

POLYETHYLENIMINE-LOADED SILICA WITH A HIERARCHICAL PORE STRUCTURE FOR H₂S ADSORPTIVE REMOVAL

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Introduction

H₂S is one of the major toxic gases from various industrial gas streams such as natural gas, synthesis gas and hydrogen gas. For low concentration of H₂S, the method of catalytic oxidation of H₂S over alkali-impregnated carbons is usually employed, due to their high activity and fast kinetic of reaction [1]. H₂S can be oxidized to elemental sulfur and sulfate during the oxidation, which are mainly loaded in the pores of the catalysts. However, one of the disadvantages of catalytic oxidation is the difficult regeneration of the spent carbons, since the removal of elemental sulfur and sulfate from the catalyst and the re-impregnation of the activated carbons are very complexity and uneconomical [2, 3]. Therefore, searching for a desulfurization agent with large saturation sulfur capacity and good regeneration performance is very useful for low concentration of H₂S removal in industry. In this work, hierarchical porous silica was prepared and loaded with Polyethyleneimine (PEI) and used for H₂S removal for the first time. The effect of PEI loading and regeneration performance of the adsorbent on H₂S removal was studied.

Experimental

The silica monolith was prepared based upon the method of Smatt et al. [4] using tetraethoxysilane (TEOS), polyethylene glycol (PEG) dissolved in an aqueous nitric acid solution, and cetyltrimethylammonium bromide (CTAB) at a gel composition of TEOS :HNO₃:H₂O:PEG:CTAB =1.00 : 0.25 : 14.69 : 0.54 : 0.0899. PEG has been used together with CTAB to control the particle aggregation and internal structure, respectively.

The PEI loaded hierarchical porous silica sorbent was prepared by a wet impregnation method. In a typical preparation, the desired amount of PEI (Mw of 600, from Aldrich) was dissolved in 3 g methanol at 40 °C under stirring for ca. 20 min, then 0.2 g of the porous silica was added to the above solution and further stirred at room temperature for 8 h. The slurry was then dried with continuous stirring. The as-prepared sorbent was denoted as HPS-xPEI for supporting on hierarchical porous silica, where x represents the loading of PEI in weight percentage in the sample (PEI+ the hierarchical porous silica). Before the sorption test, all the sorbents were pretreated at 100 °C under a nitrogen (99.999%) flow at 100 mL/min for 12 h.

Dynamic tests were carried out to evaluate capacity of the hierarchical porous silica sorbent for H₂S removal [2]. A simulated mixture (99 % of N₂ and 1% O₂ at 22 °C) containing 0.1 % (1000 ppm) of H₂S was passed through the column of the catalysts with a flow rate of 150 mL/min. In this test, the breakthrough concentration of H₂S was defined as 50 ppm. The

breakthrough and saturation sulfur capacities are referred as Q_B and Q_S, respectively.

N₂ adsorption-desorption isotherms of the samples were measured using a Micromeritics ASAP 2020M analyzer. The BET surface areas (S_{BET}) were analyzed by Brunauer-Emmett-Teller method. Micropore volumes (V_{mic}) are obtained by t-plot method. Average mesopore sizes (D_m) were obtained by Barrett-Johner-Halendar (BJH) desorption model. Total pore volumes (V_t) and pore size distributions were calculated from the analysis of the desorption branch of the isotherms using the BJH method. Mercury porosimetry was carried out with an AutoPore IV 9500 V1.03 apparatus. The morphology of the samples was observed under scanning transmission electron microscopy (TEM, JEOL 2100F).

Results and Discussion

Fig.1 shows the TEM images of the hierarchical porous silica. It is found that the porous silica is composed of a 3-D network structure of interconnected nano-sized primary particles. Both the interconnected macropores and textural mesoporosity among the nano-particles are observed in Fig. 1 a. The sizes of these pores are from several tens to hundreds nm. Small mesopores with the size of several to 20 nm are also seen from Fig. 1 b. These results indicated that the hierarchical pore structure of the porous silica.

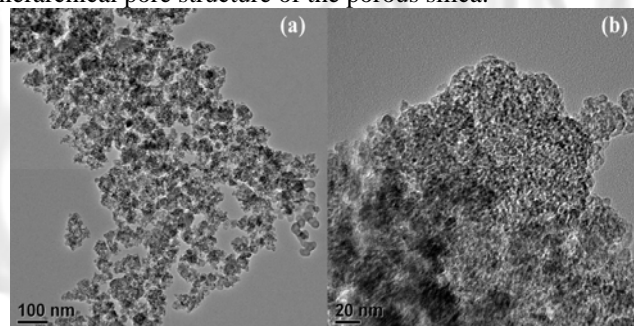


Fig 1. TEM images of the hierarchical porous silica

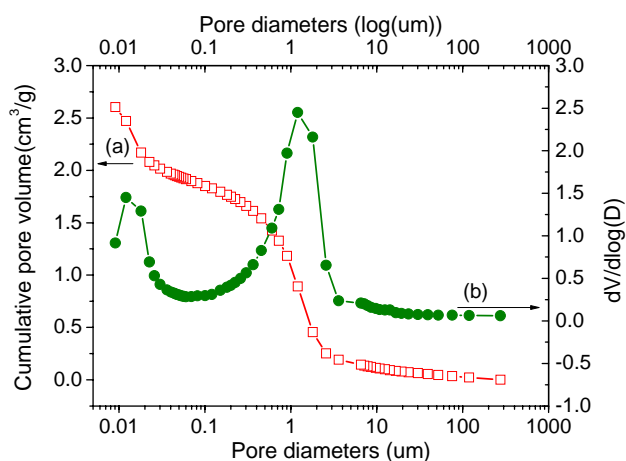


Fig. 2 Cumulative pore volume (a) and pore size distribution (b) of the hierarchical porous silica determined by Hg porosimetry.

The Hg porosimetry results of the hierarchical porous silica are presented in Fig. 2. The cumulative pore volume calculated from the Hg porosimetry curve is about 2.6 cm³/g, which is much higher than that of the SBA-15 and MCM-41 (about 1 cm³/g). The huge pore volume enables the porous silica to impregnate large amount of PEI and to improve the H₂S adsorption capacity. The pore size distribution curve by Hg porosimetry shows two peaks centered at 15 nm and 1.5 μm corresponding to the textural mesopores and macropores, respectively.

The N₂ adsorption results of the hierarchical porous silica are summarized in Table 1. The hierarchical porous silica has a large BET surface area of 469 m²/g and a mesopore volume of 1.26 cm³/g. The micropore volume of the material is only about 0.01 cm³/g, making neglectable contribution to the total pore volume. After PEI was introduced, the N₂ adsorption capacity decreased as expected. The BET surface area and pore volume of the porous silica adsorbents decreased with the increase of the PEI loading. The BET surface areas of the adsorbents with the PEI loading of 15, 30 and 65 wt. % are 137, 90, and 15 m²/g, respectively. When the PEI loading is 75 wt. %, the BET surface and pore volume decreased to zero and almost all the pores are filled by the PEI.

Table 1. Pore Parameters of the hierarchical porous silica

Samples	S _{BET} (m ² /g)	V _t (cm ³ /g)	V _{mic} (cm ³ /g)	D _m (nm)
HPS	62	0.43	0.01	15.00
HPS-30%PEI	90	0.55	0	17.60
HPS-65%PEI	15	0.01	0	36.30
HPS-75%PEI	0	-	-	-

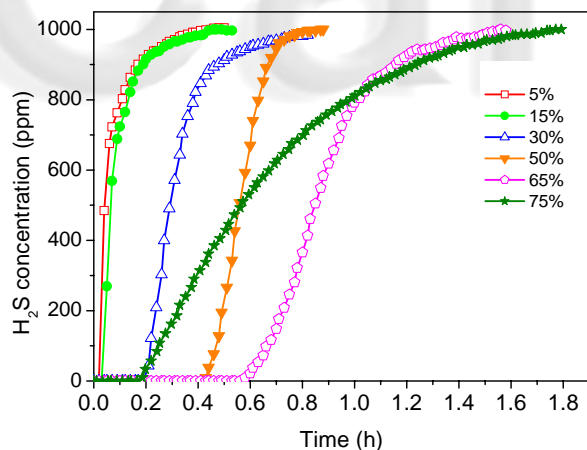


Fig. 3 Breakthrough curves of H₂S over the hierarchical porous silica adsorbents with different PEI loading

The breakthrough curves of H₂S over the hierarchical porous silica adsorbents with different PEI loading are shown in Fig. 3. The original porous silica exhibits neglectable breakthrough and saturation sulfur capacity (0, and 0.04 mmol H₂S/g adsorbent), which might be caused by the physisorption of H₂S on this materials. After the impregnation of PEI, the H₂S adsorption capacity of the adsorbents was improved significantly. The loading of 65 wt% PEI in porous silica gives

the largest breakthrough and saturation sulfur capacity of 1.23 and 1.85 mmol H₂S/g adsorbent. When the loading of PEI increased from zero to 65 wt%, the breakthrough capacity increased from 0 to 1.26 mmol H₂S/g adsorbent, and then, decreased remarkably with increasing in the loading to 75 wt.%. The increase in the capacity of the sorbent by loading PEI can be considered as a contribution from the amine groups in the loaded PEI. When the PEI loading is larger than 65 wt. %, the H₂S adsorption capacity decreased quickly. It seems that the surface area of the sorbents decreased significantly and the thickness of PEI films covered on the surface increased, which led to a substantial decrease of the kinetic capacity and certain amount of PEI not to be utilized for H₂S capture.

The regeneration performance of H₂S adsorbent is a crucial factor for practical application. Desorption of the spent HPS-65%PEI, was performed 75 °C using N₂ as a purge gas at a flow rate of 100 mL/min. The HPS-65%PEI demonstrated very reversible and stable H₂S sorption-desorption performance during 7 repeated runs. This result indicated that the PEI loaded hierarchical porous silica may be one of the promising sorbents for removal of H₂S.

Conclusions

The present work has shown that PEI loaded porous silica sorbents could effectively remove H₂S from gas streams at ambient conditions. The amount of PEI loading on the mesoporous molecular sieve has a strong influence on the sorption performance of the sorbents. The loading of 65 wt% PEI in porous silica gives the largest breakthrough and saturation sulfur capacity of 1.23 and 1.85 mmol H₂S/g adsorbent 22 °C and the GHSV of 15000 h⁻¹. In addition, the developed sorbents can be regenerated easily at mild conditions (temperature range of 75-100 °C), and have the excellent regenerability and stability.

Acknowledgment. The authors gratefully acknowledge the financial supports from the National High-Tech Research and Development Program (No. 2007AA05Z311), and the Natural Science Foundation of China (No. 50730003).

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