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Synthesis of Zeolite ZSM3 from Faujasite: Effects of Post-synthesis Ageing and *Insitu seeding*.

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ABSTRACT

The crystallization of ZSM3 via faujasite metamorphosis, synthesized from dealuminated metakaolin, was achieved without the addition of any structure directing agent. The XRD, XRF, and SEM/EDXS analyses carried out on the sample indicated successful synthesis of matrix, containing zeolites X, Y and sodium aluminosilicate, in various proportions, which was later transformed completely into ZSM3. The XRD peaks and SEM morphologies attributed to ZSM3 increased in intensity and crystallinity, as reaction and ageing time progressed. Post synthesis effects i.e. exposure to dampness and longer contact time in the presence of residue/unwashed NaOH used for the synthesis earlier, were totally responsible for the metamorphosis. Anatase and quartz were observed to persist in the raw, intermediate and as-synthesized product, pointing to their high level of resistances to treatments. The formation of competitive zeolite phases, was prevented by controlling factors responsible for its nucleation and formation.

Keywords: metamorphosis, insitu seeding, kaolin, ZSM3, faujasite, dealumination, aging

1. Introduction

Zeolites are advanced materials of crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions. Some recently known materials which are structurally identical to the classical zeolite, but consisting of structural oxide other than silica and alumina have extended this definition.

ZSM3, possessing 10 ring and 8 ring aluminosilicate framework with defined channel structures, has been widely used in many catalytic reactions as catalysts owing to its excellent catalytic property and shape selectitvity (Perez-Pariente et al,1988). ZSM3 was first synthesized by Plank *et al* (1977) in an aqueous system, using ethylenediamine or pyrrolindine as template. Wenyang *et al* (1982) studied the kinetics of ZSM3 crystallization and also reported on the synthesis of zeolite ZSM3 in the system ethylenediamine-Na_2O-Al_2O_3-SiO_2-triethylamine (Wenyang *et al*, 1989), with the possibility of recycling the organic compound to reduce cost and pollution. In 2004, Xuewu et al, synthesized zeolite ZSM35 by vapor phase transport method in the system of NH_4F -Al_2O_3-SiO_2- ethylenediamine-H_2O, with good result and reduced consumption of organic materials. There exist various other reports in patents on synthesis of ZSM3 (US Pat. 4107195 (Rollman, 1978), US Pat. 4,584,286 (Valyocsik, 1986), and PCT/US90/03827 (Rubin, 1989)), *inter-alia*.

The application of ZSM3 in variety of life makes its continuous synthesis imperative. Furthermore, recent environmental protection concerns discourage the use of organic template; accordingly the need arise to opt for alternative more economical and ecofriendly means of its synthesis.

Various researchers in this field reported formation of zeolite ZSM family series from prolonged aging method using soluble salts as source of silica and alumina. Wulff-Döring and Lechert (1991) reported on co-crystallization of zeolite Y and ZSM-3, while Rubin et al (1978) and Dwyer et al (1981) during the synthesis of ZSM34 and ZSM39, showed that crystallization time of 98 and 90 days are required, respectively. They also claimed that the period for crystallization reduces with increase in crystallization temperature. The work of Rosinski et al (1992), though on synthesis of zeolite ZSM45, confirmed the aforementioned claim, and further shed more light on the metastability of zeolite materials.

The rate at which the metastable faujasite zeolite changes to an equilibrium stable material is dependent upon intrinsic properties of the zeolite, level of impurities in the gangue liquor and the chemical environment in which it exists and aging period (Breck, 1974). For example, if zeolite A, after crystallization, is allowed to remain in its mother liquor, it will recrystallize to zeolite P. Changes in the composition of amorphous reaction mixture, sources of silica and alumina, inherent impurities, temperature and time of crystallization, have been identified as promoter of recrystallization of zeolite X and Y to zeolite P and subsequently, analcime (Dwyer and Chu, 1979).

Dwyer and Chu (1979) were the first to report on metamorphosis of faujasite zeolite into ZSM4, using pure analytical soluble salts as reagents. The work presented here treats transformation of impure kaolinite based faujasite into zeolite ZSM3 promoted by only post-synthesis aging and *insitu* seeding.

2. Experimental

2.1 Kaolin Pretreatment

The beneficiation of kaolin from Kankara (a village in Katsina State, Nigeria) was done as reported by Emofurieta et al (1992). The beneficiated kaolin was calcined to metakaolin, for enhanced reactivity (Caballero et al,2007 and Zheng et al,2005). The calcination was done at 900^0C for 3hrs in a furnace. The silica-alumina (SiO_2/Al_2O_3) molar ratio of 9 required for the desired zeolite was obtained by dealumination process. The dealumination was done using 98% H_2SO_4, for ten minutes, in a reflux condenser. The product obtained was washed with hot deionized water to near neutrality, dried at 40^0C for 24hrs and later at 125^0C in an electric oven, for another 24hrs. The compositional analysis was carried out using EDXS and X-Ray fluorescence machine (model PW1660 X-ray analyzer), while the structural pattern was observed on D500 X-ray diffractometry machine. The morphological analysis was done using Jeol, JSM 5800.

2.2 Gelation and Zeolite Formation

The dealuminated sample was mixed with calculated amount of NaOH to obtain a reaction mixture consisting of $SiO_2/Al_2O_3=9$, $Na_2O/ SiO_2=0.6$ and $H_2O/ Na_2O=45$. The resulting gel was left to age for 5 days at room temperature in an airtight polypropylene bottle. At the end of the aging period, the gel was heated in an autoclave (WS2-84-64 model-7101) set at 100^0C, for 24hrs. The resulting product was washed thoroughly with deionized water, to remove excess sodium hydroxide and dried at 90^0C for 3hrs. Thereafter, the thus obtained product was divided into two parts. A part was characterized immediately, while the other part was post-aged for 95 days under ambient conditions, prior to analyses.

3. Results and Discussions

3.1 Kaolin Beneficiation, Calcination and Dealumination

The compositional analysis indicated in Table 1 combined with the crystallographic analysis (Figure 1) revealed that the raw kaolin contains associated impurities, i.e. muscovite, quartz, clinochlore and gmelinite, resulting in SiO_2/Al_2O_3 ratio of 2.55, as against SiO_2/Al_2O_3 ratio of 2, for theoretical kaolin. The presence of fibrous layers in between the silica-alumina plates as shown in Figure 2(a), further justifies this claim.

The effect of beneficiation (even though marginal with respect to bulk compositional changes, shown in Table 1), was able to reduce muscovite, quartz, and gmelinite beyond the XRD detection limit, as depicted in Figure 3.

The phase transformation of kaolin into a more reactive one (i.e. semi-amorphous) was achieved via calcinations as reflected in Figures 2(b) and Figure 4. It was observed that the kaolinite structure further decomposed into less crystalline phases via dealumination and gellation (Figures 2c and d referred).

Oxides of potassium and iron were known to respectively, promote formation of zeolite P or D, in place of zeolite Y and retard the growth and nucleation of zeolite Y (Murat et al,1992). Accordingly, particular attention was paid to monitoring these oxides, as can be seen in Table 1. The two oxides were observed to reduce with increase in mode of pretreatment, i.e. both physical and chemical method of beneficiations. Dealumination process targeted at improving the SiO_2/Al_2O_3 molar ratio also assisted in reducing the amounts of impurities in the sample as shown in Table 1 and

Figure 2(c). Figure 2 (c) further shows a breakdown of the metakaolinite structure, as result of acid attack. Evidently, the silica-alumina plate-like-sheet observed earlier in the SEM picture apparently disappeared in Figure 2 (c).

The SiO_2/Al_2O_3 ratio was deliberately kept relatively low, i.e. 9, in order to avoid co-crystallization of zeolite P – a readily formed zeolite from high silica content than zeolite A or X (Breck, 1974). The Na_2O/Na_2O+K_2O ratio was determined from Table 1 and found to be very close to unity making the gel a potential ingredient for not only zeolite X but also zeolite Y synthesis (Ruren *et al*, 2007).

3.2 Faujasite Synthesis and Characterization

The XRD pattern for the fresh product analyzed (Figure 5) confirmed synthesis of mixed crystalline phases quantitatively determined as: zeolite X (39.37%), zeolite Y (13.01%), quartz (13.13%), anatase (8.22%) and unnamed zeolite (6.56%). This unnamed zeolite was confirmed through further analysis to be ZSM3. The SEM pictures (Figure 2e) in agreement with the XRD analysis gave insight to the formation of the above named materials. The tetragonal crystallite was attributed to presence of anatase, cubic to faujasite and the ZSM3 zeolite, while the hexagonal, for quartz.

This observation is in agreement with the work reported by Chandrasekhar and Pramada (1999) and Erdem and Sand (1979), on the formation of multiphase zeolite crystalline products from heterogeneous aluminosilicates as against the use of soluble active silicates and aluminates that often result in formation of pure single phase zeolite.

3.3 ZSM3 crystallization

Figure 6 shows the XRD patterns for the product obtained after 95 days of post synthesis aging of the second half product. The pattern shows disappearance of peaks responsible for faujasite zeolite and increase in the intensity of peaks attributed to ZSM3 zeolite. The anatase and quartz still persists and remained in the system, aside the remaining unconverted sodium alumino-silicate that could serve as ingredient for further transistion. The results obtained clearly substantiate the crystallization mechanism: $Amorphous \rightarrow Faujasite \rightarrow ZSM3$

The XRD analysis (Figure 5) shows the presence of unidentified zeolite in the matrix along with faujasite zeolites which was later observed to transform almost completely into ZSM3 as ageing time progresses. The two main mechanisms that have been proposed for zeolite crystallization have been from a “solid gel phase” or a “solution phase”. In this case, it was suggested that the mechanism could have been a combination of both, with the solution phase serving as the initiation stage leading to crystallization. The dried sample left to age for 95 days was not calcined, enabling some intercalated water molecules present in the sample, which apparently were enough to further the progress of the reaction. This observation is in agreement with reports of other researchers in this field who claimed that zeolitic materials are metastable and continuously metamorphosis from one state to another, provided there is a favourable condition and ingredient. For example Dwyen and Chu (1974) observed the transformation of faujasite to ZSM4 although in the presence of templating agent. The transition noticed in the current report was achieved without the use of any templating agent but due to prolonged aging period. It was speculated that the available un-depolymerized silica and unwashed/unconverted NaOH in the presence of dampness continue to react, while the already formed faujasite in the system, serve as seeding agent for the autocatalytic reaction, as reported by Hong-Jiang et al (2004). It should also be noted that ZSM3 zeolite is of the faujasite family (Breck, 1974) and a relatively more stable phase of the family.

4. Conclusion

Kankara kaolinite clay provided the needed ingredients, i.e. silica and alumina for the successful synthesis of zeolite X and Y matrix. The initially synthesized faujasite ***might have served*** as *insitu* seeding agent, catalyzing the transformation process of faujasite to ZSM3 observed in this work. The XRD, SEM and XRD analyses depicted the transformation of faujasite zeolite to ZSM3 (a relatively more stable state) without the need of organic template or structure directing agent. This approach makes this route an economically and environmentally viable means of ZSM3 synthesis.

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Table 1: Compositional Analysis of the Samples

Sample ID	**RKK**	**BKK**	**MK 93**	**DMK**	**Gel**	**Zeo-Matrix**	**ZSM3**

Al_2O_3	32.2	35.2	36.2	14.8	15.5	20.3	24.4
BaO	0.03	0.02	0.03	0.05	0.04	0.06	0.08
CaO	0.15	0.14	0.15	0.11	0.10	0.16	0.16
Fe_2O_3	3.16	2.28	2.28	1.69	0.64	0.89	0.74
K_2O	1.26	0.68	1.31	0.32	0.20	0.28	2.15
MgO	1.04	0.64	1.10	0.66	0.04	0.05	1.05
MnO	0.09	0.04	0.06	0.01	-0.01	0.00	0.03
Na_2O	0.12	0.07	0.09	0.10	10.5	10.9	5.89
SiO_2	48.3	46.5	54.6	77.6	60.3	53.2	50.2
TiO_2	0.84	0.34	1.00	1.42	4.53	6.51	7.44
SO_3	0.09	0.09	0.06	0.16	3.50	0.24	0.010
LOI	11.43	12.31	2.24	2.18	1.76	nd	nd
Total	98.7	98.3	99.2	99.1	97.1	92.6	92.2

Legend:

RKK-Raw Kankara Kaolin	BKK-Beneficiated Kankara Kaolin	MK93-Metakaolin@900^{0}C for 3hrs
DMK-Dealuminated metakaolin	Gel-from metakaolin	Matrix-zeolites X, Y and Unnamed

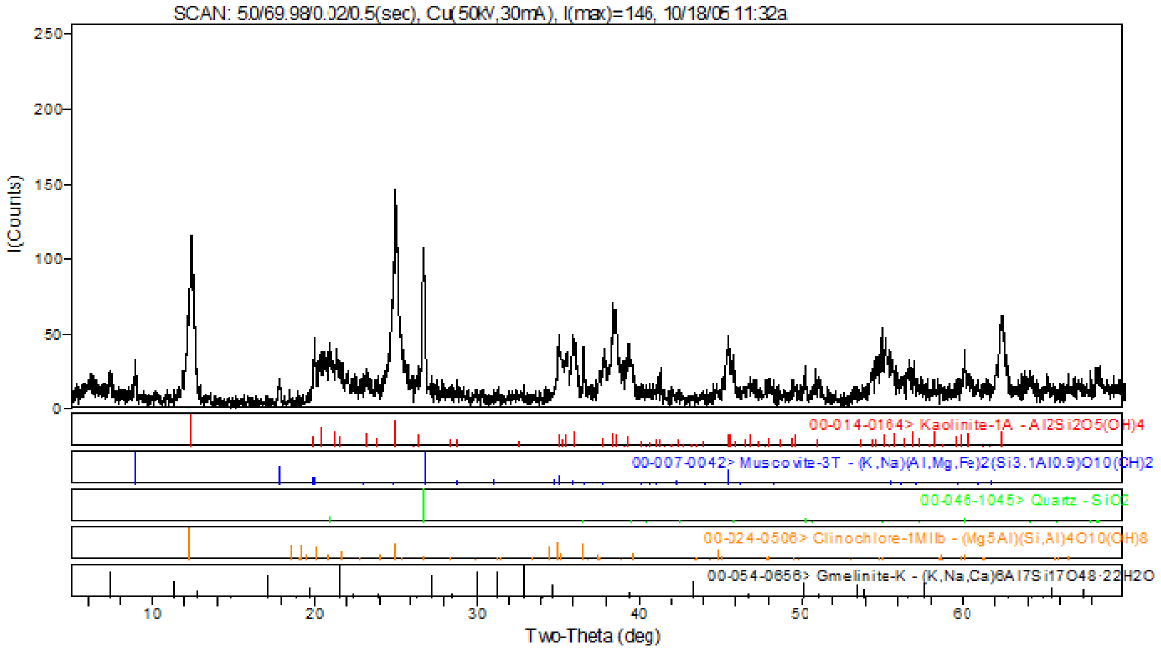

Figure 1: XRD Pattern for Raw Kaolin

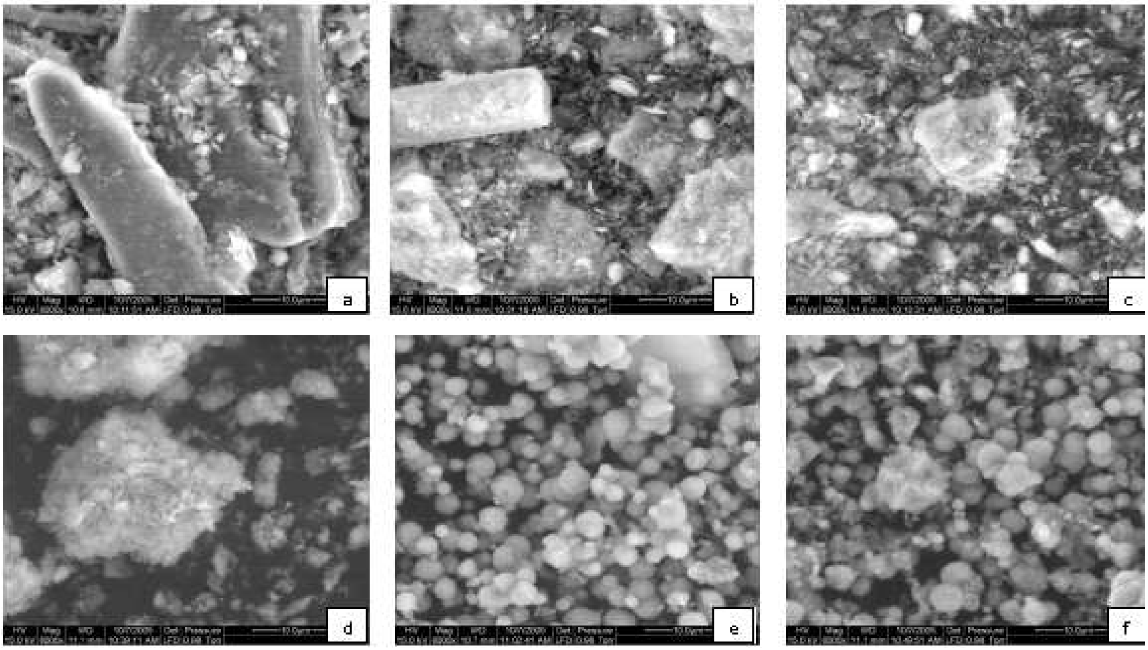

Figure 2: Scanning Electron Micrographs of (a) RKK, (b) MK93, (c) DMK93, (d) Gel, (e)Zeolite -Matrix and (f) ZSM3

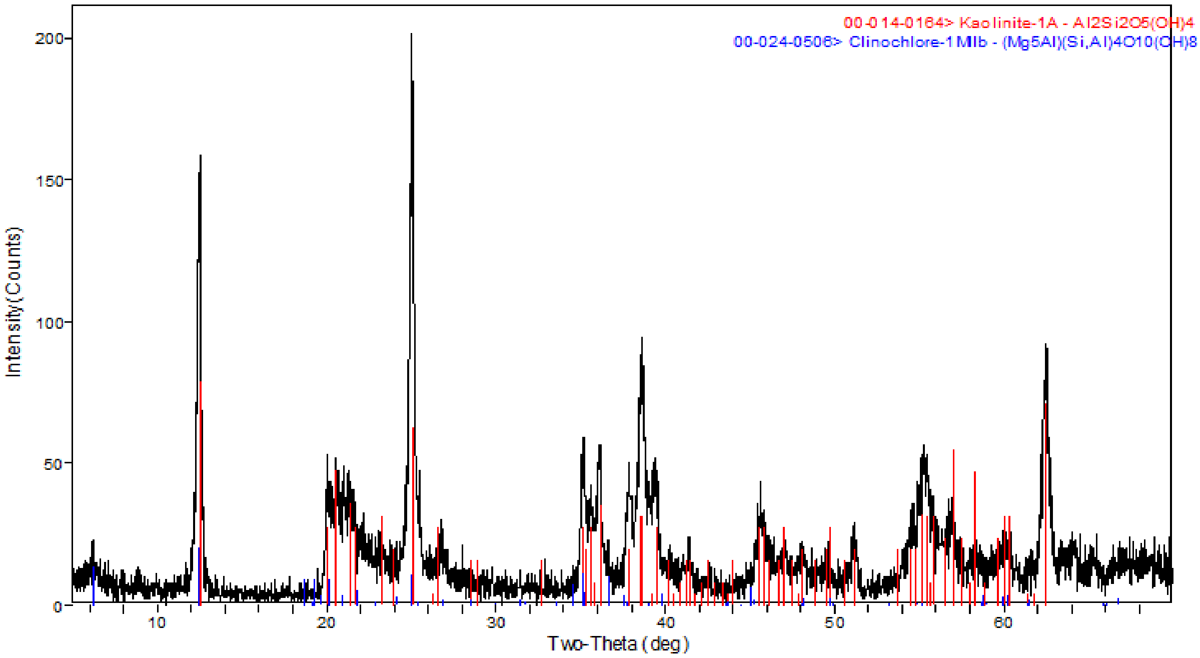

Figure 3: XRD Pattern for Beneficiated Kaolin

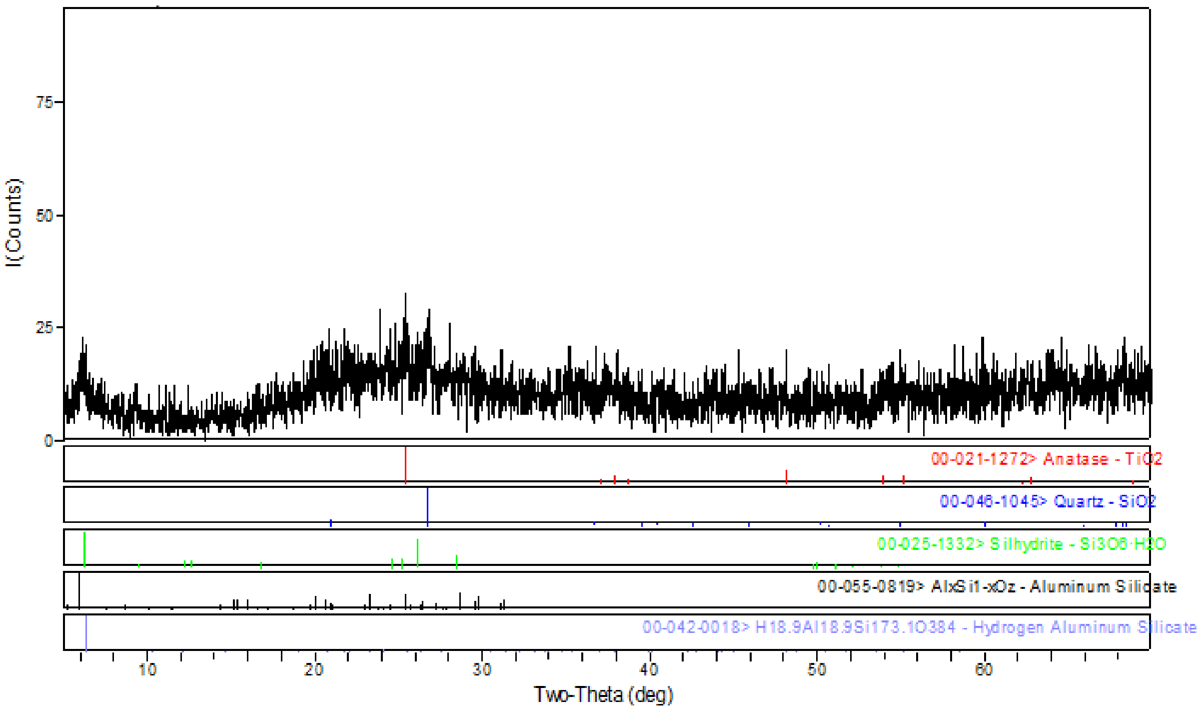

Figure 4: XRD Pattern for Kaolin calcined at 900^{0}C for 3hrs.

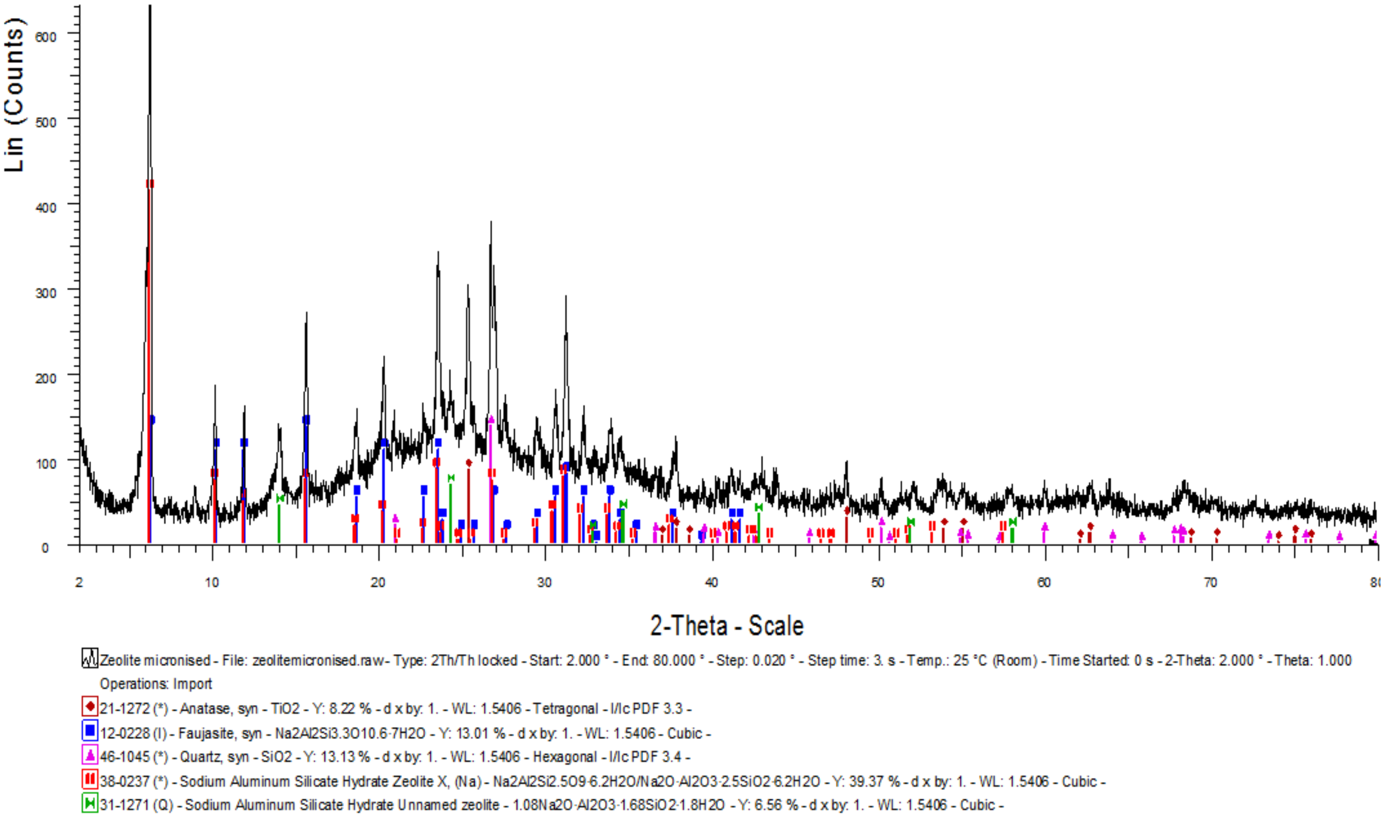

Figure 5: XRD Pattern for matrix/composite zeolitic material

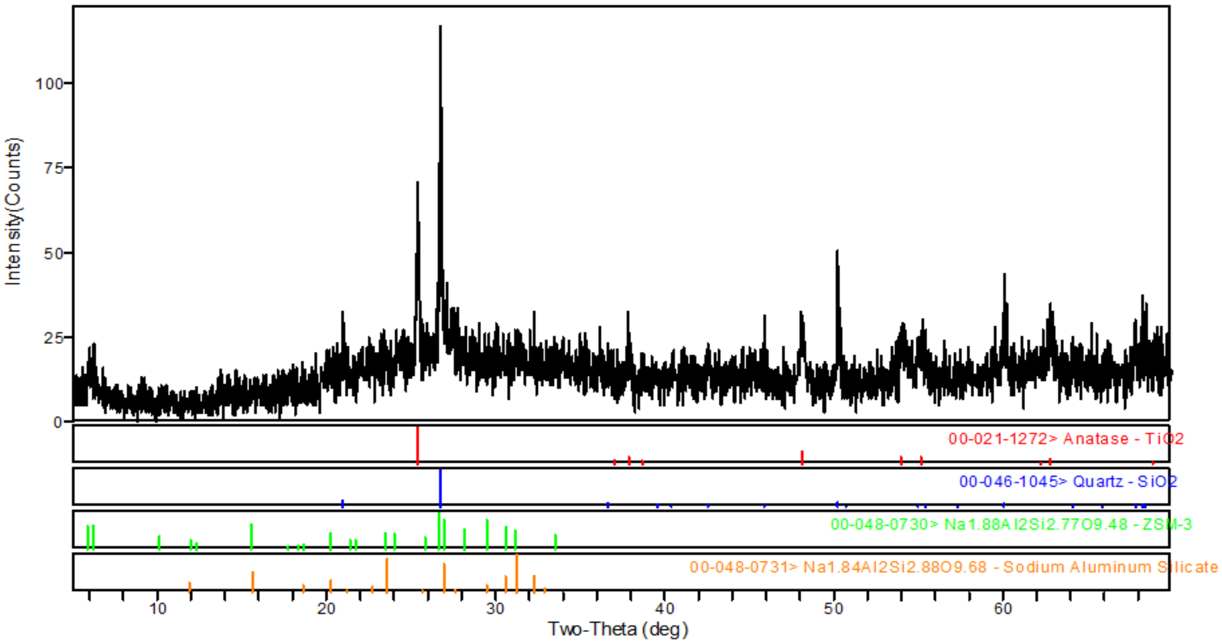

Figure 6: XRD Pattern for Zeolite ZSM3

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