UvA-DARE (Digital Academic Repository)

Temperature Programmed Desorption on n-Nonane: The method to measure the micropore size distribution

Mittelmeijer-Hazeleger, M.C.; van der Linden, B.; Blik, A.

DOI

[10.1007/BF00486567](https://doi.org/10.1007/BF00486567)

Publication date

1995

Published in

Journal of porous materials

[Link to publication](#)

Citation for published version (APA):

Mittelmeijer-Hazeleger, M. C., van der Linden, B., & Blik, A. (1995). Temperature Programmed Desorption on n-Nonane: The method to measure the micropore size distribution. *Journal of porous materials*, 2, 25-34. <https://doi.org/10.1007/BF00486567>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Temperature Programmed Desorption of *n*-Nonane; The Method to Measure the Micropore Size Distribution

MARJO C. MITTELMEIJER-HAZELEGER, BART VAN DER LINDEN AND ALFRED BLIEK

Department of Chemical Engineering, University of Amsterdam

Abstract. TPD of *n*-nonane gives a micropore size distribution of micropores in the range of 0.4 to 2 nm. This method is independent of the shape of the pore entrances. It is proven that *n*-nonane fills these micropores. The Temperature Programmed Desorption patterns of five activated microporous carbons and three zeolites will be shown.

The difference in adsorption behaviour of CO₂ and SF₆ at 273 K and of CH₄ at 315 K on the carbons is explained with the aid of the obtained micropore size distributions.

Keywords: TPD of *n*-nonane, micropore size distribution, zeolites, activated carbons, heat of desorption of *n*-nonane

Introduction

Although *n*-nonane preadsorption in combination with N₂ adsorption isotherms is known over twenty-five years [1] as a method to determine the micropore volume, there still exists a controversy, regarding filling or blocking the pores by *n*-nonane [2, 3]. Also discussions are reported in the literature about the size of the micropores that are filled or blocked by *n*-nonane [3, 4]. Because of the importance of micropores in many processes like separation, adsorption and so, since long scientists are trying to determine the micropore size distribution. Many methods have been published. For instance, the Horvath-Kawazoe [5] method, the M-P method [6] and the molecular probe technique [7, 8]. Each method has its own disadvantages.

The Horvath-Kawazoe method needs lots of accurate data points in the low relative pressure range and is dependent on the adsorbent-adsorbate pair. This method is also not very accurate for pores larger than 1.6 nm.

The M-P method is applied to measuring points in the relative pressure range of 0.2 to 0.8 that gives information about the pores that are filled below a relative pressure of 0.01.

The molecular probe technique is very laborious and is based on the knowledge of the size of the adsorbing molecule.

McEaney and Masters [9] stated twenty years ago; "a reliable method to obtain micropore size distribution from a single isotherm is a highly desirable goal, which

has so far proved elusive". This still holds. The proposed new method [10] can be a start to come to a simple and reliable method to measure the micropore size distribution, although still two isotherms (before and after *n*-nonane pre-adsorption) and a TPD need to be measured. Micropores can be measured in the range of 0.4 to 2 nm. The results are independent of the shape of the pore opening and independent of the nature of the porous material (carbon, zeolite).

Experimental

After outgassing the samples for 24 hrs at 473 K and $<10^{-3}$ mbar, the samples are cooled down to roomtemperature or in an icebath. For samples with a high degree of acidity an icebath is preferred because of the heat of adsorption can cause some cracking of the *n*-nonane. While keeping the sample under vacuum, an excess of *n*-nonane is added, totally immersing the sample. After 30 minutes the immersed sample is brought to atmospheric pressure, for at least 24 hr, allowing *n*-nonane to enter the pores. Subsequently the excess of *n*-nonane is removed by applying vacuum for 24 hrs ($T = 300$ K; $P = <10^{-3}$ mbar).

The TPD patterns were measured in a thermobalance and in a DSC. In the thermobalance, Setaram TG85 16–18, the heating rate was 1 K/min under an argon flow of 100 ml/min. In the DSC, Setaram DSC111, the heating rate was 5 K/min under an argon flow

of 20 ml/min. Mass spectrometry analysis were performed with a Balzers QME112 MS.

The sample size used in the TPD measurements was 20 mg in the thermobalance and varied in the DSC depending upon the porevolume of the sample, but was limited to 100 mg. The samples of the zeolites with *n*-nonane preadsorbed were prepared within one week before the measurements. The adsorption isotherms were measured on a Carlo Erba Sorptomatic 1800.

The Samples

Three zeolites and a carbon molecular sieve were used as calibration samples.

The molecular sieves used are 4A and 5A (nominal pore size 0.4 and 0.5 nm) from Merck and 13X (nominal pore size 1.0 nm) from Chemische Fabrik Uetikon. A Carbon Molecular Sieve 5A was obtained from Takeda Chemical Industries Ltd. This carbon has slit shaped pores with openings of 0.5 nm [11]. The other activated carbons are from Norit (the RX-1 and the RB-1), Calgon and from Kureha (spherical BAC-QM).

Results and Interpretation

In Fig. 1 the results of the TPD of *n*-nonane from the four calibration samples are given. For clarity the results have been given an offset along the *Y*-axis. With decreasing poresize the temperature, at which the maximum desorption rate occurs, increases. This Desorption maximum ($D_{\max}$) is found around 400 K for the sample with pores of 1 nm. For both the zeolite 5A and the carbon molecular sieve 5A the $D_{\max}$ lies around 490 K, whereas the $D_{\max}$ of the zeolite 4A is found at 570 K. The most striking observation is that both the Carbon Molecular Sieve 5A and the zeolite 5A show a $D_{\max}$ at the same temperature, while their pore openings have a completely different shape, i.e. a slit shape for the CMS [11] and more or less round for the zeolite. So, the shape of the pore mouth is not determining the temperature of the $D_{\max}$.

In Fig. 2 the results of the TPD of the five activated carbons are given. The poresizes corresponding to the $D_{\max}$ of the calibration samples are indicated on the top of the figure. Basically three samples, the Calgon, the Norit RB-1 and the Norit RX-1 show the same pattern, only a difference in the amount of *n*-nonane desorbed can be seen. The Kureha sample shows the $D_{\max}$ at a lower temperature than the others and shows more or

Table 1. The heat of desorption of *n*-nonane as measured by DSC at 5 K/min till 670 K.

Sample	Heat of desorption (kJ/mol <i>n</i> -C ₉)
Zeolite 4A	233
Zeolite 5A	137
Zeolite 13X	193
Takeda CMS 5A	126
Calgon	131
Norit RB-1	128
Norit RX-1	114
Kureha BAC-QM	123

less two peaks. The Takeda sample has the broadest TPD pattern that continuous till high temperature.

In Table 1 the heat of desorption of *n*-nonane, as measured with the DSC, from the zeolites and the carbons are given till 673 K. All the carbons show about the same heat of desorption of 123 kJ/mol $\pm$ 9 kJ/mol independent of the temperature where the $D_{\max}$ is situated. At 370 K (for the Kureha sample) or at 570 K (for the Takeda sample).

Also for the zeolite 5A and the CMS 5A the heat of desorption of *n*-nonane is about the same (137 and 126 kJ/mol respectively).

The other two zeolites 4A and 13X show a higher heat of desorption. For this higher heat of desorption one explanation can be occurring of cracking reactions on the acidic surface of the zeolites, although no fragments could be detected by the mass spectrometer. If 1% of the *n*-nonane was cracked during TPD some fragments should have been detected. Some cracking of the *n*-nonane occurs when the prepared samples are stored at roomtemperature for a longer period. This effect of cracking of *n*-nonane at roomtemperature was the strongest for the 13X sample (the most acid one of the three samples), causing a completely different TPD pattern. None of the carbon samples showed such cracking behaviour, not even when the prepared samples are stored for one year. So, besides a small effect of cracking causing a slightly higher heat of desorption, the CMS 5A and the zeolite 5A, have the same heat of desorption. Also the $D_{\max}$ is situated at the same temperature. These facts prove that *n*-nonane fills these pores rather than blocking them. If blocking of the pores by *n*-nonane would have occurred, certainly the temperature of the $D_{\max}$ and the heat of desorption would have been completely different for the CMS 5A and the zeolite 5A because of their different pores shapes. In Table 2 three types of micro porevolumes are given for the five carbons.

Fig. 1. Temperature programmed desorption patterns of the calibration compounds: Zeolite 4A, Zeolite 5A, Zeolite 13X and Takeda Carbon Molecular Sieve 5A. Heating rate 1 K/min.

1 the volume of *n*-nonane adsorbed in the pores,
 2 calculated from the CO₂ (273 K) isotherms (given in Fig. 5) with the aid of the Dubinin–Radushkevich equation [13] and

3 from the N₂ isotherms at a relative pressure of 0.01 [14].

For the Takeda, and the Calgon samples there is a very good agreement for all the three different methods of

Fig. 2. Temperature programmed desorption patterns of the five carbons. Heating rate 1 K/min.

measuring the micro porevolumes. For the two Norit samples the micro porevolumes measured with CO₂ and *n*-nonane agrees very well. The volumes from

the nitrogen isotherms are somewhat lower. For the Kureha sample there is not a very good agreement among the three different methods. This is not very

Table 2. Micropore volumes of the carbons.

Sample	V_0 (cm ³ /g)		
	CO ₂ (DR)	<i>n</i> -nonane	N ₂ ($p/p^0 = 0.01$)
Takeda CMS 5A	.211	.209	.214
Calgon	.287	.288	.295
Norit RB-1	.365	.372	.325
Norit RX-1	.487	.485	.405
Kureha BAC-QM	.373	.534	.465

surprising as this is the only sample that still showed a remarkable adsorption capacity after *n*-nonane pre-adsorption (Figs. 3 and 4). Also the fact that CO₂ is known to measure only the smallest micropores [15, 16] proofs that this sample contains larger micropores or small mesopores. The fact that for four of the samples the micro porevolumes, measured with CO₂ are identical with the volumes of *n*-nonane also proofs that *n*-nonane fills the pores. Blocking would have given an lower micro porevolume for the *n*-nonane than for the CO₂.

Because *n*-nonane fills the pores, the weight loss during the TPD can be converted to a volume, we can interpret the TPD patterns immediately as micro pore-size distributions in the temperature range of 300 K to 670 K, corresponding to 2 till 0.4 nm.

In Fig. 3 the N₂ (77 K) adsorption isotherms of the five carbons and in Fig. 4 the corresponding isotherms after *n*-nonane preadsorption are given. In Table 3 the monolayer equivalent surface area's according to BET [12] and the pore volumes at a relative pressure of $P/P^0 = 0.95$ of the isotherms from Figs. 3 and 4 are given. From the table and Figs. 3 and 4 it can be seen that in the Takeda sample all the pores are filled with *n*-nonane. The Norit and the Calgon samples still show some N₂ adsorption of N₂ after *n*-nonane preadsorption. For these three samples the angle of the plateau stays the same before and after *n*-nonane preadsorption, indicating that in these cases only large pores and outer surface are left for adsorption. The Kureha sample shows after *n*-nonane preadsorption still a remarkable adsorption capacity. Even a more or less pronounced knee in the adsorption isotherm can be observed. As the resulting surface area is too high to be attributed to outer surface and larger mesopores, this sample must still have small mesopores or large micropores that do not stay filled with *n*-nonane during outgassing at roomtemperature.

In Fig. 5 the isotherms of CO₂ at 273 K are given. It can be seen that only the isotherm of the Takeda samples shows a pronounced curvature, which flattens out already at a relative pressure as low as 0.03, indicating that all the adsorption sites are occupied.

Fig. 3. Nitrogen adsorption isotherms (77 K) of the five carbons.

Fig. 4. Nitrogen adsorption isotherms of the five carbons after *n*-nonane preadsorption.

Looking at the adsorption capacity in the measured pressure region, we observe that the Kureha sample adsorbs less than all the other samples. As can be seen from Fig. 2, the Kureha sample has an amount of pores smaller than 0.5 nm that is the least of all the samples. Thus, such an adsorption behaviour can be understood.

In Fig. 6 the adsorption isotherms of SF₆ (273 K) on the five carbons are given. In Table 4 the monolayer equivalent surface area's ($a_m = .415 \text{ nm}^2$) [18] calculated from these isotherms are given. Comparison of the results of nitrogen and sulfurhexafluoride clearly shows a molsieve effect. For all the samples the surface area's measured with SF₆ is lower than with N₂. Although the adsorption capacity, in the measured pressure region, for the Kureha sample is lower than for the Norit RX-1 sample, the calculated surface area

is higher. Here the adsorption behaviour can also be understood by looking at the patterns of Fig. 2. SF₆ is a large molecule (>0.5 nm) so, it can only adsorb in larger pores. That part of the TPD patterns below a temperature of 490 K may be used to explain the adsorption behaviour of SF₆ in these carbons. Adsorption on the Kureha sample takes also place in the pores that are not shown in the TPD pattern, because they are not filled with *n*-nonane.

This method can also be of use in explaining the adsorption behaviour of gases above the critical temperature. Adsorption under such conditions is of interest for those who are developing microporous carbons for storage, adsorption and separation purposes, like adsorption of hydrogen and natural gas and pressure swing adsorption.

Table 3. Monolayer equivalent surface areas and pore volumes measured with nitrogen before and after *n*-nonane preadsorption.

Sample	Before <i>n</i> -nonane preadsorption		After <i>n</i> -nonane preadsorption	
	Sa (m ² /g)	V _p (cm ³ /g)	Sa (m ² /g)	V _p (cm ³ /g)
Takeda CMS 5A	617	.283	6	.01
Calgon	956	.506	71	.08
Norit RB-1	1143	.539	82	.09
Norit RX-1	1543	.773	76	.07
Kureha BAC-QM	1504	.757	228	.14

Fig. 5. Carbon dioxide adsorption isotherms (273 K) of the five carbons.

Fig. 6. Sulfurhexafluoride adsorption isotherms (273 K) of the five carbons.

An example of this is given in Fig. 7; the adsorption of CH_4 at 315 K. Remarkable in this figure is that the adsorption capacity of the Takeda sample is in the same

order of magnitude as that of the two Norit samples. At very low pressure it is even larger. Again combining Fig. 2 with this figure makes such an adsorption

Table 4. Monolayer equivalent surface area's from the SF₆ isotherms.

Sample	Sa (m ² /g)
Takeda CMS 5A	272
Calgon	651
Norit RB-1	875
Norit RX-1	1223
Kureha BAC-QM	1261

behaviour easier to understand: The ratios of the micro porevolumes of pores smaller than 0.4 nm and the ratios of the adsorption capacity at 1 atmosphere are the same.

Discussion

In this article is it proven that *n*-nonane fills micropores as small as 0.4 nm. This is in contrast to the results of other authors [2, 3, 4, 17]. The reason must be found in the different way the *n*-nonane preadsorption was applied. In our case the *n*-nonane was allowed to penetrate as a liquid (high pressure compared to gasphase adsorption), at roomtemperature while other investigators preadsorb *n*-nonane from

the gasphase and sometimes at a lower temperature than roomtemperature. Under our conditions blocking of very small micropores (<0.4 nm) can occur, as was showed before [10].

Certainly at this moment the method needs much more calibration points before coming to a complete scale of poresizes versus the temperature of the maximum desorption rate. Especially data points between 0.5 and 1 nm and above 1 nm are needed, because now it is not clear what the exact size is of the pores that stay filled with *n*-nonane after outgassing at roomtemperature. As can be seen in Fig. 4 for the Kureha sample, not all the small pores are filled with *n*-nonane, resulting in an isotherm that is still more or less of type 1. Probably these pores belong to the type that can be called large micropores or small mesopores. Although no strong evidence can be given now, in our opinion these pores are larger than 2 nm, but smaller than 3 nm.

Another point that certainly needs some attention is the fact that even the TPD patterns of the zeolites, knowing to have a uniform size of the pore entrances, do not give very sharp peaks. Changing the heating rate does not give rise to much sharper peaks as can be seen in Fig. 8. In this figure the TPD patterns of the Kureha sample are given at three different heating rates. A disadvantage of a low heating

Fig. 7. Methane adsorption isotherms (315 K) of the five carbons.

Fig. 8. Temperature programmed desorption pattern of the Kureha sample at a heating rate of 0.2 K/min, 1 K/min and 10 K/min.

rate is the almost unacceptable measuring time of 42 hours.

Conclusions

n-Nonane fill pores in the range of 0.4 to 2 nm.

The method of Temperature Programmed Desorption of *n*-nonane is a good and simple way to measure the micro pore size distribution.

The temperature at which the $D_{\max}$ is found depends on the pore size and not on the shape of the pore opening.

The heat of the desorption of *n*-nonane from pores between 0.4 and 2 nm is $123 \text{ kJ/mol} \pm 9 \text{ kJ/mol}$ on non acidic surfaces.

This method can be used for both microporous carbons and zeolites. For the latter care should be taken in interpretation of the desorption patterns, as the acidity of the zeolites may give rise to cracking of *n*-nonane.

Samples with a high acidity should always be prepared shortly before the TPD measurement.

The shape of the adsorption isotherms of different gasses can be explained with the aid of the obtained micro pore size distributions.

References

1. S.J. Gregg and J.F. Langford, *Trans. Faraday Soc.* **65**, 1394 (1969).
2. J.N. Bohra and K.S.W. Sing, *Adsorption Science & Technology* **2**, 89 (1985).
3. P.J.M. Carrott, F.C. Drummond, M.B. Kenny, R.A. Roberts, and K.S.W. Sing, *J. Colloids and Surf.* **37**, 1–13 (1989).
4. F. Stoeckli, D. Huguenin, and P. Rebstein, *J. Chem. Soc. Faraday Trans.* **87**(8), 1233 (1991).
5. G. Horváth and K. Kawazoe, *J. Chem. Eng. of Japan*, **16**(6), 470 (1983).
6. R.Sh. Mikhail, S. Brunauer, and E.E. Bodor, *J. Colloid, Interface Sci.* **26**, 45 (1968).
7. R.L. Bond and D.H.T. Spencer, *Industrial Carbon and Graphite*, Soc. Chem. Ind., London (1958), p. 231.
8. J. del Lopez-Gonzales, J.M. Martín-Martínez, A. Mendez, M. Molino, and F. Rodriguez-Reinoso, (Abstracts of the 16th American Carbon Conference, (American Carbon Soc., San Diego, 1983), p. 307.
9. B. McEaney and K.J. Masters, *Thermochimica Acta* **82**, 81 (1984).
10. M.C. Mittelmeijer-Hazeleger, B.v.d. Linden, J.M. Martín-Martínez, and A. Blik, (Proceedings of the 1993 AIChE Summer National Meeting, August 15–18, Seattle, Washington USA), Lecture 76h.
11. K. Kawazoe, M. Suzuki, and K. Chiharo, *J. Chem. Eng. of Japan* **7**, 31 (1974).
12. S. Brunauer, P.H. Emmet, and E. Teller, *J. Am. Soc.* **60**, 309 (1938).
13. M.M. Dubinin, *Progress in Surface and Membrane Science* 9, edited by E. Matijevich, (Academic Press, London, 1975).
14. S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, (Academic Press, London, 1982).
15. F. Rodríguez-Reinoso, A. Linares-Solana, J.M. Martín-Martínez, and J.D. López-Gonzalez, *Carbon* **22**, 123 (1984).
16. J.M. Martín-Martínez, M. Molina-Sabio, F. Rodríguez-Reinoso and R. Torregrosa, *Fuel* **68**, 204 (1989).
17. V.S. Tripathi, *Indian Journal of Technology* **31**, 98 (1993).
18. A.L. McClellan and H.F. Harnsberger, *J. Coll. Interface Sci.* **23**, 577 (1967).