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STUDY OF Na–A MOLECULAR SIEVE DEGENERATION BY THERMAL ANALYSIS

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The degenerations on heat treatment and the thermal stabilities of Na–A molecular sieve zeolites of different crystallinities were studied by thermal analysis. The degenerations of the sieves were computed from the decreases of the zeolitic water content. The thermal stabilities were determined from the commencement of the exothermic peaks. Heating at 600° causes considerable degeneration of these sieves. The degeneration and thermal stability depend on the crystallinity of the sieve. Poorly-crystalline sieves are degenerated to a greater extent than well-crystaline ones. The thermal stabilities on poorly-crystalline sieves also decrease during heating at 600°.

Molecular sieve zeolites are regenerated for subsequent application by heating to a suitable temperature. This activation depends on the thermal stability of the sieve. Different workers have studied the activation and thermal stability by heating the zeolite to various temperatures and determining the water adsorption ability.

It was reported that, if the activation temperature is raised beyond a certain limit, the activity of Na–A zeolite gradually decreases due to the development of macroporosity [1, 2]. Beyond a certain temperature, the zeolite completely loses its adsorption capacity as a result of total structural breakdown. For Na–A type zeolite, this temperature lies around 700° [3].

In zeolite, water is held in both primary and secondary surfaces. The primary surface comprises the intra-crystalline pores and cavities, whereas the secondary surface includes the external surface of the grain and macropores. The selectivity of a molecular sieve is due only to the primary surface. Although the primary adsorption surface of a molecular sieve is directly related to the activity and is affected by degeneration, the earlier workers used the total water adsorption data relating to primary and secondary surfaces to study the activity [1, 2].

Thermal analysis has been employed by various workers for characterization and evaluation of molecular sieve zeolites [4, 5]. The degeneration of a molecular sieve on heating is a very slow process and it is therefore not detected in the differential thermal analysis curve. It has been reported that thermal analysis curves (DTA, DTG) can distinguish the water adsorbed in primary and secondary surfaces [4]. It is therefore expected that a change of primary surface due to heat treatment can be effectively studied from the thermal analysis of sieves. The exo-

thermic peak of the thermal analysis curve also indicates the structural breakdown of a sieve [5]. Accordingly, the authors have investigated by thermal analysis the degenerations and structural stabilities of Na—4 molecular sieves of different crystallinities, heated below the temperature of structural breakdown.

Experimental

Three samples of Na-A type molecular sieve zeolite were taken for the present study. Sample *A* was Linde molecular sieve. The samples *B* and *C* were prepared in this laboratory from a locally-available clay [6]. The natures and crystallinities of these samples were identified and compared by X-ray powder diffraction, using iron-filtered cobalt K_αX-radiation.

The molecular sieve samples were powdered to 100—150 μm. Portions of the powdered samples were activated by heating at 600° for 4 hr in a laboratory muffle furnace. These activated samples, along with the unactivated samples, were placed in a closed vessel maintained at 100% relative humidity till saturation.

The equilibrated samples were thermally analyzed in a derivatograph [7]. α-Al_2O_3 calcined at 1500° was taken as reference material. Samples and reference material were kept in platinum crucibles. Analysis was performed at a heating rate of 7.5°/min under normal atmospheric conditions. Identical conditions were maintained for all analyses.

Results and discussion

Derivative weight loss (DTG), weight loss (TG), differential thermal analysis (DTA) and temperature (T) curves were recorded in thermal analysis. The DTA curves of samples *A*, *B* and *C*, both activated and unactivated, have been redrawn from the original curves as a function of temperature. The general natures of the DTA curves, as shown in the Figure, are the same. The curves exhibit endothermic changes starting from room temperature to around 600° and exothermic changes beyond 750°. The endothermic changes are associated with weight loss due to removal of water, as evidenced by corresponding changes in the DTG and TG curves. The exothermic changes are not accompanied by weight change, and therefore represent structural changes. The endothermic parts of the DTA curves indicate that the weight change takes place in three distinct temperature regions; from room temperature to 120°, from 120° to 400°, and from 400° to 600°. An inflexion around 120° is observed in the broad endothermic part of the DTA curves. This indicates that the physically-adsorbed surface moisture is removed from room temperature to 120°. Most of the water is eliminated in the temperature region of 120° to 400° and this water represents the zeolitic water. The endotherm from 400° to 600° is due to the removal of strongly-associated water in the zeolite. The weight losses in various temperature regions for all the activated and unacti-

vated samples are calculated from the DTG and TG curves and are listed in the Table.

The activated and unactivated samples display considerable differences in the endothermic regions. The Figure reveals that the unactivated samples exhibit a weak inflexion, whereas the corresponding activated samples show a pronounced break around 120°. In the case of sample *C*, the break is so prominent that a peak appears.

The total water adsorption capacities of all the molecular sieve zeolites, as shown in the Table, remain more or less same, around 20%, for both the activated and unactivated samples. This clearly indicates that the total water adsorption capacities of all the samples of molecular sieve are not affected by activation at 600°. However, there are considerable differences between the activated and unactivated samples as regards the water adsorption capacities in different temperature regions. Although the amount of strongly-associated water remains the same, the amount of physically-adsorbed surface moisture increases and the zeolitic water decreases on activation. This increase of physically-adsorbed surface moisture results in the appearance of a prominent break around 120° in the DTA curves of activated samples.

The reversibility of water adsorption is considered to be regenerative value of a molecular sieve zeolite. The regeneration of a zeolite on activation is determined by the non-alteration of the pores and cavities. Obviously, any change in the zeolitic water content on activation will indicate the degeneration of the zeolite. The de-

Table 1

Weight changes in different temperature regions

Sample	Sample treatment	Total loss (percentage by weight of zeolite)	Physically-adsorbed surface moisture		Zeolitic water		Strongly-adsorbed water	
			percentage by weight of zeolite	percentage of total loss	percentage by weight of zeolite	percentage of total loss	percentage by weight of zeolite	percentage of total loss
Sample *A*	Unactivated	20	3	15	15	75	2	10
	Activated	20.4	5	24.6	13.4	65.7	2	9.7
Sample *B*	Unactivated	20.2	1.8	8.9	17	84	1.4	7.1
	Activated	19.1	5.8	29.2	11.8	61.8	1.5	9
Sample *C*	Unactivated	18.1	3.4	18.8	13.5	74.6	1.2	6.6
	Activated	20.2	7	34.3	11.9	59	1.4	6.7

crease of zeolitic water content for all the samples, as shown in the Table, clearly indicates that heating at 600° causes considerable degeneration to the sieves. Although the reversibility of water adsorption was considered to be the regenerative value of a molecular sieve, the results clearly indicate that the same value can be maintained even when there is considerable degeneration. Therefore, thermal analysis, which differentiates zeolitic water from surface moisture, can be used to identify the degeneration.

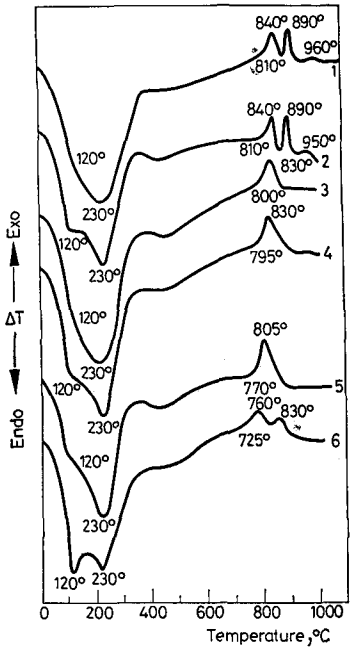

Fig. 1. DTA curves of Na — 4 Å type molecular sieve: 1. Sample *A* — unactivated; 2. sample *A* — activated; 3. Sample *B* — unactivated; 4. sample *B* — activated; 5. sample *C* — unactivated; 6. sample *C* — activated

The secondary surface of a molecular sieve zeolite is insignificant in comparison to the primary surface. The percentages of total water adsorption in the secondary surfaces of *A*, *B* and *C*, as shown in the Table, are 15%, 8.9% and 18.8%, respectively. On activation at 600°, the secondary surface changes to 24.6%, 29.9% and 34.3%, respectively. The significant increase of adsorption in the secondary surface may be due to the development of macroporosity, as reported by Thomas *et al.* [1].

The exothermic peaks are due to the structural changes of the zeolites and are related to their natures and crystallinities. The natures and temperatures of the exothermic peaks of the unactivated samples are different (Fig. 1). Sample *A* exhibits prominent exothermic peaks around 840, 890 and 960°. In the cases of sam-

ples *B* and *C*, the peak temperature lies around 830 and 805°, respectively. These peaks are not so sharp. Although activation at 600° does not affect the exothermic peak temperatures for samples *A* and *B*, a considerable drop, from 805 to 760°, is observed for sample *C*. X-ray powder diffraction analysis indicates that all the samples *A*, *B* and *C* are Na—A type zeolites. The intensities and sharpnesses of the lines in the X-ray diffraction patterns of all the samples were compared, and it was found that samples *A* and *B* are well-crystalline, but sample *C* is poorly crystalline in comparison. The exothermic peak temperatures are in conformity with the crystallinity. Therefore, the higher the peak temperature, the better the crystallinity of a given type of molecular sieve.

The initiation temperature of the first exotherm can be regarded as an index of the thermal stability of a molecular sieve. The characteristic properties of molecular sieves are completely lost on heating to this temperature region. In the investigated samples, these temperatures are 810, 800 and 770°, respectively, for the unactivated samples *A*, *B* and *C*. On heating to 600°, which is much lower than the stability temperature, considerable degeneration of the zeolite structure takes place, leading to a decrease of the sieve value. After activation, the peak initiation temperature remains the same for samples *A* and *B*, but for sample *C* it drops from 770° to 725°. Thus, it appears that on heating at 600° the well-crystalline samples *A* and *B* are not significantly affected in comparison to the poorly-crystalline sample *C*.

Conclusions

1. The degeneration of a molecular sieve zeolite on heating can be detected from the thermal analysis curve. The total water adsorption capacity of even a degenerated zeolite may remain the same, but the zeolitic water content changes on degeneration.

2. Although the thermal stability of a molecular sieve zeolite is judged from the exothermic changes in the differential thermal analysis curve, the degeneration takes place at a much lower temperature.

3. The temperature range of thermal stability and the extent of degeneration of a given type of molecular sieve depend on the crystallinity.

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RÉSUMÉ — On a étudié, par analyse thermique, la dégénération causée par traitement thermique ainsi que la stabilité thermique de tamis moléculaires aux zéolithes Na— A de cristallinité différente. On a mesuré la dégénération des tamis à partir de la diminution de la teneur en eau zéolithique. On a déterminé la stabilité thermique à partir du commencement du pic exothermique. Le chauffage à 600° cause une dégénération considérable des tamis. La dégénération et la stabilité thermique dépendent de la cristallinité des tamis. Des tamis à faible cristallinité dégénèrent plus fortement que ceux à haute cristallinité. La stabilité thermique des tamis à faible cristallinité diminue également lors du chauffage à 600°.

ZUSAMMENFASSUNG — Die infolge der Wärmebehandlung auftretende Degenerierung und die Hietzebeständigkeit von Na— A Molekularsiebzeolithen verschiedener Kristallinität wurden durch Thermoanalyse untersucht. Die Degenerierung der Siebe wurde an der Abnahme des Zeolithwassergehaltes gemessen. Die Hitzebeständigkeit. wurde aus dem Anfang des exothermen Peaks abgeleitet. Aufheizen auf 600° verursacht eine bedeutende Degenerierung der Siebe. Degenerierung und Hitzestabilität hängen von der Kristallinität der Substanzen ab. Wenig kristalline Siebe werden in höherem Maße degeneriert als hochkristalline. Die Hitzebeständigkeit wenig kristalliner Spezies wird durch Aufheizen auf 600° ebenfalls herabgesetzt.

Резюме — С помощью термического анализа была изучена термическая стабильность Na— A молекулярных ситовых цеолитов с различной степенью кристалличности и их вырождение, обусловленное термической обработкой. Вырождения сит было измерено, исходя из уменьшения содержания цеолитной воды. Термическая стабильность была определена из начала экзотермического пика. Нагревание при 600° вызывает значительное вырождение сит. Такое вырождение, а также их термическая стабильность зависят от кристалличности сит. Низкокристаллические сита вырождались в большей мере, чем хорошо кристаллические. Термическая стабильность низкокристаллических сит также уменьшается при нагревании при 600°.