

# Synthesis of Hydrophobic Silicalite Adsorbent from Domestic Resources: The Effect of Alkalinity on the Crystal Size and Morphology

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**ABSTRACT:** A new polymorph crystalline silica composition having uniform pore dimensions were synthesized by calcining a crystalline hydrated alkyl-ammonium silicate. The pore dimensions approximately were 6 angstrom for silicalite-1 and 11 angstrom for silicalite-2 units. The silicalite-1 was prepared hydrothermally at a pH of about 10 from a reaction mixture consist of water, amorphous silica and a quaternary ammonium compound. Domestic water glass was ion-exchanged to produce silicasol. In this work we also investigated the influence of alkalinity percent in the starting gel mixture on the crystal shape and size.

**KEY WORDS:** Silicalite, Polymorph crystalline silica, Amorphous silica, Tetrapropylammonium-bromide.

## INTRODUCTION

Some of the crystalline forms of silica are found in nature and some of them exist as synthetic forms which apparently have no natural counter part. Among those found in nature are quartz, tridymite and cristobalite, each having polymorphic forms stable in different ranges of temperature [1]. Silicalite was first prepared by *Flanigen et al.* [2]. It is a new hydrophobic crystalline silica molecular sieve and has a crystal structure like zeolite ZSM-5 ( Fig. 1). It can be considered as the Al-free analogues of ZSM-5 and was termed silicalite-1. Another form of silicalite (silicalite-2) has the same structure as

the ZSM-11. Crystallization region of silicalite in ternary phase diagram has been shown in Fig. 2.

Due to the surface area and pore volume, silicalite possesses a good adsorption capacity. The competitive adsorption of a binary mixture (e.g. water and alcohols) on silicalite molecular sieve has shown that hydrophobicity increases with decreasing of Na<sub>2</sub>O content of the adsorbent. This matter can be considered as an advantage of silicalites compared to ZSM type zeolites [7].

*Bibby* [3] has synthesized silicalite in NH<sub>4</sub>OH-TBAOH (tetrabutylammonium hydroxide) system. He

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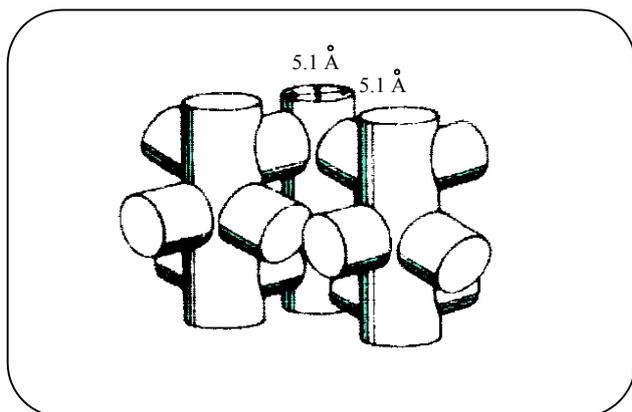


Fig. 1: The framework structure of zeolite ZSM-5 ( or Silicalite ).

has shown clearly the major difference between the X-ray powder diffraction patterns of silicalite-1 and silicalite-2 [4]. Generally, a liquid crystal templating mechanism (LCT) in which surfactant liquid crystal structure serves as organic templates has been proposed for the formation of shape selective with defined pore size material.

The use of TPABr is an one-step procedure while the use of  $\text{NH}_4\text{OH}$ -TPAOH is a two-step procedure in which the first step is preparing of TPAOH by TPABr ion-exchange and then the use of produced template. So the use of TPABr is easier respect to another one [4].

It is apparent that some various inorganic cations play an essential role during the zeolite synthesis and some references reported this effect [5,6]. It was found that various alkali metal cations play this role during the crystallization of silicalite [4]. For instance, nucleation and genesis of zeolite cages, decreasing of crystallite size and crystal-habit (height to width ratio) are improved by increasing the amount of  $\text{Na}_2\text{O}$ . However, the influence of alkali metal cations on the stability of silicalite is as  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ , while particle size and morphology increase vice versa [4].

This adsorbent has a very useful hydrophobic and organophilic characteristics which make it suitable to use in selective adsorption of some materials from water, either in liquid or in vapor phases [1,7,8]. Therefore, the synthesis of this material will be desirable due to its excellent potential for separation of polar organic compounds from gaseous or liquid mixtures (e.g. separation of small amounts of ethanol from fermentation products).

Due to the availability of domestic resources used in

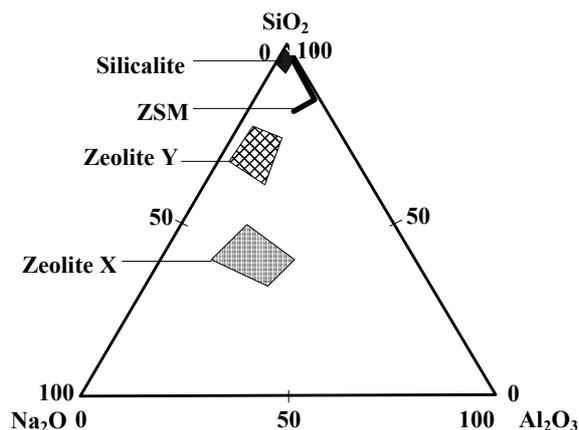


Fig. 2: Ternary composition diagram of  $\text{Na}_2\text{O}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system for synthesis of silicalite.

this synthesis, the production of this material is economical. On this basis, working on a pilot plant scale production of this material can also be justifiable.

## EXPERIMENTAL

### Reagents

Reagents used in this work were domestic sodium silicate ( PARS SILIS, technical grade water glass) with  $\text{Na}_2\text{O}:\text{SiO}_2$  molar ratio of 1:2.9 used for production of silicasol ( $\text{Na}_2\text{O}:\text{SiO}_2$  molar ratio  $\leq 0.10 : 2.90$  ), sodium hydroxide (BIPC, technical grade) and tetrapropylamm-oniumbromide (Riedel-de Haen).

The sodium and silica content of the reagents were analyzed by following methods:

- Sodium and silica in water glass (UOP method 627-85).
- Sodium in silicasol by atomic absorption method.
- Silica in silicasol (UOP method 436-87).

### Silicalite Synthesis

The reaction mixture was prepared by adding the silicasol solution (20-30 wt%  $\text{SiO}_2$ , 0.1-0.5 wt%  $\text{Na}_2\text{O}$ ) to the stirred solution of sodium hydroxide. The mixture was stirred vigorously for about 10 minutes and then the TPABr solution was added to the mixture with proper stoichiometric ratio and mixed for 5 minutes. Then the crystallization was carried out in an unagitated closely sealed autoclave system for 72 hours at  $200^\circ\text{C}$  and autogeneous pressure equivalent to the vapor pressure of water at the temperature concerned (about 16 bars). Crystallization was continued until an extensive supernat-

ant solution was separated from the reaction mixture.

The solid formed was settled into a compact layer of crystalline phase at the bottom of the vessel. When reaction was completed, the reaction mixture was immediately cooled. Product was filtered off from the mother liquor and thoroughly washed with distilled water. Finally it was dried at 90°C and calcined at about 650°C for one hour. A summary of the synthesis is shown in Fig. 3.

## CHARACTERIZATION

### XRD

Phillips X-ray diffractometer model "PW 1840" (Cu  $\alpha$ , APD-Software package and JCPDF search files) was used for the qualitative phase analysis, and relative crystallinity ASTM-D5758- Vol. (05.03).

### SEM and Image Analysis

Scanning electron micrographs were taken using a "Cambridge stereo scan" scanning electron microscope model 360. progressive trend of silicalite formation was taken as SEM photoes.

### TGA

TGA (Thermal Gravimetry Analysis) was determined using a "TGS-2, Perkin-Elmer" system. In this system the sample was activated by heating to 670°C. Desorption measurements were made at various temperatures and pressure of 750 torrs. Desorption measurement of uncalcined silicalite (containing TPABr) is shown in Fig. 4.

### Surface Area and Water Adsorption Capacity of Silicalite

The surface area of the products determined by using "Quantasorb" system with nitrogen adsorption method.

## RESULTS AND DISCUSSION

It was found that silicalite can be prepared in the presence of certain amounts of alkali metal cations (in form of sodium hydroxide) and tetrapropylammonium-bromide [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub> NBr].

Fig. 5 shows the XRD patterns of synthesized silicalite and standard ZSM-5 [9]. As it is seen, there is good similarity in the most intense peaks at 2 $\theta$  from 7 to 10 and 22 to 25 degrees between the two patterns and no other peaks which would show an impurity were detected. This is an indication that the sample obtained was pure silicalite-1. Fig. 6 shows the SEM photographs

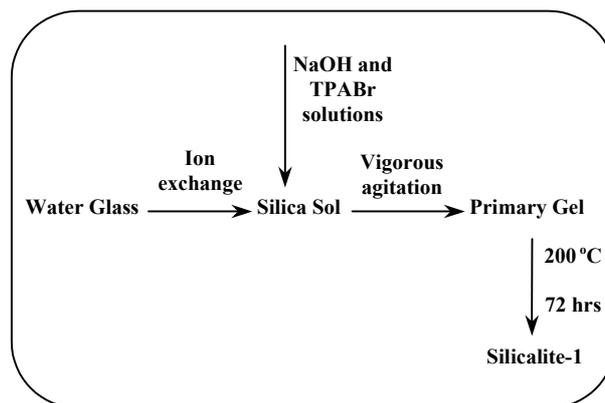


Fig. 3: A Summary of the Synthesis.

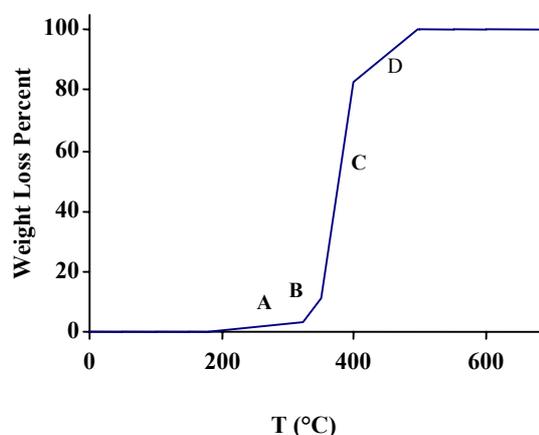


Fig. 4: The TGA graph of synthesized silicalite-1.

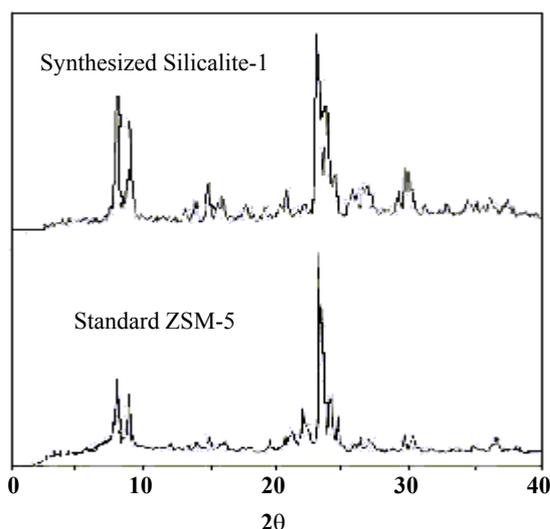
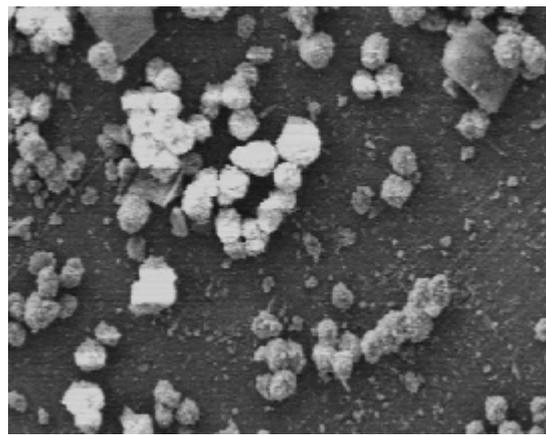
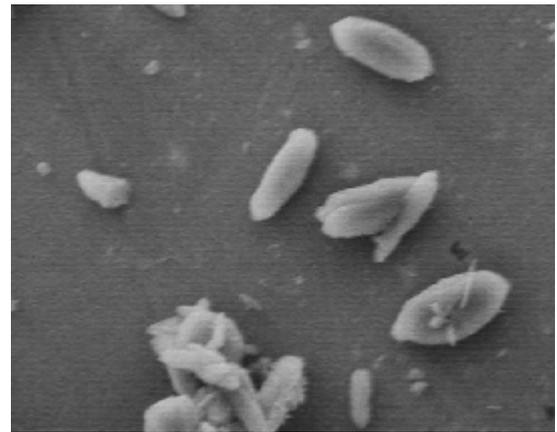


Fig. 5: XRD patterns of synthesized silicalite-1 and standard ZSM-5.



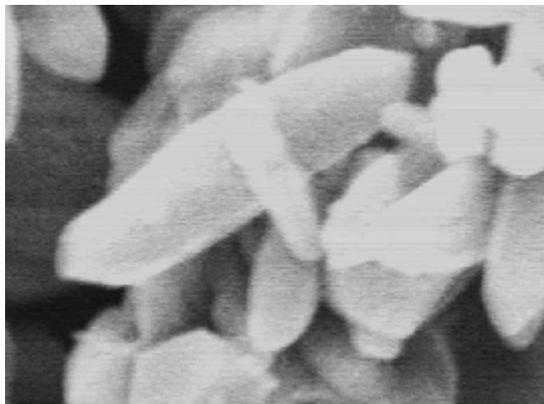
50.0 μm

(a)



10.0 μm

(b)



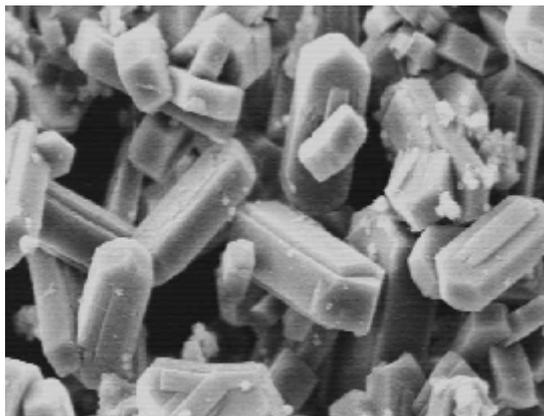
2.0 μm

(c)



50.0 μm

(d)



20.0 μm

(e)



5.0 μm

(f)

**Fig. 6:** The scanning electron micrographs of : (a) cyclic alpha quartz, (b) ovate alpha quartz, (c) prolonged ovate alpha quartz, (d) and (e) coffin shape silicalite-1 ( $\text{SiO}_2\text{:Na}_2\text{O}$  molar ratio 50:2.04), (f) coffin shape silicalite-1 ( $\text{SiO}_2\text{:Na}_2\text{O}$  molar ratio 50:4.10).

**Table 1: The comparison of silicalites with different ratios of  $\text{SiO}_2:\text{Na}_2\text{O}$ .**

| $\text{SiO}_2:\text{Na}_2\text{O}$<br>molar ratio | TPABr<br>(moles) | Crystal<br>size<br>( $\mu\text{m}$ ) | Relative<br>Purity<br>(%) | Surface<br>Area<br>( $\text{m}^2/\text{gr}$ ) | Humidity<br>Absorption<br>(wt. %) |
|---|------------------|--------------------------------------|---------------------------|---|-----------------------------------|
| 30  | 1.33             | 32.0                                 | 90-95                     | 305   | 0.5                               |
| 24  | 1.33             | 27.5                                 | 100                       | 332   | 0.5                               |
| 12  | 1.33             | 12.6                                 | 90-95                     | 363   | 0.6                               |
| 10  | 1.33             | 8.3                                  | 80-85                     | 375   | 0.8                               |

of the three forms of alpha quartz and two forms of silicalite-1 crystals in terms of alkalinity amounts.

Typical SEM pictures of the five product samples synthesized in different  $\text{SiO}_2:\text{Na}_2\text{O}$  ratios were compared (Table 1). It was found that the morphology of crystals depend on alkali metal cations concentrations could have three different shapes (cyclic, ovate and prolonged ovate alpha quartz and coffin- silicalite shapes).

Surface area of products varied from 305 to 375  $\text{m}^2/\text{gr}$ , and their equilibrium water adsorption capacity varied between 0.5 to 0.8 weight percent.

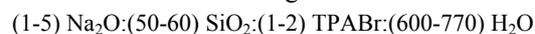
In order to find the appropriate temperature for calcination of the product, TGA graph was taken from produced silicalite as is showed in Fig. 5 in which four significant zones are observed. It seems that from room temperature to about  $320^\circ\text{C}$  (zone A) physically adsorbed water is eliminated, from about  $320^\circ\text{C}$  to about  $350^\circ\text{C}$  (zone B) the crystal water is released, from about  $350^\circ\text{C}$  to about  $400^\circ\text{C}$  (zone C) the major part of organic template is decomposed and finally, from about  $400^\circ\text{C}$  to about  $470^\circ\text{C}$  (zone D) decomposition of remained part of the template (probably protonic or cationic form of the template) is occurred.

Sodium metal cations depending on their intrinsic properties may influence the nucleation step by various ways. At first because of their valuable ability to order water molecules around them, they will favor the super saturation of the solution, the formation of sol species and their further agglomeration and precipitation as a gel; the second, is that the intimate mixture of silicate complexes with  $\text{TBA}^+$  which can leads to silicalite nuclei. Finally, it seems that decreasing of alkalinity ( $\text{Na}_2\text{O}$  wt.%) grows

the particle size and affects on the morphology (more exact habit) of various silicalite crystals (table1).

## CONCLUSIONS

Pure silicalite type zeolite was obtained from the reaction mixture of the following molar ratios:



In general, many uses can be considered for synthesized silicalites in industry. This zeolite could be used as organophilic and hydrophobic adsorbent in purification of the hydrocarbons and alcohols in chemical industries [7,8]; furthermore, silicalite has an excellent potential to apply for elimination of hydrocarbonaceous pollutions from water and air to approach to environmental health purposes [8]. Also, it can be employed to separate the coloured organic molecules from aqueous phases.

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