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Primary Article

Thermo-Analytical And Sem Methods Of Studing High Silica Zeolites

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ABSTRACT

Thermal treatment is the main force for crystallization and phase transformation, the behavior of precursors on heating revels a lot of information about the possible phenomena of involving stability, sensitivity and some predictive ability of zeolites. Thermo-gravimetric (T.G.) in combination with differential thermal analysis (D.T.A.) changes in precursor samples including the structure collapse and phase transformation at high temperatures were checked by recording T.G./DTA plots of Highi silica H-US Y zeolites using SETERAM T.G.DTA-92 instrument in air atmosphere 30ml//min. at a heating rate of 5^0c //min. the range of temperature studied using this instrument is from room temperature (RT) to 1000^0c . The selective samples are post Synthesized and are obtained from low silica Na-Y zeolite converted in to high silica USY zeolites, are studied in the present paper. The post synthetic modification of the original samples affects the pore dimension, crystalinity, void volume, frame work structure, catalytic activity, selectivity, stability etc of the original sample. The Na-Y zeolite is made available from Union carbide corporation, USA (Linde,SK-40) for the post Synthetic modification having ratio of Si/Al=2.4.Scanning electron microscopy(SEM) technique is used to measure the particle size distribution and morphology of the crystals. The amorphous materials present can be determined from the micrographs. In the present study TG/DTA and the SEM technique is also used for the purpose of the above study.The importance of thermal stability and the interest in the high temperature properties of zeolites is largely related to their use in petrochemical catalytic cracking reaction. All the samples are characterized by using XRD, AAS, FPS, UV-VISIBLE, NMR, FTIR,TG/DTA, SEM, techniques etc.

Keywords:
1)Potassiumtitaniumoxalate$K_2TiO(C2O4)2H_2O$,(oxa),i($O(CH_2)_3CH_3$),(buto),Ti$[(OCH)(CH_3)_2]_4$,(iso),are used as Ti sources
(2)Synthesized Faujasite Na-Y zeolite.
(3) SETERAM T.G.DTA-92 instrument.

Introduction:

What are Zeolites?

Zeolites are crystalline hydrated alumino- silicates having rigid three dimensional infinitely extended framework structure. It encloses the cavities and channels of molecular dimensions.The framework structure contains corner sharing of $[SiO4]^{-4}$ and $[AlO4]^{-5}$ Tetrahedral linked through common oxygen atoms as the primary building units. The general empirical crystallographic unit cell formula of zeolite is expressed as

M x/n[(AlO2)x (SiO2)y] zH2O

where

M= charge compensating cat ions of valency , n .

x and y represents the no. of moles of SiO2 & AlO2 where $y \geq x$ and

z= no. of water molecules.

Most of the zeolites are very unstable and lose their catalytic activity

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easily under the severe conditions of catalytic reactions and hydrothermal conditions at high temperatures. By large dealumination of zeolite framework may leads to collapse its structure. To overcome this problem synthesized zeolites are dealuminated in a very carefully controlled manner under hydrothermal conditions. Which is found to be a best method for increasing catalytic activity as well as stability of the zeolite? The extra lattice aluminum species formed are removed by acid leaching. Abundant literature is available on Y type zeolite as it is most promising zeolite due to its 3D pore structure. It is best suited to produce large numbers of petrochemicals. Such zeolites are treated under steam at different temperatures and are called as ultra stable Y zeolite. The zeolite fujasite type-Y is low silica, large 3D pour zeolite, hence can be easily synthesized in the laboratory and in the industry

The unit cell of Y type zeolite is cubic with a large dimension of 25^0A and contains 192(Si, Al) O_4 tetrahedral, has remarkably stable and rigid framework structure with largest void space, which amounts to be nearly40% by volume of the dehydrated crystal.

Experimental: 10g of Na-Y is added in to 200 ml 2N NH_4NO_3 to ion exchange it for the Preparation of NH_4-Y zeolite from it. The Solution is taken in a round bottom flask. This mixture is then heated at 100^0C by stirring it for 12h by using reflux method. The sample is then filtered, washed several times with hot de-ionized water till free from any traces of nitrate ions and dried at 100^0C over night, the above procedure is repeated at list three times to obtain more than90% of NH_4-Y from Na-Y by above method ..As Sodium is added to the zeolite the total no. of acid sites is reduced. Effect of sodium poisoning is found to be dramatic over the entire range of Si/Al ratio examined. one sodium atom could effectively poison 5 non frame work acidic Al atoms which found to reduce the catalytic activity of the zeolite. The amount of Ti incorporated into the Frame work is found to be increased as the presence of Na (alkali metals) in the gel decreased. In view of this report Na-Y is converted into NH_4-Y zeolite and is used for Ti incorporation in it. Still It is used in the Synthesis of zeolite, because it can be easily ion exchanged with any metal.

Procedure of Preparation of Different samples of USY zeolites by using NH_4-Y with different methods:

Preparation of USY zeolites; Most of the zeolites are very unstable and lose their catalytic activity easily under the severe conditions of catalytic reactions and in hydrothermal conditions. Due to large dealumination of zeolite framework which leads to collapse of zeolite structure to overcome this problem synthesized zeolites are dealuminated in controlled manner and extra lattice aluminum species formed are removed by acid leaching The NH_4 -Y zeolite prepared is further dealuminated under carefully controlled steam in the cylindrical reactor by keeping the sample in the silica glass sample holder to increase hydrothermal severity at 550 ^{0}C for 4 h. There after the sample is kept for cooling very slowly till its temperature reaches to 100 ^{0}C then the steam passing over the sample is stopped it takes about 3h to reach to 100 ^{0}C from 550 ^{0}C temperature. The sample holder is taken out of the reactor at a temperature about 50-60 ^{0}C. Then it is transferred in to the conical flask containing 2N NH_4NO_3 solution in proportionate to about 20ml of it for 1gm of the sample. All the samples prepared are ion exchange with 2N NH_4 NO_3 as per above procedure and finally the samples are calcined at 500 ^{0}C to obtain H-USY zeolite.

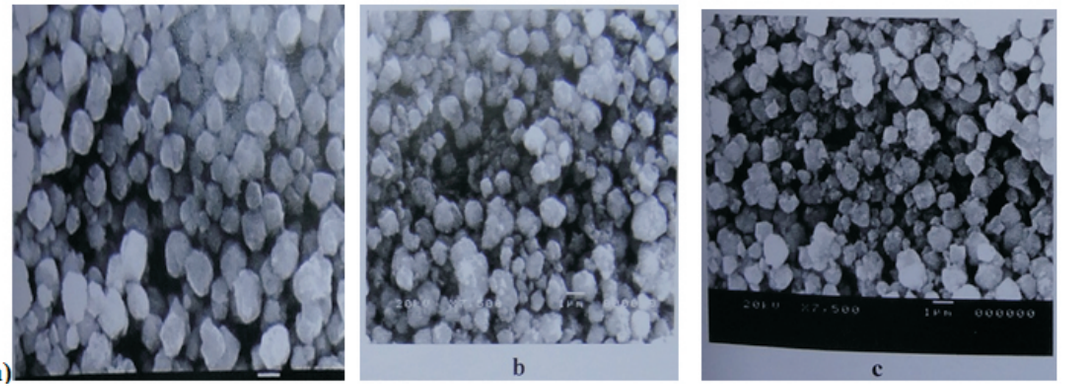
2) Preparation of high silica USY zeolites;

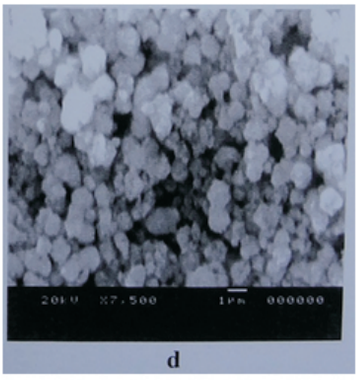
The zeolites are very unstable and lose their catalytic activity easily under the severe conditions of catalytic reactions and in hydrothermal conditions.Large dealumination of zeolite framework leads to collapse of zeolite structure.

Procedure of Preparation of the different Materials used for TG/DTA and SEM studies.

Starting material and its different modified forms	Preparation procedure	Identification of the product
Na-Y	Commercial Sample obtained from, Linde division,USA.Ion exchanged thrice by 2N NH_4NO_3 at 100^0C for 4h and clearly washed with hot de-ionized water and calcined at 500^0C for 4h	Na,NH_4-Y
Na,NH_4-Y	Steam treated at 550^0C for 4hfollowed by ion exchange thrice by 2N NH_4NO_3 at 100^0C for 4h and washed with hot de-ionized water and calcined at 500^0C for 4h	550-MSTP high silica zeolite
550-MSTP	Steam treated at 700^0C for 4h followed by ion exchange thrice by 2N NH_4NO_3 at 100^0C for 4h and washed with hot de-ionized water and calcined at 500^0C for 4h	550-700-MSTP intermediate high silica zeolite
550-700-MSTP	Steam treated at 850^0C for 4h followed by ion exchange thrice by 2 N NH_4NO_3 at 100^0C for 4h and **clearly** washed with hot de-ionized water and calcined at 500^0C for 4h	550-700-850MSTP (high silica USY zeolite.)

To overcome this problem synthesized zeolites are dealuminated in very controlled manner and extra lattice aluminum species formed are removed by acid leaching .The above prepared NH_4 Y zeolite is further dealuminated under carefully controlled steam in the cylindrical reactor to increase hydrothermal severity at 550 ^{o}C for 4 h, 700 ^{o}C for 4 h, 850 ^{o}C for 4 h, in succession by using the previous sample as the mother sample for the next sample. After hydrothermal treatment at each temperature interval the samples are ion exchanged with 2N NH_4-Y as per above procedure and finally samples are washed several times with hot de -ionized water and then filtered dried powdered and calcined at 500 ^{o}C to obtain H-USY zeolites. The procedure is narrated in the Table-1.The above condition of the sample is standardized before further study of the samples.





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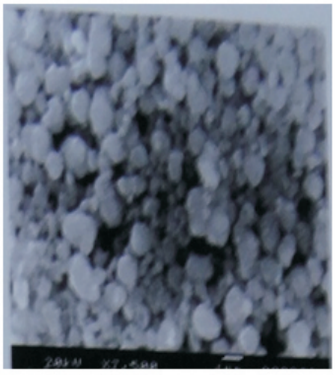

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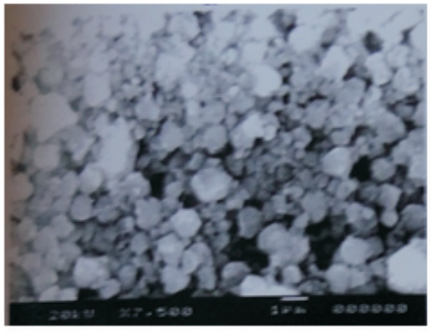


(g)

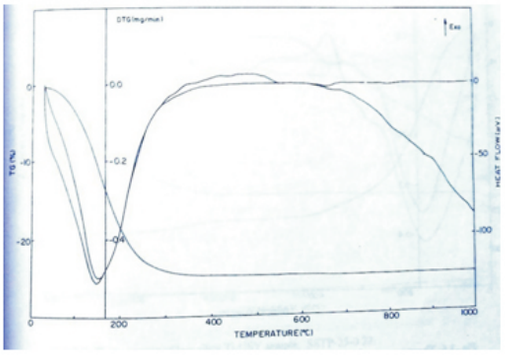
Scanning electron Micrographs of USYSamples prepred by Hydrothermal dealumination of NH_4-Yzeolite (a) origanal sampleNH4-Y(b)550-MSTP(c)550-700-MSTP(d) 550-700-850-MSTP.(e)Oxa-MSTP-200-0.33(f) Buto-MSTP-200-0.33(g) Iso-MSTP-200-0.33

Procedure of Preparation of the different Materials used for TG/DTA and SEM studies.

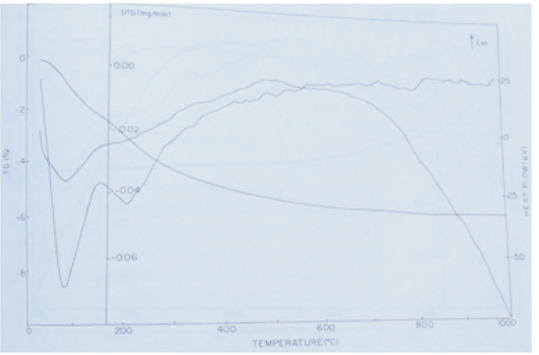
Starting material and its different modified forms	Preparation procedure	Identification of the product
550-700-850MSTP	Reacted with 0.33 mole fraction of K-Ti oxalate at 200^0C for 8h, acid treated with0.01NHNO_3 at100^0C for 4h and clearly washed with hot de-ionized water to remove all traces of $NO_3$from it and calcined at 500^0C for 4h	Oxa-MSTP-200-0.33 (high silica Ti-USY)
550-700-850MSTP	Reacted with 0.33 mole fraction of Ti-buto- Oxide at 200^0C for 8h, acid treated with0.01NHNO_3 at100^0C for 4h and clearly washed with hot de-ionized water to remove all traces of $NO_3$from it and calcined at 500^0C for 4h	Buto-MSTP-200-0.33 high silica Ti-USY)
550-700-850MSTP	Reacted with 0.33 mole fraction of Ti-(IV) iso-propoxide at 200^0C for 8h, acid treated with0.01NHNO_3 at100^0C for 4h and clearly washed with hot de-ionized water to remove all traces of $NO_3$from it and calcined at 500^0C for 4h	Iso-MSTP-200-0.33(high silica Ti-USY)

Chemical composition and unit cell properties of high silica Ti-HUSY from high silica HUSY-550-700-850 MSTP by multiple step method using $K_2TiO(C2O4)2H_2O$,(oxa) $Ti(O(CH2)3CH_3)$,(buto) Ti $[(OCH)(CH_3)_2]_4$,(iso).

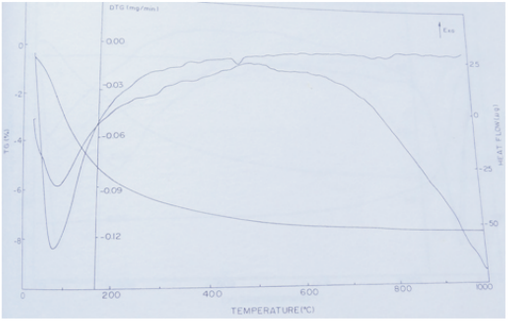
S.N.	Name of the sample	Unit cell Const.	Frame work Si/(Al+Ti)	F Al/ Unit cell	Unit cell composition	%de-alumination
1	Na-Y	24.71	2.4	56	Na20(AlO2)56 (SiO2)136	4
2	NH4-Y	24.68	2.56	54	Na20(AlO2)54 (SiO2)136	10
3	550-700-850-MSTP	24.21	26.29	4	Na1-3(AlO2)7(SiO2)135	87.5
4	Oxa-MSTP-200-0.33	24.25	16.95	11	-	-
5	Buto-MSTP-200-0.33	24.23	14.98	12	-	-
6	Iso-MSTP-200-0.33	24.23	40.06	5	-	-



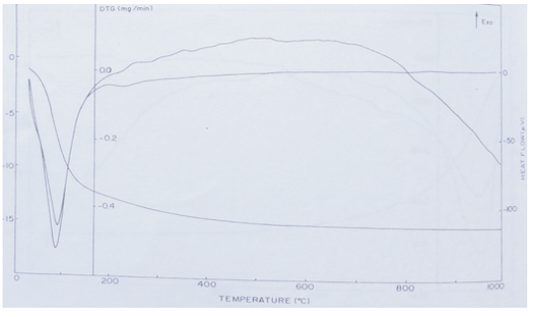
Therograms of high silica USY sample,



Thermograms of NH-Y zeolite 550-700-850-MSTP



Therograms of high silicate-USY sample 550-700-850-Oxa-MSTP.-200-.33



Therograms of high silicate-USY sample 550-700-850-Iso-MSTP.-200-.33

TG/DTA data of high silica TiUSY From high silica USY-550-700-850 sample by multiple step method using $K_2TiO(C2O4)2H_2O$,(oxa) $Ti(O(CH_2)_3CH_3)$,(buto) Ti $[(OCH)(CH_3)_2]_4$,(iso) as Ti Sources.

S.NO.	Name of the sample	Peak temp.in^{O}C	Weight loss%	Peak temp.in^{O}C
1	NH_4-Y	44(sh),148	24.67	Broad
2	**550-700-850-MSTP**	**42(sh),84,333,484**	**7.23**	-
3	**Oxa-MSTP-200-0.33**	**32(sh),91,251**	**14.9**	**701**
4	**Iso-MSTP-200-0.33-10**	**40(sh),80, 225,485**	**5.6**	-

TG/DTA data of high silica TiUSY From high silica USY-550-700-850 sample by multiple step method using $K_2TiO(C2O4)2H_2O$,(oxa) Ti $[(OCH)(CH_3)_2]_4$,(iso) as Ti Sources.

Result and discussion:

The SEM photographs of the steamed dealuminated samples prepared by hydro thermal Methods are taken; these samples are found to retain their crystalinity up to 850 C. The crystal size of NH_4Y is around 0.5 to 1.5 micro meters which remains unchanged in all the dealumintated USY samples. Where as the SEM photographs shows that the morphology of samples of high silica titanium- USY changes noticeably depending upon the method of their preparation. The crystallites agglomerate in the Ti- USY samples and in those samples where concentration of titanium is high some smaller particles may be of TiO2 agglomerates are noticeable. Over al;.all the samples look highly crystalline.

Thermo gravimetric Analysis:

TG/DTA

Curves of high silica are presented in the figures. In the table 2, the loss in weight and peak in temperatures for different stages are given.

DTA curve shows a very low temperature shoulder around 45 C in all the samples and, most of the weight loss due to occluded water occurs below 35^{0}C in all the samples. The temperature of the endothermic peak appears around 15^{0}C for NH4-Y sample but for all Ti-USY it occurs at much lower temperature even though micro pore volume which is available for adsorption of water is much more. The loss in weights is very small for different USY samples because of their very high hydrophobicity. Presence of titanium in the framework or outside does not influence the adsorption of water positively because Ti-USY is relatively hydrophobic. Some important differences occurs in nature of thermo grams of these samples, 3 stages of weight loss can be considered in all the samples, only the first stage is very much clear and prominent, the second stage which is very minor and occurs around 300C and the peak temperature cannot be definitely pointed out. The third stage also cannot be pointed out which is continuous to the highest temperature of 1000^{0}C. The weight loss in this state is due the dehdro-xylation of structural hydroxyl groups. Such structural hydroxyl groups are less on NH_4-Y but significant in all USY and Ti-USY samples because these zeolites have so many defect sites and Silanol groups.

A notable feature in these curves is the exothermic peak due to structural collapse occurs at higher temperature as the Al content in the sample decreases and the Ti content in it increases.

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