A Study of Thermal Effects on Molecular Sieve, Type 13X

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Summary: Thermal effects on molecular sieve, type 13X have been studied by employing thermogravimetry (TG) and X-ray diffraction (XRD) techniques. The weight loss free and entrapped water equals 17.5% was observed, which corresponds to 132 water molecules. The dehydration of molecular sieve is obviated by changes observed in the relative intensities of the diffraction peaks of samples heated at various temperatures.

Introduction

Molecular sieves are crystalline zeolitic alumino-silicates, used as adsorbent because of their selective adsorptive properties [1]. Their adsorptive properties are due to their crystal structure, incorporating inter-connecting channels and cavities of definite and uniform size. These internal cavities contain water molecules that may be removed reversibly. Molecules having appropriate dimensions with respect to these channels can enter and be adsorbed in the internal cavities [2]. The molecular sieve (13X) has already been used for the adsorption of uranium [3-4] and thorium [5-6] ions from aqueous solutions. The use of molecular sieve as catalyst is also well documented [7-8].

It is known [9] that thermal dehydration produces changes in the frame work of molecular sieves. The dehydration process is a complex phenomenon in which step wise transformation take place at different temperatures [9]. The aim of the present work is to study dehydration and the structural modifications that occur in molecular sieve (type 13X) as a result of thermal treatment.

Results and Discussion

The dehydration of molecular sieve mapped by thermogravimetry is reproduced as TG curve in Fig. 1. The TG curve shows a single step weight loss in the temperature range studied. Weight loss starts at 50°C and continues up to 400°C. The weight loss of 17.5% from 50-400°C results from the loss of moisture that may be present in free or bound form.

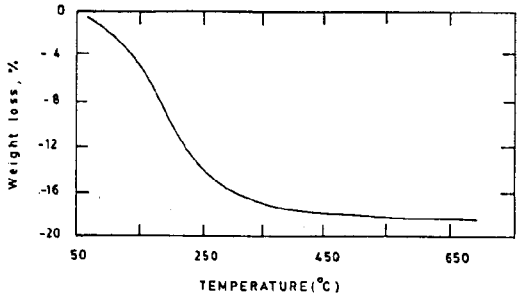

Fig. 1: TG curve of molecular sieve, 13X type.

Moisture present on the surface of material is removed initially up to 110°C, it is considered as free moisture. Whereas, the moisture entrapped in inter-molecules is termed as entrapped moisture. The XRD results supplement this observation as the structural changes are evident only above 600°C. No further loss suggests that no moisture is present in the sample at temperature beyond 400°C. The activation energy for dehydration process calculated using Horowitz Metzger method [10] is 46.92 kJ/mol.

The x-ray diffraction data of the untreated molecular sieve and samples heated at 100, 350, 600 and 900°C in air are given in Table 1. It is evident from XRD data that these samples are crystalline in nature. Characteristics XRD peaks in the untreated sample are at 2.88 Å (1.0), 3.7 Å (0.8) and 3.30 Å (0.78). Major peak at 2.88 Å also appears in sample heated at 100 and 350 °C. In addition to this, peaks at

Table-1:XRD Data of Molecular Sieve, Type 13X

Untreated		Heated at 100 °C		350 °C		600 °C		900 °C	
d(Å)	I/I_o	d(Å)	I/I_o	d(Å)	I/I_o	d(Å)	I/I_o	d(Å)	I/I_o
4.82	16	4.80	20	4.81	22	4.81	22	4.98	18
4.43	30	4.41	38	4.41	38	4.43	38	4.31	46
4.02	30	3.82	98	3.82	95	3.82	100	4.16	61
3.70	80	3.33	91	3.35	90	3.34	85	3.81	85
3.30	78	3.04	17	3.00	20	3.05	18	3.24	78
3.15	22	2.93	47	2.95	40	2.94	30	2.99	100
2.94	56	2.88	100	2.88	100	2.88	87	2.86	51
2.88	100	2.79	38	2.79	40	2.79	35	2.54	31
2.80	34	2.66	44	2.65	47	2.67	42	2.48	19
2.65	42	2.61	23	2.62	21	2.61	21	2.07	48
2.61	20	2.20	26	2.24	30	2.40	25	1.98	14
2.42	24	2.18	24	2.18	24	2.21	23	1.92	25
2.23	23	2.11	22	2.11	22	2.19	22	1.61	33
2.17	23	1.95	15	1.95	16	2.12	24	1.56	75
2.11	17	1.92	15	1.92	15	1.95	11	1.46	19
1.94	11	1.78	17	1.78	17	1.92	14	1.42	33
1.92	15	1.76	20	1.76	18	1.82	12	1.38	54
1.79	15	1.71	33	1.71	30	1.76	18	1.31	24
1.76	22	1.60	31	1.60	30	1.71	30		
1.72	28	1.47	20	1.47	20	1.60	28		
1.60	31	1.44	16	1.44	16	1.56	61		
1.47	18					1.47	18		

3.82 Å and 3.3 Å have high relative intensities. In the XRD data the decrease in relative intensities of peak 2.94 Å can be observed with rise in temperature (upto 600°C). This decrease in relative intensities of peak 2.94 Å can be attributed to the loss of water in the sample upon heating. The diffraction patterns of these samples pointed out the hydrated form of the molecular sieve having represented formula $Na_2[(Al_2O_3)_{86}(SiO_2)_{106}.132\ H_2O]$.

A different diffraction patterns were observed in the sample heated at 600°C and 900°C as compared to the samples heated at temperatures below 400°C. Major diffraction peaks appear at 3.83 Å (1.0), 2.88 Å (0.87) and 3.34 Å (0.85) in the sample heated at 600°C. The sample heated at 900°C has major diffraction peaks at 2.99 Å (1.0), 3.81 Å (0.85) and 3.24 Å (0.78). In addition to these peaks, a new peak (absent in samples heated at low temperature up to 350°C) appears at 1.56 Å in both the samples. The intensity of this peak appears to be increased as the temperature is raised from 600 to 900°C which may be attributed to the changes in crystal structure.

It can be concluded from the above discussion that at lower temperature i.e., 400°C loss of water takes place. However, at higher temperatures crystalline changes of the molecular sieve take place as revealed by the XRD data.

Experimental

Molecular sieve, 13X (Aldrich No. 20863-9) was ground to a fine powder in an agate ball mill. This powder was used for further studies. The powder samples were heated at 100, 350, 600 and 900°C respectively for 60 minutes before recording XRD patterns.

NETZSCH Simultaneous Thermal Analyzer (STA) model 409 was used for dehydration studies. The dehydration was carried out from ambient temperature to 750°C at a heating rate of 10°C/min. The experiment was conducted in dynamic nitrogen atmosphere with a gas flow rate of 200 ml/min.

X-ray diffraction pattern were recorded on a Philips PW 1060/70 diffractometer. The detector was an argon filled proportional counter linked to a PW 1390 rate meter and channel analyzer. The radiation Cu K_α was generated at 1.5418 Å from a PW 1730 generator operated at 40 kV and 30 mA current.

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