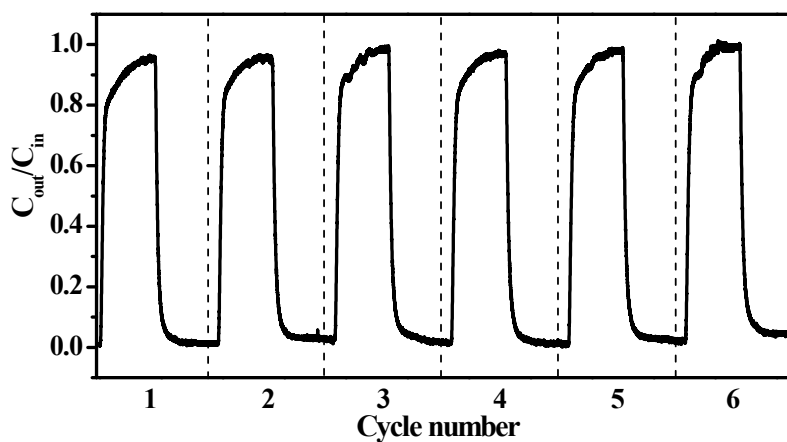
## 5. Effects of CO<sub>2</sub> and H<sub>2</sub>O

CO<sub>2</sub> breakthrough experiments were carried out on TMG-AlPO-5 particles. SO<sub>2</sub> breakthrough experiments were then carried out with the addition of CO<sub>2</sub> in the feed. FT-IR results in Figure S3 show that CO<sub>2</sub> adsorption on TMG-AlPO-5 forms hydrogen bond, similar to that of SO<sub>2</sub>. However, Figure S4 shows that the capacity is much lower than that of SO<sub>2</sub> and SO<sub>2</sub> breakthrough curve is barely affected by the addition of 15% CO<sub>2</sub> in the feed.

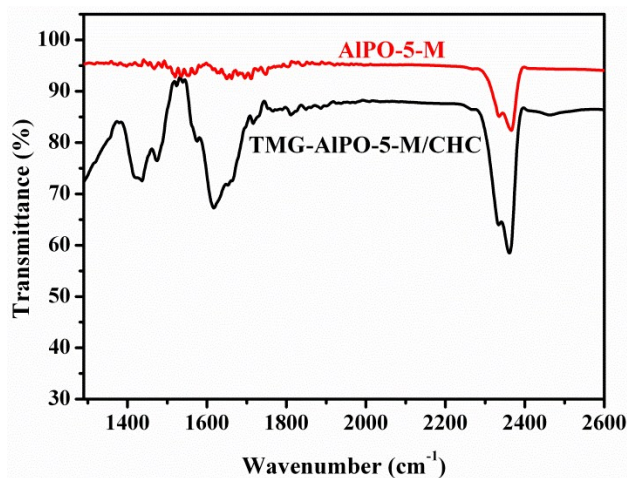
The setup shown in Figure S5 was used to introduce H<sub>2</sub>O into the system. A water bath (F34-ED Series, Julabo, German) was used to control the bottle at a constant temperature of 25 °C, such that a relatively stable partial pressure of water was maintained. As shown in Figure S4, the addition of H<sub>2</sub>O does not have significant effects on SO<sub>2</sub> breakthrough curve.

In order to evaluate effects of aqueous acid solutions on the stability of AlPO-5, 1.0 g AlPO-5 particle sample was immersed in 50 ml deionized water. After being bubbled with CO<sub>2</sub> and SO<sub>2</sub> (20 and 0.5 v%, in N<sub>2</sub>) at room temperature for 5 h, the sample was filtered and degassed at 100 °C for 24 h. XRD patterns were then measured for both untreated and treated AlPO-5 samples. It may be seen from Figure S6 that the AFI structure and high crystallinity of AlPO-5 zeolite were maintained after the acid treatment. In addition, both untreated and treated samples have similar

XRD patterns, justifying the stability of AIPO-5 under acidic conditions.



**Figure S1.** Cyclic adsorption and desorption of SO<sub>2</sub> on TMG-AIPO-5-M/CHC. Space velocity: 25 min<sup>-1</sup>. Total pressure: 0.1 MPa. N<sub>2</sub> carrier. Adsorption: 90 min, SO<sub>2</sub> 0.2%. Desorption: 100 min, SO<sub>2</sub> 0%.



**Figure S2.** FT-IR spectra of AIPO-5-M and TMG-AIPO-5-M/CHC samples. Compared with AIPO-5-M sample, TMG-AIPO-5-M samples shows broad bands between 1300 and 1780 cm<sup>-1</sup> corresponding to the characteristic C-N and C=N absorption and stretching vibration modes. This result further testified the existence of TMG in the TMG-AIPO-5-M samples.

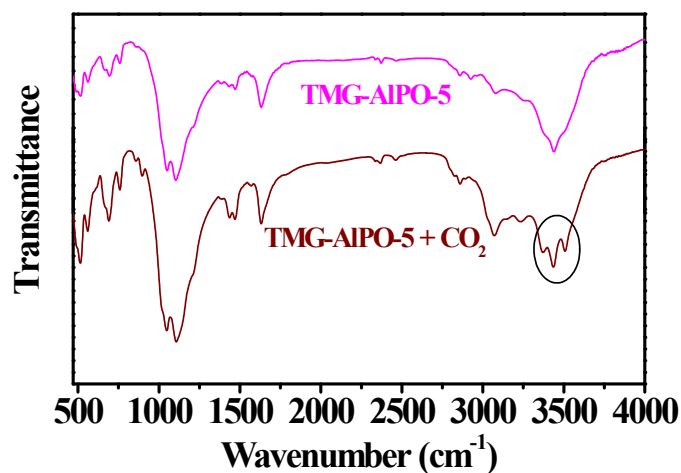


Figure S3. Comparison of FT-IR spectra. Pink: TMG-AlPO-5; Black: TMG-AlPO-5 after being saturated with CO<sub>2</sub> (15 v% in N<sub>2</sub>) at room temperature. The highlighted extra peaks correspond to the formation of hydrogen bond.

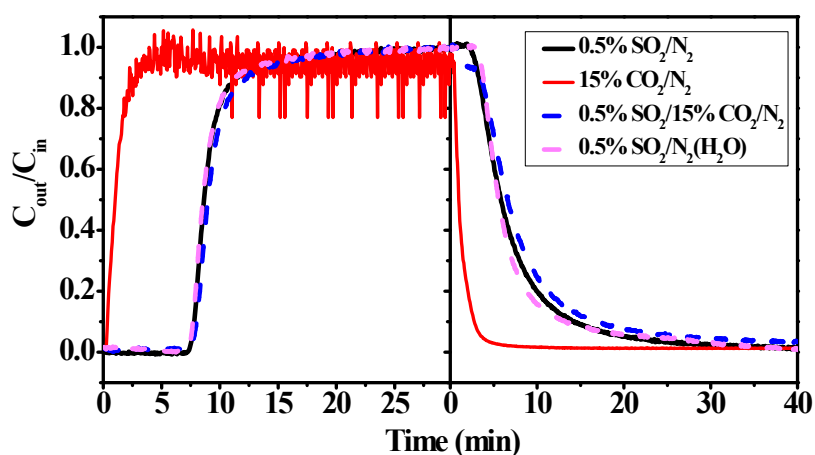


Figure S4. Dynamic sorption behaviors of various feeds on TMG-AlPO-5 particles. Black solid line: 0.5 v% SO<sub>2</sub> in N<sub>2</sub>; Red solid line: 15 v% CO<sub>2</sub> in N<sub>2</sub>; Blue dash line: 15 v% CO<sub>2</sub> and 0.5 v% SO<sub>2</sub> in N<sub>2</sub>; Pink dash line: 0.5 v% SO<sub>2</sub> in N<sub>2</sub>, H<sub>2</sub>O introduced by bubbling N<sub>2</sub> carrier in a water bottle controlled at 25±2 °C. Space velocity: 25 min<sup>-1</sup>. Concentrations were detected by In-situ FT-IR (3787.2-3489.9cm<sup>-1</sup> for CO<sub>2</sub> and 1260-1055.6 cm<sup>-1</sup> for SO<sub>2</sub>). Both adsorption and desorption processes are operated at 25±2 °C. The comparison shows that neither CO<sub>2</sub> nor H<sub>2</sub>O has significant effects on SO<sub>2</sub> breakthrough curves on TMG-AlPO-5.

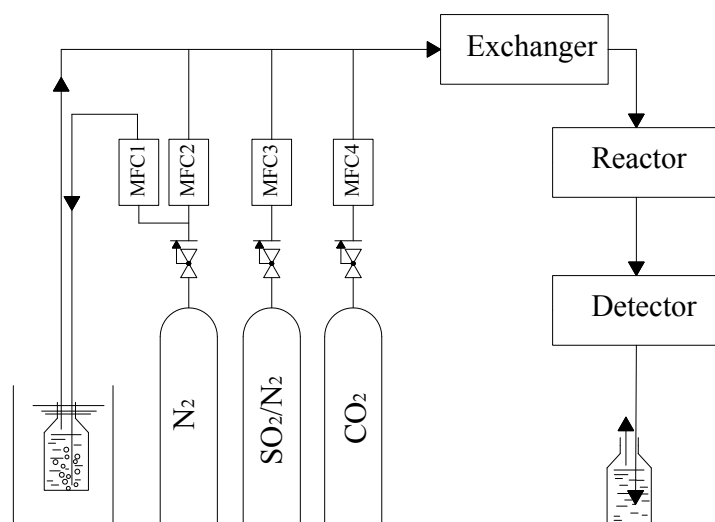


Figure S5. Schematic diagram of the setup for the breakthrough experiments with H<sub>2</sub>O. The water bottle was put in a water bath controlled at 25±2 °C.

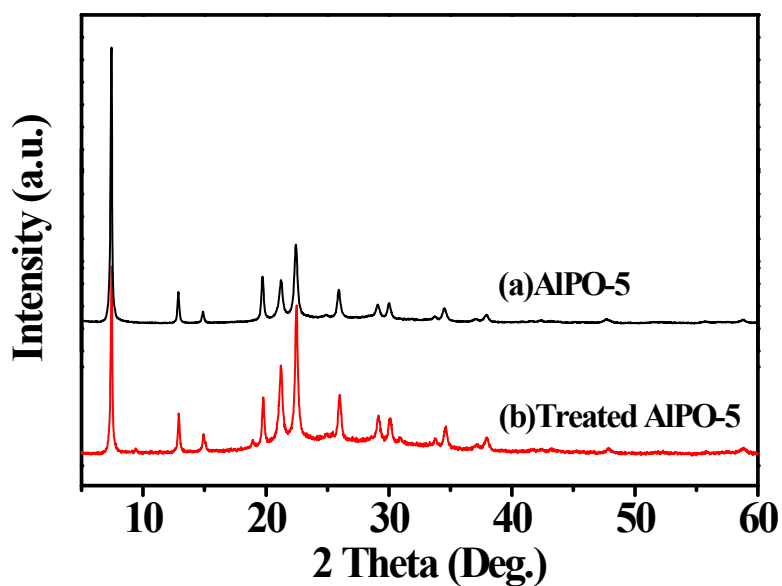


Figure S6. XRD patterns of AlPO-5 and treated AlPO-5 samples. The treated AlPO-5 sample was obtained as follows: 1 g of AlPO-5 sample was added into 50 mL water, then a gas mixture of CO<sub>2</sub>/SO<sub>2</sub>/N<sub>2</sub> (20/0.5/79.5, v%) was bubbled into the water for 5 h (room temperature). The sample was filtered and degassed at 100 °C for 24 h before XRD measurements.

## References.

1. Wang, J.; Song, J.; Yin, C.; Ji, Y.; Zou, Y.; Xiao, F.-S., Tetramethylguanidine-templated synthesis of aluminophosphate-based microporous crystals with AFI-type structure. *Micro. Meso. Mater.* **2009**, *117* (3), 561-569.
2. Yu, C.; Jin, H.; Tao, W.; Mu, T., Determination of Absorption Rate and Capacity of CO<sub>2</sub> in Ionic Liquids at Atmospheric Pressure by Thermogravimetric Analysis. *Energy Fuels* **2011**, *25* (12), 5810-5815.
3. Fogler, H. S., *Elements of chemical reaction engineering*. 4th ed.; Prentice Hall: 2005.
4. Xu, J.; Jiang, X.; Guo, J.; Chen, Y.; Yu, W., Competitive adsorption equilibrium model with continuous temperature dependent parameters for naringenin enantiomers on Chiralpak AD column. *J. Chromatogr. A* **2015**, *1422*, 163-169.
5. Li, X.; Zhang, L.; Zheng, Y.; Zheng, C., SO<sub>2</sub> Absorption Performance Enhancement by Ionic Liquid Supported on Mesoporous Molecular Sieve. *Energy Fuels* **2015**, *29* (2), 942-953.