

## A NEW TMA ADSORPTIVE EXPANSION TEST FOR MOLECULAR SIEVES

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Until recently, it has been believed that during adsorption and desorption cycles of molecular sieve pellets, the pellets have been passive participants in the process. It has lately been shown by others using X-ray diffraction technique that the molecular sieve structure undergoes expansion and contraction as a result of moisture content changes.

A new thermomechanical analyzer (TMA) technique has been developed that allows the dimensional change to be measured continuously as a function of time and, concurrently, moisture content, thus creating an unique method for measuring adsorption rates.

The instrument modifications (DuPont 990 and 943), collection and evaluation of data, and the sensitivity of the adsorption rate due to various parameters are discussed in the paper.

A useful technique has been developed to measure the adsorption rate of water by molecular sieve pellets. This technique involves establishing a relationship between dimensional change and molecular sieve adsorption rates. It has been shown [1–5] that molecular sieves undergo a structural dimension change during adsorption. The change has been observed on a unit-cell scale by X-ray lattice parameter shifts, with corresponding macro-scale detection by dilatometry [3]. This change manifests itself as a volumetric change in a molecular sieve pellet, but it can be estimated by a measurement in one dimension with a commercial dilatometer.

After a molecular sieve pellet has been dehydrated or activated, it will expand upon contact with water vapor. This expansion is measured by continuous recording of the dilatometer probe displacement. The expansion continues until the sample has reached an equilibrium state with the moisture available. The curve, plotted by the continuous displacement of the probe, can then be analyzed to give comparative rates.

### Experimental

The equipment used in this technique consists of a DuPont 943 Thermomechanical Analyzer (TMA) module, in conjunction with a DuPont 990 Recorder-Controller. The TMA module has a moveable core linear variable differential transformer (LVDT) attached to a probe, which is operated under negligible load. The

movement of the LVDT core through the primary coil generates an electrical signal which is proportional to the distance the core has moved. The signal is amplified and recorded on the calibrated Y-axis of the recorder chart as the absolute displacement of the probe in mils. The X-axis records either temperature or time, or both, if both pens are used.

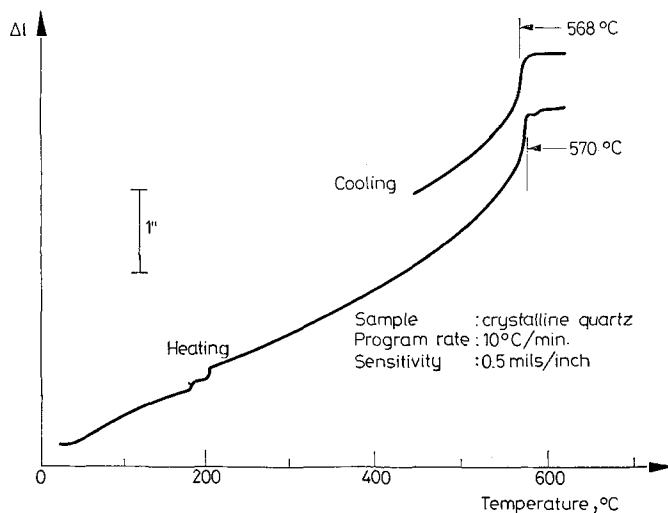


Fig. 1. Temperature scale calibration for TMA cell.

The manufacturer claims [6] that the linearity of the LVDT should be within 0.5% of the selected scale. This was confirmed by comparing the manual displacement of the probe (by a micrometer graduated in mils), with the recorded displacement. The accuracy of sample temperature measurement in this system was also tested. This was done by scanning a sample of  $\alpha$ -quartz and reconrding the  $\alpha$ - $\beta$  transition, which was observed at 570°, in good agreement with the accepted value of 572°. These data are shown in Figure 1.

A special modification of the DuPont 943 module was necessary to meet experimental requirements for this technique. To insure efficient and reproducible sample-atmosphere contact, the purge system had to be changed. A modified sample holder tube was fabricated, consisting of a coiled Inconel-600 tube (0.056" O.D. - 0.046" I.D.) spiralling downward along the inside wall of the sample holder tube and terminating in the sample area. This system allows the adsorbate-laden gas stream to be thermally equilibrated before coming in contact with the sample, and also insures good sample-atmosphere contact, essential for successful operation.

The samples used in data collecting were a series of laboratory and commercial bonded molecular sieve pellets. All samples were equilibrated at 50% relative hu-

midity prior to testing. The property being studied was the rate of change in linear dimension as a function of water adsorption. This was used to compare differences in adsorption rate due to such factors as pellet density, pellet diameter, and pore damage or blockage. Although water was the only adsorbate used in this investigation, other adsorbates that initiate a similar response [1, 4] can be accommodated by the system.

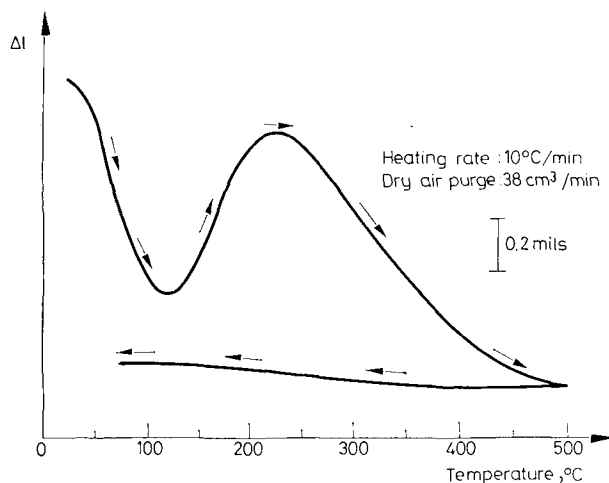


Fig. 2. Typical TMA programmed temperature curve (activation cycle).

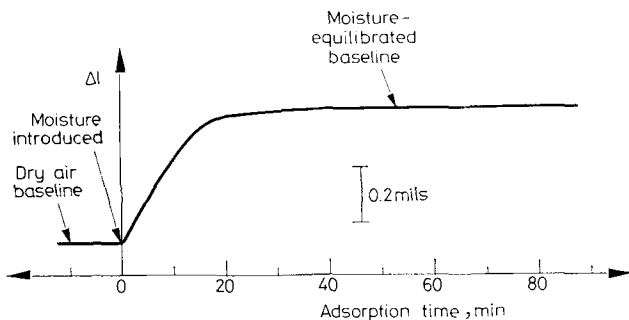


Fig. 3. Typical TMA moisture adsorption curve

The testing of the molecular sieve samples involves heating a 50% relative humidity-equilibrated pellet to 500° in dry air flowing at 38 cm<sup>3</sup>/min, followed by cooling to room temperature in dry air at the same flow rate. A typical curve is shown in Figure 2. Once the sample has reached room temperature, a stream of air at 38 cm<sup>3</sup>/min containing approximately 20 torr of water vapor is passed into the chamber. The probe displacement, due to moisture adsorption by the molecular

sieve, is then recorded as a function of time. A typical curve illustrating this displacement is shown in Figure 3.

The rate of adsorption is determined by taking the slope of the line tangent to the adsorption curve at the point equivalent to one-half the total equilibrated displacement. The time corresponding to this point is referred to as  $T_{1/2}$ , or time

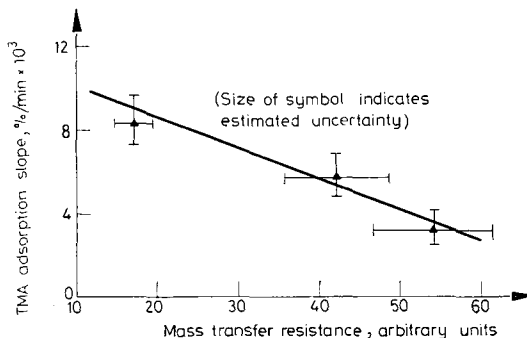


Fig. 4. TMA adsorption slope vs. mass transfer resistance in a packed column

for 50% equilibration. The slope is then converted to % elongation of the pellet per minute. The total time for equilibration, total equilibration being the point at which the adsorption curve attains a nearly horizontal slope, is also recorded. The total equilibration displacement is also normalized for difference in pellet size by calculating the % total change in the pellet length, from the activated to the fully equilibrated state. These four features of the curve can all be used in comparison of samples, but most emphasis has been placed on the % displacement/min value.

### Results and discussion

The effect of pellet density on adsorption properties, as measured by TMA expansion, is shown in Table 1. As expected, the faster rate is associated with lower density and is reflected in all the rate-related values for this laboratory-prepared sample. The total change, measured at equilibrium, is the same, however, for both samples.

Differences in pellet diameter would also be expected to give rise to different rates of adsorption, as illustrated by the data in Table 2. The larger pellet exhibits a much slower rate, reflecting its higher mass transfer resistance. The total percentage change is again the same for both materials.

Resistance to mass transfer in a given sample can be increased as a consequence of thermal or hydrothermal treatments. Table 3 shows these effects in samples exposed to both types of damage. The samples are the same as those used for the

Table 1  
Effect of density on adsorption properties measured by TMA

	Pellet density, g/cm <sup>3</sup>	TMA adsorption data			
		Slope, % expansion per min × 10 <sup>3</sup>	T <sub>1/2</sub> (half-time), min	Equilibration time, min	Total expansion, %
Sample 1	1.26	5.82	27.5	178	0.349
Sample 2	0.98	8.28	21.5	157	0.340

Data represent mean values of 4 to 5 measurements.

Table 2  
Effect of pellet diameter on adsorption properties measured by TMA

	Pellet diam., mm	TMA adsorption data			
		Slope, % expansion per min × 10 <sup>3</sup>	T <sub>1/2</sub> (half-time), min	Equilibration time, min	Total expansion, %
Sample 1	1.6	13.7	9.0	106	0.357
Sample 2	3.2	6.09	23.5	187	0.378

Data represent mean values of 4 to 5 measurements.

Table 3  
Effect of thermal and hydrothermal treatments on TMA adsorption data

	Treatment	TMA adsorption data			
		Slope, % expansion per min × 10 <sup>3</sup>	T <sub>1/2</sub> (half-time), min	Equilibration time, min	Total expansion, %
Sample 1	none	13.7	9.0	106	0.357
Sample 1a	cyclic hydrothermal at 250°	8.84	11.8	114	0.276
Sample 2	none	6.09	23.5	187	0.378
Sample 2a	isothermal at 600°	3.07	40.3	183	0.274

Data represent mean values of 4 to 5 measurements.

pellet diameter comparison. There is a loss in total adsorptive capacity, as measured by TMA expansion, in these cases, showing that the damage has been severe, but the change in adsorption rate clearly exceeds this. The data illustrate that degradation of these molecular sieve materials occurs in stages, and that they are damaged under severe treatment conditions [3, 7].

The mass transfer resistance of molecular sieve pellets and beads can be assessed by means of adsorption rate measurements in an instrumented packed column or bed. Such data can be correlated with TMA adsorption rate measurements, as shown in Figure 4. The data represent 3.2 mm pellets with different histories, and show that the TMA adsorption rate measurement reflects differences in mass transfer resistance, and can be used to make quick and convenient estimates.

The sensitivity of the adsorption rate data to changes in flow rate of moist air through the modified TMA cell was investigated with several 3.2 mm Type 4A molecular sieve pellet samples. Table 4 shows the result of successively decreasing the flow rate for four test cycles, from 38 cm<sup>3</sup> per minute to 9 cm<sup>3</sup> per minute. Similar data on another pellet sample are shown in Table 5, where the flow rate was successively increased.

Table 4  
Effect of moist air flow rate on TMA adsorption data

Cycle	Flow rate, cm <sup>3</sup> per min	TMA adsorption data		
		Slope, % expansion per min $\times 10^3$	$T_{1/2}$ (half-time), min	Equilibration time, min
1	38	6.83	21	235
2	28	6.91	20	215
3	19	6.46	17	154
4	9	0.98	140	515

3.2 mm type 4A pellet activated in situ at 500° before each cycle.

Table 5  
Effect of moist air flow rate on TMA adsorption data

Cycle	Flow rate, cm <sup>3</sup> per min	TMA adsorption data		
		Slope, % expansion per min $\times 10^3$	$T_{1/2}$ (half-time), min	Equilibration time, min
1	9	1.79	124	294
2	19	5.64	33	160
3	28	6.19	24	165
4	38	6.05	21	200
5	19	4.54	29	178

3.2 mm type 4A pellet activated in situ at 500° before each cycle.

These flow rate results indicate that the test is bulk mass transfer-limited only at moisture-saturated gas flow rates below about 20 cm<sup>3</sup> per minute. At very low flow rates, the expected large effect is clearly observed. At higher rates there is

little effect due to modest variation in the flow rate such as might be expected in normal operation. These data provided the basis for selection of a standard flow rate to be used in the test system that would not significantly contribute to measurement error.

### Conclusions

Combining the factors of rapid, inexpensive sample testing, small amounts of sample, and correlatable data, this TMA technique can provide a useful tool in the investigation of the properties of molecular sieves.

The data obtained from the described TMA technique were related to data from other sources on the characteristics of the studied materials. The technique showed how high-temperature damage to a molecular sieve pellet could cause a drastic reduction in adsorption rate, and it also showed that the equilibrium capacity was only modestly changed. This type of information can lead to a better understanding of the mechanism of high-temperature damage. It appears that the damage causes pore opening obstruction or reduction in some manner, but does not greatly affect total micropore volume until the damage becomes severe.

A sample known to have pore obstruction, by other measurements, showed a reduced adsorption rate, compared to the same material without pore blockage. This shows that the technique could be used as a screening tool for pore obstruction susceptibility.

The technique also showed comparable data in mass-transfer resistance due to pellet diameter and pellet density. A higher rate of adsorption was observed for the smaller diameter pellet, and for the pellet of lower density. Once again, the technique demonstrated variance in rate of adsorption, but showed the respective total capacities to be about the same.

It appears, from the study of the data collected, that the TMA technique of measuring rate of adsorption can be a useful tool in determining properties and in identifying potential problems. Also, as compared to other methods, TMA is a faster method requiring only a small amount of material for testing.

### References

1. A. I. SARAHOV, V. F. KONONYUK and M. M. DUBININ, *Molecular Sieves*, *Advan. Chem. Ser.*, 121 (1973) 403.
2. T. N. IVANOVA, A. I. SARAHOV and M. M. DUBININ, *Izv. Akad. Nauk. SSR, Ser. Khim.*, (1975) 1471.
3. W. H. FLANK and G. W. SKEELS, paper presented at the Fifth North American Meeting of the Catalysis Society, Pittsburgh, Pa., April, 1977.
4. O. K. KRASIL'NIKOVA, A. I. SARAHOV and M. M. DUBININ, *Izv. Akad. Nauk SSR, Ser. Khim.*, (1977) 1479.
5. A. DYER, T. R. NOWELL and M. J. WILSON, in *Proc. of First European Symposium on Thermal Analysis*, D. Dollimore, ed., Heyden, London, p. 313, 1976.

6. Instruction Manual, Model 990 Thermal Analyzer and Modules, Instrument Products Division, E. I. duPont de Nemours & Co., Wilmington, Delaware.
7. W. H. FLANK, Analytical Calorimetry, Vol. 3, Plenum Press, New York, p. 649, 1974.

RÉSUMÉ — Jusqu'à tout récemment on pensait que lors des cycles d'adsorption et de désorption des tamis moléculaires, les particules des tamis étaient des participants passifs. Depuis peu de temps des auteurs ont montré, en se servant de la technique de diffraction des rayons X, que par suite à des variations de l'humidité, la structure des tamis moléculaires subit des dilatations et des contractions.

On a développé une nouvelle technique d'analyse thermomécanique qui permet de mesurer, en continu, les variations de dimension en fonction du temps simultanément avec la teneur en humidité, créant ainsi une méthode unique de mesure des vitesses d'adsorption.

Les modifications apportées à l'appareil (Du Pont 990 et 943), l'acquisition et l'évaluation des données, ainsi que la sensibilité de la vitesse d'adsorption due à divers paramètres sont discutées.

ZUSAMMENFASSUNG — Bis vor kurzem wurde angenommen, dass während der Adsorptions- und Desorptionszyklen an Molekularsiebpellets, diese sich als passive Teilnehmer an dem Vorgang beteiligen. Durch andere Autoren wurde unter Anwendung der Röntgendiffraktionstechnik gezeigt, daß die Molekularsiebstruktur infolge von Änderungen des Feuchtigkeitsgehalts Expansionen und Kontraktionen ausgesetzt ist.

Eine neue thermomechanische Analysentechnik wurde entwickelt, welche die kontinuierliche Messung der Dimensionsänderung als Funktion der Zeit unter gleichzeitiger Messung des Feuchtigkeitsgehalts gestattet und somit eine einzigartige Methode zur Ermittlung von Adsorptionsgeschwindigkeiten schafft.

Die Varianten des Instrumentes (DuPont 990 und 943), die Datensammlung und -verarbeitung, sowie die durch verschiedene Parameter bedingte Empfindlichkeit der Adsorptionsgeschwindigkeit werden in der Veröffentlichung erörtert.

Резюме — До недавних пор считалось, что молекулярные ситовые гранулы являлись только пассивными участниками в процессе адсорбционных и десорбционных циклов. Совсем недавно, используя рентгено-дифракционный метод, было показано, что молекулярные ситовые структуры подвергаются расширению и сжатию, вследствие изменения содержания влаги. Разработан новый метод термометрического анализатора, с помощью которого изменение размерности может быть измерено непрерывно как функция времени и, одновременно, содержание влаги. Таким образом создан уникальный метод для измерения скоростей адсорбции. В статье обсуждены модификации инструментов (Дюпон 990 и 943 модели), сбор и оценка данных, а также чувствительность скорости адсорбции, обусловленная различными параметрами.