resulted in xerogels with larger mesopores and more robust structure, similarly as before. The ES-APT and ES-ATM xerogels were thermally stable up to 250 and , respectively.

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CO₂ adsorption in synthetic hard carbons

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1. INTRODUCTION

Carbon aerogels, sol-gel derived, open porous hard carbons, show a two step adsorption kinetics for CO₂ at 273K (and 295K) that is not detected for N₂ at 273 K. A similar behavior, however, with different adsorption rates has also been reported for other types of hard carbons [1-4]. A detailed investigation of the two adsorption steps for carbon aerogels as a function of relative pressure reveals that the slower step actually corresponds to a larger micropore size; this suggests two well defined types of micropores to be present in the same sample, an easily accessible one and a wider, however, bottleneck type set of micropores [5]. The comparison of samples with different macropore sizes but similar microporosity shows that the adsorption rate for the bottleneck type micropores is not affected by the morphology of the samples on the macropore scale nor the sample dimensions. The investigation presented here focuses on the adsorption kinetics of the fast adsorption step of CO₂ in these synthetic hard carbons.

2. EXPERIMENTAL

2.1. Samples

The carbon aerogels investigated were monolithic solids prepared from sol-gel derived organic precursors via pyrolysis at 1050 °C [6,7]. The starting solution used for the synthesis of the organic gels consisted of resorcinol, formaldehyde (37,5 wt.% in water), water as the solvent and Na₂CO₃ as the catalyst. The relative volume of the solid phase in the organic precursors was adjusted via the mass ratio

$$R_M = \frac{M_{\text{resorcinol}} + M_{\text{formaldehyde}}}{M_{\text{resorcinol}} + M_{\text{formaldehyde}} + M_{\text{water}} + M_{\text{catalyst}}}, \quad (1)$$

with M_x the mass of the respective component; for the samples presented here the mass ratio R_M was set to 30 % resulting in a carbon aerogel density of about 0.3 g/cm³. For all samples the molar ratio of resorcinol to formaldehyde was kept constant (R/F= 0.5). At fixed mass

ratio the meso- and macrostructure of the organic gels was varied via the catalyst concentration and by changing the time that the gelling sol was kept at room temperature (see Table 1) prior to further aging the samples for 1 day at 90 °C. The so called R/C ratio, i.e. the molar ratio of resorcinol to sodium carbonate catalyst, was set to 1000 and 1500, respectively. The time at room temperature was 0 and 4 days, respectively. After aging, the water in the pores of the aquagels was replaced by acetone prior to drying the samples at 50 °C and ambient pressure.

Table 1
Synthesis parameters for the three different samples prepared.

sample	R_M	R/C	R/F	aging /gelling time at room temperature
#1	0.3	1500	0.5	4
#2	0.3	1500	0.5	0
#3	0.3	1000	0.5	0

2.2. Morphological characterization of the samples

The morphology of the porous carbons was characterized by small angle X-ray scattering (SAXS) as well as nitrogen sorption at 77K and sorption of carbon dioxide at 273 K.

SAXS was performed at the beam-line JUSIFA at the synchrotron source HASYLAB, Hamburg. To determine the scattering cross section for the sample investigated on an absolute scale, the scattering of the sample was calibrated using a glassy carbon standard as a reference.

The sorption isotherms were taken with a commercially available volumetric instrument (ASAP 2000, software 2010, Micromeritics).

2.3. Measurements of adsorption kinetics

The adsorption kinetics was recorded using cylindrical carbon aerogel monoliths (diameter about 1.6 cm, height about 1cm) in combination with a volumetric sorption instrument (designed at Wuerzburg University) that is equipped with a standard and a fast pressure transducer [8]. Upon dosing of carbon dioxide the maximum pressure increase in the sample chamber (volume about 125 ccm) of the instrument was set to about 5 mbar. Due to the restrictions of the instrument the experiments were performed at a temperature of 295 K rather than 273 K.

3. RESULTS

3.1. Morphological characteristics

Fig. 1 shows the small angle X-ray scattering for the three samples investigated. The curves qualitatively show that the micropore characteristics are almost identical for all aerogels investigated while the scattering related to the envelope surface of the particle forming the open porous skeleton of the hard carbons clearly varies.

Fig.1. SAXS data for the three samples investigated; note that the data are given on an absolute scale. The cartoons indicate the morphology of the different carbon aerogels consisting of a network of microporous particles with different average diameters.

The data were quantitatively evaluated with respect to the total micropore volume and the external surface area of the carbon skeleton. Details of the procedure applied can be found in ref. [5]. The characteristic particle and pore sizes as well as the micropore volume of the samples are given in Table 2.

Table 2

Morphological parameters derived from SAXS and sorption data, with ρ the sample density, V_{micro}/m the specific micropore volume, S/m_{particle} the external specific surface area of the microporous particles and d_{mesopore} and d_{particle} the average diameter of the mesopores and the particles, respectively.

sample	SAXS					N ₂ sorption (77K)		CO ₂ sorption (273 K)
	density (g/cm ³)	V_{micro}/m (cm ³ /g)	$(S/m)_{\text{particle}}$ (m ² /g)	d_{pore} (nm)	d_{particle} (nm)	V_{micro}/m (cm ³ /g)	V_{micro}/m (cm ³ /g)	
#1	0.33±0.02	0.27±0.02	1.7±0.06	5400±280	2700±160	not detectable	0.24±0.01	
#2	0.31±0.02	0.29±0.02	17.9±0.6	550±29	261±15	0.24±0.01	0.30±0.01	
#3	0.34±0.02	0.36±0.02	155±5	55±3	33±2	0.20±0.01	0.26±0.01	

3.2. Adsorption kinetics

The adsorption kinetics for carbon dioxide at 295 K is shown versus square root of time in Fig.2, both, for sample #2 at different relative pressures as well as for all samples at a relative pressure of 0.0017. The plots clearly show two distinct adsorption steps except for sample with the smallest macropores (#3).

Fitting of the curves with a superposition of two adsorption steps yields for the slow adsorption step an almost sample and pressure independent diffusion coefficient.

Left: Adsorption kinetics of carbon dioxide at 295 K for sample #2; the dashed lines represent corresponding fit curves (see text). The parameters given are the relative pressures of each run. Right: Adsorption kinetics of carbon dioxide at 295 K for all three samples at a rel. pressure of 0.0017.

Diffusion coefficients D as derived from a fit of the experimental data in Fig.2 with the solution diffusion equation for cylindrical sample (open circles); in addition, values corrected for the amount of gas to be transported ($D \cdot \Phi_{\text{pseudo}}$, full circles) are depicted. For comparison the theoretical values for gas phase diffusion in cylindrical pores are also included (dashed lines); the value of the macroporosity (50%) and a tortuosity factor of 3 are taken into account. The porosity was calculated from the bulk density of the sample and the micropore volume: $\text{porosity} = \text{total porosity} - \text{microporosity} = 86\% - 36\%$.

The fast adsorption provides the diffusion coefficients plotted in Fig.3. To account for the different amounts of gas to be transported to the sorption site, the experimental diffusion coefficients have been corrected by the so called "Pseudoporosity"

$$\Phi_{\text{pseudo}}(p/p_0) = \Phi + \frac{V_{\text{ads}}(p/p_0)}{V_{\text{pore, total}}} \quad (2)$$

that includes both, the actual porosity Φ of sample and the apparent porosity that corresponds to the amount removed from the gas phase via adsorption. V_{ads} is the volume adsorbed (in STP) and $V_{\text{pore, total}}$ is the total pore volume of the sample. For comparison, the diffusion coefficient (molecular diffusion plus viscous flow) for capillaries of different sizes are included.

4. DISCUSSION

The analysis of the adsorption kinetics of the fast adsorption step (sample #2) yields a pressure dependence that is characteristic for surface diffusion: the diffusion coefficient varies as the derivative of the corresponding sorption isotherm which is governed by micropore adsorption [9].

The "surface" diffusion is therefore related to transport along the micropores rather than the external surface of the particles that form the skeleton of the aerogels. In addition, gas phase transport takes place that can be described by a superposition of molecular diffusion and viscous flow in capillaries with an average diameter of about the pore size in the respective sample and a tortuosity of about 3. The value of 3 was chosen to match the experimental data; it is slightly higher than the value of about 1.8 detected for other carbon aerogels ([10]: $1.8 = 1.35^2$).

Comparing aerogels with different pore macropore sizes (samples #2 and #3), however, a similar microporosity yields diffusion coefficients that differ by about a factor of 10, i.e. the ratio of the respective macropore sizes. I.e. despite the same microporosity and an even larger external surface the surface transport component decreases with the pore size (see also ref. [10]).

5. SUMMARY AND CONCLUSIONS

CO₂ adsorption at 295K in carbon aerogels pyrolyzed at 1050 °C takes place via two sorption steps:

The step with the slow adsorption kinetics is essentially independent of the morphology of the samples on the meso- and macropore scale indicating restricted diffusion at the mouth of the micropores.

In contrast, the fast adsorption step reflects the different macropore sizes of the samples under investigation. In particular the diffusion coefficients determined from the experimental data reveal a superposition of "surface" and gas phase diffusion, with the latter corresponding

to the theoretically expected value for a bundle of capillary that have about the size of the pores present in the samples investigated.

The "surface" contribution clearly correlates with the isotherm resulting from the adsorption in the micropores. Comparing samples with different macropore sizes, the absolute value of the (total, transient) diffusion coefficients is found to be proportional to the macropore size of the carbons; this indicates a transport that is dominated by molecular diffusion coupled with surface transport at low relative pressures.

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Characterisation of Nanoporous Aluminosilicate Monoliths Derivatised with Metal Cations for Selective Propene-Propene Adsorption

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Monoliths SiO₂-Al₂O₃ with a desired shape and size have been synthesized via direct liquid crystal templating pathway (DTLC) combined with sol-gel method and subsequently functionalised with metal cations. Effects of metal loading and metal addition method on structural properties of functionalised materials were tested and discussed. The technique of copper and silver addition used in the present work included the conventional impregnation, wetness impregnation and ion exchange, as well as the direct incorporation during synthesis. Additionally, for the functionalised adsorbents, the metal cation effect, Cu²⁺, Ag⁺, and Ag⁺, on the propene adsorption capacity was investigated.

1. INTRODUCTION

Cryogenic distillation has been used for over 60 years for the recovery and refining of ethylene and propylene from olefin plants, refinery gas streams, and other sources [1]. In addition to this highly energy intensive distillation process, a number of alternative separation technologies, e.g. extractive distillation, physical or chemical adsorption or absorption, membrane separation have been investigated [2, 3-5]. Especially, adsorption has been explored in the last years to carry out olefin/paraffin separations because the adsorbent can increase the separation factor several times and also diminish cost demands. Yet only a few reports are devoted to separation by selective adsorption onto solid substrates, such as carbon black [6], zeolite 13X [7], activated carbon, silica gel and zeolite A [8, 9] or ordered mesoporous silica [10, 11-12]. The most promising technological approach is separation based on the mechanism of π -complexation between the alkene double bond and transition metal cations, mostly Cu or Ag. CuCl in the form of crystals has been considered for olefin/paraffin separations as early as 1939 [13, 14]. Preferential sorption of the alkene via formation of π -complexes, resulting from charge donor-acceptor interactions between appropriate atomic and molecular orbital, was first explained by Dewar [15]. The bonds formed between the metal cations and the olefins are stronger than those formed by Van der Waals forces alone and thus, selective olefin adsorption is expected. Therefore, it is possible