

***N*¹-(3-trimethoxysilylpropyl)diethylenetriamine grafted ordered mesoporous silica KIT-6 for CO₂ adsorption**

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Abstract. Pure KIT-6 was synthesized by using tri-block copolymer P123 as the structure directing agent and tetraethyl orthosilicate (TEOS) as the silica source. It was functionalized with *N*¹-(3-trimethoxysilylpropyl)diethylenetriamine (denoted as 3N) by grafting in solvent at 80 °C. The materials were characterized by X-ray powder diffraction (XRD) and nitrogen adsorption/desorption and thermal gravimetric analysis (TGA). The CO₂ adsorption capacity was studied in a gravimetric analyzer. The results showed that the pore structure of KIT-6 was well kept after grafting of amine groups while surface area, pore size and pore volume were decreased. The CO₂ adsorption capacities of 3N-KIT-6 increased first and then decreased with the increase of 3N loading. The maximum adsorption capacity is 3.017 mmol/g.

1. Introduction

Greenhouse effect has become a threat across the globe especially on the marine ecosystem. Carbon dioxide is the main greenhouse gas that causes global warming and the capture and sequestration of CO₂ is an effective method to reduce CO₂ emissions^[1]. Compared with the traditional liquid amine scrubbing technology, adsorption approach has the advantages of low energy penalties and high selectivity^[2]. Therefore, more and more researchers begin to focus on solid adsorbents. In the recent years amine functionalized silica have earned much attention for CO₂ capture. Various kinds of silica, such as MCM-series, KIT-series, and SBA-series^[3], were employed as the support because of their high surface area, large and uniform pores and tunable pore sizes. The impregnation and grafting are two common ways to introduce amine into the solid supports^[4]. Amines can be evenly distributed on the surface of the support by grafting method^[5-6]. Compared with grafting method, impregnation can make more amines loaded on support, but their distribution is inferior because the amine groups often conglomerate^[7]. Nowadays, more and more literatures reported on amine grafted MCM series and SBA series for CO₂ adsorption^[8]. But only few of them reported on the CO₂ adsorption behavior in amine grafted KIT-6.

In this paper, we synthesized KIT-6 and grafted it with different volumes of *N*¹-(3-trimethoxysilylpropyl)diethylenetriamine (denoted as 3N). Characteristics of grafted KIT-6 were investigated through various techniques. The CO₂ adsorption performance was tested in the thermal gravimetric analyzer at 60 °C.

2. Experimental

2.1. The Synthesis and Modification of KIT-6

Pure KIT-6 was synthesized according to the previous report^[9]. KIT-6 was grafted by using *N*¹-(3-trimethoxysilylpropyl)diethylenetriamine (denoted as 3N) as modifier. In a typical grafting process, 2



g of KIT-6 was dispersed in a 60 ml of toluene in a flask. The given amount of 3N was added in the mixture and refluxed at 80 °C for 12 h. Finally the modified materials were prepared and recorded as 3N-KIT-6-X, where X(X=0.5,1,1.5,2) is the 3N volume.

2.2. Characterization of Materials

The powdered X-ray diffraction (XRD) patterns were obtained on a X'Pert PRO powder diffractometer in the 2θ range of 0.5–8°. N_2 adsorption/desorption isotherms were measured at liquid N_2 temperature. The samples were degassed at 80 °C for 10 h prior to measurement. The surface areas of samples were calculated using the Brunauer–Emmett–Teller (BET) equation and the pore size were determined by the Barrett–Joyner–Halenda (BJH) method. Thermal gravimetric analysis (TGA) was carried out under N_2 atmosphere from 25 to 750 °C with a heating rate of 5 °C/min.

2.3. Adsorption of carbon dioxide

CO_2 adsorption experiments were carried out by thermal gravimetric analyzer (TGA) in the mixed gases (15 vol.% CO_2 and 85 vol.% N_2) under a flow of 60 ml/min at 60 °C. Prior to the adsorption of CO_2 , the samples were heated in N_2 with a flow rate of 100 ml/min at 110 °C for 1 h and then cooled to 60 °C.

3. Results and Discussion

3.1. XRD characterization

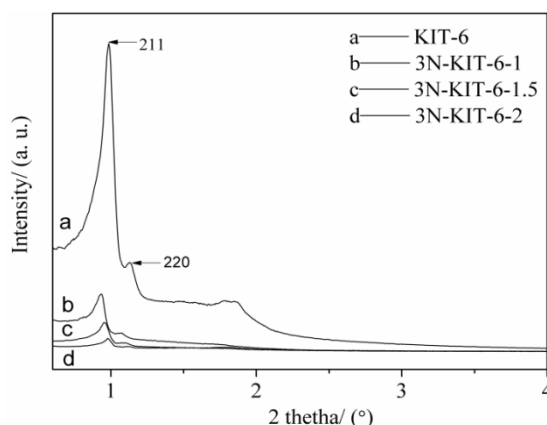


Figure 1. XRD patterns of the KIT-6 and 3N-KIT-6-X

As shown in Figure 1, the XRD pattern of KIT-6 has the clear diffraction peaks at (211) and (220) planes, indicating that KIT-6 has the double continuous cubic structure^[9]. The major peaks of 3N-KIT-6 were retained but the intensity of these peaks were diminished with increasing amounts of grafting 3N. This indicated that the mesoporous structure of KIT-6 is preserved and 3N successfully grafted onto KIT-6.

3.2. N_2 Adsorption/Desorption

The N_2 adsorption/desorption isotherms of KIT-6 before and after modification with 3N are displayed in Figure 2. The surface area, pore volume and pore diameter of materials are summarized in Table 1. It can be seen that all samples displayed type IV isotherms, which is the features of mesoporous materials. The surface area and pore volume of KIT-6 are 646.57 m²/g and 1.4015 cm³/g, respectively. With the increase in the 3N amount, the pore channels of materials were blocked and the surface area and the pore volume decreased rapidly. These features are in harmony with the results of XRD characterization which confirmed that 3N were successfully grafted onto KIT-6.

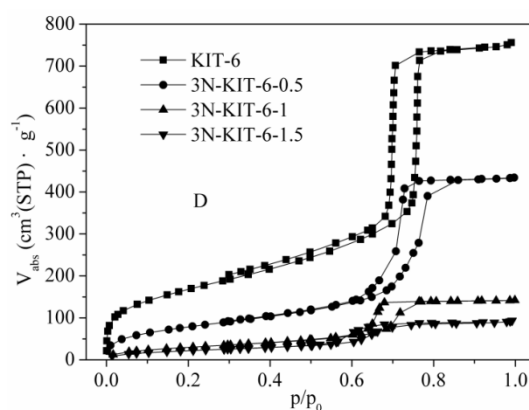


Figure 2. N₂ adsorption/desorption isotherms of samples

Table 1. Physicochemical properties of samples

Sample	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Pore diameter (nm)
KIT-6	646.57	1.4015	4.61
3N-KIT-6-0.5	292.65	0.6892	4.61
3N-KIT-6-1	115.96	0.2313	3.53
3N-KIT-6-1.5	83.06	0.1514	2.71

3.3. TG studies

Figure 3 shows the TG curves of KIT-6 and 3N-KIT-6-X. For all samples, the weight loss below 100 °C was attributed to the impurity gas and physically adsorbed water. From 100 °C to 750 °C, KIT-6 has none obviously mass loss. As for 3N modified KIT-6, the weight loss between 200 °C and 500 °C was assigned to the thermal decomposition of 3N and the surfactant. Above the temperature of 200 °C, 3N-KIT-6-X shows different mass loss due to the decomposition of 3N with different ratios grafted onto KIT-6. These results indicate that 3N was successfully grafted onto KIT-6 and all samples have good thermal stability below 200 °C.

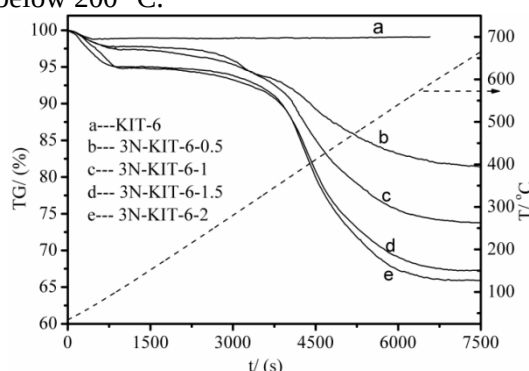


Figure 3. TG curves of KIT-6 and 3N-KIT-6-X

3.4. CO₂ Adsorption

Figure 4 depicts the CO₂ adsorption capacities of 3N-KIT-6-X. The CO₂ adsorption capacity of adsorbent was depends on pore size, pore volume and amine loading. For pure KIT-6, the CO₂ adsorption capacity was 0.642mmol/g. The CO₂ adsorption capacities of 3N-KIT-6-X increased first and then down with the increasing of the amount of 3N grafted. The sample shows an adsorption capacity of 1.474, 1.797, 3.017 and 1.882 mmol/g when it is modified with 3N of 0.5, 1, 1.5 and 2 ml,

respectively. Among them, 3N-KIT-6-1.5 has a best adsorption capacity. The adsorption capacity increased was due to the chemisorption between amine functional group grafted on the surface and CO₂. But in higher 3N concentration, the adsorption capacity decreased, indicating that extra amine groups were covered on the outer surface of KIT-6 and limited the spread of CO₂.

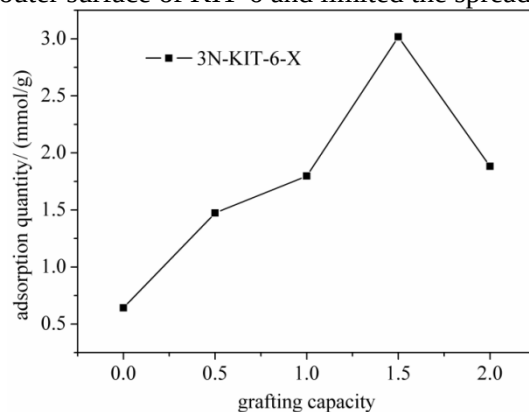


Figure 4. CO₂ adsorption performance of samples

4. Conclusions

In this study, a novel 3N grafted KIT-6 material (3N-KIT-6-X) for CO₂ adsorption was synthesized. Characteristics of 3N grafted KIT-6 and the adsorption performance were tested. The XRD and N₂ adsorption/desorption results indicate that after grafting the pore structure keeps well. TG analysis confirmed that 3N was successfully grafted onto KIT-6 and all samples have good thermal stability below 200 °C. The adsorption results indicate that 3N-KIT-6-X has larger CO₂ adsorption capacity. Under similar conditions, 3N-KIT-6-1.5 has a best adsorption capacity of 3.017 mmol/g.

5. References

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