

AMINE FUNCTIONALIZED KIT-6 FOR CO₂ ADSORPTION AT DIFFERENT TEMPERATURES

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Abstract

In this paper, pure KIT-6 was synthesized and functionalized with 3-aminopropyl triethoxysilane (APTES) by grafting in aqueous solvent at 80°C. The as-prepared composites were characterized by X-ray diffraction at low angles, FT-IR spectroscopy, TGA-DTA coupled with mass-spectrometry, SEM and N₂ physisorption techniques followed by testing for CO₂ adsorption at different temperatures. The CO₂ adsorption/desorption performance was investigated by TGA-DTA coupled with mass-spectrometry using TPD method. The results showed that the CO₂ adsorption capacity decreases with increasing temperature from 40 to 70 °C.

Introduction

A major problem in recent years is the high level of CO₂ emissions on the environment with serious negative effects. In the last half century large quantities of carbon dioxide have been released into the atmosphere, which contributes substantially to global warming - the greenhouse effect. Thus, the research directions were directed towards obtaining materials with CO₂ adsorption-desorption properties [1-3].

There is a direct correlation between increasing CO₂ concentration and the greenhouse effect that causes global warming. In recent decades, there has been growing interest in developing materials that can be used to capture and store CO₂. In the literature, CO₂ adsorption has been studied under various conditions on a series of mesoporous silica adsorbents composed of conventional silica molecular sieves MCM-41, SBA-15 and KIT-6 [4].

Mesoporous silica, KIT-6 is of particular interest to other materials such as MCM-41 and MCM-48, due to its three-dimensional structure with a large diameter mesopore and an easy method of synthesis. [5].

Experimental

KIT-6 mesoporous silica was synthesized following the method described by Kleitz *et al.* [6]. First, 3.69 g triblock copolymer pluronic P123 (EO₀₂PO₇₀EO₂₀) was dissolved in 132 g distilled water and 6.75 g 37% HCl under vigorous stirring at 35 °C for 8 h. After complete dissolution, 3.63 g n-butanol was added to this solution. The mixture remained under stirring at 35 °C for 1 h. To this, 7.92 g tetraethyl orthosilicate (TEOS, 99% Fluka) was added to the homogeneous solution and stirring for 24 h at 35 °C. Then, this mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h under static hydrothermal conditions. The solid product obtained after hydrothermal treatment was separated by vacuum filtration and washed with a 2% HCl-ethanol solution. Finally, the sample was calcined in air atmosphere at 550 °C for 6 h to remove the organic template. The resulting sample was denoted KIT-6.

Modified KIT-6 denoted as KIT-6 Sil was prepared as follows: 0.5 g of KIT-6 was dispersed in 50 ml toluene and 0.79 ml of 3-aminopropyl triethoxysilane was added later to the solution. The above mixture was refluxed at 110 °C for 12 h, and then the solid was

collected by filtration, washed by ethanol and air-dried at 80 °C. The grafting reaction was carried out at 110 °C for 5 h. After filtration and drying, the adsorbents were obtained as white solids.

The thermal analyses were carried out using a thermoanalyzer system Mettler TGA/SDTA 851/LF/1100 coupled with mass-spectrometry (MS). The measurements were conducted in dynamic atmosphere of air (50 ml/min), using the alumina plates crucibles of 150 μ l.

The FTIR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm^{-1} range, 256 scans, and resolution 2 cm^{-1}) using KBr pellets

Powder X-ray diffraction data were obtained with a XD 8 Advanced Bruker diffractometer using the Cu $K\alpha$ radiation in the range $2\theta = 0.5\div 5^{\circ}$ and $2\theta = 5\div 60^{\circ}$.

The specific surface areas of samples were calculated from the nitrogen adsorption-desorption isotherms using a Quantachrome instrument, Nova 2000 series.

Scanning electron micrographs (SEM) were recorded using Jeol JMS 6460 LV instrument equipped with an Oxford Instruments EDS (energy dispersive spectroscopy) analyser.

Adsorption tests were carried out using the same thermogravimetric analyzer connected to a gas delivery manifold. High-purity CO_2 and 30% CO_2 in N_2 at 1 atm was used for the adsorption runs, and N_2 was used as a regenerating purge gas for CO_2 desorption. Each sample was pretreated in flowing N_2 at 150 °C, then cooled to the desired adsorption temperature (60 °C), and exposed to 30% CO_2/N_2 (70 ml/min) for 90 min. The CO_2 adsorption capacity of the adsorbent in milligrams of CO_2 per gram of adsorbent was calculated from the weight gain of the sample in the adsorption process.

Results and discussion

The XRD model of KIT-6 and KIT-6 Sil are shown in Fig. 1. and confirm the cubic structure Ia3d specific to mesoporous sieves of KIT -6 type [7] by the presence of the two diffraction peaks at small angles of 0.96 and 1.83°, corresponding to the crystal planes Miller (211) and (220).

In the case of KIT-6 Sil, the peaks were also retained but the intensities decreased with introduction of 3-aminopropyl triethoxysilane. This also shows that APTES was successfully grafted onto KIT-6.

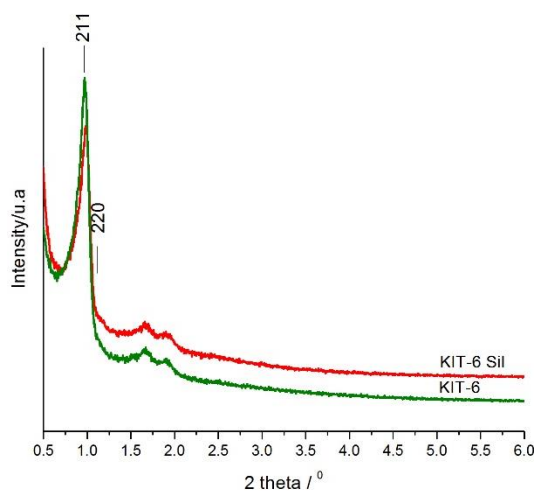


Fig. 1. XRD patterns of KIT-6 and KIT-6 Sil

The FT-IR spectra were recorder in the range 500-4000 cm^{-1} to confirm the APTES in the absorbent as can see in Fig. 2. In the APTES grafted, the peaks around 1387 cm^{-1} and 1548 cm^{-1} represent the $-\text{NH}_2$ and $-\text{NH}$ groups associated with the surface [5]. The peaks intensity of KIT-6 Sil was found higher compared with KIT-6.

The broad peaks at around 3734 and 3844 cm^{-1} represent the $-\text{NH}$ and $-\text{OH}$ stretching vibrations. The other peaks at 2042 cm^{-1} and 1632 cm^{-1} represent CO_2 and the physically adsorbed water [8, 9].

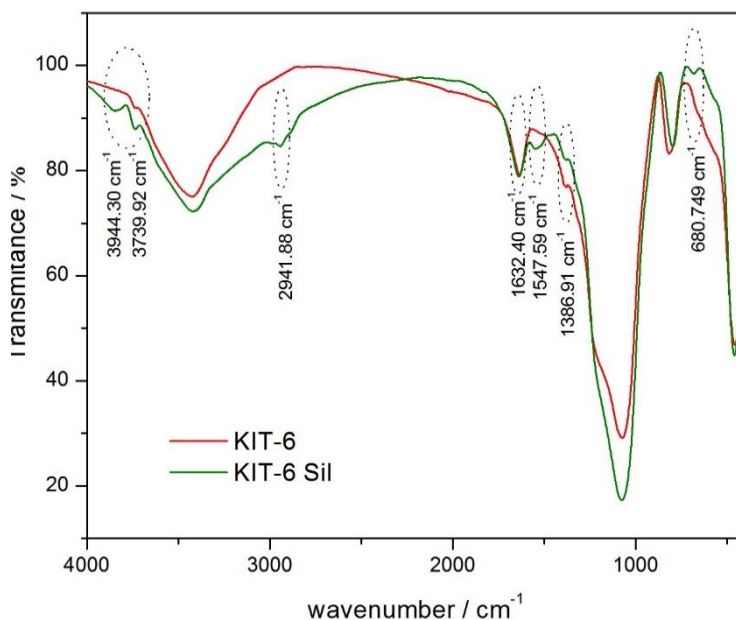


Fig. 2. FTIR spectra of parent KIT-6 and KIT-6 Sil

The textural parameters of synthesized KIT-6 and KIT-6 Sil are shown in Table 1. After grafting of APTES the surface area and pore volume decreased from 715 to 560 (m^2/g) and from 0.967 to 0.950 (cm^3/g) respectively. The data reveal a gradual reduction in surface area and pore volume after modification with silane coupling agent 3-aminopropyl triethoxysilane. These decrease can be attributed to the increase in agglomeration of silica particles or/and the filling of pore with APTES.

All composites display a type IV isotherm with H1 hysteresis loop according to the IUPAC classification, which is characteristic of mesoporous materials. It could be observed a sharp increase in volume adsorbed at $p/p_0 = 0.5-0.8$ characteristic of highly ordered of composite (not shown).

Table 1. Textural properties of KIT-6 and KIT-6 Sil composites

No.	Samples	Specific surface area (m^2/g)	Pore volume BJH_{Des} (cm^3/g)	Average pore diameter BJH_{Des} (nm)
1	KIT-6	715	0.967	6.570
2	KIT-6 Sil	560	0.950	5.462

Scanning electron micrographs images were used to observe the morphology of the KIT-6 and KIT-6 Sil particles. The image of KIT-6 shows that the particles are appeared to be spherical (Fig.3a) due to aggregation of fine threads of KIT-6. The spherical morphology is

slightly modified after amine functionalization as seen in (Fig. 3b). After introduction of APTES, the threads are easily dispersed and thus destroyed the spherical morphology [10]

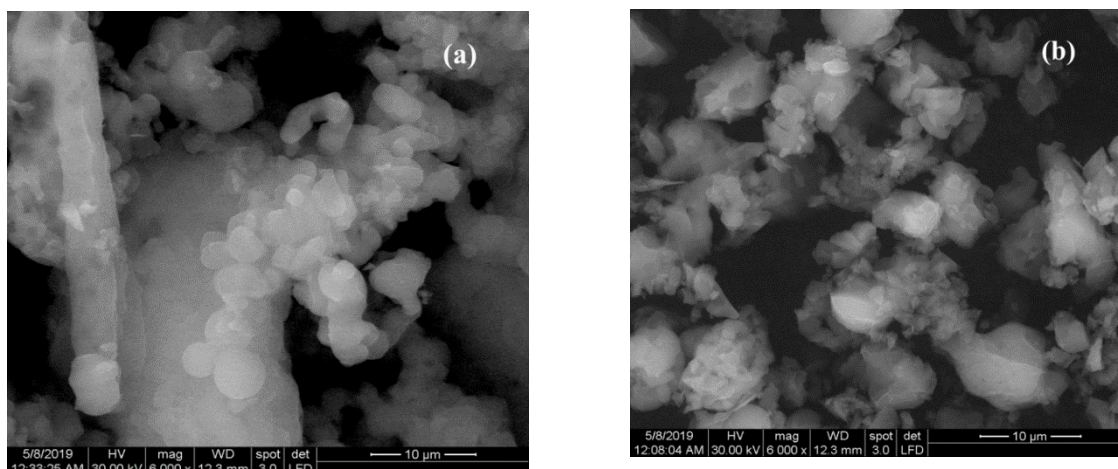


Fig. 3. SEM images of KIT-6 (a) and KIT-6 Sil (b)

The CO₂ adsorption capacity of the adsorbent in mmol of CO₂ per gram of adsorbent was determined from the mass gain of the sample in the adsorption process and was calculated more precisely from the mass loss during the desorption step. In Table 2, the amounts of the captured CO₂ on KIT-6 Sil adsorbent in the temperatures between 40-70 °C are shown. By increasing the temperature, the adsorption capacity and efficiency of amino groups decrease from 2.23 to 0.95 mmol CO₂/g SiO₂, and from 0.51 to 0.22 mmol CO₂/mmol NH₂ respectively. The best result was obtained for KIT-6 Sil at 40 °C which means an adsorption capacity of 2.23 mmol CO₂/g SiO₂ and an efficiency of amino groups of 0.51 mmol CO₂/mmol NH₂.

The results are promising and showed that both the adsorption capacity (mmol CO₂/g adsorbent) and the efficiency of amino groups (mmol CO₂/mmol NH₂) depend of the temperature at which the experiment performed.

Table 2. The amounts of the capture CO₂ using KIT-6-Sil at different temperatures

No.	Sample	Temp (°C)	n _{CO₂} /gSiO ₂ (mmol/gSiO ₂)	n _{CO₂} /n _{NH₂} (mmol/mmol)
1	KIT-6-Sil	40	2.23	0.51
2	KIT-6-Sil	50	1.76	0.40
3	KIT-6-Sil	60	1.31	0.29
4	KIT-6-Sil	70	0.95	0.22

The results are promising and showed that both the adsorption capacity (mmol CO₂/g adsorbent) and the efficiency of amino groups (mmol CO₂/mmol NH₂) depend of the temperature at which the experiment performed.

Conclusion

In this paper, the preparation of KIT-6 and KIT-6 Sil by grafting of amino-functionalized using a silane coupling agent 3-aminopropyl triethoxysilane (APTES) were carried out.

The small angles of XRD showed that KIT-6 has a cubic structure which indicates that the synthesis was successful. In the case of KIT-6 Sil appears a decrease in peaks intensity by partial blocking of pores and result that APTES was successfully grafted onto KIT-6. The FT-IR indicated that the KIT-6 Sil present all the characteristic bands of amino-functional groups, providing the grafting of amines onto KIT-6.

The CO₂ adsorption/desorption of KIT-6 Sil showed that both the adsorption capacity (mmolCO₂/g adsorbent) and the efficiency of amino groups (molCO₂/mol NH₂) depend on the temperatures. The best results were obtained for KIT-6-Sil at 40 °C.

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