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# Structural Characterization of Micro- and Mesoporous Carbon Materials Using In Situ High Pressure <sup>129</sup>Xe NMR Spectroscopy

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Supporting Information

ABSTRACT: In situ high pressure <sup>129</sup>Xe NMR spectroscopy in combination with volumetric adsorption measurements were used for the textural characterization of different carbon materials with well-defined porosity including microporous carbide-derived carbons, ordered mesoporous carbidederived carbon, and ordered mesoporous CMK-3. Adsorption/desorption isotherms were measured also by NMR up to relative pressures close to  $p/p_0 = 1$ at 237 K. The <sup>129</sup>Xe NMR chemical shift of xenon adsorbed in porous carbons is found to be correlated with the pore size in analogy to other materials such as zeolites. In addition, these measurements were performed loading the samples with *n*-nonane. Nonane molecules preferentially block the micropores. However, <sup>129</sup>Xe NMR spectroscopy proves that the nonane also influences the mesopores, thus providing information about the pore system in hierarchically structured materials.



# INTRODUCTION

Porous carbon materials are crucial components in various fields including adsorption/separation of gases,<sup>1–3</sup> electro-chemical energy storage,<sup>4–6</sup> catalysis,<sup>7,8</sup> capacitive desalination of water,<sup>9</sup> and biomedicine.<sup>10,11</sup> They stand out due to their high thermal stability, chemical inertness, and electrical conductivity. Appropriate materials need to exhibit a large and well-defined contact area between the carbon surface and the surrounding species because many applications include adsorption processes. High specific surface areas are provided by high contents of micropores (<2 nm according to the IUPAC classification). Therefore, their controlled integration into porous carbon materials is of fundamental interest in present day's materials science. The selective removal of metal atoms from carbide precursors using a treatment in hot halogens (most commonly chlorine gas) is one method for the production of microporous carbon materials (carbide-derived carbons, CDCs) with sub-Ångstrøm accuracy.<sup>12</sup> The pore size and carbon microstructure can be controlled by the halogenation conditions and the distribution of carbon atoms in the carbide precursor. The very narrow pore-size distribution together with high specific surface areas of up to  $3000 \text{ m}^2/\text{g}$  make CDCs attractive candidates for gas storage,<sup>2,13,14</sup> catalysis,<sup>15,16</sup> or as electrode materials in electrochemical double-layer capacitors (EDLCs).14,17,18

However, certain applications, such as drug delivery or the removal of cytokines from blood plasma require the adsorption of large organic molecules, which cannot be immobilized in narrow micropores due to their dimensions exceeding the size of the cavities. In such a case, mesopores (2-50 nm) are required as adsorption sites.<sup>10,11</sup> In addition, they serve for enhanced materials transport within the adsorptive system. This makes their presence highly important.<sup>14,17</sup> The synthesis of mesoporous carbon materials is mostly carried out using methods based on structure-directing agents (denoted as softtemplating)<sup>19,20</sup> or solid-state templates (denoted as hardtemplating or "nanocasting").<sup>21</sup> One of the most widely known families of materials produced by nanocasting are the so-called CMKs (Carbons Mesostructured by KAIST). They are produced by infiltration of carbon sources (e.g., sucrose) into ordered mesoporous silica (e.g., SBA-15 or KIT-6) followed by carbonization and template removal. The resulting carbon materials offer a system of ordered and uniformly sized

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mesopores and are therefore highly suitable for size-selective applications.  $^{\rm 22}$ 

Both, the CDC approach and the nanocasting technique can be combined, and the resulting materials exhibit an ordered mesopore system coupled with well-defined micropores. These ordered mesoporous carbide-derived carbons (OM-CDCs) are obtained by infiltration of polycarbosilane polymers into ordered mesoporous silica followed by pyrolytic conversion to silicon carbide (SiC) and wet chemical template removal. The resulting ordered mesoporous SiC (OM-SiC) is then transferred to OM-SiC-CDC by selective silicon extraction associated with the insertion of large micropore volumes in the carbon nanorods under the conservation of the mesopore structure.<sup>14,23</sup> These materials offer outstanding performance in various electrochemical energy storage applications and capacitive deionization of water due to their impressive specific surface areas of up to  $3000 \text{ m}^2/\text{g}$  and total nanopore volumes as high as 2.0 cm<sup>3</sup>/g.<sup>9,14,23</sup> Whereas the microporous carbon nanorods serve for high capacities, the mesopore channels in between facilitate efficient materials transport and rapid access of guest molecules to the adsorption sites. Consequently, OM-CDCs offer advanced kinetics when used as electrode materials in EDLCs<sup>23</sup> or in adsorption processes.<sup>14</sup>

The use of such complex materials in applications related to adsorption processes requires a detailed understanding of their pore structure (i.e., their size distribution, curvature, accessibility, volume, and surface properties) in order to optimize them for a specific field of interest and to understand basic mechanisms. While characterization based on spectroscopy, Xray scattering, electron microscopy, calorimetry, or mercury intrusion as well as combinations of them are very suitable, the physisorption of gases will likely remain the most frequently used technique for textural imaging of porous solids because it enables the calculation of important properties such as the specific surface area, total pore volume and pore-size distribution.<sup>24</sup> Commonly, physisorption of nitrogen (77 K), argon (87 K), and carbon dioxide (273 K/298 K) or combinations of these techniques are useful for the characterization of various nanoporous structures.<sup>25</sup> However, the most complex and hierarchical structures are often difficult to analyze. Therefore, additional adsorption techniques have been developed.

For instance, nitrogen physisorption before and after preadsorption of *n*-nonane is a useful tool to better distinguish between the meso- and micropores because the latter are selectively blocked by the hydrocarbon molecules. This method was proven to deliver deep insights into the pore structure of ordered mesoporous silica materials (OMS) as well as hierarchical activated carbons with a cavitation-linked mesostructure.<sup>26,27</sup> Very recently, this method was used for the characterization of carbide- and carbon materials with ordered mesopores and varying amounts of micropores.<sup>28</sup> Preadsorption of *n*-nonane provides information about the pore connectivity, and contributions of the different pore systems to the total pore volume can be directly determined. However, while some effects of the *n*-nonane adsorbed in the micropores upon the mesopore system of the materials were already observed, these phenomena are still neither fully understood nor quantified.

<sup>129</sup>Xe NMR spectroscopy of adsorbed xenon is another very useful method for the characterization of porous solids because it allows us to directly investigate the physical state of adsorbed molecules. Xenon is an inert, nonpolar spin-1/2 atom with a high NMR sensitivity and a large electron cloud which is very sensitive to different interactions with various environments, resulting in a wide chemical shift range. Consequently, <sup>129</sup>Xe NMR spectroscopy offers many interesting parameters, such as the chemical shift, the line width, the chemical shift anisotropy, and the longitudinal relaxation time  $T_1$  that can be correlated to structural properties of the porous materials. This technique was first described by Ito and Fraissard in 1980.<sup>29</sup> Since then, different porous solids, such as silica, zeolites, and carbons were characterized.<sup>30–48</sup> Recently, <sup>129</sup>Xe NMR spectroscopy was also used to monitor the adsorption-induced breathing transitions in metal–organic frameworks (MOFs).<sup>49–51</sup>

In general, the overall chemical shift of adsorbed <sup>129</sup>Xe depends on xenon-surface interactions and density-dependent xenon-xenon interactions:<sup>29</sup>

$$\delta(T,\rho) = \delta_{\rm S}(T) + \delta_{\rm Xe-Xe}(T,\rho) \tag{1}$$

where  $\rho$  denotes the xenon density and T the absolute temperature. For low xenon densities, i.e., low relative pressures, the density-dependent term can be written as follows:

$$\delta_{\mathrm{Xe-Xe}}(T,\rho) = \Delta_{\mathrm{Xe-Xe}}(T)\rho \tag{2}$$

with the temperature-dependent slope  $\Delta_{Xe-Xe}(T)$ . Extrapolation of the measured <sup>129</sup>Xe chemical shift to zero density/ pressure therefore yields the xenon-surface interaction term  $\delta_S(T)$ . Previous investigations on various amorphous carbon materials revealed that this value depends on a number of different materials properties. It could be shown to be correlated with the concentration of acidic groups,<sup>38</sup> strong adsorption sites, heteroatoms,<sup>40</sup> and the average pore size.<sup>42</sup> The virial coefficient  $\Delta_{Xe-Xe}$ , i.e., the slope of the chemical shift with increasing xenon density inside the pores can also deliver information about the microporous carbon material under study.<sup>41,43,44</sup> However, the previously published <sup>129</sup>Xe NMR investigations on carbon materials were limited to rather low relative pressures.<sup>30-47</sup>

Within the present work, we investigated a series of nanostructured carbon materials (CMK-3, OM-SiC-CDC-800, and two purely microporous TiC-derived carbons) with well-defined or even hierarchical porosity in the range from 0.6 to 4.5 nm using high-pressure in situ <sup>129</sup>Xe NMR spectroscopy up to 18 bar at 237 K. This allowed the NMR study of adsorption/ desorption isotherms up to a relative pressure close to 1. The NMR parameters can be well correlated with the pore structures, rendering this spectroscopic method as highly useful for the characterization of complex porous carbon structures. The shift of the NMR signals after saturation of micropores with *n*-nonane provides additional information about the mesopore systems, pore connectivity, and the adsorption state of the hydrocarbon molecules.

#### EXPERIMENTAL SECTION

**Synthesis of CMK-3.** Hexagonally ordered mesoporous carbon (CMK-3) was synthesized by mixing a 10 mL aqueous solution of 2.5 g sucrose and 0.28 g concentrated (96%) sulfuric acid with SBA-15 (hydrothermally treated at 403 K)<sup>28</sup> in a Petri dish. This mixture was then heated to 373 K and kept there for 6 h followed by heating to 433 K and keeping for another 6 h ensuring complete polymerization of the carbohydrate molecules. For complete infiltration of the SBA-15 pore system, the infiltration was repeated with a 10 mL solution of 1.6 g sucrose and 0.18 g sulfuric acid in water again followed by heating to 373 and 433 K. Carbonization was achieved by heating the composite up to 1173 K for 2 h under flowing argon (150 K/h heating rate) in an

alumina tube in a horizontal tubular furnace. Template removal was performed by a 3 h treatment in a 1:1:1 mixture (by volume) of water, ethanol, and 35% aqueous hydrofluoric acid solution followed by filtration, washing with large amounts of ethanol, and drying at room temperature.

Synthesis of OM-SiC-CDC-800. For the synthesis of ordered mesoporous carbide-derived carbons (OM-SiC-CDCs), 2.0 g of SBA-15 (hydrothermally treated at 403 K)<sup>28</sup> were infiltrated with a mixture of 2.1 mL liquid allylhydridopolycarbosilane (SMP-10, Starfire Systems) and 0.5 mL of the cross-linker para-divinylbenzene by the incipient wetness method. The polymeric precursor was thermally decomposed at 1073 K for 2 h under flowing argon atmosphere (60 K/h heating rate) in an alumina tube in a horizontal tubular furnace. Silica removal was achieved under the same conditions as described for the CMK-3. Approximately 1.0 g of the obtained OM-SiC was then transferred to a quartz boat and placed in a quartz tube (inner diameter: 25 mm) into the isothermal zone of a horizontal tubular furnace. The precursor was heated to 1073 K under an argon flow of 150 mL/min (450 K/h heating rate) and subsequently, the gas flow was changed to a mixture of 70 mL/min argon and 80 mL/min chlorine for 3 h. Cooling of the OM-SiC-CDC-800 to a temperature of 873 K under an argon flow of 150 mL/min was followed by 1 h of postreductive treatment under 80 mL/min of flowing hydrogen for the removal of chlorine and chlorides from the porous carbon.

Synthesis of Microporous TiC-CDCs. The microporous CDCs were obtained by high-temperature chlorination followed by postreductive hydrogen treatment of crystalline TiC powder (Sigma-Aldrich, 95%; particle size ~4  $\mu$ m) under the same conditions as for the above-described OM-SiC-CDC-800. The maximum chlorination temperature was either 873 K/600 °C (TiC-CDC-600) or 1273 K/ 1000 °C (TiC-CDC-1000).

*n***-Nonane Preadsorption.** Preadsorption of *n*-nonane was performed in a homemade manometric equipment developed at the Advanced Materials Group (LMA, University of Alicante), now commercialized as N2Gsorb-6 (Gas to Materials Technologies) using the following procedure: after degassing the material at 523 K for 4 h, the sample was exposed to *n*-nonane (Aldrich, 99%) for 30 min at 77 K and then left in contact with the liquid for 3 h at room temperature.

Characterization. After degassing for at least 5 h at 423 K, nitrogen physisorption experiments were carried out at 77 K on a Quadrasorb apparatus (Quantachrome Instruments, U.S.A.). The high resolution nitrogen physisorption isotherms were collected at 77 K on an Autosorb 1C instrument (Quantachrome Instruments, U.S.A.). Specific surface areas were calculated according to the Multi-Point BET method  $(p/p_0 = 0.05-0.2$  for OM-SiC-CDC-800 and CMK-3 and 0.01-0.1 for the TiC-CDCs). Total pore volumes (TPVs) were determined from the amount adsorbed at  $p/p_0 = 0.97$ . Pore size distributions (PSDs) were calculated using the Quenched Solid Density Functional Theory (QSDFT) method for nitrogen on carbon (slit/cylindrical pores, adsorption branch kernel).<sup>52</sup> Micropore volumes (MPVs) are estimated from the cumulative pore volumes at a diameter of 2 nm. The Autosorb 1C was also used for the carbon dioxide physisorption measurements at 273 K. Volumetric xenon adsorption/desorption measurements at 237  $\pm$  3 K were performed on a Belsorb HP apparatus (Bel, Japan). Raman spectroscopic investigations were carried out on a Holospec f/1.8 Spectrograph (Kaiser Optical systems, U.S.A.) working at 785 nm excitation wavelength.

<sup>129</sup>Xe NMR Spectroscopy. All <sup>129</sup>Xe NMR experiments were carried out using a homemade in situ high-pressure apparatus.<sup>49</sup> Samples were transferred into the single crystal sapphire tube under argon atmosphere (Glovebox). Afterward, the samples were activated overnight using high vacuum  $(10^{-8} \text{ to } 10^{-7} \text{ bar})$  to prevent artifacts due to surface adsorption of atmospheric molecules. The application of relative pressures  $p/p_0$  up to 1 would require an absolute pressure of ca. 60 bar at room temperature. Although the sapphire tube withstands such pressures, the tubing connecting the tube inside the magnet with the outside pump rack and xenon reservoir does not allow this pressure. At the chosen lower temperature (237 ± 3 K), however, a relative pressure of 1 corresponds to ca. 19 bar which is well accessible

for our apparatus. After pressurizing the samples, a subsequent equilibration phase of at least 15 min has been deferred. In the case of cooled samples a further phase of at least 1 h was incorporated for thermal equilibration. All experiments were performed using an Avance 300 (Bruker, Karlsruhe, Germany) NMR spectrometer coupled with a BIOSPIN SA BCU-Xtreme unit (Bruker, Karlsruhe, Germany). The <sup>129</sup>Xe NMR spectra were recorded at a resonance frequency of 83.02 MHz using a 10 mm HR probe, a pulse length of 6  $\mu$ s, and relaxation delays of 5 s. Temperature calibration and referencing of the <sup>129</sup>Xe NMR chemical shift have been performed as previously described.<sup>49</sup>

#### RESULTS AND DISCUSSION

The structural properties of the four investigated carbon materials derived from the nitrogen adsorption/desorption measurements (Table 1 and Supporting Information (SI)

Table	1.	Porosity	Data	of	the	Porous	Carbon	Samples <sup><i>a</i></sup>
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sample	SSA (m²/g)	TPV (cm <sup>3</sup> /g)	MPV (cm <sup>3</sup> /g)	APS (nm)						
CMK-3	1396	1.42	0.1	1.0/4.5						
TiC-CDC-1000	1652	0.74	0.59	0.8						
TiC-CDC-600	1412	0.60	0.54	0.6						
OM-SiC-CDC-800	2838	2.05	0.55	1.0/4.1						
<sup>a</sup> SSA: Specific Sur	rface Area,	TPV: Total	Pore Volur	ne, MPV:						
Micropore Volume, and APS: Average Pore Size.										

Figure S1) have been previously described.<sup>53</sup> Due to the purely microporous character of the TiC-CDCs, their nitrogen physisorption isotherms are of type I according to the IUPAC classification. In the semilogarithmic plots of the isotherms (SI Figure S2), higher nitrogen uptake at low relative pressures can be observed for the TiC-CDC-600 due to the presence of rather narrow micropores of 0.6 nm diameter in this sample compared to TiC-CDC-1000 containing 0.8 nm sized pores (SI Figure S3). The largest micropores of 1.0 nm are present in OM-SiC-CDC-800. CMK-3 shows a relatively low uptake of nitrogen below a relative pressure of  $p/p_0 = 0.1$ due to the small micropore volume (Table 1). In contrast to the controlled insertion of the micropores into OM-SiC-CDC-800, the presence of micropores in CMK-3 is due to the formation of defects during decomposition of the carbon precursor. In consequence, they are not as well connected to the mesopore system as the micropores in the hierarchical CDC material.

Carbon dioxide physisorption measurements at 273 K up to 1 bar ( $p/p_0 \approx 0.03$ ) additionally show the large differences in the micropore structure of the investigated samples (Figure 1). Under these conditions, CO<sub>2</sub> adsorption is very sensitive to the presence of narrow micropores.<sup>1,28</sup> As a consequence, the highest amount of gas at 1 bar is adsorbed in the pore system of the TiC-CDC-600 due to the presence of the narrowest micropores followed by TiC-CDC-1000 and OM-SiC-CDC-800 in agreement with their increasing micropore size. CMK-3 shows the lowest uptake due to the lower micropore volume and relatively large micropore diameter of 1.0 nm.

The presence of distinct hysteresis loops in the nitrogen physisorption isotherms of the OM-SiC-CDC-800 and CMK-3 at relative pressures of  $0.4 < p/p_0 < 0.7$  indicates the presence of small and narrowly distributed mesopores in these carbon materials. Their sizes were calculated to be 4.1 and 4.5 nm for OM-SiC-CDC-800 and CMK-3, respectively (SI Figure S3). The good agreement between the QSDFT method and the



Figure 1. Carbon dioxide adsorption/desorption (filled symbols/ empty symbols) isotherms of OM-SiC-CDC-800 (circles), CMK-3 (squares), TiC-CDC-1000 (triangles), and TiC-CDC-600 (diamonds) measured at 273 K.

experimental data for all samples (SI Figure S4) indicates that this method calculates reliable pore-size distributions for the investigated samples.

The <sup>129</sup>Xe NMR spectra measured at a temperature of 237 K and a xenon pressure of 11 bar show at least two resolved <sup>129</sup>Xe NMR signals (Figure 2). The signals at low chemical shifts of



**Figure 2.** <sup>129</sup>Xe NMR spectra for isothermal xenon adsorption on OM-SiC-CDC-800, CMK-3, TiC-CDC-1000, and TiC-CDC-600 measured at 237 K at a xenon pressure of 11 bar  $(p/p_0 = 0.64)$ .

ca. 0–20 ppm are due to xenon in the gas phase. The signals of adsorbed xenon occur at higher chemical shifts of 100–300 ppm. In addition to the intense signal of adsorbed xenon and the gas phase signal, a third signal appears for TiC-CDC-600 (denoted by an asterisk in Figure 2) at ca. 35 ppm. Its intensity amounts to only 4% of the signal of adsorbed xenon at 264 ppm. Due to the low chemical shift and intensity, the signal can be attributed to macropores, e.g., between the particles. Xenon in these macropores interacting with the outer surface of the TiC-CDC-600 particles would give rise to such a chemical shift.

Two of the samples under study, TiC-CDC-1000 and TiC-600 exclusively show micropores of 0.8 and 0.6 nm average diameter. Correspondingly, the <sup>129</sup>Xe NMR spectra of these samples only exhibit one signal due to adsorbed xenon (Figure 2). The highest chemical shift is observed for xenon adsorbed at TiC-CDC-600. It should be noted that an inverse correlation between the pore size and the <sup>129</sup>Xe chemical shift is wellknown, e.g. for zeolites.<sup>54</sup> The observed behavior therefore indicates that the micropore diameter in TiC-CDC-600 is smaller than in TiC-CDC-1000-in agreement with the nitrogen and carbon dioxide adsorption data (Table 1, Figure 1, and SI Figure S1). It is also remarkable that the line width in TiC-CDC-600 strongly exceeds the line width in the other samples (Figure 2). This can be explained in two ways: (i) Xenon is more strongly adsorbed in TiC-CDC-600, probably due to the narrow micropores of 0.6 nm in size that is close to the kinetic diameter of xenon (0.44 nm). (ii) Surface inhomogeneity (despite the well-defined pore size) due to the rather amorphous carbon microstructure in this sample can be another reason for line broadening.<sup>38</sup> Recently, the higher concentration of hydrogen atoms on the surface of TiC-CDC-600 compared to materials obtained at higher chlorination temperature such as TiC-CDC-1000 has been shown by <sup>1</sup>H MAS NMR measurements.<sup>53</sup> (iii) In addition, xenon clusters of different size may be formed within the micropores which would give rise to a chemical shift distribution.

To better characterize the degree of graphitization of the materials under study, Raman spectroscopic investigations have been performed (SI Figure S5). Two characteristic bands in the Raman spectra of such materials denoted as D and G are usually considered (SI Figure S5,A).<sup>55,56</sup> The disorder-induced D-band arises from a double-resonance process (intervalley scattering), whereas the graphitic G-band is related to in-plane stretching vibrations of sp<sup>2</sup> sites. The increasing intensity of both bands in carbon materials prepared at increasing temperature indicates an increasing graphitization (i.e., the growth and enlargement of the sp<sup>2</sup>-bonded sites in the pore walls). Up to a sample treatment temperature of ca. 1000 °C, the D-band intensity increases even stronger than the Gband.<sup>55</sup> That means, the initially increasing  $I_{\rm D}/I_{\rm G}$  band intensity ratio in carbide-derived carbon materials prepared at increasing temperature indicates the proceeding graphitization, i.e., the growth and enlargement of the sp<sup>2</sup>-bonded sites in the pore walls. Finally, at very high temperatures, the D-band starts to decrease. The highest  $I_D/I_G$  ratio of 1.44 is observed for TiC-CDC-1000. The lowest value of 1.26 occurs for TiC-CDC-600, while OM-SiC-CDC-800 (1.43) and CMK-3 (1.43) are comparable in graphitization to TiC-CDC-1000 (SI Figure S5,B). These observations are characteristic for CDCs prepared at comparable temperatures.<sup>9,13,17,55,56</sup> In addition, the decreasing full width at half-maximum of the D band indicates a lower degree of graphitization in the carbon materials prepared at lower temperatures (SI Figure S5,C).<sup>13,16</sup> That means the surface of TiC-CDC-600 is less graphitized and contains more hydrogen atoms than the other porous carbon materials.

Interestingly, two distinct signals can be detected for adsorbed xenon in CMK-3 (Figure 2): signal (1) at ca. 190 ppm and signal (2) at ca. 230 ppm with an intensity ratio of approximately 90:10, in agreement with previous observations for CMK-3.<sup>46</sup> These signals were interpreted as being due to mesopores (1) and micropores (2). In agreement with nitrogen and carbon dioxide physisorption isotherms, (Table 1, Figure 1,

and SI Figure S1), the chemical shifts of the micropore signal are lower than those observed for the micropores in the TiC-CDCs due to the larger micropores in CMK-3. The mesopores represent a more than ten times higher fraction of the overall pore volume. At 11 bar, signal (1) exhibits an asymmetry which becomes even more pronounced at higher pressure, finally resulting in two closely neighbored signals (SI Figure S6). This can be attributed to the presence of two slightly different mesopores due to the partial presence of tubular structures within the carbon nanorods. At lower pressures, rapid exchange results in an averaged signal. However, this exchange obviously becomes slow at increasing pore filling.

The pressure-dependence of the NMR chemical shift of the xenon adsorbed in purely microporous samples TiC-CDC-600 (Figure 3) and TiC-CDC-1000 (SI Figure S7) closely



Figure 3. <sup>129</sup>Xe NMR chemical shift for TiC-CDC-600 measured at 237 K as a function of relative pressure.

resembles a type I adsorption/desorption isotherm. Note that the chemical shift steeply increases up to a relative pressure p/ $p_0$  of ca. 0.2 for the micropores. Beyond a relative pressure of ca. 0.2, the chemical shift levels off and reaches a constant value. This indicates that the pore system is filled with xenon at relative pressures of  $p/p_0 = 0.2$  for microporous samples. This behavior could be expected for the signal intensity since the <sup>129</sup>Xe NMR signal intensity represents the amount of adsorbed xenon in an isothermal adsorption/desorption measurement. However, the <sup>129</sup>Xe NMR chemical shift is also correlated with the xenon density  $\rho$ , i.e., the amount of adsorbed xenon (eq 1). Therefore, the pressure-dependence of the chemical shift should also resemble the shape of the adsorption/desorption isotherm-as it is indeed observed. Over the entire relative pressure range, TiC-CDC-600, which exhibits the smallest average pore diameter, shows the highest chemical shift, followed by TiC-CDC-1000. It is furthermore remarkable that the "saturation value" of the chemical shift of xenon in micropores clearly exceeds the chemical shift value of 203 ppm observed for liquid xenon at 237 K.49 This is due to the fact that xenon-wall interactions are predominating in microporous materials even if the pore system is completely filled. In contrast, the final chemical shift values for xenon inside mesopores is close to 200 ppm since the xenon condensed within the mesopores is similar to the bulk liquid (see below).

It is interesting to compare these observations with the pressure-dependence of the <sup>129</sup>Xe NMR chemical shift and the

signal intensity of the two signals in CMK-3 (Figure 4). Both the chemical shift as well as the intensity of the signal (1)



**Figure 4.** Top: <sup>129</sup>Xe NMR chemical shift of the signals due to mesopores and micropores observed for CMK-3 at 237 K as a function of relative pressure. Bottom: <sup>129</sup>Xe NMR signal intensity of the signals due to mesopores and micropores observed for CMK-3 at 237 K as a function of relative pressure.

follow a dependence characteristic for adsorption isotherms of mesoporous materials (cf. Figures 2 and 4). In contrast to TiC-CDCs, the final chemical shift value for xenon inside the mesopores is close to 200 ppm, since the xenon condensed inside the pores is similar to the bulk liquid xenon. For signal (2), the curves resemble type I adsorption isotherms which are characteristic for microporous materials. Over the entire range of relative pressure, the chemical shift of the signal (2) is lower compared to the TiC-CDCs due to the larger size of the micropores in CMK-3.

The advantage of the chemical shift measurement is its inherently high accuracy compared with the measurement of the signal intensity. At the chosen measurement temperature of 237 K, neither the volumetrically measured adsorption/desorption isotherm (SI Figure S8) nor the <sup>129</sup>Xe NMR signal intensity measurements (Figure 4, bottom) show a hysteresis which is observed at lower temperature in the nitrogen adsorption isotherms (SI Figure S1). However, the very sensitive <sup>129</sup>Xe NMR chemical shift clearly reflects the onset of a corresponding hysteresis behavior at relative pressures  $p/p_0$  of ca. 0.5–0.6 (Figure 4, top and Figure 5).



**Figure 5.** <sup>129</sup>Xe NMR spectra of CMK-3 measured after xenon adsorption and during xenon desorption at 237 K for 8 bar  $(p/p_0 = 0.46)$  and 10 bar  $(p/p_0 = 0.58)$ . Note that the chemical shift for xenon inside the mesopores (signal (1)) is different for the adsorption and desorption spectra at identical pressures (hysteresis) in contrast to the micropore signal (2).

The presence of two distinct signals for mesopores and micropores in CMK-3 shows that the exchange between the two pore systems must be slow at the NMR time scale, i.e., compared with the critical time constant which is defined by  $(2\pi\Delta\nu)^{-1}$ .  $\Delta\nu$  denotes the frequency difference between the two signals which amounts to 3300 Hz (40 ppm) at 11 bar (Figure 2). Thus, the exchange of xenon between micro- and mesopores must be considerably slower than the critical time constant of 50  $\mu$ s. Indeed, 2D Exchange Spectroscopy (EXSY) was unable to detect any exchange between the different pore systems even at a mixing time of 500 ms (SI Figure S9). It should be noted that an exchange of xenon between micro- and mesopores of CMK-3 could be detected at room temperature and low xenon pressure  $p_{Xe} = 0.53$  bar within a mixing time of 50 ms.<sup>46</sup> At 237 K and high pressure, the mobility of xenon is obviously very limited, which effectively suppresses xenon exchange between the two pore systems in CMK-3. In addition, the accessibility of the micropores in CMK-3 might be hindered due to narrow entrances resulting from their uncontrolled growth during carbonization further hindering the exchange of xenon between both pore systems.

Note that the micropores in the three samples, TiC-CDC-600, TiC-CDC-1000, and CMK-3 exhibit a similar general dependence on the relative pressure resembling a type I adsorption isotherm—but with pronounced quantitative differences. In particular, the "plateau value"  $\delta_{\text{max}}$  of the chemical shift obtained by extrapolation of the chemical shift to  $p/p_0 = 1$ is obviously influenced by the pore size. It amounts to  $260 \pm 3$ ppm for TiC-CDC-600 (0.6 nm average pore diameter),  $250 \pm$ 3 ppm for TiC-CDC-1000 (0.8 nm average pore diameter), and  $235 \pm 3$  ppm for the micropores in CMK-3 (1 nm average pore diameter). These values are all larger than the chemical shift of 203 ppm expected for liquid xenon at the experiment temperature of 237 K.<sup>49</sup> In contrast, the signal due to xenon atoms in the mesopores of CMK-3 only exhibits a  $\delta_{max}$ -value of 205 ± 3 ppm close to the value expected for liquid xenon. This observation shows that the  $\delta_{max}$ -value pronouncedly depends on the presence of xenon–wall interactions and is obviously correlated with the average pore diameter. Advantageously,  $\delta_{max}$  can be easily measured since the slope of the chemical shift in the high-pressure regime is small and the signal intensity is high—in contrast to the chemical shift  $\delta_{\rm S}$  determined by extrapolation to zero pressure (see above, eq 1). We, therefore, suggest the use of  $\delta_{max}$  as a measure for the pore size which can be determined precisely in an inherently sensitive high-pressure <sup>129</sup>Xe NMR experiment.

In addition to the mesoporous CMK-3 and the TiC-CDCs, we have investigated the hierarchically ordered mesoporous carbon sample, OM-SiC-CDC-800, which contains significant amounts of both, mesopores and micropores (Table 1). In contrast to CMK-3, however, only one single narrow signal of adsorbed xenon is observed for OM-SiC-CDC-800 (see Figure 2). Interestingly, the signal appears at 209 ppm, i.e., in between the chemical shift values of micropores (230-260 ppm) and the chemical shift of xenon inside the mesopores of CMK-3 (190 ppm) at 11 bar xenon pressure. In contrast to CMK-3, the well interconnected micro- and mesopores in OM-SiC-CDC-800 obviously allow a fast exchange of adsorbed xenon between micro- and mesopores. As a result of this fast exchange, a signal at the averaged chemical shift is detected as previously reported for the adsorption of electrolyte ions in this hierarchically structured carbon material.53 This is observed over the full relative pressure range up to  $p/p_0 = 1$  (Figure 6). It is also



**Figure 6.** <sup>129</sup>Xe NMR chemical shift for OM-SiC-CDC-800 measured at 237 K as a function of relative pressure. For comparison, the corresponding data for CMK-3 are given.

remarkable that the chemical shift  $\delta_{max}$  extrapolated to a relative pressure of 1 amounts to ca. 225 ± 3 ppm. This is in between the value observed for mesopores (205 ppm) and micropores (235 ppm) in CMK-3 (see above). This is in line with the conclusion that the xenon atoms exchange rapidly between mesopores and micropores in OM-SiC-CDC-800. Moreover, the observed average signal exhibits a lower line width than the other samples under study. This also indicates a high mobility of the xenon and/or well-defined pore size of this material.

Finally, we have characterized the hierarchical samples after n-nonane loading using <sup>129</sup>Xe NMR spectroscopy. This

treatment preferentially closes the micropores thus making them practically inaccessible for other molecules, whereas the mesopore system remains accessible. Note that the presence of a low but measurable amount of micropores in CMK-3 as well as a well-interconnected hierarchical pore structure in the OM-SiC-CDC-800 with large contributions from both micro- and mesopores were demonstrated by nitrogen physisorption measurements before and after *n*-nonane-preadsorption.<sup>28</sup> The <sup>129</sup>Xe NMR spectra of the two mesoporous samples CMK-3 and OM-SiC-CDC-800 before and after *n*-nonane loading at a pressure of 11 bar and 237 K (Figure 7) prove the



Figure 7. <sup>129</sup>Xe NMR spectra of the mesoporous samples CMK-3 and OM-SiC-CDC-800 before and after loading with *n*-nonane measured at 237 K at a xenon pressure of 11 bar  $(p/p_0 = 0.64)$ .

different pore structures present in both samples. The quantitative blocking of the micropores by the hydrocarbon molecules causes the disappearance of the signal due to adsorbed xenon in the micropores of CMK-3 at ca. 230 ppm. However, the signal of xenon adsorbed in the mesopores is located at higher chemical shift after n-nonane loading. This observation indicates that the mesopores are also modified by hydrocarbon loading. The pressure-dependence of the chemical shift (SI Figure S10) shows that the hysteresis loop shifts toward a slightly lower relative pressure compared to the nonane-free material. These observations indicate that the mesopores become smaller during *n*-nonane loading. Moreover, the chemical shift value  $\delta_{\max}$  of the xenon adsorbed in the mesopores extrapolated to relative pressures of 1 is also slightly larger than before *n*-nonane loading indicating a stronger influence of xenon-wall interactions caused by the presence of *n*-nonane in the mesopores. It is known for hierarchically structured materials-especially for materials with an ordered mesopore structure-that n-nonane molecules blocking the micropores in the neighborhood of mesopores can also partly

penetrate into the larger pores explaining the shift of the hysteresis loop toward lower relative pressure.  $^{26,28}\!$ 

A similar situation is observed in OM-SiC-CDC-800. An even larger volume of micropores is blocked by the hydrocarbon molecules significantly decreasing the overall porosity of OM-SiC-CDC-800 + n-nonane compared with CMK-3.<sup>28</sup> This should result in a significantly decreasing <sup>129</sup>Xe NMR chemical shift provided the mesopores remain uninfluenced by the nonane. However, the signal of the adsorbed xenon atoms shows a minor change toward higher chemical shift (Figure 7, bottom and SI Figure S11). That means, loading with *n*-nonane also influences the mesopores as observed for CMK-3, which gives rise to the increased chemical shift. Two effects may contribute to this chemical shift increase, namely (i) the decreasing pore size of the mesopores due to the presence of *n*-nonane at the pore walls and (ii) a stronger interaction between xenon and the nonane molecules compared with the graphene-like pore walls in nonane-free samples.53

#### CONCLUSIONS

In situ high pressure <sup>129</sup>Xe NMR spectroscopy in combination with volumetric adsorption measurements and n-nonane preadsorption were used for the textural characterization of different carbon materials with well-defined porosity. While xenon adsorbed in the micro- and mesopores of CMK-3 gives two different signals due to their spatial separation, only one averaged signal can be observed in the strongly hierarchical OM-SiC-CDC-800, due to the well-connected pore systems allowing fast exchange of adsorbed xenon. This method can be used to clearly distinguish between different micropore sizes as shown by the investigations on two TiC-derived carbons with different pore size. Full adsorption/desorption isotherms up to relative pressures  $p/p_0$  close to 1 were recorded. The chemical shift  $\delta_{\max}$  extrapolated to a relative pressure of 1 is suggested as a sensitive measure for the micropore diameter. It can be measured with high accuracy and sensitivity. The agreement with the volumetric adsorption data renders this method as highly useful for the pore structure analysis of different carbon materials. The changes in the spectra of the hierarchical materials after the blocking of the micropores with *n*-nonane provides information about the adsorption state of the hydrocarbon molecules in the carbon structure leading to a better understanding of the connectivity of micro- and mesopores which is of interest for various applications.

#### ASSOCIATED CONTENT

# **Supporting Information**

Figure S1: Nitrogen adsorption/desorption isotherms measured at 77 K. Figure S2: Semilogarithmic plot of the nitrogen adsorption/desorption isotherms. Figure S3: QSDFT pore-size distributions. Figure S4: QSDFT fitting comparisons. Figure S5: Raman spectra,  $I_D/I_G$  ratio and fwhm of the D band. Figure S6: Pressure-dependence of the <sup>129</sup>Xe NMR spectrum of xenon adsorbed on CMK-3 measured at 237 K. Figure S7: <sup>129</sup>Xe NMR chemical shift for TiC-CDC-1000 measured at 237 K as a function of relative pressure. Figure S8: Volumetric xenon adsorption/desorption isotherm of CMK-3 at 237 K. Figure S9: 2D EXSY spectrum of xenon adsorbed at 10 bar and 237 K on CMK-3. Figure S10: <sup>129</sup>Xe NMR chemical shift for CMK-3 after *n*-nonane loading measured at 237 K as a function of relative pressure. Figure S11: <sup>129</sup>Xe NMR chemical shift for OM-SiC-CDC-800 after *n*-nonane loading measured at 237 K as a function of relative pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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# **Author Contributions**

<sup>#</sup>The manuscript was written through contributions of all authors. M.O., H.C.H., J.P., and J.S. contributed equally to the presented work. All authors have given approval to the final version of the manuscript.

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#### Notes

The authors declare no competing financial interest.

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