EFFECT OF TEMPLATES ON THE SYNTHESIS OF ORGANIZED MESOPOROUS ALUMINA

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Abstract

Organized mesoporous materials represent a class of molecular sieves because of its high potential for commercial applications in adsorption and catalysis. In this study, organized mesoporous alumina was synthesized by the sol-gel method using various organic templates, i.e. cationic, neutral and anionic surfactants. Surface porosity of the synthesized aluminas obtained exhibit materials in the mesopore ranges. The morphology of the samples consists of wormhole-like mesostructure in the nano-region (20 – 70 nm). Sample with cetyl trimethylammonium bromide as cationic templates has the narrowest pore distribution centred at 8 nm as compared to samples synthesized with Triton X-114 (neutral) and stearic acid (anionic). All samples showed only Lewis acidity. Acidity and mesoporous character present in these mesoporous alumina samples showed that this material has potential as catalyst support and also used in Lewis acid catalyzed reactions. Study showed that the cationic surfactant is a better template to obtain uniform mesoporous alumina that might be due to the weak interaction between the template and the surface of the alumina.

Abstrak

Bahan berliangmeso teratur adalah mewakili kelas bahan penapis molekul kerana berpotensi tinggi dalam penggunaannya dalam penjerapan dan pemangkinan. Dalam kajian ini alumina berliangmeso teratur disintesis mengikut kaedah sol-gel menggunakan berbagai templat organik iaitu surfaktan bersifat kation, neutral dan anion. Keliangan permukaan alumina yang disintesis memperlihatlan bahan berada dalam julat berliangmeso. Morfologi sampel mengandungi strukturmeso berupa seperti ulat dalam julat nano (20 - 70 nm). Sampel dengan setil trimetilammonium bromida sebagai templat kation mempunyai taburan liang yang paling sempit berpusat di 8 nm berbanding dengan sampel yang disintesis dengan Triton X-114 (neutral) dan asid stearik (anion). Semua sampel menunjukkan hanya keasidan Lewis. Keasidan dan keliangan meso yang diberikan oleh sampel alumina menunjukkan yang bahan ini berpotensi sebagai penyokong mangkin dan berguna juga dalam tindak balas bermangkinkan asid Lewis. Kajian menunjukkan yang surfaktan kation adalah templat yang lebih baik untuk mendapatkan alumina berliangmeso yang seragam, berkemungkinan disebabkan oleh interaksi lemah templat dengan permukaan alumina.

Introduction

Aluminas are important industrial chemicals that have found wide application as adsorbents, ceramics, abrasives, catalysts and catalyst supports [1]. Alumina, mainly in its ? form, is widely used in catalysis as an inert carrier of metal catalysts and as part of bifunctional catalysts, largely because it is inexpensive, reasonably stable, and can provide high surface area for many catalytic applications. As a general rule, the alumina used in catalytic reactions always requires a controlled pore size distribution [2].

Present day heterogeneous catalysts are involved in the processing of high-molecular weight hydrocarbons. Because of this reason, the demand for mesoporous materials (pore radius higher than 1.0 nm and lower than 25 nm) has triggered major synthetic efforts in academic and industrial laboratories [3]. As these materials have very-well scattered acid sites and large-pore diameters with less diffusional constraints, they are expected to discourage consecutive alkylations and deactivation of the catalyst by coke deposition [4]. In addition, unlike microporous zeolites, where simultaneous diffusion of many molecules is prevented due to the limitation of the pore size and the pore geometry, these materials, in contrast, allow simultaneous entry of many reactant molecules into their pores, thereby permitting high conversion [2].

Organized mesoporous materials represent a class of molecular sieves having a high potential for commercial applications in adsorption and catalysis. Their regular pore arrangement is responsible for their extraordinary properties, such as high surface area and narrow pore size distributions [5]. Despite enormous importance of organized mesoporous alumina, which exhibits narrow pore size distribution, higher surface areas and abundant of surface hydroxyl groups compared to conventional aluminas, for catalyst supports or adsorbents, the number

of papers dealing with the synthesis and characterization of organized mesoporous alumina is still limited [6]. This is mainly due to the fact that synthesis of organized mesoporous alumina is not as straightforward as synthesis of organized mesoporous silica. Previous works done by other researchers using the existing sol gel method to synthesize mesoporous alumina [3 -10] showed that the key aspect to obtain mesoporous alumina is the surfactant which acts as the pore-directing reactant to form pore in the meso range.

In this paper, we report the synthesis of mesoporous alumina by using different charge property of surfactants and study the effect of the different templates on the formation of the mesoporous alumina.

Experimental

Synthesis of mesoporous alumina

Different mesoporous aluminas were prepared by following three kinds of method with different structure directing agent. Aluminum *iso*-propoxide, $Al(C_3H_7O)_3$ (Merck, 98%) was used as the aluminum source and *iso*-propanol, C_3H_7OH (Fluka, 99%) as solvent. Other reagents used were hydrochloric acid, HCl (Merck, 37%), sodium hydroxide, NaOH (Merck, 99%) and distilled water.

The mesoporous aluminas were prepared from gels with the following molar composition:

$$1 \; Al(C_3H_7O)_3 : 0.2 - 0.3 \; Surfactant : 1.8 \; HCl : 5 - 36 \; C_3H_7OH : 3.2 - 22 \; H_2O$$
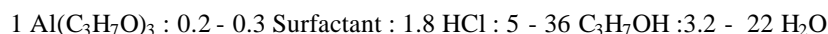
The cationic surfactants used were cetyltrimethylammonium bromide, CTABr, (Fluka, 99%) and dimethyldistearylammonium chloride, DDAC (Alfa Aesar, 97%), the non ionic surfactant used was Triton X-114 (Fluka) and stearic acid (Merck, 98%) acted as the anionic surfactant. The alumina was prepared according to a literature [11] while the anionic templating was done according to procedures described in a literature [8] with slight modifications. The procedure compromises three steps: hydrolysis, condensation and thermal treatment. Firstly, the hydrolysis of aluminum *iso*-propoxide at room temperature was carried out for 4 hours in the presence of the surfactants and *iso*-propanol as solvent. The second step was the condensation of aluminum hydrolyzed species by heating the reacting mixture at 80 °C and subsequent drying at 100 °C. Finally, the resulting material was calcined at 550 °C for 5 hours.

Characterization of mesoporous alumina

The crystallinity of the prepared samples was analyzed by powder X-ray diffraction (XRD) patterns using a Bruker Avance D8 diffractometer with the Cu Ka (? = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. Typically, powder samples were ground and spread into a sample holder and then analyzed. The pattern was scanned in the 2? range of 1.5 – 10 ° at a step of 0.020° and step time 1 s. Infrared (IR) spectra of the samples were collected on a Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer, with a spectral resolution of 2 cm^{-1}, at temperature 20 °C as KBr pellets. The framework spectra were recorded in the region of 1700–1300 cm^{-1}. The samples' morphologies were observed with field emission scanning electron micrographs (FESEM), obtained with Zeiss Supra Series model. N_2 adsorption/desorption experiments were carried out using a Micrometrics ASAP 2010 analyzer. Specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) and the pore size distributions were obtained according to the Barret-Joyner-Hallender (BJH) model on the desorption branch. For acidity study, about 10 mg of the sample was pressed at 2–5 tonnes for a minute to obtain a 13mm disk. The sample was introduced in the infrared cell with calcium fluorite, CaF_2 windows. The sample was heated at 400 °C in vacuum condition for 16 h. The infrared spectra were collected at room temperature using Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer, with a spectral resolution of 2 cm- 1. The types of acid sites were examined using pyridine as a probe molecule. Pyridine was adsorbed at room temperature for a minute, continued by desorption at 150 °C for an hour and another hour of desorption at 400 °C. The infrared spectra were monitored at room temperature.

Results and Discussion

XRD patterns for all the alumina synthesized showed half of a peak sloping down at 2? between 1.5° and 3°, as shown in Figure 1.Wide angle XRD gave no discernable structure indicating that the alumina in the mesoporous powders was amorphous [11]. Low-angle XRD patterns reported before for mesoporous alumina showed one peak at 2? between 0.5 and 3° [4, 6, 8, and 12]. This indicates that the mesoporous aluminas prepared has different pore structures as compared to hexagonal or cubic mesoporous silica such as MCM-41, SBA-15 or MCM-48, which exhibit three peaks at 2? between 0.5° and 5° [8, 13]. MCM-41 has one-direction cylindrical

pore structure with a highly regular pore distribution, whereas mesoporous alumina has interconnected pore channel structure with a random pore distribution. The interconnected pore system can reduce transport limitations, enhance accessibility to the active sites and contribute to the adsorption uptake elevation. As the XRD patterns obtained were scanned starting from 2? at 1.5°, only the later half of the peak can be seen.
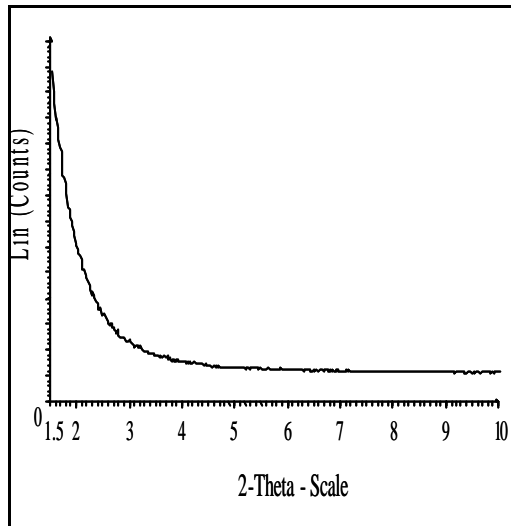

Figure 1: XRD pattern for the synthesized mesoporous alumina samples
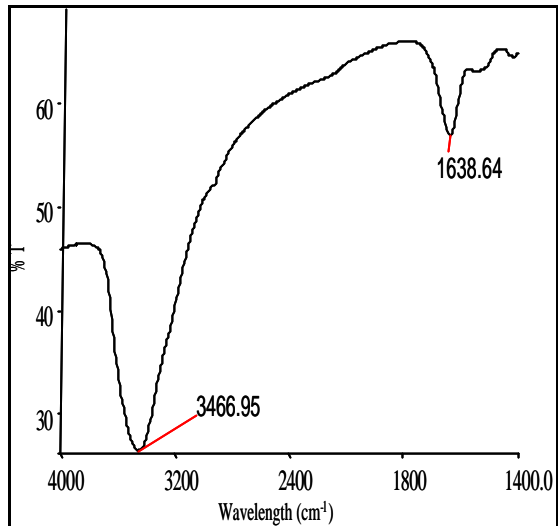
Figure 2: FT-IR spectrum of the mesoporous synthesized aluminas

The FT-IR spectra in Figure 2 shows that mesoporous aluminas synthesized can be distinguished by two bands in the region of 4000 cm^{-1} – 1500 cm^{-1}. The broad band around 3450 – 3500 cm^{-1} may be attributed to the adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the adsorption band at 1623 -1640 cm^{-1} [14]. The broad band shown for the adsorbed water is a characteristic of porous materials which are usually found in zeolites and mesoporous materials.

The Field Emission SEM (FESEM) images shown in Figure 3 reveal the morphology of all three mesoporous alumina samples prepared, magnified by 50,000 times. In the case of mesoporous alumina prepared by CTABr templating (Figure 3 (a)) the morphology shows a wormhole like appearance with no significant shapes. This confirms the advantage of a highly interconnected pore system [11]. This is also in good agreement with the absence of high order peaks in the XRD patterns [15]. Although the samples prepared using Triton X-114 (Figure 3(b)) and stearic acid (Figure 3(c)) as the templates exhibit wormhole like appearance too, agglomeration among the particles can be clearly seen.

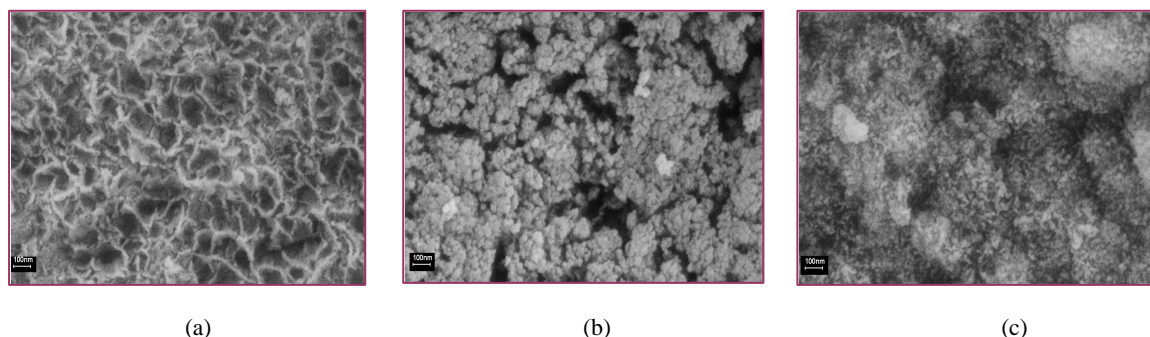(a)   (b)   (c)

Figure 3. FESEM images of the samples prepared by using (a) CTABr, (b) Triton X-114 and (c) stearic acid as the templates.

The porosity of the mesoporous alumina varied with the template used, is shown in Figure 4. While the properties of synthesized mesoporous aluminas using different templates are listed in Table 1. The nitrogen adsorption-desorption isotherms for all three samples show that they are of typical type IV (defined by IUPAC), [16], which is the characteristics of mesoporous materials. For the mesoporous alumina prepared using CTABr as the template, the shape of the large hysteresis loop (type H1) in the isotherm, Figure 4(a), indicates the capillary condensation in open-ended cylindrical channel with uniform size and shape. On the other hand, isotherms for samples prepared using Triton X-114, Figure 4(b), and stearic acid, Figure 4(c), consists of slit shape pores with non-uniform size and shape (Type H3). As for the pore size calculated from the desorption branch by the BJH method, only cationic templated mesoporous alumina has a narrow distribution over the range from 5 to 11 nm centered at 8 nm, indicating that the sample has uniform pore size and ordered mesostructure. Sample prepared from non ionic templating showed a wider distribution over the range from 20 to 110 Å while the alumina prepared from stearic acid has the widest distribution among all three samples, over the range from 4 to 60 nm, indicating the existence of some macropore aluminas.

Table 1. Properties of synthesized mesoporous aluminas using different templates

Type of template	Template	Pore size (nm)	BET Surface area (m^2/g)	External Surface area* (m^2/g)	Internal Surface area* (m^2/g)	Pore volume (cm^3/g)
Cationic	CTABr	9.4	280	267	13	0.6574
Cationic	DDAC	11.3	171	274	**	0.4841
Non Ionic	Triton X-114	6.7	413	592	**	0.6940
Anionic	Stearic Acid	7.7	294	253	41	0.5714

* calculated using Harkins-Jura equation

** gave a negative value. Can conclude that no micropores are present in the sample

The mesoporous alumina precursors were prepared in solution at a pH that would favour the formation of a predominant number of positive charges on their surface [13]. Alumina obtained through the cationic templating, CTABr showed the narrowest pore size distribution and sufficient surface area. The nitrogen adsorption-desorption shows a Type IV (Figure 4(d)) isotherm with a Type H1 hysteresis loop. Another cationic template, DDAC also displayed a narrow pore size distribution centering at 11 nm which proves that cationic templating is the better way to prepare organized mesoporous alumina. This may be due to the weak but sufficient interaction between the cationic surfactant and the negative charges that might still exist on the surface of the alumina precursors. Mesoporous alumina synthesized using Triton X-114, a non ionic surfactant, gave non uniform pore distributions, which could be due to the lack of interactions between the polyethylene surfactants and the alumina surface. On the other hand, the alumina synthesized using stearic acid displays very wide pore distribution with some macropore structure. In this case, the sintering probably readily occurs because the polar surfactant head groups COO^- strongly interact with the positive charges of the alumina surface, hence to some extent is embedded into the alumina walls. Their further removal upon calcination leaves an alumina surface that would readily sinter and collapse at high temperature.
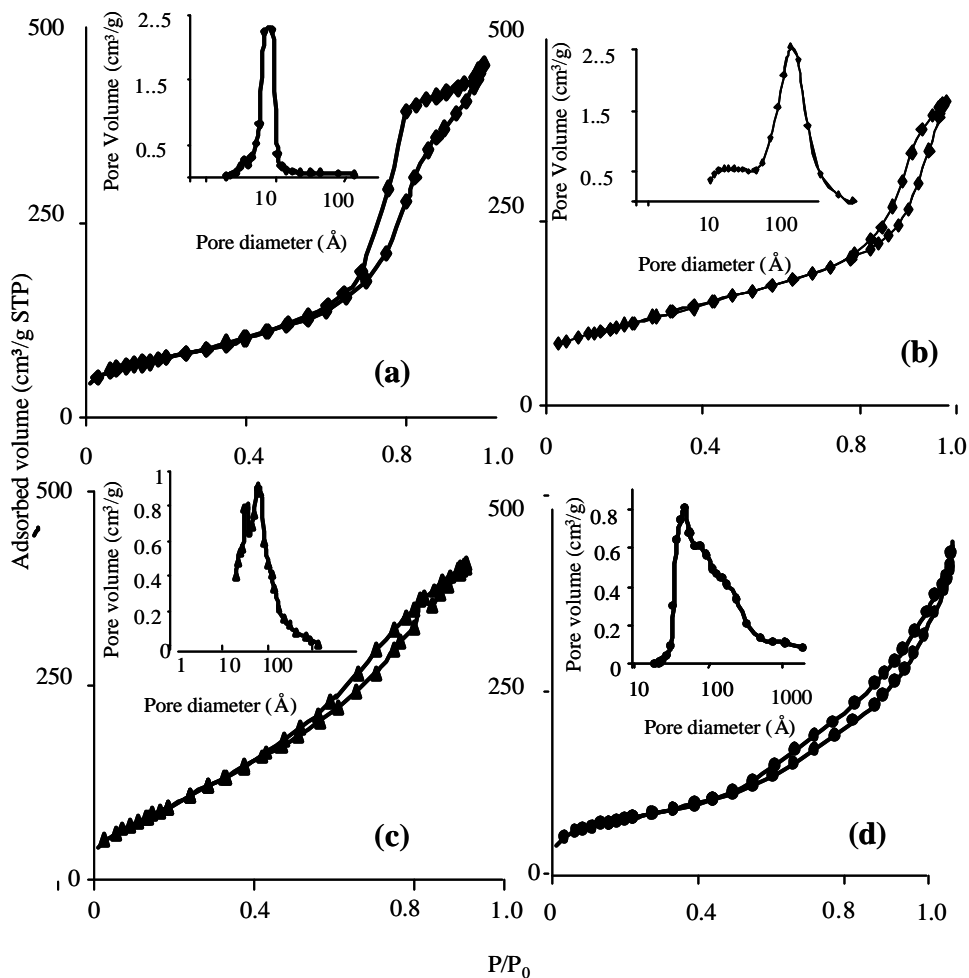
Figure 4. N_2 isotherms and pore size distributions (inset) of mesoporous aluminas templated by (a) CTABr, (b) DDAC, (c) Triton X-114 and (d) stearic acid.

Results obtained by pyridine adsorption on aluminas at temperatures between room temperature and 400 °C shows only the presence of Lewis type acidity. As expected, the FTIR results shown in Figure 5 confirm the absence of Brönsted type acidity with the absence of adsorption bands near 1540 and 1640 cm^{-1}, the characteristics of weak Brönsted acid sites, whereas the characteristics bands at 1578 and 1451 cm^{-1} which correspond to the vibration of pyridine in Lewis acid sites are present. As the desorption temperature increased up to 400 °C, the intensity of these bands decreased. The fact that the band at 1456 cm^{-1} is still detected at 400°C indicates that the sample has high strength of Lewis acidity. There were no significant differences in the amount of acid sites between the samples.
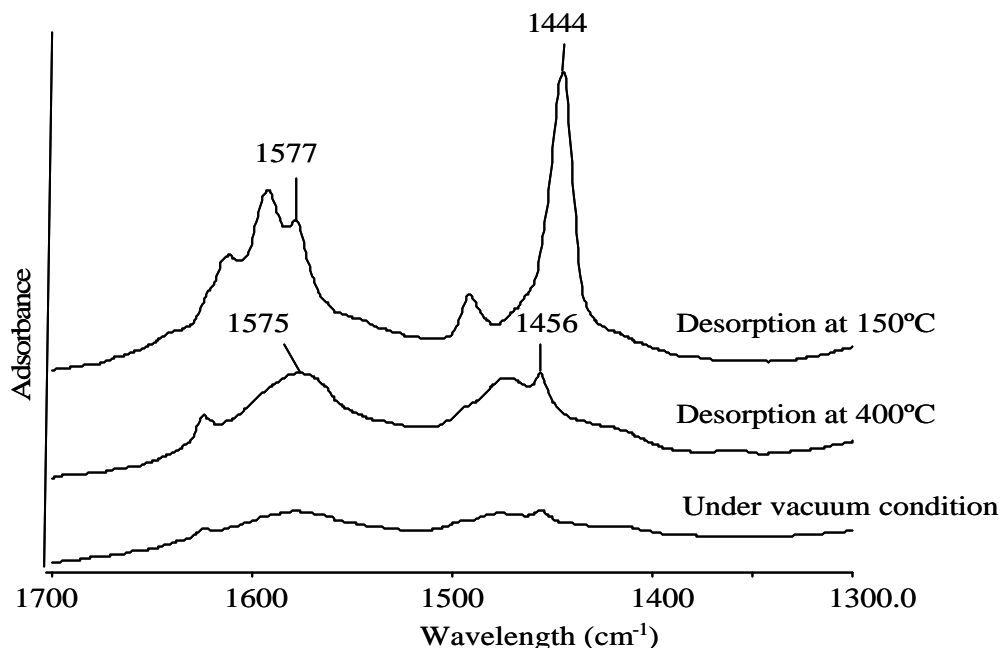
Figure 5. FT-IR spectrum of the sample prepared using CTABr after the adsorption of pyridine

Conclusion

The present study was aimed at understanding the significance of different templates on the properties of mesoporous alumina prepared via cationic, non ionic and anionic templating. The mesoporous alumina prepared using CTABr as the template displays high surface area (up to 280 m^2g^{-1}), uniform narrow pore size distribution and wormhole-like mesostructure. Acidity studies also show that the mesoporous alumina prepared displayed Lewis type acidity, which make it a potential catalyst for reactions catalyzed by Lewis acid catalyst and also those involving bulky molecules thanks to its mesosized pores. As this project is still on-going and only in its preliminary step, hopefully a more thorough conclusion can be made in the future. The cationic and non ionic templating is more suitable to produce alumina in the meso range.

Acknowledgements

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