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Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis

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Abstract

Physisorption methods as routine tools for the characterization of micro- and mesopores of new materials have been explored. Crystalline zeolite structures of Na-Y and Na-ZSM-5, amorphous microporous mixed oxides, mesoporous SiO₂ and MCM-41 materials have been investigated and tested by a variety of methods to differentiate between meso- and microporous structures. Problems encountered with micropore analysis by routine application of the *t*-plot and the Horvath–Kawazoe method (HK) are identified. It is shown that neither type I isotherms nor *t*-plots, α_s -plots or HK-pore-size distributions are reliable evidence for microporosity. The pore sizes in micropore-size distributions derived from the adsorption isotherm are very sensitive to adsorbate gas and adsorption temperature. Only with argon as the adsorbate at the temperature of liquid argon, reliable pore sizes in the micropore range are obtained. This manuscript attempts to guide scientists in the selection of suitable methods for the *routine* characterization of porous solids with commercial equipment based on our experiences. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: High-resolution physisorption; Microporous and mesoporous solids; AMM; MCM-41; Na-Y; Na-ZSM-5; Isotherm; Horvath–Kawazoe; Pore-size distribution; *t*-plot; Argon; Nitrogen

1. Introduction

Surface area and porosity are important properties in the field of catalyst design and heterogeneous catalysis. Total surface area is a crucial criterion for solid catalysts since it determines accessibility of active sites and is thus often related to catalytic activity. The pore architecture of a heterogeneous catalyst controls transport phenomena and governs selectivity in catalyzed reactions. Properties, such as pore volume and pore-size distribution, are therefore

essential parameters especially in shape selective catalysis. Today, pore size and distribution are often a target of catalyst design.

Gas sorption among other methods [1] is routinely used in heterogeneous catalysis to characterize porous materials with mesopores (diameter 2–50 nm) as well as with micropores (diameter <2 nm). This manuscript is an attempt to guide scientists engaged in catalyst development in the selection of suitable physisorption methods that can be used to identify, differentiate and characterize materials with pores in the range of micro- and mesopores (0.5–50 nm). Scopes and limitations of these methods are discussed and illustrated by examples. This attempt to stress and clarify pro-

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blems involving physisorption analysis can and will, by no means, be complete. It covers mainly aspects, problems and reliable solutions encountered with physisorption analysis of micro- and mesoporous materials. Emphasis is placed on amorphous microporous materials, such as the amorphous microporous mixed oxides (AMM) catalysts, prepared via a modified sol–gel process, which are characterized by a narrow micropore distribution comparable to that of zeolites [2]. According to pulsed field gradient NMR studies of small molecule diffusion, AMM materials contain a one-dimensional pore structure with distances between channel intersections smaller than ca. 0.6 μm [3]. Since the materials are amorphous, no X-ray data related to pore size can be obtained. Therefore, reliable physisorption isotherms have been essential to evaluate the pore structure of these AMM materials and to unambiguously distinguish between micro- and mesoporosity and associated border line cases.

2. Experimental

Crystalline microporous materials selected for this study were Na-ZSM-5 (Si/Al=55) and Na-Y. Na-ZSM-5 was provided by Alsi–Penta GmbH and Na-Y by Grace GmbH. The micropore sizes of these samples are well known. They have been determined by single crystal X-ray diffraction to 0.53×0.56 and 0.51×0.55 nm for Na-ZSM-5 and 0.74 nm for Na-Y, respectively [4]. An amorphous microporous SiO_2 (AMM-Si) prepared by a modified sol–gel process described elsewhere [2], a mesoporous SiO_2 material prepared according to a MCM type synthesis [5] and a mesoporous MCM-41 were investigated in detail. All samples were outgassed prior to the measurement at 523.15 K and 10^{-4} mbar for 12 h. Adsorption isotherms were recorded in static volumetric technique with a modified Omnisorp 360 by Coulter. Both nitrogen and argon were used as analysis gas at 77.3 and 87.5 K, respectively. The Milestone 200 Sorption Software Advanced Data Processing, version 3.03 (Porotec GmbH) was used for all calculations based on isotherm data.

3. Isotherms

The first important information about surface and porosity obtained from a physisorption experiment is

the isotherm. It can reveal the kind of porosity present in unknown samples. Brunauer has defined five different types (Fig. 1) [6]. Type I isotherms are characteristic for microporous adsorbents, such as zeolites and carbons. Type IV isotherms are typical for mesoporous goods. Important features are the increase in volume adsorbed at higher p/p_0 caused by adsorption in mesopores as well as a hysteresis loop. A distinct increase in adsorbate volume in the low p/p_0 region in type IV isotherms indicates the presence of micropores associated with mesopores. Experimental isotherms of both types, obtained with argon at 87.5 K are presented in Fig. 2. According to the definition of Brunauer the zeolites Na-ZSM-5, Na-Y, the AMM-Si, and the mesoporous SiO_2 material are characterized by type I isotherms. A type IV isotherm is encountered for the MCM-41 sample with a typical adsorbate uptake starting at 0.3 p/p_0 .

4. Mesoporosity

The increase in adsorbed volume at higher p/p_0 in type IV isotherms is caused by capillary condensation below the expected condensation pressure of the adsorbate. Capillary condensation is a secondary process that requires the preformation of an adsorbed layer on the pore walls formed by multilayer adsorption. Both processes generally occur simultaneously in the region of 0.3–1 p/p_0 . The latter is described by the Kelvin equation (Eq. (1)) that relates the curvature of the meniscus present in a pore to the p/p_0 value associated with condensation.

$$r_K = \frac{-2\sigma v_1}{RT \ln(p/p_0)} \quad (1)$$

where r_K is the Kelvin radius, v_1 the molar volume of the liquid condensate, and σ the surface tension of the liquid condensate.

The Kelvin radius, the radius of the condensed adsorbate, is obtained via this method. The pore radius for cylindrical pores is given by the Kelvin radius and the film thickness of the adsorbed multilayer t (Eq. (2)).

$$r_p = r_K + t \quad (2)$$

where r_p is the pore radius and t the statistical thickness of adsorbed film. Values for t can be derived from standard isotherms.

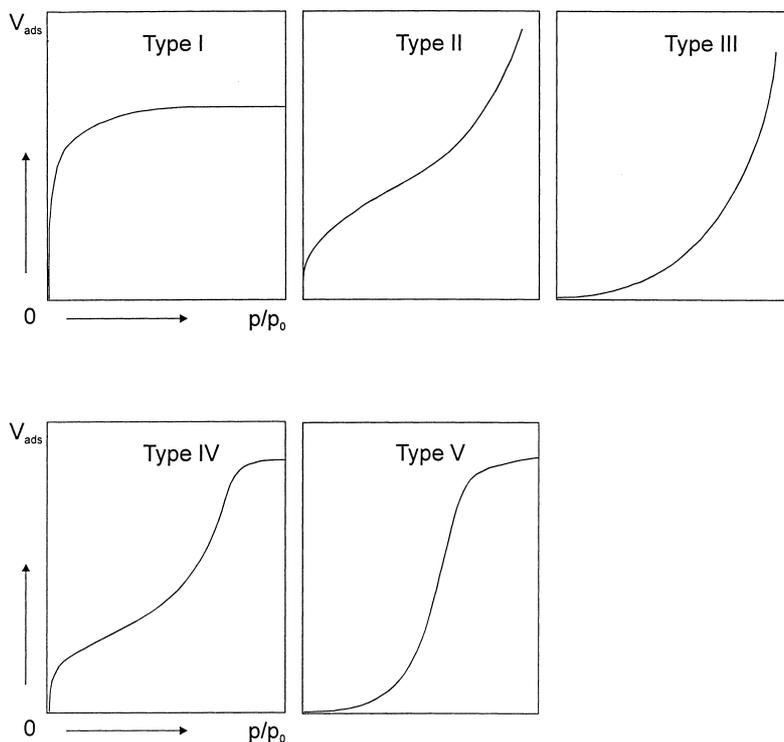


Fig. 1. Adsorption isotherm types defined by Brunauer [6].

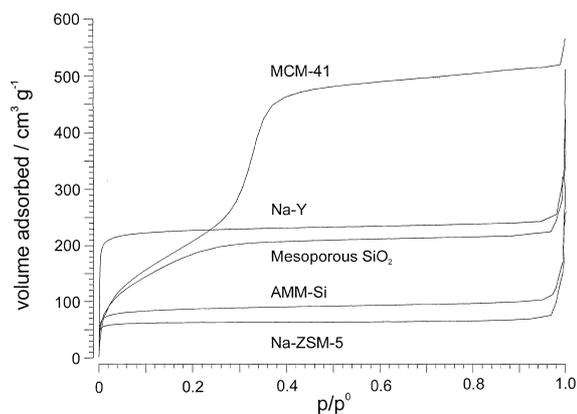


Fig. 2. Adsorption isotherms of the samples tested with Ar at 87.5 K.

Several methods to calculate the mesopore-size distribution from adsorption isotherm data have been developed [7,8]. Most computational methods are based on the BJH model by Barrett, Joyner and Halenda [9]

Isotherm data can be derived either from the desorption branch or from the adsorption branch of the isotherm to calculate the mesopore-size distribution. The pore-size distribution of the mesoporous SiO_2 material and the MCM-41 material shown in Fig. 3 have been calculated from the adsorption branch of the isotherm by the BJH method. A pore-size maximum for the MCM-41 material at 2.5 nm has been found. The mesoporous SiO_2 exhibits smaller mesopores (2–2.5 nm) associated with larger micropores (1–2 nm) according to the BJH method. BJH-pore-size distributions in the small mesopore to large micropore region should be interpreted with caution because the Kelvin equation (basis of BJH) is reliable only for pores >2 nm. Due to lack of materials with well-defined narrow pore-size distributions ranging from 1–2 nm, little can be said about the reliability of pore-size assignments in this pore-size range. However, there is no doubt that the pore sizes of mesoporous SiO_2 are in this region, since below 1 nm and above 2 nm pore-size assignments are reliable.

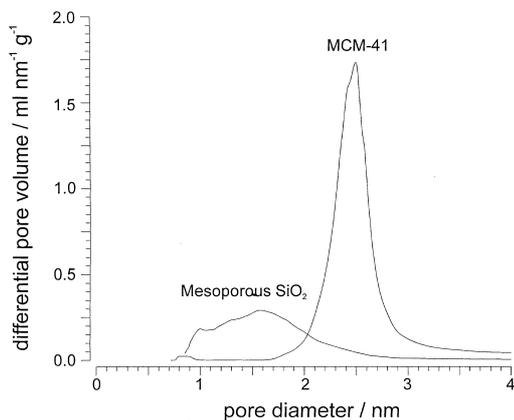


Fig. 3. Pore-size distribution according to the BJH method.

5. Microporosity

5.1. Micropore filling

The assessment of micropores (diameter <2 nm) is by no means trivial. Generally, two mechanisms of pore filling of micropores have been described by Sing [10]. ‘Primary’ micropore filling occurs at low relative pressures ($p/p_0 < 0.01$) and involves pores with diameters comparable to the size of the gas molecules used. Adsorption forces (adsorbent–adsorbate) across the pores cause the filling of these narrow pores. Larger micropores are filled by cooperative effects in a ‘secondary’ process involving adsorbent–adsorbate interactions in the relative pressure region between $p/p_0 \approx 0.01$ – 0.2 .

5.2. Identification of micropores

5.2.1. t -Plot and α_s -plot

In order to judge the presence and the amount of micropores in catalysts revealing type IV isotherms, it is necessary to evaluate pore-size distributions in the micropore region. Experimentally, micropores can be analyzed by adsorption calorimetry along with isotherm measurements and by preadsorption of larger molecules to block micropores [1]. Empirical methods that allow a semiquantitative analysis of the micropore surface area are the t -plot and the α_s -plot [11,12]. Both methods are based on the comparison of adsorption isotherm data of a porous sample and of a nonporous sample of identical chemical composition and surface character (reference isotherm, type II).

The t -plot is considered to be the graph of V_{ads} vs. t . If both reference and sample isotherm are identical, as is the case for nonporous solids, a straight line passing through or passing close to the origin, should result (Fig. 4). Horizontal departures from the straight line indicate the presence of micropores while vertical plots reveal mesopores. The micropore volume present is obtained from a straight line extrapolated to a positive intercept on the ordinate (Fig. 5). Although the method could be used quantitatively to determine the micropore surface area, for routine analysis it is, however, difficult to obtain reference isotherms of nonporous solids and ensure a precise analysis. For semiquantitative investigations Lecloux suggested the use of reference isotherms with approximately identical BET C constant as the solid to be tested [13,14]. This method has been subject of debate in Ref. [8].

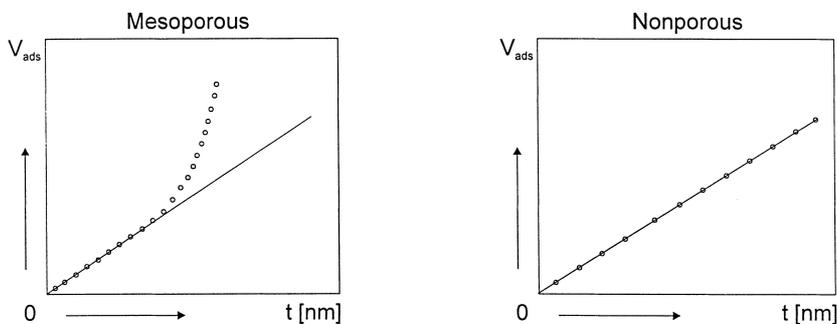
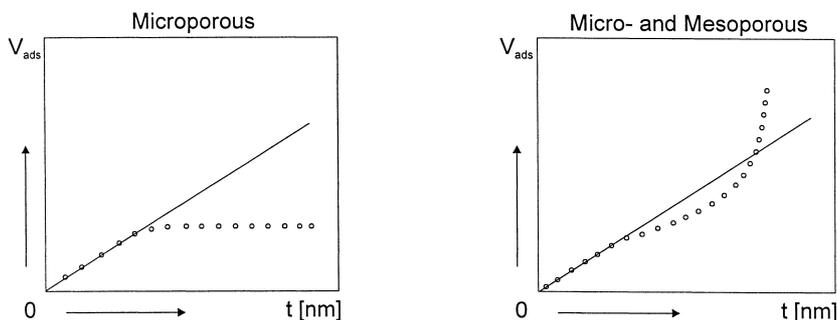
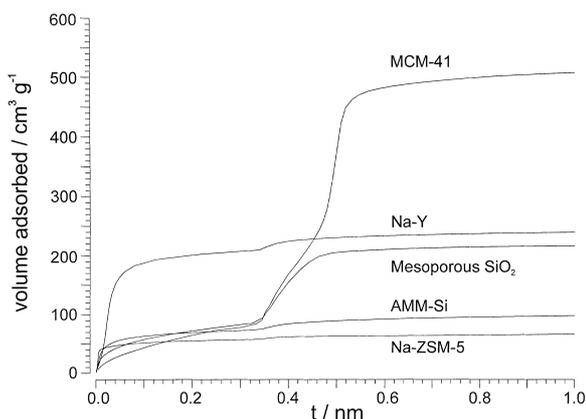


Fig. 4. t -Plots of mesoporous and nonporous solids.

Fig. 5. t -Plots of microporous and micro- and mesoporous solids.Fig. 6. t -Plots of the tested samples.

The t -plots of our samples were calculated for a qualitative interpretation by the Lecloux method. In Fig. 6 the intercepts on the y-axis indicate larger micropore volumes for Na-Y, Na-ZSM-5 and the AMM-Si. However, some micropore volume seems also to be present in the mesoporous SiO₂ material and in the MCM-41 material. Additional small adsorption steps ca. 0.34 nm present in the t -plots of three microporous materials could be interpreted as adsorption in larger micropores or on the outer surface. However, since this step at 0.34 nm appears in all materials, an artefact of the evaluation software is more likely.

A clear upward deviation at large film thickness (0.35 nm) which is typical for mesopore volume is observed for the MCM-41 and the mesoporous SiO₂ materials. A positive intercept combined with an upward deviation suggests the presence of a small micropore volume associated with dominating mesoporosity for the MCM-41 and the mesoporous SiO₂ in

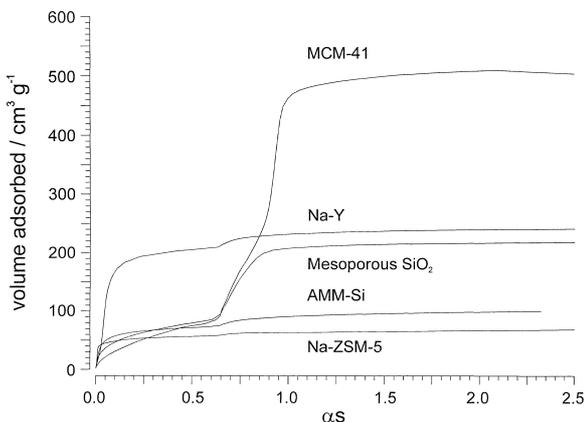
Fig. 6. The shapes of the calculated t -plots strongly deviate from the ideal t -plots shown in Figs. 4 and 5. We believe that these differences are mainly caused by the use of the Lecloux method. To obtain t -plots more similar to their expected ideal shape, reference isotherms stemming from nonporous materials of identical chemical compositions would be required. For routine applications, such as ours, this is usually not possible and the scientist has to rely on such non-idealized t -plots as shown in Figs. 4 and 5.

The α_s -plot [11] takes a similar approach to the assessment of micropores. The advantage here is the use of a reduced standard isotherm. Evaluation of micro- and mesopores remains the same as for the t -plot method, also the presence of small micropore regions in the two mesoporous samples is confirmed. The results of the chosen samples are identical to those found in the t -plot as Fig. 7 depicts. The indication of micropore volume for the MCM material is in clear contradiction to the Ref. [15].

5.3. Isotherms of microporous materials

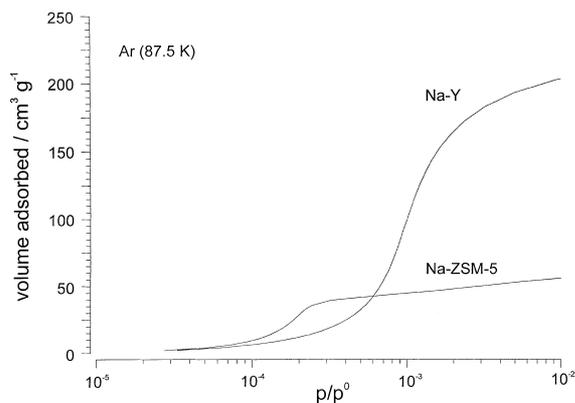
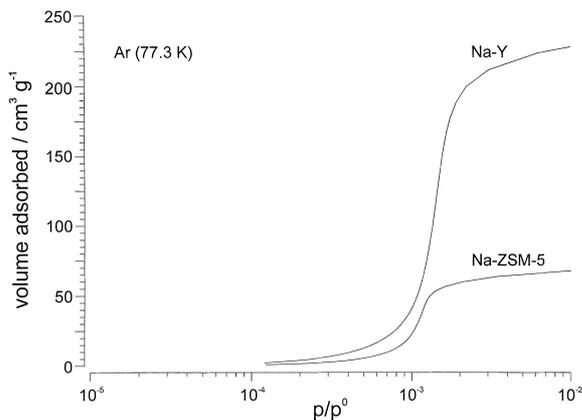
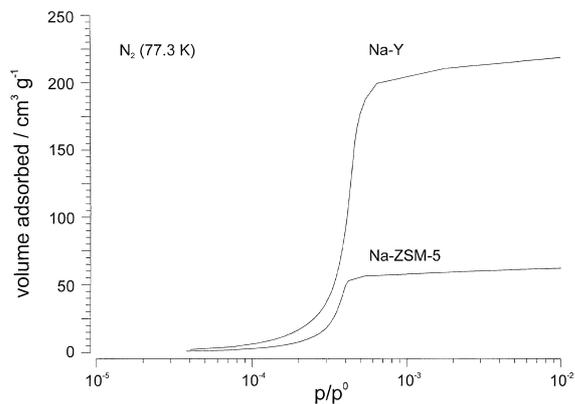
Information about possible microporosity present in a material can be obtained from points of inflection at very low p/p_0 in the isotherm plotted in logarithmic scale (high-resolution isotherm). The point of inflection corresponds to the pore size of the materials. For materials with smaller pores the pressure transitions should be observable at lower pressures. Different plots have been reported in the literature to locate pressure transitions in adsorption isotherms of crystalline porous materials.

Venero and Chiou [16] have investigated the zeolites Ca-A, Na-ZSM-5 and Na-Y with nitrogen and

Fig. 7. α_s -Plots of the tested samples.

argon as adsorbates using a continuous volumetric technique at 77.3 and 87.5 K. They report characteristic ‘S’ shaped isotherms in the low-pressure region plotting w/w_0 (volume adsorbed divided by volume adsorbed at $p/p_0=0.5$) vs. $\log p/p_0$. Only for argon as the adsorbate the first-transition regions correlate with the pore diameters of the zeolites. The argon data used in conjunction with the Horvath–Kawazoe (HK) model provides realistic pore-diameter values. The same plot has been used by Saito and Foley [17] and Hathaway and Davis [18]. Borghard et al. presented their results of argon sorption experiments with ZSM-5 by plotting the first derivative of the adsorption isotherm vs. the log of the relative pressure [19]. The two maxima obtained were attributed to 21 and 30 argon atoms per unit cell, respectively. We have investigated the test samples using a plot volume adsorbed vs. log of the relative pressure. It should be emphasized, that the use of one of these methods is crucial for a reliable assignment of microporosity.

From the series of test samples, Na-Y and Na-ZSM-5 have been selected as suitable microporous test materials. The two zeolites should show a difference of ca. 0.2 nm in pore size. The isotherms in the low-pressure region below $10^{-3} p/p_0$ have been obtained with N_2 (77.3 K), Ar (77.3 K) and Ar (87.5 K) to document the effect of adsorbate/temperature combination for physisorption experiments of microporous materials. From Fig. 8(a–c) it can clearly be seen that points of inflections at the correct relative pressure can only be obtained with Argon at 87.5 K. With the use of nitrogen as adsorbate it is not possible to differentiate

Fig. 8. Low-pressure regions of the adsorption isotherms of Na-Y and Na-ZSM-5 with N_2 at 77.3 K, Ar at 77.3 K and Ar at 87.5 K.

between the two zeolites, presumably due to its large quadrupole moment.

Therefore, the isotherms of all samples obtained with Ar (87.5 K) have been investigated (Fig. 9)

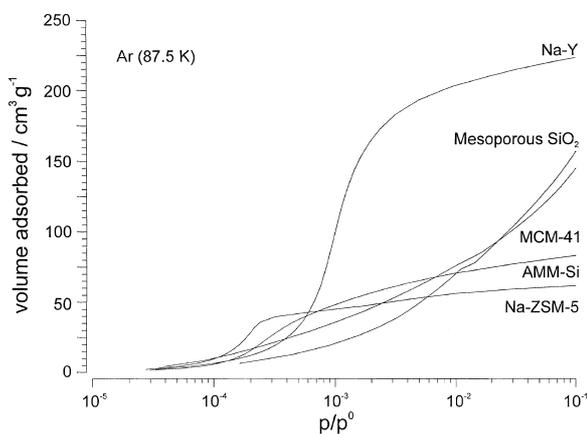


Fig. 9. Low-pressure regions of the adsorption isotherm of all tested samples with Ar at 87.5 K.

confirming that the AMM-Si material shows a point of inflection and is purely microporous. However, Fig. 9 also shows that the pore-size distribution of the AMM-Si material is not as narrow as that of the two crystalline materials. This might be caused by the presence of a variety of micropore sizes in the AMM material, but it may also be a consequence of differences in chemical composition and the amorphous nature of the pore walls. Na-ZSM-5 with the smallest micropores adsorbs at $2 \times 10^{-4} p/p_0$ followed by the AMM-Si at $5 \times 10^{-4} p/p_0$. A distinct transition for Na-Y appears at $1 \times 10^{-3} p/p_0$. The plot allows a qualitative classification of micropore sizes according to the pressure transitions. The mesoporous MCM-41 and the mesoporous SiO₂ materials show a continuous increase in adsorbed volume with p/p_0 from 10^{-5} up to 10^{-1} with no pressure transitions and no inflection point indicative of the complete absence of micropores and in perfect agreement with the Ref. [15]. There are two explanations for the absence of a distinct point of inflection at low p/p_0 . Either there is an extremely homogeneous distribution of micropores of all sizes ranging from 0.3 to 3 nm (which is theoretically possible but unlikely in a real system) or there are no micropores at all and the continuous adsorption with p/p_0 is due to continuous adsorption on a large surface. The continuous adsorption in the low pressure region of MCM-41 and mesoporous SiO₂ (Fig. 9) does not indicate the presence of micropores, since such continuous adsorption is also present in the low pressure regions of the well defined zeolites. However,

this is in contradiction of the qualitative assignment derived from the t -plot method and the α_s -plot above, both of which seem to suggest the presence of small amounts of micropores in these mesoporous materials. Since no micropores are present (see above), we conclude that both t -plot and α_s -plot assignments must be wrong. Reasons for this deviation of the t -plot and α_s -plot must be the lack of a suitable nonporous standard material and the use of the standard parameters supplied by the software. Both methods should, therefore, be applied with caution in routine applications.

The low resolution isotherm of the mesoporous SiO₂ material (Fig. 2) is remarkable because it shows a type I isotherm typical of microporous materials while apparently no micropores are present. This finding emphasizes the crucial importance to double check sorption data for the presence of micropores. The shape of the isotherm, as recommended in the traditional literature, is clearly no longer a sufficient criterion. We emphasize the inspection of the low-pressure range of the isotherm as already recommended by Davis and others.

To document the high resolution by the use of Argon at 87.5 K together with proper vacuum conditions, we have performed a competitive adsorption experiment with a physical mixture of Na-Y and Na-ZSM-5. As shown before by Saito and Foley [17], both transitions are present and indicate volume uptake in different p/p_0 regions (Fig. 10). This procedure of competitive adsorption assures identical adsorption conditions and should be recommended as a suitable test procedure for equipment characterization. Only such equipment, capable of differentiating among different pore sizes of zeolites should be entrusted with micropore analyses.

5.4. Pore-size distributions

Micropore-size distributions are derived from physisorption isotherm data and provide valuable microstructural information. The HK model [20] relates relative pressure (p/p_0) to a micropore radius described by a Lennard–Jones potential [2]. Isotherm data acquisition at very low pressure in the region of micropore filling ($p/p_0 < 0.01$) is necessary for the HK model to obtain reliable data. [21] However, the HK method shows some major drawbacks which limit its reliability. The HK slit model was proposed for the

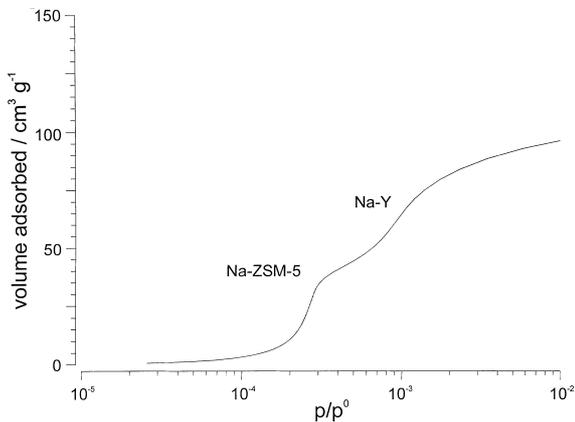


Fig. 10. Low-pressure regions of the adsorption isotherm of the competitive adsorption of Na-Y and Na-ZSM-5 with Ar at 87.5 K.

evaluation of micropores in carbon molecular sieves. For zeolites, oxides and aluminophosphates, this HK model may not be adequate because the effects of curvature on the forces of adsorption are neglected. Nor are there parameters that distinguish between crystalline and amorphous materials. Further problems are caused by the assumption that the adsorbate–adsorbate and adsorbate–adsorbent interactions are considered to be equal within the narrow micropores. To overcome some of these problems modifications have been suggested in the past. The polarizability and the magnetic susceptibility in the potential term have been adjusted to the adsorbate and adsorbent used. But it has been found that the influence of the potential parameter on the position of the distribution maxima is only small [1]. It is striking that we could obtain correct distribution maxima for silicon oxide based materials using a nitrogen on carbon potential while calculations performed with an argon on silicon dioxide potential did not lead to satisfying results for the same materials. A problem of the method is the limited availability of physical parameters required in the Lennard–Jones potential term especially for new catalyst materials. Nevertheless, the method can be used for routine analysis effectively, if based on careful calibration with defined microporous structures. Zeolites are well suited for this task since they have been characterized in detail using a variety of methods to determine their pore size.

The isotherms discussed above have been used to calculate HK-pore-size distributions. Fig. 11(a–c)

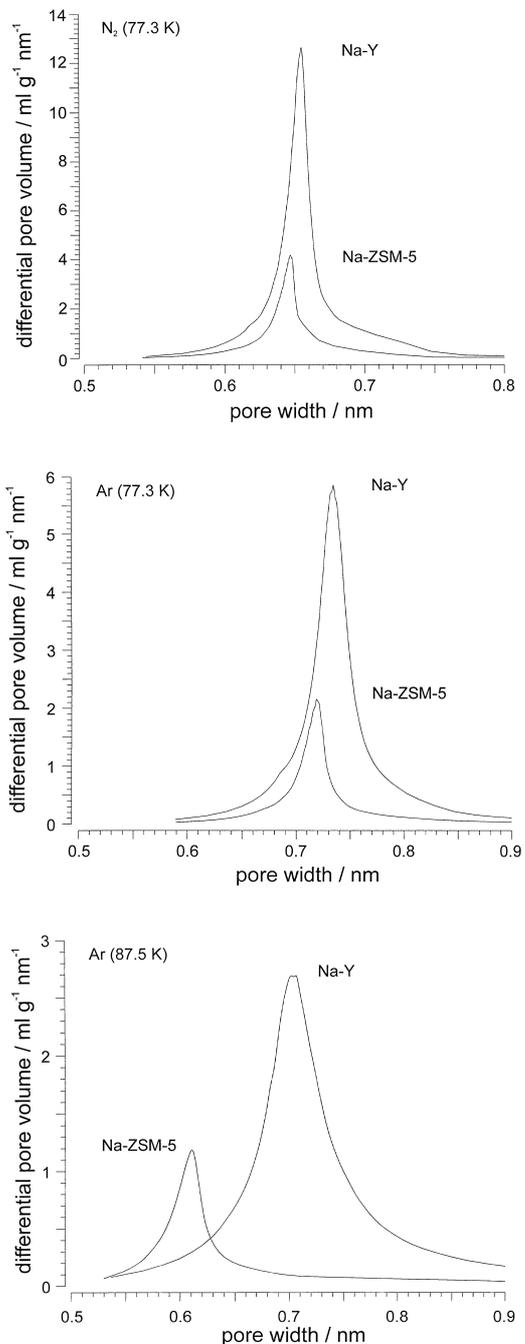


Fig. 11. Pore-size distributions of Na-Y and Na-ZSM-5 according to the HK method with N_2 at 77.3 K, Ar at 77.3 K and Ar at 87.5 K.

confirm our results that only with the use of Ar at 87.5 K it is possible to distinguish between pore sizes of Na-Y and Na-ZSM-5. The HK-pore-diameter dis-

Table 1

Mean pore diameters of Na-ZSM-5 and Na-Y according to the HK method with N₂ at 77.3 K, Ar at 77.3 K and Ar at 87.5 K

Adsorbant	N ₂	Ar	Ar	Data of Ref. [5]
<i>T</i> (K)	77.3	77.3	87.5	
Na-Y				
Pore size (nm)	0.66	0.74	0.70	0.74
Na-ZSM-5				
Pore size (nm)	0.65	0.72	0.62	0.53×0.56 0.51×0.55

tribution plots for N₂ at 77.3 K and Ar at 77.3 K show inaccurate pore-size maxima. The results are summarized in Table 1. This calibration procedure allowed a precise pore-diameter determination for the AMM-Si material. Fig. 12 shows the AMM-Si catalyst with a pore-size maximum of 0.62 nm located between both zeolite structures. As already expected from the broad transition region in the plot adsorbed volume vs. log p/p_0 , the AMM material has a broader micropore distribution than the zeolites. The HK method can be applied to differentiate micro pore size distribution maxima located close to each other in a physical mixture of two different zeolite materials as shown in Fig. 12. According to Fig. 13, HK indicates also the presence of micropores in both mesoporous materials, the MCM-41 and the mesoporous SiO₂. Fig. 14, the micropore distribution of these mesoporous materials plotted with a different scale of the y-axis suggest the clear presence of micropore volume confirming the t -plot and the α_s -plot as discussed above. However, as

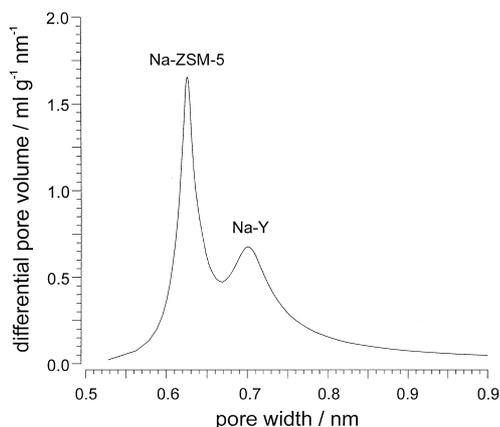


Fig. 12. Pore-size distribution of Na-Y and Na-ZSM-5 in competitive adsorption (from Fig. 10).

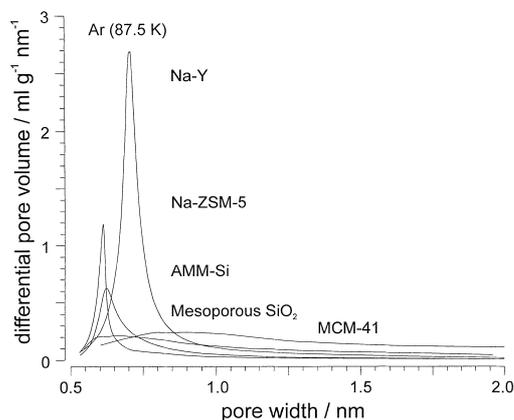


Fig. 13. Pore-size distributions of all tested samples according to the HK method with Ar at 87.5 K.

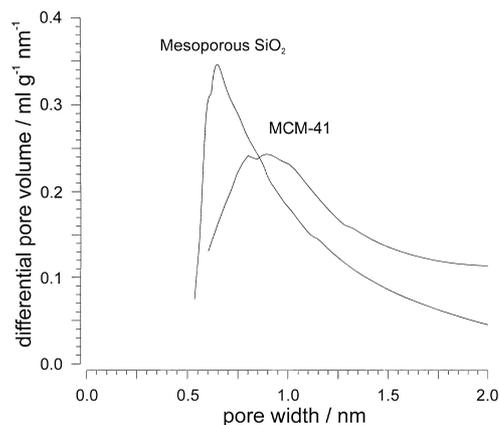


Fig. 14. Pore-size distributions of MCM-41 and mesoporous SiO₂ samples according to the HK method with Ar at 87.5 K from Fig. 13 with different scale of the y-axis.

already outlined above, the absence of a point of inflection in the high-resolution isotherm is direct evidence for the absence of micropores in these materials. Therefore, this micropore assignment of the HK method as well as of the t -plot and the α_s -plot must be an error. We recommend to apply these secondary methods only, if the high-resolution isotherm shows a clear point of inflection in the micropore region.

6. Conclusions

For the analysis of new microporous materials, a calibration procedure with substances of defined pore

sizes to find the proper adsorbate and temperature conditions was shown. It has been confirmed that only with the use of argon as adsorbate at the temperature of boiling argon, adsorption isotherms can be used to differentiate between the transition pressures and pore-size maxima of micropores of different sizes. The presence of micropores should exclusively be identified by inflection points in the high-resolution isotherm at low p/p_0 and we recommend strongly to use the plot of adsorbed volume against $\log p/p_0$ as already suggested by others. Isotherm shape, HK treatment, α_s -plot and t -plot have been shown to be misleading. Pore-size distributions obtained by the HK method and assignments from α_s - and t -plots should only be trusted, if the former condition is fulfilled. We have shown that the physisorption analysis of microporous solids can be carried out routinely with commercial technical equipment if proper calibration and calculation procedures have been applied.

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