Effect of SrO content on Zeolite Structure

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Abstract. The aims of current studies is to investigate the effect of strontium oxide content (SrO) on synthesized zeolite. Zeolite was synthesized from Tetraethyl orthosilicate (TEOS) as precursors of SiO2 and aluminum isopropoxide (AIP) precursors. The mixture was aged for 3 days and hydrothermally treated for 6 days. The SrO content was added by impregnation method. The products were then characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), and Surface Area Analyzer (SAA). The diffractogram confirmed the formation of Faujasite-like zeolite. However, after the addition of SrO, the crystallinity of zeolite was deformed. The diffractograms shows the amorphous phase of zeolite were decrease as the SrO content is increase. The structural changes was also observed from FTIR spectra which shows the shifting and peak formation. The surface area analysis showed that the increasing loading of SrO/Zeolite reduced the catalyst surface area.

1. Introduction

Zeolite Y is a large-pore high-silica material first synthesized in 1967 [1]. Its structure has been recently reported to be an intergrowth of two or three polymorphs having a 3-dimensional system of interconnected 12-membered ring channels. Its crystallization kinetics and mechanism have been investigated in a Na, K, TEA-containing system with tetraethylorthosilicate (TEOS) as source of silicon in static conditions [2-3]. Amorphous and colloidal silica have also been used as raw materials [4-7]. In these studies, the effect of the relative amounts of Na and K in the parent gel was also systematically investigated. However, the nature and concentration of alkali metals have been shown to influence the crystallization rate and the crystal size and morphology of other high-silica zeolites [7].

In the case of zeolite Y, the possibility of synthesizing a pure sample of one of the polymorphs by control of their relative nucleation and crystallization rates provides an additional strong reason for studying the effect of the synthesis parameters. Furthermore, both the crystal intergrowth and the crystal size and morphology are known to influence the catalytic behavior of zeolites.

In the present work, the effect of Sr2+ cation on the crystallization of zeolite Y is reported. Special attention has been given to the chemical changes in the liquid and solid phases, as well as to the functional group and diffractogram pattern of the products.
2. Experimental

The tools used in the study were equipment glass (glass beaker, erlenmeyer, funnel glass, funnel, measuring cup, pipette, pipette measuring, pipette volume, flask, a stirrer, a spatula), hotplate magnetic stirrer (IKAMAG), magnetic stirrer, oven (Memmert), furnaces (Barnstead Thermolyne 1400), analytical balance (AND GR-200), the reactor autoclave stainless steel, thermometer, instrument X-Ray Diffraction Zhimadzu, FTIR Shimadzu instruments Spectrum One 8400S, a set of tools Reflux, fine filter paper, GC-MS (Shimadzu QP2010S).

The materials needed in this research are Strontium Nitrate Sr(NO$_3$)$_2$. (99%) (Merck), tetraethyl orthosilicate (TEOS) 99% $\rho = 0.94$ kg/L, sodium hydroxide (NaOH) (99%), tetramethylammonium hydroxide (TMAOH) (acidimetric 24.0 to 27.0% (m)) $\rho = 1.02$ kg/L, C$_6$H$_{21}$AlO$_3$Aluminium isopropoxide (ALP) 98%, deionized water (Aqua Demin), Methanol Merck (Mr 32.04 g / mol, about 99% of $\rho 0.792$ g/cm$^3$), used cooking oil, alcohol 95%, Potassium Hydroxide (KOH) Merck (Mr 56.11 g/mol, purity 85%), Merck phenolphthalein indicator (Mr 318.33 g/mol, about 99%), natural zeolites bayah Banten, aqueous HCl Merck (Mr. 36.46 g/mol, 32% purity, $\rho 1.16$ g/cm$^3$).

2.1. Synthesis of Zeolite

Zeolite were synthesized in accordance with the methods conducted by Taufiqurrahmi et al., (2011) with some modifications [8]. Preparation of zeolite begins with making a 0.065 mol NaOH solution. The next stage added 17.744 grams of tetramethylammonium hydroxide (TMAOH) and 16.34 grams of aluminum isopropoxide (ALP) to a solution of NaOH while stirring using a magnetic stirrer until a homogeneous or formed sol. At the same time TEOS of 30.796 mL was added to the mixture dropwise until the solution is white as milk. The mixture was stirred using a magnetic stirrer for 3 days while continuously stirring at room temperature. In this preparation obtained a molar composition ratio of 4.964 TMAOH: 0.065 NaOH: 2 ALP: 3.448 TEOS: 125 H$_2$O. The next stage was hydrothermal by incorporating the mixture into a stainless steel autoclave heated in an oven at 100°C for 6 days. The solid obtained at this stage was further separated by centrifuge at a rate of 3,000 rpm for 20 min. The solid was washed with distilled water until the pH of neutral laundry, then dried in an oven at 100°C for 2 hours. The obtained solids were calcined using a furnace with a temperature of 550°C for 8 hours. The zeolite solids were characterized by Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD).

2.2 Preparation of SrO-modified Zeolite

In this research, the Sr content was calculated as SrO. Preparation of zeolite with 1% of Sr (w/w) was carried out by first immersing of zeolite within NH$_4$OH solutions, followed by putting zeolite solids into 10 mL of Sr(NO$_3$)$_2$ solution. The solution mixture was then stirred for 30 minutes, while heated until the mixture was shaped like a slurry. The mixture was dried in an oven at a temperature of 100°C for 2 hours. The obtained solids were then calcined in the furnace at 550°C for 5 hours. The SrO/Zeolite catalysts were characterized by Fourier Transform Infrared (FTIR), X-RayDiffraction (XRD) and Surface Area Analyzer (SAA). The similar treatment was also done for different concentration of SrO.

3. Result And Discussion

3.1 Synthesis of Zeolite

3.1.1 Crystallinity Analysis X-Ray Diffraction (XRD)

Crystallinity Analysis Using X-Ray Diffraction (XRD) synthesis of Zeolite was matched with a standard faujasite zeolite diffractogram according to Treacy and Higgins [9].
The diffractogram of synthesized zeolite Y shows a characteristic peak at 2θ = 10.84°; 21.98°; 25.40. However, the zeolite is still containing high amorphous phase. Zeolites had the best performance since the channel was good and the range of 3-15 Å cavity [10]. Because of the zeolite Y type faujasite standard first peak appears at an angle 2θ smaller than 10, the Zeolite also have the distance d which is equal to the zeolite comparison, possible arrangement of polyhedral cage sodalite on this product is perfect [9].

3.1.2 Zeolite Function Analysis of Fourier Transform Infrared Nanoparticles (FTIR)

FTIR spectra results of synthesis of Zeolite can be seen in Figure 2. It can bee seen that the Zeolite had formed the zeolite framework. The band at 3435.98 cm\(^{-1}\) indicate -OH group and 1639.82 cm\(^{-1}\) was overtone vibration of -OH group. While the band at 1052.08 cm\(^{-1}\) was a vibration asymmetric span. The presence of a curved peak in an area of about 1000 cm\(^{-1}\) arose because of the vibration of the Al-OH cage formed by a cation vacancy, and 722.25 cm\(^{-1}\) was a symmetric spacer vibration. The presence of vibration and bending indicates the formation of aluminosilicate framework [11]. This results was in accordance with Zahro et al [12] which states that in structure of zeolite Y was known character of aluminosilicate had internal and external network, which was internal network of zeolite shown at absorption area about 500-420 cm\(^{-1}\), 820-650 cm\(^{-1}\), and 1250-950 cm\(^{-1}\). The absorption area of about 820-650 cm\(^{-1}\) represents the vibration of O-Si-O and O-Al-O symmetry, while the absorption region of about 1250-950 cm\(^{-1}\) represents the asymmetric stretching vibration.

Figure 1. Diffragogram Synthesis of Zeolites Using X-Ray Diffraction (XRD)
Figure 2. Clustered Spectrum Function of Zeolite Using FTIR

3.2 Synthesis of SrO/Zeolites

SrO metal bonding in Zeolite was done by impregnation method. The SrO/zeolite solids of the formed nanoparticles are separated from the solvent by being filtered. The obtained solid is dried to remove any residual demineralized water solvent present in SrO/Zeolites. The result of impregnation was obtained by slurry solids.

3.2.1 Analysis of Crystallinity SrO/Zeolites Using X-Ray Diffraction (XRD)

Diffractogram of crystallinity SrO/Zeolites can be shown in Figure 3.

Figure 3. Diffractogram of (a) H-zeolite, (b) 1% SrO/Zeolite, (c) 2% SrO/Zeolite, (d) 4% SrO/Zeolite, and (e) 8% SrO/Zeolite

XRD data analysis results show that SrO metal cannot be embedded in Zeolite. This was known by the peak loss of SrO/zeolite. The loss of zeolite peak was due to SrO formed on the pore of zeolite, urging the aluminosilicate skeleton on the zeolite. New emerging peaks were characterized
as strontium oxide, which was presented in zeolites [12]. After the impregnation process, the zeolite structure becomes amorphous, indicating a pure silica composition. The diffraction pattern of FIG. 3 shows a peak width at 20 between 21°-25° for all types of catalysts. The peak was similar to the peak of the amorphous silica [13], so it can be said that all synthesized materials were mostly amorphous materials.

Based on this, the zeolite of the impregnated nanoparticles was transformed into a silicalite zeolite, a zeolite having high Si and it was hydrophobic and had an affinity for hydrocarbons. Aluminium in the zeolite framework was a weak point of zeolite crystals. Al easily knocked out of the framework caused damage to the zeolite structure and lost its activity [1]. According Kasmui et al. [14] stated that the silicon zeolite faujasite was derived from zeolite Y and it was caused the formation of the faujasite framework can experience a metastable state.

The impregnated catalyst with SrO had a pattern similar to that of H-Zeolite but with different intensities. It shows that the six catalysts still have the same minerals as the nanoparticle zeolite but with different amounts. The decrease in XRD peak intensity was also experienced by [14] which developed CuO in Titanium Silicalite (TS-1). They stated that the decrease in intensity in TS-1 was due to the agglomeration of CuO oxide that closed the pores of TS-1.

3.2.2 Analysis of Cluster Function SrO/Zeolites Using Fourier Transform Infrared (FTIR)

Comparison of FTIR spectra of catalyst H-Zeolite, SrO, SrO/Zeolites 1%, 2%, 4% and 8% can be seen in Figure 4.

![Figure 4. a) SrO/Zeolites 8% b) H-Zeolite c) SrO d) SrO/Zeolites 4% e) SrO/Zeolites 1% f) SrO/Zeolites 2%](image)

According to Figure 4, the emerging absorption can be seen that the zeolite of the SrO/zeolite spectrum of nanoparticles had formed. The absorption peak that appeared in the area around 400-1300 cm\(^{-1}\) was the typical peak of zeolite faujasit [5]Typical vibration band zeolite Y at wave number 1055.5; 1052.14; 1052.04; 1051.78; And 1043.91 cm\(^{-1}\). According Sudiyono (2016) was typical of zeolite Y vibrational band at wave number 1020 cm\(^{-1}\) (internal asymmetric stretch vibration) after bonding experiencing widening, so that indicated the zeolite structure changes. This was in accordance with the XRD results data showing the increment made causing zeolite Y to shift the value of 20 [15]. The new absorption peaks after loading were present at wave numbers at about 2360-2380 cm\(^{-1}\), which assumed the uptake of the hydrocarbon impurities [16].

3.2.3 Surface Area Analysis of SrO/Zeolites Using Surface Area Analyzer (SAA)

The results of catalyst surface area measurement SrO/Zeolites are synthesized and H-Zeolite and SrO are presented in Table 1.
Table 1. Surface Surface Results

| No | Sample          | Surface Area (m²/g) |
|----|-----------------|---------------------|
| 1. | H-Zeolite       | 46,969              |
| 2. | SrO             | 386,395             |
| 3. | SrO/Zeolite 1%  | 382,818             |
| 4. | SrO/Zeolites 2% | 148,851             |
| 5. | SrO/Zeolites 4% | 81,008              |
| 6. | SrO/Zeolites 8% | 279,394             |

Table 1 shows that on the stand alone SrO catalyst and SrO the synthesis results decreased the specific surface area along with the percent increase loading. This decrease in surface area indicated that the formation of smaller particle size and the breakdown of crystal structure of SrO/zeolite synthesized nanoparticle catalyst. The smaller the particle crystal size, the larger the surface area of the catalyst [17-18].

In addition to the SrO/zeolite catalyst nanoparticles produced large particle size crystals and small surface area. This was inversely related to the synthesis results of SrO/Zeolites 1%, 2%, and 4% catalysts. However, in this case it can be reinforced with the crystallinity yield resulting from an 8% SrO/Zeolite catalyst that there is a better 2θ peak than the H-Zeolite catalyst, SrO/Zeolites of 1%, 2%, and 4%.

4. Conclusion

SrO/Zeolites 8% shows a shift in the wave number 1043.91 cm⁻¹ and the emergence of new absorption bands at 2359.97 cm⁻¹ indicating the interaction between SrO and H-Zeolite. The highest surface area was obtained at 8% of SrO was added into zeolite.

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