

H₂S CATALYTIC OXIDATION OVER Na₂CO₃ IMPREGNATED MESOPOROUS CARBON AEROGELS: PROGRESS FROM MICROPORES TO MESOPORES

Qingjun Chen, Donghui Long, Zhi Wang, Xiaojun Liu,
Wenming Qiao, Xiaoyi Liang, Licheng Ling

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.

Introduction

H₂S is not only an extremely toxic and malodorous gas, but also a corrosive gas towards pipelines and equipments, as well as one of main poisons for many industry catalysts. Alkali-impregnated activated carbons are usually used as low concentration H₂S oxidation catalysts, due to their high activity and fast kinetic of reaction. However, the saturation sulfur capacity of these desulfurization agents is only about 0.2-0.8 g H₂S/g catalyst [1,2]. Recently, we have reported that Na₂CO₃ impregnated mesoporous carbon aerogels served as a novel catalyst for H₂S oxidation which exhibited particularly high saturation sulfur capacity (~3 g H₂S/g catalyst) [3]. The high catalytic activity of impregnated carbon aerogels was attributed to the large pore volume and 3-dimension mesoporosity of the support, which allow easy diffusion and storage of reactants and products. The effect of pore structure (pore volume, pore size distribution) on performance and products of H₂S oxidation are discussed.

Experimental

Carbon aerogels were prepared by aqueous sol-gel polymerization of resorcinol(R) and formaldehyde (F) using sodium carbonate as basic catalyst (C) [3]. The as-prepared carbon aerogels are denoted as C_x, where x represents concentration of the catalysts (mole ratio of R/C). For example, when the mole ratio of R/C is 100, the prepared carbon aerogel is referred as C100. In addition, in order to investigate the effect of micropores, C100 was activated with CO₂ at 900 °C for 3 and 9 h, respectively. The resultant carbon aerogels are designated as C100-CO₂-3h and C100-CO₂-9h, respectively.

H₂S oxidation catalysts were prepared by incipient wetness impregnation [1]. The weight percentage of Na₂CO₃ in the catalyst is fixed at 25 wt. %. The impregnated carbon aerogel is designated by an additional letter, I, in the name of the carbon aerogel. After exhaustion for H₂S removal test, an additional letter E is added to the name of impregnated carbon aerogel. Dynamic tests were carried out to evaluate capacity of impregnated carbon aerogels for H₂S removal [1]. A simulated mixture (99 % of N₂ and 1% O₂ at 30 °C) containing 0.1 % (1000 ppm) of H₂S (with 80 % moisture) 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. Breakthrough and saturation sulfur capacity is referred as Q_B and Q_S, respectively.

N₂ adsorption-desorption isotherms 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. The X-ray diffraction (XRD) patterns were acquired on a Rigaku D/max 2550 diffractometer operating at 40 KV and 20 mA using Cu Kα radiation (λ = 1.5406 Å).

Results and Discussion

The N₂ adsorption results of the initial, impregnated and exhausted carbon aerogels are shown in Fig. 1 and Table 1. For the carbon aerogels prepared at different catalyst concentrations, the mesopore volume increases from 1.02 to 3.60 cm³/g, whereas the micropore volume are all about 0.2 cm³/g. For C100, after activation of 3 h, the micropore and mesopore volume increases by 35 % and 6.6 %, respectively. This result suggests that activation mainly improved the micropore structure of the materials. With increasing activation time, micropore volume increases gradually. From C50 to C300, the pore size distribution becomes wider, and the mean mesopore size increases from 7.49 to 29.79 nm (Table 1). However, Activation with CO₂ does not change the pore size distributions significantly as shown in Fig. 1 (b). After impregnation, both the specific surface area and pore volume of the carbon aerogels decrease as expected. After esulfurization, micropores are almost filled or blocked by the products of H₂S oxidation. But there are still some mesopores in the exhausted carbon aerogels.

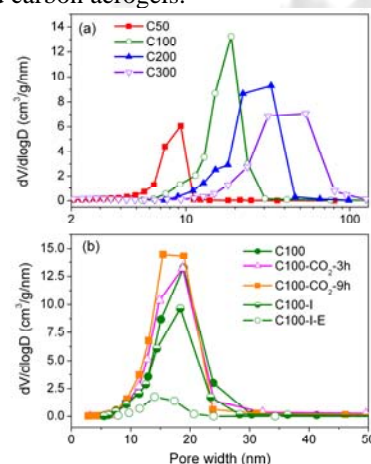


Fig. 1 Pore size distributions of the carbon aerogels

Table 1. Pore Parameters of the Carbon Aerogels

Samples	S _{BET} (m ² /g)	V _t (cm ³ /g)	V _{mic} (cm ³ /g)	D _m (nm)
C50	833	1.20	0.18	7.49
C100	908	3.06	0.20	16.30
C200	834	3.52	0.21	23.36
C300	838	3.81	0.21	29.97
C100-CO ₂ -3h	1079	3.32	0.27	16.22
C100-CO ₂ -9h	1302	3.70	0.31	15.04
C100-I	651	2.32	0.12	15.64
C100-I-E	62	0.43	0.01	15.00

The breakthrough and saturation sulfur capacity of the carbon aerogels is collected in Table 2. For carbon aerogels with different mesopores, the breakthrough and saturation sulfur capacity (g H₂S/g catalyst) increases in the order of C300-I < C50-I < C200-I < C100-I, which is not in agreement with the increase order of mesopore size or pore volume. Moreover, the materials exhibiting larger pore volume would not always obtain higher saturation sulfur capacity. It can be found that mesopore sulfur capacity is strongly depended on pore volume and pore size, both of which have significant but different effects on performance of impregnated carbon aerogels. But the increase of pore volume is at the cost of the increase of pore size, which is unfavourable for improving the catalytic activity. Therefore, there is a compromise between pore volume and pore size of carbon aerogels, which gives a highest sulfur capacity for C100 with pore volume of 3.0 cm³/g and a pore size in the range of 6-30 nm. We believe that the material exhibiting high pore volume and relatively small pore size should be a good candidate for H₂S removal. For the carbon aerogels, micropore volume almost decreases to zero after desulfurization (Fig. 1 and Table 1), which means that micropores are filled or blocked by products of H₂S oxidation. Consequently micropore sulfur capacity of carbon aerogels mostly depends on micropore volume.

Table 2 H₂S adsorption capacity of the samples

Samples	Q _B		Q _S	
	gH ₂ S/g adsorbent	gH ₂ S/cm ³ ^a	gH ₂ S/g adsorbent	gH ₂ S/cm ³ ^a
C50-I	0.77	0.64	1.08	0.90
C100-I	1.04	0.34	1.64	0.54
C200-I	0.96	0.27	1.56	0.44
C300-I	0.68	0.19	1.07	0.28
C100-CO ₂ -3h-I	1.61	0.48	2.26	0.68
C100-CO ₂ -9h-I	1.58	0.42	2.17	0.58

Note: ^a represents the breakthrough and saturation sulfur capacity per pore volume of the carbon aerogels.

The products of H₂S oxidation over the impregnated carbon aerogels can also be detected by X-ray diffraction technology. Fig. 2 shows the XRD spectra of initial, impregnated, and exhausted carbon aerogels. No obvious X-ray diffraction peaks are observed for initial carbon aerogels. For impregnated carbon aerogels, high intensity diffraction peaks corresponding to the phase of Na₃H(CO₃)₂•2H₂O are discerned. After desulfurization, the diffraction peaks for Na₃H(CO₃)₂•2H₂O disappeared and some new diffraction peaks appeared, which can be resolved as crystalline sulfur (S₈), Na₂SO₄ and Na₃H(SO₄)₂, respectively. From C50-I-E to C300-I-E, the intensity of peaks for elemental sulfur increases while these for Na₂SO₄ and Na₃H(SO₄)₂ decreases gradually. It can be concluded that elemental sulfur is more readily produced in larger mesopores and sulfuric acid is easier formed in smaller mesopores. For samples with different microporous structures, the relative intensity of sulfate (Na₂SO₄ or Na₃H(SO₄)₂) increases in the order of C100-I-E < C100-CO₂-3h-E < C100-CO₂-9h-E. It can

be concluded that sulfuric acid rather than elemental sulfur is more readily formed in micropores.

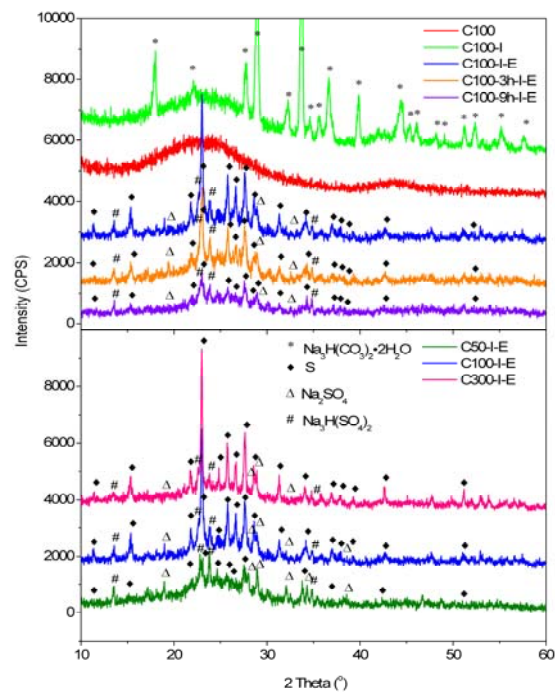


Fig. 2 XRD spectra of initial, impregnated, and exhausted carbon aerogels.

Conclusions

Na₂CO₃ impregnated carbon aerogels exhibited excellent performance for H₂S removal. It was found that micropore sulfur capacity was mainly determined by micropore volume of carbon aerogels. Mesopore sulfur capacity was mostly affected by mesopore volume and mesopore size. Products of H₂S oxidation over impregnated carbon aerogels were mainly elemental sulfur and small amount of sulfuric acid (in the form of Na₂SO₄ or NaHSO₄). H₂S is more readily oxidized to sulfuric acid in micropores and with the increase of mesopore sizes more elemental sulfur was produced.

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