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OPTIMIZATION OF STABILIZATION PROCESS OF NH_4-NaY BY DTA-TGA AND OTHER CHARACTERIZATION METHODS

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ABSTRACT

Thermal stabilities and changes in the framework resulting from hydrothermal treatments at different temperatures in four series of Y zeolites each of which with the same Na_2O content were studied by DTA,XRD and infrared spectroscopy in the OH and framework skeletal vibration regions. Low Na_2O content zeolites were obtained by combination of thermal and exchange treatment, but only after final deep bed calcination at high temperatures stable structures were attained.

INTRODUCTION

Dealuminated Y zeolites have raised great interest due to their chemical and thermal stabilities in view of their use in cracking catalysts. The aluminium content in the zeolite structure is also important in defining catalyst activity and selectivity.

The aluminium-deficient zeolites have been prepared by different methodologies like hydrothermal treatment,chemical treatment and combination of both (1-5). According to the preparation methods some characteristics of the resulting zeolite are common but others are strongly affected by the method used. Several techniques such as MAS-NMR spectroscopy,X-ray diffraction,SIMS, sorption measurements,infrared spectroscopy in the hydroxyl and skeletal regions and DTA-TGA help to define changes in the framework and surface resulting from dealumination process. For example,a lot of the properties of the final product can be interpreted by their final silica-to-alumina molar ratio (SAR). Some works (6) tend to attribute the final thermal stability differences to the type and distribution of the non-framework species generated, which are dependent on the process of stabilization employed. Yet,a wide comparison between samples was often difficult due to different sets of samples containing different final levels

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of Na_2O,which could also be a factor that controls the stability of the product.

In this work,thermal stabilities and changes in the framework as a result of hydrothermal treatment at different temperatures in different series of Y zeolite each with the same Na_2O content were studied by some of the above mentioned techniques.

EXPERIMENTAL

Four series of samples were prepared:

Series 1-2-NH_4NaY zeolite with 4.0% Na_2O and 3.0% Na_2O respectively,and SAR 5.0, were submitted to deep bed calcination at different times and temperatures.

Series 3 - NH_4NaY zeolite with 4.0% Na_2O and SAR 6.0, was also submitted to deep bed calcination at different times and temperatures.

Series 4 - NH_4NaY zeolite with Na_2O content below 1.0% was prepared by exchange of different NH_4NaY starting material.

The thermal stabilities of these samples were studied using a Thermoflex Rigaku simultaneous TG-DTA analyser and the changes in the framework as a result of different treatments were studied by infrared technique using a Perkin Elmer 283-b equipment with techniques of self supporting wafers and KBr pellets.

The sample crystallinities were determined by XRD using a JDX-8P Jeol equipment,and their Na_2O content were determined by chemical analysis.

RESULTS AND DISCUSSION

Table I shows the thermal stabilities and silica-to-alumina molar ratio (SAR) of samples of series 1 to 3 and Table II shows the characteristics of samples of series 4 with Na_2O content below 1.0%.

Figures 1a and 1b show plots of collapse temperatures for the resulting products versus corresponding silica-to-alumina ratio and versus their number of aluminium per unit cell repectively. Figure 2 shows the infrared spectra in the OH region for some zeolites of series 4.

Data from Table I show that for samples with Na_2O content higher than 3.0% even treatment at 700^oC/4 h did not result in a final SAR >0.9. This is in contrast with the data from Table II,where a similar treatment leads to higher SAR. Probably the presence of sodium ions in samples from series 1-3 inhibits further aluminium extraction. The relationship between SAR and thermal stability,as measured by collapse temperatures of the structures was also observed,so that the more siliceous zeolite corresponds to the more stable

TABLE I:
Collapse Temperature and Silica-to-alumina Ratio of Samples: Series 1-3

SAMPLE	DEEP BED CALCINATION TEMP °C	TIME h	SAR	COLLAPSE TEMPERATURE (MAX, °C)
SERIES 1				
1	450	1	5.26	993
2	450	3	5.78	999
3	450	4	6.22	1004
4	600	0.5	6.58	999
5	600	1	6.87	1009
6	600	4	7.21	1014
7	700	1	7.70	1013
8	700	4	7.83	1020
SERIES 2				
1	550	2	5.50	940
2	620	3	5.83	965
3	700	4	8.01	1021
SERIES 3				
1	550	2	6.36	992
2	550	4	6.88	1021
3	620	3	8.12	1027
4	700	4	8.74	1045

TABLE II:
Characteristics of Samples of Series - 4 (x NH_4 NaY T_1XT_2)

SAMPLE	x	T_1	FINAL SAR	COLLAPSE TEMP (MAX, °C)	DRX CRYSTALLINITY	Na_2O
SERIES 4						
1	5.0	SB calcination 550°C/2h	21.53	1040	63	0.77
2	5.0	DB calcination 550°C/4h	25.63	1040	90	0.41
3	5.0	DB calcination 500°C/1h	11.16	1043	75	1.00
4	5.0	DB calcination 500°C/3h	16.78	1050	84	0.64
5	5.0	DB calcination 500°C/4h	20.04	1058	81	0.45
6	6.0	SB calcination 550°C/4h	21.98	1070	100	0.38

SB and DB - shallow bed and deep bed conditions, respectively
x - silica-to-alumina ratio of starting NH_4NaY zeolite.
T_1 - treatment before ammonium exchange step.
X - ammonium exchange step with ammonium salt
T_2 - deep bed calcination at 700°C/4h
X and T_2 - conditions were applied for all samples of series 4.

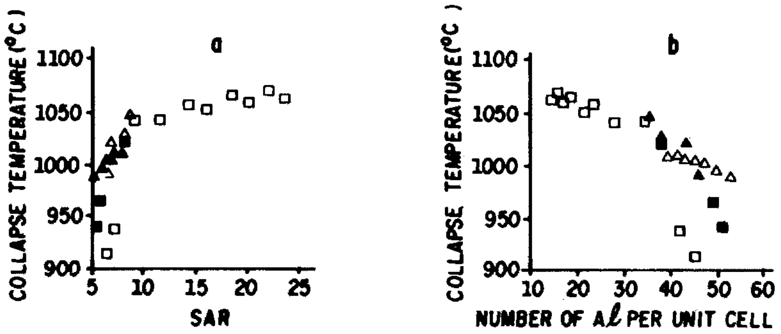

FIGURE 1- THERMAL STABILITIES OF SERIES I TO 4 Y ZEOLITES AS A FUNCTION OF: (a) SAR; (b) NUMBER OF Aℓ PER UNIT CELL.
□-Na_2O<1.0%, ■-Na_2O=3.0%; ▲-Na_2O=4.0%(SERIES 1)
△-Na_2O = 4.0%(SERIES 3)

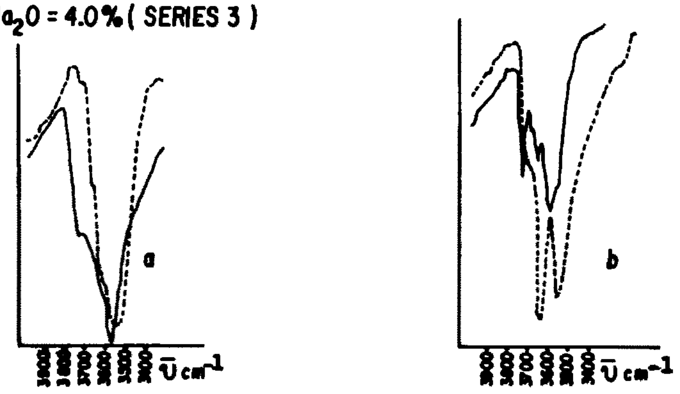

FIGURE 2- INFRA RED SPECTRA IN OH REGION OF: (a) SAMPLE 6, (b) SAMPLE 7, SERIES 4, PRETREATED AT 200 °C / 10^{-5} TORR, (---) AFTER T_1 STEP; (—) AFTER T_2 STEP

structure.

From Table II, it can be seen that the heating procedure of T_1 in shallow or deep bed conditions to redistribute the sodium ions into a more accessible location, seems to be important for the crystallinity retention. However, it does not affect thermal stability, according to sample 1 and 2 data. Also, from samples 3 to 5 we can see that the effectiveness of sodium removal increases with the time of deep bed heating at 500°C. If the starting material was a more stable precursor like a 6.0 NH_4NaY, the heating treatment in T_1 can be done in shallow bed conditions without prejudice to the final crystallinity.

In Figure 1a it is clearly shown that in samples with SAR from 5.0 to 9.0 a slight increase in the silica-to-alumina ratio resulted in a great improvement of stability although for samples of SAR in the range from 9.0 to 25.0 a very slight enhancement in stability was accomplished. Instead of plotting the crystal collapse temperature against the SAR as in Figure 1a,it is interesting to plot this temperature against the number of aluminium per unit cell. When such a plot was made,as in Figure 1b,a roughly linear correlation was found. In both Figure 1a and 1b,four samples behaved in an anomalous way. Such samples have a Na_2O content below 3.0% and probably belong to a kind of material described by Mc Daniel and Maher (7) as "unstable" zeolites. According to the authors, zeolites with Na_2O level below 3.0% are fragile structures which can be converted to the ultrastable structure with a further increase in stability, otherwise they will show a sharp decrease in stability,if not properly stabilized.

In Figure 2 the infrared spectra in the OH region of samples 6 and 7 from series 4 are shown after T_1 and T_2 steps. Generally the HY zeolite obtained by deamination of NH_4Y has three absorption bands in the OH stretching region (8):

3750 cm^{-1} assigned as due to terminal silanol groups or silical gel impurities

3650 cm^{-1} assigned as due to type Y structural hydroxyl generated by OH groups containing "bridge-oxygen" (O_1 type atoms forming the hexagonal prism between cubo-octahedrons) and are considered responsible for the Bronsted type acidity in zeolites,interacting with pyridine and NH_3

3550 cm^{-1} also assigned as due to type Y structural hydroxyl generated by OH groups but involving "ring-oxygens" probably O_3 - type atoms. This band interacts only with NH_3.

The OH region of ultrastable Y zeolite infrared spectra has been extensively investigated (9-11). It was reported that hydrothermal treatment of NH_4 Y zeolites generates four absorption bands in the OH stretching region:

3750 cm^{-1} assigned as due to terminal silanol groups or amorphous silica

3710 cm^{-1} assigned as due to OH nests generated in the dealumination process

3693 cm^{-1} assigned as due to highly condensed non framework aluminium species, present in the supercages,containing edge-shared octahedral $Al_m(O,OH)_n$ chains and probably having bohemite-type topology.

3606 cm^{-1} assigned as due to slightly condensed,mobile,non framework aluminium species such as $Al(OH_2,OH)_4$ present in the sodalite cages.

From Figure 2,differences in the framework healing are suggested by the OH region infrared spectra. With sample 6,Figure 2a shows that although a significant overlap of OH bands had occurred,the presence of the original OH bands can be distinguished from HY zeolite at 3650 cm^{-1} and 3550 cm^{-1} ,with the high frequency band shortened in its original intensity,aside of the new bands at 3690 cm^{-1} and 3600 cm^{-1} generated with the hydrothermal treatment. After the exchange plus hydrothermal treatment at 700°C/4h, an increase in 3750 cm^{-1} band intensity was observed. With the 6.0 NH_4NaY precursor, Figure 2b shows that well defined bands at 3650 cm^{-1} and 3550 cm^{-1} were present, but after the final treatment, the intensity of the 3750 cm^{-1} band strongly increased, the 3650 cm^{-1} band became greatly reduced and a strong absorbance at 3600 cm^{-1} appeared aside of additional band of medium intensity at 3690 cm^{-1} indicating generation of nonframework aluminium species. The spectra of samples 6 and 7 were quite distinct.

CONCLUSIONS

Rather stable zeolites were obtained by deep bed calcination with low Na_2O contents. It was confirmed that collapse temperature increased almost linearly as the framework aluminium content decreased. At least two features arose from different Na_2O content. When the content was equal or higher than 3.0 wt% it was difficult to obtain low framework aluminium and hence did not lead to stable structures. Yet for very low Na_2O contents mild final stabilization (low final steaming temperature) led to even less stable structures.
Finally, different starting materials when subjected to similar stabilization process can lead to similar final stability but distinct surface properties as indicated by infrared spectroscopy.

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