

SYNTHESIS OF MESOPOROUS SODALITE BY USING DIFFERENT TEMPLATES

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Abstract: Zeolites can be considered as green catalysts due to their benign nature from an environmental point of view. Zeolites are microporous crystalline solids with open three-dimensional framework with pores and channels in the size range less than 2 nm. Sodalite is type of zeolites having ultramicropore size and high thermal stability, but it has several drawbacks in the catalyst application due to its smallest pore size (2.8Å) and low surface area. To overcome these disadvantages mesoporous sodalite can be modified having mesoporous structure. This study focused on the synthesis of mesoporous sodalite by using various organic structure directing molecules. The sodalite was synthesized hydrothermally for 6 hours at 150°C for crystallization by using different silica sources. The synthesized samples were characterized using XRD, FTIR and BET surface area. XRD and FTIR results showed that pure sodalite was formed during 6 hours crystallization time by using dimethyldioctadecylammonium bromide (DDAB) and organosilane (trimethoxysilylpropyldimethyloctadecylammonium chloride). However only sodalite synthesized by using organosilane (trimethoxysilylpropyldimethyloctadecylammonium chloride) showed mesoporosity as proved by BET surface area.

Keyword: zeolite, mesoporous sodalite, different templates

1.0 INTRODUCTION

Zeolites are microporous (1-20 Å diameters) crystalline solids with well-defined structures. Zeolites are crystalline, hydrated aluminosilicates with open three-dimensional framework structure built of $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetrahedral linked by sharing of an oxygen atom, to form regular intracrystalline cavities and channels of molecular dimensions. The framework structure may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter the limiting pore sizes are roughly between 3 and 10 Å in diameter. Zeolites are crystalline aluminosilicates, compositionally similar to clay minerals, but differing in their well-defined three-dimensional neon- and micro-porous structure. Aluminum, silicon, and oxygen are arranged in a regular structure of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral units that form a framework with small pores (also called tunnels, channels, or cavities) of about 0.1-2 nm diameter running through the material.

Because of their unique porous properties, zeolites are used in a variety of applications. Zeolites have been used as ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to molecular sieves.

Zeolites have the ability to act as catalyst for chemical reactions which takes place within the internal cavities. An important class of reactions is that catalyzed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This has been exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts. Zeolites with uniform pore size, adjustable acidity, and good stability are widely used in petroleum refining and petrochemical production[1]. However, the relatively small pore size of the microporous zeolites (pore diameter < 1.5 nm) restricts their further applications because of slow diffusion of reactants and products from the active sites of the zeolites[2]. Several different methods have been proposed to overcome the drawback of these limitations of microporous zeolites. These approaches consist of synthesizing ordered mesoporous materials with ordered pore (2–50 nm). Up to date zeolites with mesoporosity have been successfully synthesized such as pure silica ZSM-5[3], zeolite Y[4], zeolite A [5] and zeolite X[6].

Sodalite is kind of zeolite with ultramicropore size, high aluminum content (Si/Al = 1), and high stability in basic solution. In general the composition of sodalite is $M_8[\text{TT}'\text{O}_4]_6(\text{X})_y$, where X is a monovalent guest anion such as chloride in the mineral sodalite. Sodalite is an ultra micropore zeolite, which aluminosilicate framework consists of a 4-membered ring aperture with a pore size of 2.8 Å, known to be the smallest pore size in zeolite family. Because of its small pore size and high ion exchange capacity, sodalite has been considered as a good candidate material for a wide range of applications such as

hydrogen storage, optical materials and hydrogen separation [7], but one disadvantage of sodalites is the pore sizes which are too small to allow access to bulky organic molecules. Thus it has not found any significant catalytic applications due to its inaccessibility cages with small pore openings (2.8Å). In order to crack bulky organic molecule, catalysts should have proper pores of different sizes especially of large mesopores with high activities. To overcome these disadvantages mesoporous sodalite with special properties including high aluminum content, high stability in basic solution, highly crystalline zeolitic walls and high surface area should be synthesized. This paper reported the attempt to synthesis mesoporous sodalite by utilizing different types of organic structure directing molecules.

2.0 MATERIALS AND METHODS

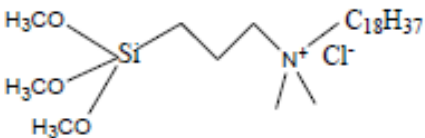
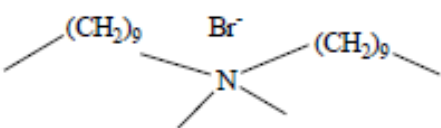
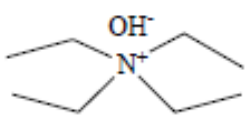
2.1 Materials

Chemicals used for the synthesis of mesoporous sodalite were sodium hydroxide, NaOH (Merck, EMSURE, >99%) as alkali source and sodium aluminate, NaAlO₂ (Riedel-de-Haën) as alumina source. The silica source that was used is fumed silica (Fluka) which was commercially purchased (~200 m²/g –as obtained from manufacturer), and different organic structure directing molecules including dimethyl dioctadecyl trimethylammonium bromide (DDAB), organosilane(trimethoxysilylpropyldimethyloctadecylammonium chloride) (organosilane), and tetraethylammonium hydroxide (TEA).

2.2 Synthesis of Mesoporous Sodalite

The hydrothermal synthesis of mesoporous sodalite was performed by preparing a sol containing oxide ratios of 1.7SiO₂:15Na₂O:1Al₂O₃:80H₂O:0.3 [(CH₃O)₃SiC₃H₆N(CH₃)₂C₁₈H₃₃]Cl (51.5wt% methanol solution) [8]. First, NaOH solution was prepared by dissolving NaOH pallet (7.98 g) in distilled water (10 g). The solution was divided into two portions equally. One portion of alkaline solution was mixed with fumed silica (0.68 g) to form silicate mixture and the other portion was mixed with NaAlO₂ (0.68 g) to form aluminate solution. Then organosilane template was added to silicate solution. Both solutions were heated at 100°C to dissolve the solid until clear solution formed. The solutions then were cooled down to RT. The silicate solution was then added dropwise into the aluminate solution. Solution formed was transferred into stainless steel autoclave and was heated at 150°C for 6 hours. Then the solid product obtained was washed using distilled water until the filtrate solution reached pH 7. The recovered solid product was dried at 60°C for 24 hours, followed by calcination at 550°C for 6 hours to remove the organic templates. The procedure was repeated for DDAB and TEA as templates. Table 2.1 shows the structural formula for the templates used for the synthesis of mesoporous sodalite.

Table 2.1: Structural formula of different templates for synthesis of mesoporous sodalite

Template	Structural formula
organosilane	
DDAB	
TEA	

2.3 Characterization

Characterization of the synthesized samples were carried out by X-Ray Diffractometer (Model Bruker D8) with radiation sources Cu K α that has $\lambda=1.542 \text{ \AA}$ at 40 kV and current of 10 mA. The diffractogram were scanned in the degree of 2θ at the range of $5 - 50^\circ$ with the step size of 0.05° [9].

The presence of tetrahedral TO_4 (T = Si or Al) bonding is determined by using Fourier transform infrared spectroscopy, FTIR (Perkin Elmer series 1600). The spectrum was elucidated for zeolite framework structure at wavelength between $400\text{-}1500 \text{ cm}^{-1}$ [10]. The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area of samples [11].

3.0 RESULTS AND DISCUSSION

The XRD of the synthesized samples using DDAB, TEA, and organosilane templates are presented in Figure 3.1. The presence of sodalite phase was confirmed by comparing the diffraction peaks at 2θ , 13.97° , 24.938° , 32.368° , 38.468° and 41.887° with that of the reference for sodalite [JCPDS 81-0705]. These peaks correspond to the plane [110], [211], [310], [222] and [330]. It can be seen from Figure 3.1 that all synthesized samples showed the formation of sodalite with different crystallinity. High crystallinity and pure sodalite has been formed by using organosilane and DDAB templates. However only low crystallinity of sodalite was formed when using TEA. In addition some other phases

were observed exist in the sodalite sample of TEA. It can be suggested that bigger size templates such as organosilane and DDAB, facilitated the formation of pure sodalite.

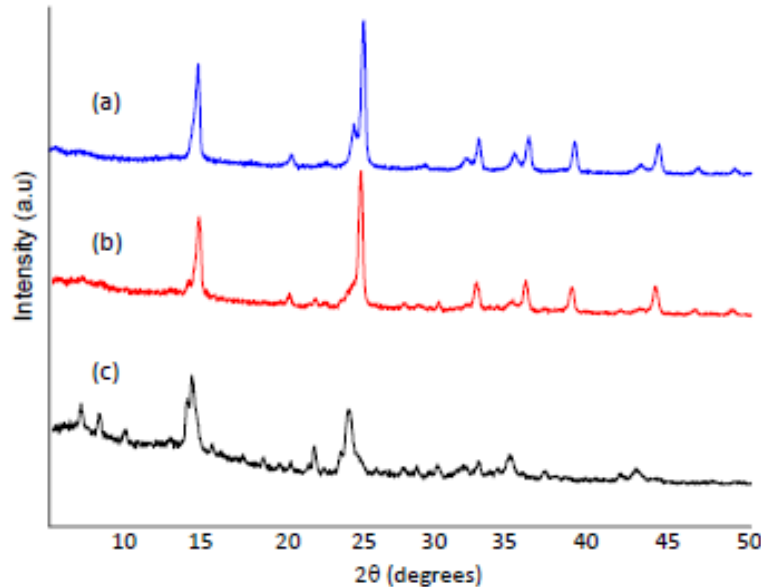


Figure 3.1: XRD pattern of synthesized samples using fumed silica as silica source, (a) organosilane, (b) DDAB, (c) TEA as templates

The crystallite size the synthesized samples were calculated theoretically using Debye-Scherrer equation(1), while the crystallinity was calculated by taking the total intensity of 2 main peaks at angle 2θ , around 13.97° and 24.938° [9]. In this study crystallinity of sodalite samples obtained by organosilane was taken to 100% crystallinity. The crystallinity of other samples was compared to organosilane sample. Table 3.1 showed the crystallinity and the crystallite size (nm) of the sodalite formation.

$$D = 0.9 \lambda / \beta \cos \theta \quad (1)$$

Table 3.1: The crystallite size and crystallinity of sodalite formed by using different templates.

Template	Crystalline size (nm)	Crystallinity(%)
organosilane	18	100*
DDAB	22	82
TEA	24	42

*The sample synthesized using organosilane is taken to 100% organosilane

Figure 3.2 shows the spectra of samples synthesized by using different templates. In general the IR spectrum of each sample shows 2 main peaks with different sharpness of the peak. The IR peak pattern shows by the IR in a typical vibration pattern for the sodalite formation [10].

IR spectra of the samples showed broad band of asymmetric stretching of T-O-T (T=Si or Al) bond was observed around 994 cm^{-1} which indicates the formation of Si-O-Al bond. The asymmetric Al-O stretch is located in the region of 950-1000 cm^{-1} while the symmetric Al-O stretch is observed in the region of 660-770 cm^{-1} . The absorption band round about 690 cm^{-1} is due to the symmetric stretch (T-O-T). The bands around 450-475 cm^{-1} shows the bending vibrations of T-O-T [11].

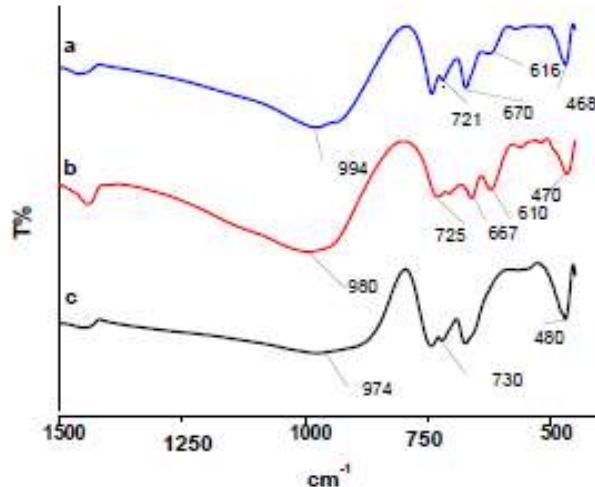


Figure 3.2: FTIR spectra of synthesized samples by using fumed silica as silica source, (a) organosilane, (b) DDAB (c) TEA as templates.

The samples were characterized using N_2 adsorption to determine their surface area. Only sodalite obtained using organosilane showed mesoporosity as proved by higher BET surface area. Another samples showed only low surface area. Since sodalite is ultramicropore zeolite, in its microporous form no N_2 molecule can penetrate the pore rendered the samples with low surface area. The fact that sodalite obtained by organosilane produced higher surface area, it can be suggested that sodalite with mesoporosity has been formed. Table 3.2 presented the BET surface area of sodalite obtained by using various templates.

Table 3.2: Results for BET surface area for synthesized samples by using different templates

Template	BET surface area(m ² /g)
organosilane	150.28
DDAB	54
TEA	46

4.0 CONCLUSION:

Synthesis of mesoporous sodalite has been investigated in this study by using different templates. XRD and FTIR results showed the pure sodalite was formed by using dimethyldioctadecylammonium bromide (DDAB) and organosilane (trimethoxysilyl propyl dimethyloctadecylammonium chloride) as templates. Sodalite synthesized by using organosilane (trimethoxysilylpropyldimethyloctadecylammonium chloride) showed mesoporosity as proved by BET surface area.

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