

Linde Type-A zeolite synthesis and effect of crystallization on its surface acidity

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An aluminosilicate zeolite, Linde Type-A (LTA) has been prepared from aluminium powder and sodium metasilicate by hydrothermal process. The zeolite was characterized by FTIR and X-ray diffraction (XRD) analysis and by measuring the surface acidity using KOH as adsorbate. The surface acidity of LTA zeolite varied greatly with varying synthesized conditions such as crystallization temperature, crystallization time and K^+ ion adsorption period. The Bronsted acid site on the zeolite surface increased with increasing crystallization temperature and the maximum surface acidity was obtained at 100°C. Crystal growth was also dependent on the crystallization time. The surface acidity increased with increasing crystallization time. The maximum surface acidity due to the maximum consumption of the K^+ ion was observed at 48 h adsorption time and the value was found to be 0.9 meq/g when Si:Al was 50:50. It was seen that the surface acidity was more pronounced when ammonium hydroxide solution as adsorbate and agitated crystallization condition were used. The surface acidity of the commercial LTA zeolite was compared with the surface acidity of the synthesized LTA zeolite. It was found that the surface acidity of synthesized LTA zeolite is slightly greater than commercial LTA zeolite.

Keywords: LTA zeolite, XRD measurement, FTIR spectroscopy, Surface acidity

Zeolites are well-defined class of naturally occurring crystalline aluminosilicate minerals. They have proved to be valuable catalysts in petroleum and polymer synthesis. The properties of zeolites such as surface acidity, shape-selectivity and thermal stability also enable them to be used for highly selective synthesis in the field of chemical intermediates and fine chemicals. They have three-dimensional structures arising from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra and are used as catalysts because of their high concentration of active acid sites. The concept of surface acidity of finely divided solid was developed primarily to explain the action of acid surfaces in catalytic reactions^{1,2}.

However, the nature of the active acid sites on surface acidity has been a subject of controversy for many years. Some workers consider them as Bronsted acid while other view them as nonprotonic Lewis acid. Therefore, measurement of surface acidity of solid catalyst is of immense importance from technological point of view. Consequently, a number of methods³⁻⁷ are available for determining the surface acidity of solid catalyst viz. aqueous method, temperature-programmed desorption method, gas chromatographic method, UV, IR, ESR, NMR, spectrophotometric and calorimetric methods etc. Above methods either determine total acidity or any

of Bronsted and Lewis types of acid sites. Bronsted acidity is generally measured by titrimetric method using aqueous solution of potassium hydroxide and base exchange method by using NH_4OH and NH_4OOCCH_3 solution. On the other hand, amine titration method (Tamele method) and Benesi titration method (by using butyl amine solution) determine total surface acidity of both Bronsted and Lewis acid sites. Furthermore, the structure of zeolite plays an important role for selectivity of reaction. So, the determination of structure of synthesized zeolite by various techniques is very important. There are many reports of zeolite characterization prepared with different Si/Al ratios by adding special aluminium or silica sources⁸⁻¹⁶. A variety of silica sources including sodium silicate and silicon alkoxides are used while the most often used aluminium sources are: sodium aluminates, aluminium sulphate, aluminium nitrate and aluminium isopropoxide.

The principal synthetic (aluminosilicate) zeolites in commercial use are Linde Type-A (LTA) and Linde Type X. The unique properties of low silica zeolites (zeolite NaA, zeolite NaX with SiO_2/Al_2O_3 ratios ~2 and ~3 respectively) such as ion exchange capacity, sorption and catalytic activity make them ideal for various industrial applications. Present study focuses on synthesis of Linde Type A zeolite for catalytic

usages. Since aluminium powder can easily be obtained from the aluminium industry at very low cost, the production of zeolite from this source has potential to become economic process for zeolite production. Besides, the efficient utilization of zeolite catalyst surface acidity is an important factor which depends on its structure and composition.

In the present work, Linde Type-A zeolite catalysts having various Si:Al ratios were synthesized from aluminium powder and sodium metasilicate. The synthesized LTA zeolite catalyst was characterized by FTIR, XRD and surface acidity measurements. The factors effecting surface acidity such as crystallization temperature, crystallization time, adsorption time, agitation etc. were optimized.

Experimental Procedure

Preparation of LTA zeolite

Linde Type-A zeolite catalyst samples were prepared using different Si:Al ratio. Firstly, 1.97 g of aluminium powder (E Merck, 99%) was taken in a 250 mL beaker. Sodium hydroxide (BDH, 97.5%) solution prepared by dissolving 2.92 g of NaOH pellets into 30 mL deionized water in the beaker was allowed to stand for completing the reaction. Metallic aluminium reacts vigorously with sodium hydroxide solution, evolving hydrogen gas and heat. Thus, care has to be taken during the reaction. Then 20.74 g of sodium meta-silicate (Loba, 99%) was dissolved in 30 mL water in a separate beaker. Another NaOH solution, which was prepared by dissolving 0.723 g of NaOH in 20 mL of water, was divided into two equal parts. One part of the solution was added into the sodium meta-silicate solution and the other part was dissolved into the aluminate solution. Both of the solutions were then placed in two separate polypropylene bottles and were shaken gently until clear solutions were obtained. Then the silicate solution was poured quickly into the sodium aluminate solution. A thick gel was formed. The pH of the resultant gel was 11.5. Then the polypropylene bottle was capped tightly and allowed to stand for an hour for homogenization. The total mass was then transferred into a 130 mL teflon inserted stainless steel autoclave reactor. The reactor was closed and tighten to make the reactor completely sealed. Then the reactor was fixed to a motor driven shaft in an oven for rotating the reactor slowly (30 cycle/min) inside the oven. The oven temperature was maintained at the temperatures, 80-160°C for crystallization under

nitrogen atmosphere. The crystallization was continued until desired times (1-24 h). After completion of the crystallization the reactor was taken out from the oven and placed into a cold-water bath for cooling. After cooling, the reactor was opened and the suspension of total mass was transferred into a Buchner funnel for washing the solid materials.

The solid mass was washed with distilled water for several times to remove alkali completely. To speed up the filtration process the funnel was connected to a high vacuum pump. The filtrate was checked by a special type of litmus paper several times to ensure whether the total alkali is removed or not. Then the solid mass was dried at 110°C and ground in a mortar by means of a pestle applying moderate pressure. They were sieved through 25-200 mesh sieve and then calcined at 550°C in a Muffle furnace for 1 h in an atmosphere of nitrogen gas. After cooling, these were further ground and sieved through 100-200 mesh sieves and stored.

FTIR and XRD measurements

IR spectra of synthesized and commercial LTA zeolites were recorded with Shimadzu IR-470 spectrophotometer (Shimadzu, Kyoto, Japan) using KBr pellet technique. A mixture of 5.0 mg LTA zeolite and 200.0 mg of KBr were pressed into a disk for IR measurement.

The crystal of the LTA sample was examined by X-ray diffraction (XRD). The XRD study was performed with a Rigaku diffractometer using $\text{CuK}\alpha$ radiation of wavelength 0.15418 nm. Diffraction data were recorded between $2\theta = 7.0^\circ$ and 34.2° at an interval of 0.01° . A scanning speed of 2° per min was used. The repetition distance of the pores 'd' was obtained by the Bragg's law using the position of the first XRD line. The lattice parameter 'a₀' of the heagonal unit cell was calculated from the equation¹⁷ $a_0 = (2/\sqrt{3})d_{100}$.

Surface acidity determination

Surface acidity of synthesized zeolite was estimated using potassium hydroxide as adsorbate: Catalyst samples of 100-200 mesh were activated for an hour at 550°C in nitrogen atmosphere and then cooled for half an hour. 0.1 g of each of the sample was placed in three separate screw-cap vials and 10 mL of 0.01 N potassium hydroxide solution was added in each vial, and the vials were shaken for a while. For blank, 10 mL of potassium hydroxide solution was taken in another vial without catalyst.

These vials were kept for 24 h to establish equilibrium between potassium hydroxide solution and catalyst sample. During this time they were agitated several times. The solution from each vial with-catalyst was decanted in three separate 50 mL volumetric flask and was shaken for a few minutes. 1 mL of potassium hydroxide solution from each flask and from the blank was then pipetted out in 4 separate conical flasks and a few drops of water and 2-3 drops of phenolphthalein indicator (BDH, 99.9%) were added to it. Titration of this solution was carried out with 0.01 N HCl (BDH, 38%) in a micro burette. The adsorption time was varied in different experiments.

Results and Discussion

LTA zeolite characterization

The FTIR and X-ray diffraction pattern of synthesized sample are presented in Figs 1 and 2 respectively and are with reference to the LTA zeolite sample. The results indicated that the spectra of synthesized zeolite agreed well with the spectra of reference zeolite A. The comparison of IR spectra of synthesized and reference zeolites showed the better matching with fingerprints of wave number values. The first class of spectra consists of the strongest vibration found in both zeolites which were assigned to the internal tetrahedron vibrations and were found at 900-1000 cm^{-1} . Stretching modes involving mainly the tetrahedral atoms were assigned in the region of 712 cm^{-1} for both zeolites. The results indicated that synthesized LTA shift to a higher frequency (wave number) more than reference LTA, since the stretching modes were sensitive to the Si-Al composition of the framework and shift to a higher frequency with increasing number of tetrahedral silica atom¹⁸.

On the other hand, the characteristic XRD peaks of LTA at 2θ : 7.0°, 10.1°, 12.5°, 16.2°, 21.9°, 24.0°, 27.2°, 30.1° and 34.2° are quite consistent with the reference sample, indicating that a pure LTA crystalline zeolite is formed in this work¹⁷.

Surface acidity of LTA zeolite

The ability of the zeolite to act as a catalyst is directly related to the acidic function of the surface. The development of acid sites on the surface is the key feature of zeolite synthesis. The acid sites of a zeolite catalyst act as active centers for catalysis of a chemical reaction. Since the active center of this catalyst is related to the surface acidity, it is measured

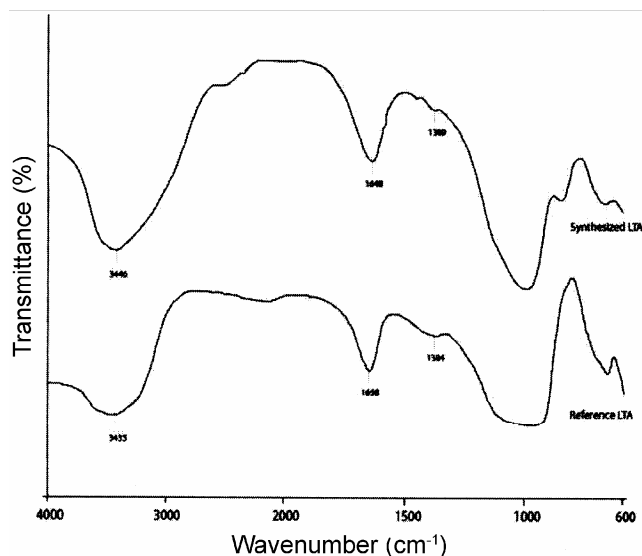


Fig. 1—FTIR spectra of reference and synthesized Linde Type-A zeolites.

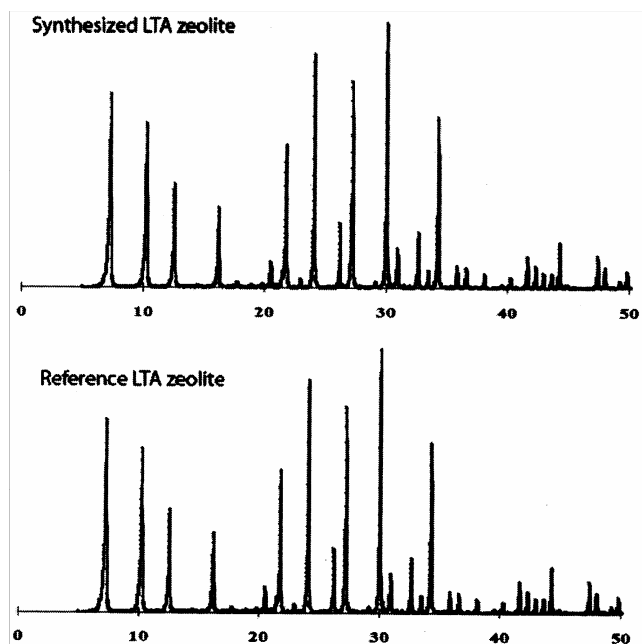


Fig. 2—X-ray diffractograms of reference and synthesized Linde Type-A zeolites.

in this work by titration method. The method involves base exchange technique using KOH as adsorbate. The surface acidity is denoted by mili-equivalent adsorbate per gram of solid zeolite. The surface acidity depends on many factors such as crystallization temperature, crystallization time, adsorption time etc. In this work all of these factors are optimized in order to find out the maximum surface acidity.

Effect of crystallization temperature

The relationship of surface acidity with crystallization temperature is shown in Fig 3. In the preparation of zeolite, amorphous aluminosilicate is formed first. Amorphous aluminosilicate possesses much of Lewis acid sites and a few of Bronsted acid sites. Bronsted acidity is much stronger than Lewis acidity. Thus, the increase of Bronsted acid sites causes the total increase of the surface acidity of the zeolite. The Bronsted acid sites develop on the zeolite surface when it forms a well defined crystal. The surface acidity at lower temperature, for example at 80°C is lower. This means that the hydrothermal crystallization of the LTA zeolite at this low temperature is not favourable and thus, the Bronsted acid sites are not formed sufficiently. At 100°C, the surface acidity is found to be the highest. Furthermore, at temperatures higher than 100°C, the surface acidity decreased gradually. This may be due to the higher nucleation rate rather than crystal growth at higher temperature. Higher nucleation rate is attributed to the smaller crystal size which ultimately causes the increase of Lewis acid sites rather than Bronsted acid sites. Therefore, the lower acidity of the LTA zeolite samples is found at temperatures higher than 100°C.

Effect of crystallization time

The LTA zeolite samples are prepared with different crystallization time from 1 to 24 h to find out the optimum crystallization time for achieving maximum surface acidity. The surface acidity of the samples is measured using 0.1 g sample size, KOH as base and upto 24 h adsorption time. The relationship between the surface acidity and the crystallization time is shown in Fig. 4. As the figure shows, the surface acidity is increased remarkably with increasing the crystallization time. At the crystallization time 1 h, the surface acidity is found to be 0.55 meq/g which is almost the same as of the amorphous aluminosilicate catalyst. This finding reveals that the nucleation of the crystals does not start within 1 h. The activation time for crystallization is 2 h. The surface acidity starts increasing after 2 h of crystallization time. The acidity increased sharply until 5 h and then gradually increased to prolong time.

Effect of adsorption time

Effect of duration of adsorption on the surface acidity is also investigated using 0.01 N of KOH as adsorbate. In this case, after adding sample to the

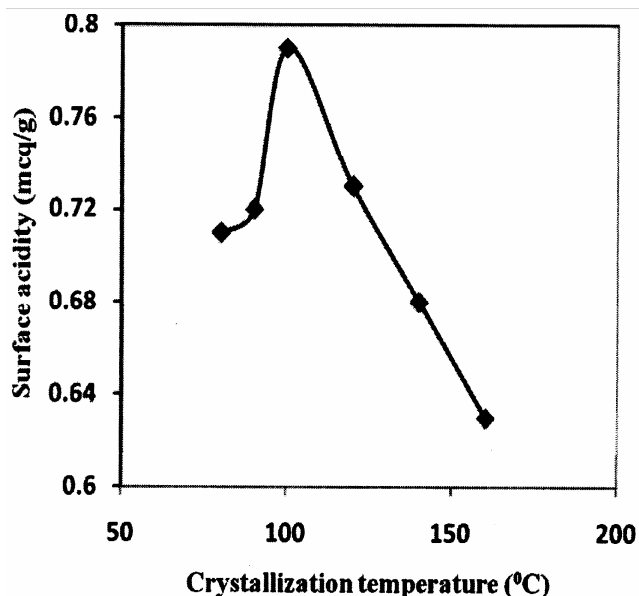


Fig. 3—Effect of crystallization temperature on the surface acidity of LTA zeolite. Sample, 0.1 g; Si:Al = 50:50; 10 mL 0.01 N KOH; 0.01 N HCl; Stirring time, 1 h; Crystallization time, 4 h; Adsorption time, 24 h

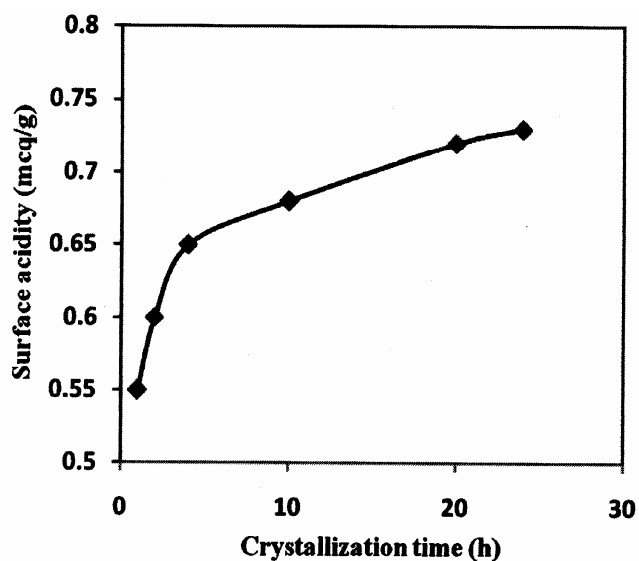


Fig. 4—Effect of crystallization time on the surface acidity of LTA zeolite. Sample, 0.1 g; Si:Al = 50:50; 10 mL 0.01 N KOH; 0.01 N HCl; Stirring time, 1 h; Crystallization temperature, 100°C; Adsorption time, 24 h.

solution the mixture is stirred for about 1 h and then kept undisturbed for different times. The duration of adsorption as a function of surface acidity is shown in Fig. 5. It is found that the increase of adsorption time resulted in increase of surface acidity. On the zeolite surface, K^+ is adsorbed by exchanging with proton of Bronsted sites, thus releasing the proton which reacts

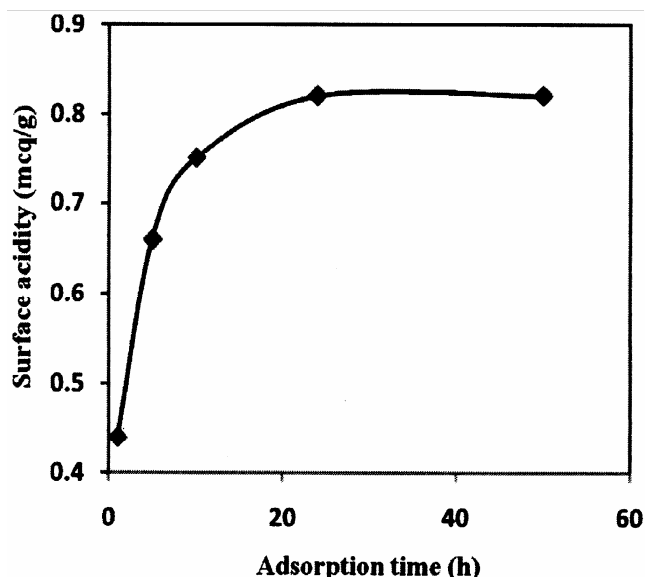


Fig. 5—Effect of K^+ ion adsorption time on the surface acidity of LTA zeolite. Sample, 0.1 g; Si:Al = 50:50; 10 mL 0.01 N KOH; 0.01 N HCl; Stirring time, 1 h; Crystallization time, 4 h; Crystallization temperature, 100°C.

with OH^- ion. On the other hand, K^+ ion is directly adsorbed by coordinating with lone pair electron of OH^- ion on Lewis acid sites. Both of the processes are somewhat slow and take time for achieving equilibrium. Furthermore, the migration of K^+ and OH^- ions through the opening of the pores to the interior sites takes time. This suggested that the saturation of all the sites with ions takes prolong time. Therefore, the surface acidity gradually increased with increasing adsorption time.

Effect of Si:Al ratio

The variation of surface acidity with the change in aluminium content in the silica-alumina zeolite has been investigated. Four samples with Si:Al ratio of 25:75 (0.33) 40:60 (0.67), 50:50 (1) and 70:30 (2.3) were prepared. The surface acidity of different composition are shown in Fig. 6. From the figure it is seen that the surface acidity varied with sample composition. The maximum surface acidity of LTA is found to be 0.9 meq/g when Si:Al = 50:50. Silica alone is either inactive or slightly active and alumina alone is better than silica but is an inferior cracking catalyst. A proper combination of silica and alumina may give a catalyst of highly active nature. The maximum acidity should result from the maximum number of Si-O-Al bonds and this occurs when the atomic ratio of Si:Al is 50:50. The total acid content is the maximum in high alumina catalyst where predominantly Lewis acid sites are present. But the Bronsted acidity is the maximum in the high silica

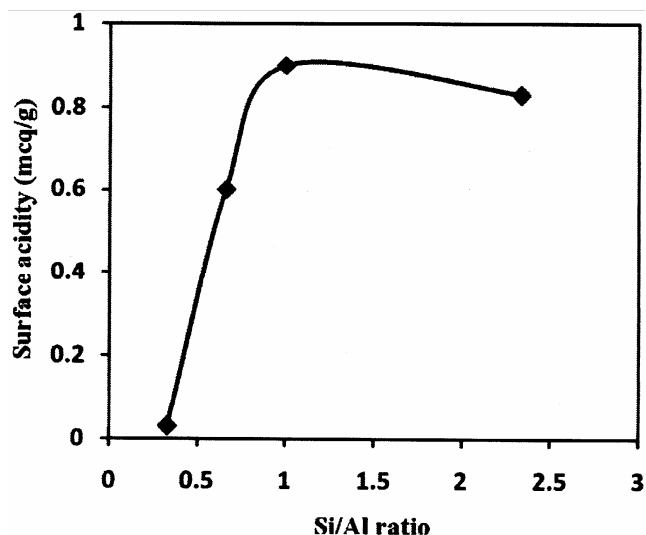


Fig. 6—Effect of Si / Al ratio on the surface acidity of LTA zeolite. Sample, 0.1 g; 10 mL 0.01 N KOH; 0.01 N HCl; Stirring time, 1 h; Crystallization time, 4 h; Crystallization temperature, 100°C; Adsorption time, 24 h.

Table 1—Effect of condition on the mean surface acidity of LTA zeolite. Sample, 0.1 g; Si:Al = 50:50; 10 mL 0.01 N KOH; 0.01 N HCl; Stirring time, 1 h; Crystallization time, 4 h; Crystallization temperature, 100°C.

Condition	Sample size (g)	Amount of K^+ adsorbed (meq)	Surface acidity (meq/g)
Static	0.1003	6.00×10^{-2}	0.598
Agitated	0.1007	7.95×10^{-2}	0.789

catalyst. However, by base exchange method total Lewis acid sites may be difficult to estimate, but the Bronsted site can be measured completely.

Effect of agitation

All of the samples of the LTA zeolite used for the determination of surface acidity under different conditions were prepared under agitated crystallization conditions. One of the samples was prepared under static condition and the surface acidity was determined by the same way. The results are summarized in Table 1. The surface acidity of the LTA zeolite prepared under static condition is much lower compared to that of agitated condition. In the static condition the amorphous aluminosilicate is separated from the homogeneous suspension. The liquid phase came to the top of the solid phase. So, the crystallization may be prohibited and thus, the surface acidity is lower than that of LTA zeolite of agitated condition.

Synthesized LTA zeolite versus commercial LTA zeolite

The surface acidity of synthesized Linde Type-A zeolite was compared with that of commercial LTA

Table 2—Comparison of surface acidity of synthesized LTA zeolite with commercial LTA zeolite. Sample, 0.1 g; Si:Al = 50:50; 10 mL 0.01 N KOH; 0.01 N HCl; Stirring time, 1 h; Crystallization time, 4 h; Crystallization temperature, 100°C; Adsorption time, 24 h.

Zeolite sample	Adsorbate	Amount of K ⁺ ion adsorption (meq)	Surface acidity (meq/g)
Commercial LTA Zeolite	KOH	0.080	0.837
Synthesized LTA Zeolite	KOH	0.087	0.867

zeolite. The acidity is measured by the same method for both the zeolites using KOH as adsorbate. For both of the samples the mixtures are stirred for 0.5 h and kept constant for 24 h. The bulk concentration of KOH is determined by titrating with 0.01 N HCl. The results are shown in Table 2. It is found that the surface acidity of synthesized zeolite is slightly higher than that of LTA zeolite. As it is known, the commercial LTA is a zeolite having greater number of Bronsted acid sites and thus the total acidity and activity for many reactions is very high, the synthesized LTA zeolite will also be a highly active acidic catalyst for many polymerization and petrochemical reactions.

Conclusion

Crystalline Linde Type A zeolite catalyst having Si:Al ratio 50:50 was prepared from aluminium powder and sodium metasilicate. The surface acidity of the synthesized LTA zeolite is varied by varying different parameters such as crystallization temperature, crystallization time, agitation during crystallization, K⁺ ion adsorption time etc. It has been observed that the surface acidity increased with increasing temperature up to 100°C and then decreased. It also increased with increasing

crystallization time and K⁺ ion adsorption time. Again, the surface acidity was much higher in the case of agitated crystallized sample than that of the crystals obtained under static conditions. Since the prepared zeolite possesses higher surface acidity, it can be used as catalyst for petrochemical processing, molecular sieve for many purification methods etc.

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