

Ceramers—functional materials for adsorption techniques

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Abstract

Ceramers were prepared by using commercially available polymethyl- and polymethylphenylsiloxanes as starting materials and converting them by pyrolysis in a nitrogen atmosphere to a hybrid state called ceramer. The microstructures were modified by adding prepolyrized polymethylsiloxanes as filler or by using a blowing agent to fabricate foamed ceramers. The porosity characteristics were quantitatively evaluated using nitrogen adsorption whereas the hydrocarbon sorption behaviour was investigated by adsorption and desorption processes via thermogravimetry. For comparison commercial activated carbons, which are especially designed for hydrocarbon adsorption, were characterized in the same way. It turns out that the new ceramer adsorbents can be used as alternative material for activated carbon. Moreover, they show a significant advantage against activated carbon as the adsorbed species can be easily released, e.g. by heating. Therefore, the ceramers are especially suitable for cyclic ad- and desorption processes as it is necessary for storage or purification applications.

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1. Introduction

The pyrolysis of preceramic precursors was established as a new processing method for advanced ceramics only some years ago.¹ Using monomeric silanes or polymeric siloxanes as starting material, SiC or SiOC materials can be obtained by shaping, cross-linking and pyrolytic conversion in inert atmosphere at elevated temperatures. The porosity of these materials depends mainly on the type and network structure of the cross-linked precursor and on the conditions of pyrolysis, especially on the final temperature. At temperatures beyond 800 °C SiOC is formed and at high temperatures (1500 °C) SiC ceramics with very low porosities can be produced. In contrast, materials with very high specific surface areas beyond 600 m²/g are obtained at lower pyrolysis temperatures. While polymer degradation starts at about 400 °C the evolution of volatile species reaches its maximum during the pyrolysis treatment in the temperature range of 500–700 °C. Stopping the pyrolysis at this stage of conversion leads to highly porous and surface-rich materials in a hybrid state where the polymer is just partly converted to

ceramic.² The resulting material is therefore called ceramer. The porosity and inner surfaces of the precursor derived ceramics can also be influenced by fillers. Dense, crack and shrinkage free monolithic ceramics can be prepared by using active fillers which react with decomposition products emerging during polymer pyrolysis.³ On the other hand, the porosity can be further adopted by using inert fillers, which prevent shrinkage.

Due to their high microporosity the ceramers are suited for applications like adsorption processes. Possible applications of these materials are then the areas of separation, gas storage, catalysis and removal of pollutants. One of the most important challenges posed by the increasingly stringent regulation of air pollution in many countries, is therefore, the search for efficient and economical control strategies for volatile organic compounds (VOCs), e.g. hydrocarbons. At present, the applicable technology for VOC control is adsorption on activated carbon with subsequent recovery or incineration.^{4,5} Sorption behaviour of activated carbons is widely investigated and owing to their large specific surface areas, high micropore volumes and rapid adsorption capabilities adsorption by activated carbons offers an efficient technology.^{6–9} However, it has been recognized that adsorption on activated carbon is also subject of disadvantageous effects,¹⁰ such as fire risk, pore plug (due to polymerisation of some VOCs

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catalysed by ashes present on activated carbon surfaces), hygroscopicity, and some problems associated with regeneration. For example it is well known that during adsorption of a multicomponent mixture of hydrocarbon (e.g. gasoline) on a bed of activated carbon, the higher molecular weight components of the vapour mixture tend to build up within the smaller pores in the carbon.¹¹ These heavier components are not completely removed from the activated carbon bed while purging (desorption) and lower the working capacity, which is defined as the amount of adsorbate purged from a saturated activated carbon bed using dry air. Thus, even if the working capacity is very high the adsorbed species either may desorb uncontrollable or cannot be totally removed by forced gas flow.

Due to described disadvantages of activated carbons the development of alternative adsorbents is necessary. Siloxane derived ceramers seem to be a promising alternative as will be shown.

In a practical VOC removal process, an ideal adsorbent is expected to offer a large amount of reversible adsorption capacity (large accessible pore volume), non catalytic activity, hydrophobic properties, high thermal and hydrothermal stability, and an easy regeneration cycle.

The objective of the present study is the investigation of the adsorption characteristics of vapourized hydrocarbons on ceramers as a function of their microstructure. In order to find relationships between the dynamic adsorption capacity and the structural properties of the ceramers their specific surface, pore size distribution and pore volumes are determined.

2. Experimentals

2.1. Materials

In order to investigate the correlation between the porosity characteristics and the adsorption properties different ceramers with and without foaming agents are produced and compared with commercially available activated carbons. As base for the production of the ceramers different industrial siloxane resins are used; the solid polymethylsiloxane PMS precursor MK (Wacker AG, Germany), the liquid polymethylsiloxane precursor M120XB (GE Bayer Silicones, Germany), where the polymer is solved in 50 wt.% Xylene, and H44 (Wacker AG, Germany), a polymethylphenylsiloxane, which was used for the foamed ceramers. Fig. 1 shows the processing route in detail. For some specimens 5 wt.% of MK which was prepyrolyzed at 600 °C in inert atmosphere and milled to particle size of less than 125 µm was added as filler to M120XB and H44, respectively. The liquid polymer M120XB was mixed with acetone under stirring and after 1 h the content of solvent was decreased by adding excess of water and finally the precursor was isolated by decanting the solvent. The foamed ceramers were prepared by dissolution of H44 and the polymeric 1 wt.% aluminum catalyst (NX 6521, Hüls, Germany) in acetone. Then the solvent was removed

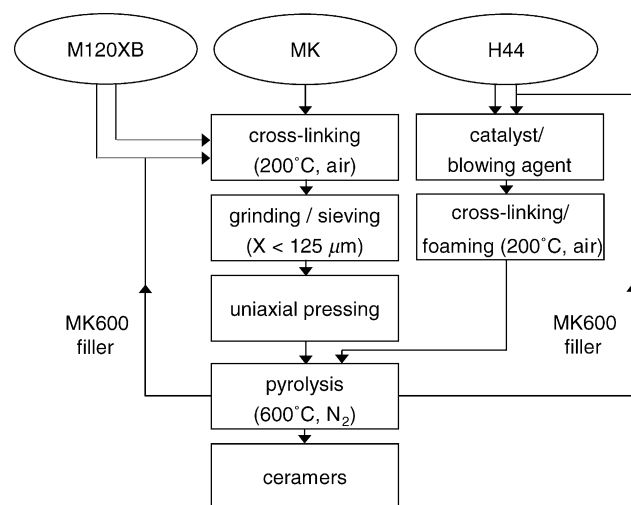


Fig. 1. Scheme of preparation of foamed and non-foamed ceramers.

in vacuum and the precursor was further dried at 60 °C and finally ground. This powder was mixed up with a commercially available blowing agent of the azodicarbonamid type (Unifoam® AZ, Hebron S.A., Spain). For some specimens the prepyrolyzed filler MK was added in this stage of processing.

In the next processing step the preceramic polymers were cross-linked upto 200 °C (2 h) in air with dwelling times at 80, 140 and 200 °C. The unfoamed materials were ground and sieved in order to obtain fine powders with particle size below 125 µm. Then the powder was pressed into samples of 30 mm × 40 mm × 5 mm. Finally the specimens were heat treated in a flowing nitrogen atmosphere at 600 °C. Some specimens were foamed and cross-linked under identical conditions as noted above. Pyrolysis was carried out under inert atmosphere at 500 °C resulting in a highly porous ceramer with large bubble like pores.

In this study the produced ceramers were compared with wood-based activated carbons (Nuchar® BAX 1500, BAX 1100 and HCA) which are commercially available (Mead-Westvaco, USA) and which are especially designed for hydrocarbon vapour adsorption. While BAX 1500 and BAX 1100 are pelletized HCA is a monolithic honeycomb. In Table 1 the various ceramers and activated carbons investigated in the work are listed.

Table 1
Ceramer and carbon materials investigated in different shapes

Ceramer	Material	Shape
Ceramer	MK600	PMS, pyrolysed at 600 °C, powder pellet
	H44	PMPHS, foam
	H44 + MK600	PMPHS containing MK600 filler, foam
	M120XB	PMS, powder pellet
	M120XB + MK600	PMS containing MK600 as filler, powder pellet
Activated carbon	BAX1500	Pellets
	BAX1100	Pellets
	HCA	Honeycomb

2.2. Characterization

The porous microstructures of the foamed and unfoamed ceramers are investigated using different methods in order to understand the adsorption and desorption processes taking place during subsequent experiments. The specific surface area, the pore volume and the pore size distribution were determined by nitrogen ad-/desorption at 77 K (Micromeritics ASAP 2010). Surface areas were calculated from adsorption data using BET equation in the P/P_0 range of 0.05–0.30.¹² The density functional theory (DFT) which is based on thermodynamical principles was used to calculate pore volumes and pore size distribution in the micro- ($r < 2$ nm), meso- ($2 \text{ nm} < r < 50$ nm) and macroporous ($r > 50$ nm) range.^{13,14} A significant feature is that the density functional theory method applies over the complete range of the isotherm and is not restricted to a confined range of relative pressures or pore sizes.

The ceramers and the activated carbon materials were tested for their hydrocarbon vapour sorption properties using a standard mixture of different hydrocarbons called CARB (California Air Resources Board) gasoline. The experiments were performed under dynamic conditions in a magnetic suspension balance (Rubotherm, Germany) by measuring mass gain and loss under different flowing conditions. The specimen was placed in a chamber, which was first heated up to 100 °C in order to remove adsorbed gas from the surface by a nitrogen flow. The hydrocarbon mixture was then transported into the chamber by a nitrogen flow through a tempered flask filled with CARB. The hydrocarbon saturated nitrogen flow (10 ml/min) entered the chamber directly resulting in mass changes of the specimens which were kept at 22 and 41 °C, respectively. After saturation, desorption was started at 41 °C by purging the specimen chamber with air (15 ml/min) for at least 14 h.

3. Results and discussion

3.1. Characteristics of porosity

Nitrogen gas adsorption isotherms were determined for evaluating the fundamental microstructural parameters of the materials (Fig. 2). The isotherms registered for the various ceramers exhibit considerable differences depending on the composition and on the type of the used polysiloxane. MK600, which was used as filler after being pyrolyzed at 600 °C and milled to powder, exhibits a type I isotherm according to IUPAC classification which is characteristic for microporous materials.¹⁵ Similar results are received for foamed ceramers made of H44 independent of the addition of MK600 powder.

In contrast to these ceramers the M120XB based material containing MK600 as filler shows type IV isotherms with a hysteresis at relative pressures above 0.4 indicating a larger amount of mesopores. The pyrolysis of the pure M120XB precursor without MK600 filler leads to isotherms which

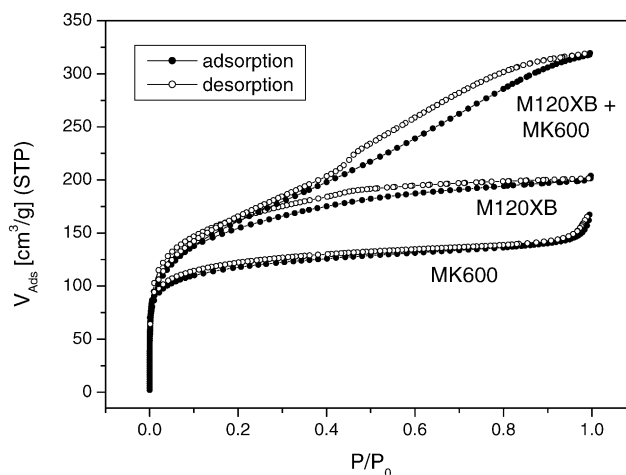


Fig. 2. N₂ adsorption–desorption isotherms of different ceramers.

show an intermediate state of type I and type IV curves. This material is mainly microporous but contains still contains a small amount of mesopores. From the maximum adsorbable gas volume it becomes clear that the ceramer MK600 has the smallest total pore volume whereas the ceramer derived from M120XB contains a higher pore volume. If MK600 is added to M120XB the total pore volume can be further increased. Obviously the filler particles enhance the pore formation as shrinkage of the bulk is prevented during pyrolysis, and therefore, the decomposition of the material during thermal treatment leads to additional mesopores.

Fig. 3 gives an overview of the pore size distribution grouped in micro-, meso- and macropores. Specific surface areas and the ratio of micro- and mesopore volumes (MMR) are also shown. All ceramers produced by pyrolysis of M120XB and MK show almost identical micropore volumes in the range of 0.12–0.16 cm³/g. Distinctive differences

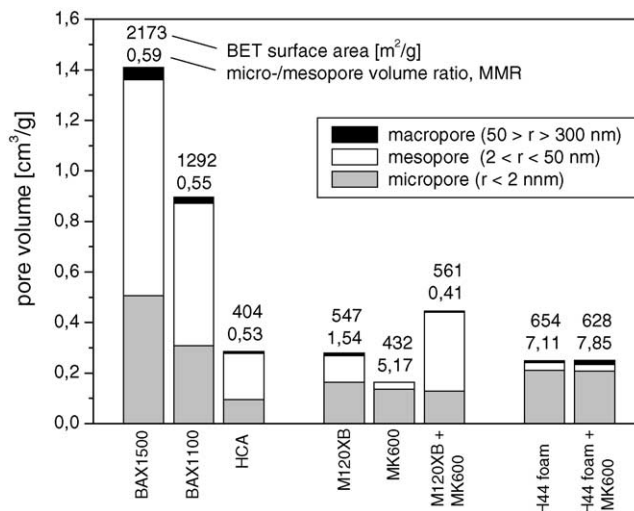


Fig. 3. Pore volume of the studied materials in the range of micro-, meso- and macropores according to DFT. Additionally BET surface areas and the ratio of micro- and mesopore volume is quoted.

are, however, manifested in their mesopore volumes. MK600 has only a small amount of mesopores whereas the mesopore volume of M120XB derived specimen is increased significantly. Adding MK600 filler to the M120XB precursor can be used to change the mesopore volume considerably. Fig. 3 shows a specimen based on this composition with a rather high mesopore volume. It should be mentioned that under identical conditions further specimens of this type were received with a wide range of mesopore volumes. The reason for this is not fully understood yet; it is, however, assumed that cross-linking is the decisive processing step. Small changes in network structure of the precursor lead then to different amounts of resulting pores when the volatile species emerge from the cross-linked body during pyrolysis. The calculated macropore volume is almost negligible in all ceramers and does not play an important role concerning the perspective applications of these materials.

The specific surface area evaluated according to BET analysis is generally rather high in the ceramers investigated. It increases with higher mesopore volume.

The foamed H44 based ceramers show a significantly higher content of micropores in combination with a very low mesopore volume. Therefore, the MMR is rather high with values between 7 and 8. The large pores resulting from the foaming process are not included in the measurement of the pore volume as only the micro-, meso- and partially the macropore range can be attributed to the N_2 -adsorption process. The resulting pore size and pore volume of the foamed H44 ceramers are independent of the use of MK600 fillers. Due to foaming the material shows a bubble like microstructure with thin walls where the volatiles may emerge easily during pyrolysis. This leads to a two-dimensional shrinkage in thickness of the cellular elements (struts, cell walls) which is fairly independent of the presence of filler particles. Therefore, the content of mesopores cannot be increased by adding MK600 filler.

The activated carbons were also analyzed concerning their pore volume and pore size distribution. It turns out that they show typical type IV isotherms characteristic for mesopore containing materials. The total pore volume is reduced from extremely high values in case of BAX1500 to about 50% in case of BAX1100 and to values in the range of the produced ceramers when a honeycomb structure is formed. The MMR, however, is not influenced by the different kinds of activated carbons.

3.2. Sorption behavior

In dynamic experiments the sorption behavior of the newly developed ceramers are investigated and compared with the performance of activated carbons. The specimens are placed in a continuous flow of carrier gas saturated with hydrocarbon vapour from CARB. MK600 shows a very low adsorption loading capacity at 22 °C while the M120XB derived ceramer adsorbs almost the double amount of vapour (Fig. 4). If MK600 is added to M120XB during processing the adsorp-

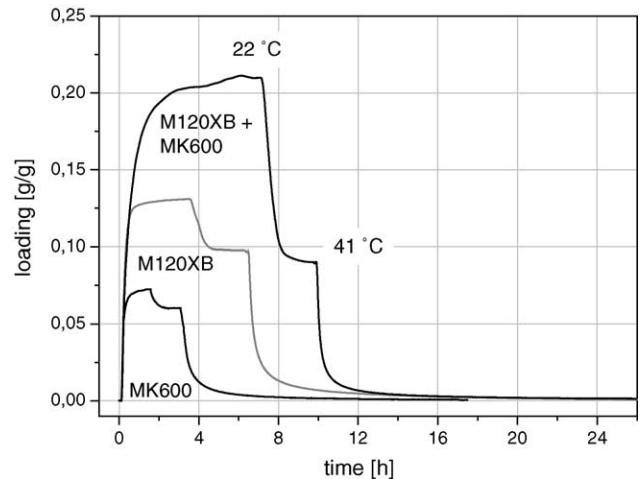


Fig. 4. Adsorption of hydrocarbon at 22 °C and 41 °C, respectively and succeeding gas flow (air) induced desorption at 41 °C. The loading ratio is determined by thermogravimetric measurements.

tion can be even more increased. Correlating these results with the pore structure it turns out that the loading capacity increases with total micro- and mesopore volume (Fig. 5). The loading capacity of the ceramers is much lower than that of activated carbon pellets. This is caused by the lower pore content; all materials investigated fit into the linear relation between the adsorbed vapour and the micro- and mesopore volume. Thus, the activated carbon honeycomb structure, which contains a pore volume comparable to that of the ceramers also shows the same amount of adsorbed vapour.

When the specimens are heated under vapour loading conditions from 22 to 41 °C the amount of adsorbed hydrocarbon is reduced. It should be noted that the amount of released vapour is much higher with decreasing MMR value (Figs. 3 and 4). This means that the vapour which is adsorbed at 22 °C in the micropores remains there during heating up to 41 °C while the vapour adsorbed in the mesopores is

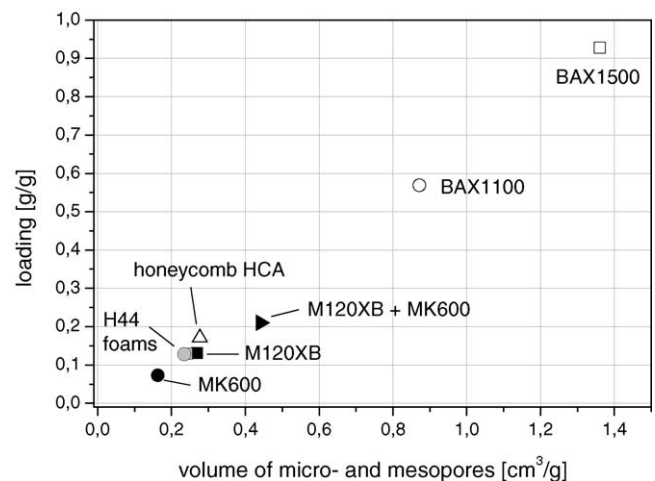


Fig. 5. Hydrocarbon loading at 22 °C dependent on volume of micro- and mesopores.

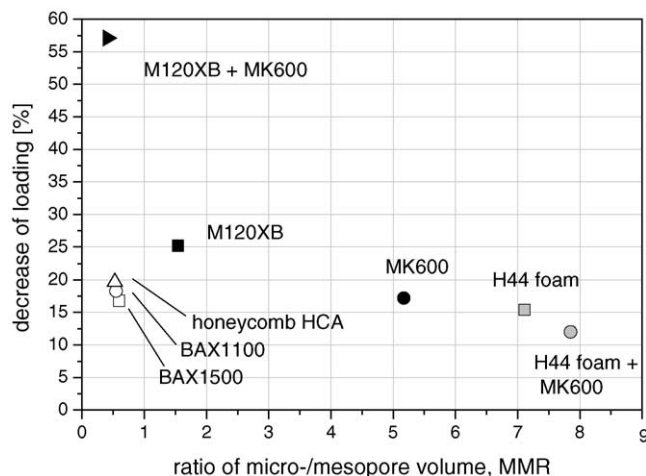


Fig. 6. Decrease of loading due to the increase of the adsorption temperature from 22 to 41 °C in relation to the ratio of micro- and mesopore volumes, MMR.

much easier released. Therefore, the remaining hydrocarbon in M120XB and in M120XB mixed with MK600 is almost on the same level after heating to 41 °C. In addition, the micropores can also be emptied completely by applying an air-flow at 41 °C (Fig. 4). Thus, it is possible to guarantee the total release of hydrocarbon vapour from these new ceramers simply by gas flow.

In Fig. 6 the amount of desorbed vapour during heating from 22 to 41 °C is correlated with the MMR value of the ceramers and activated carbons. The temperature induced desorption remains almost constant for the activated carbon materials, which corresponds with the invariable MMR of these materials. Obviously the total micro- and mesopore volume does not influence the desorption due to temperature increase. The ceramers, however, behave differently. At MMR values below 1 the release of adsorbed hydrocarbon increases dramatically with increasing mesopore content. Thus, the bonding of the hydrocarbons in the ceramer mesopores seems to be very weak. For $MMR > 1$, i.e. for lower mesopore volumes, the desorption is slightly but continuously reduced. The H44 derived foams fit well into this observed tendency. It can be concluded that a change of pore size distribution allows the controlled adjustment of the temperature induced loss of vapour (Fig. 6) while the total micro- and mesopore volume is responsible for the total amount of adsorbed hydrocarbons.

A significant difference between ceramers and activated carbons is observed if the materials are discharged by forced gas flow (Fig. 7). It is not possible to clean the activated carbons completely no matter if BAX1500, BAX1100 or the honeycomb structure is chosen. The honeycomb structure keeps the lowest amount of vapour (20%) while the BAX-materials are still loaded with even more than 30% of the maximum level at 41 °C after the desorption process. In contrast, the ceramers can be rinsed totally independent of the precursor. This is a very important advantage of these ceramers

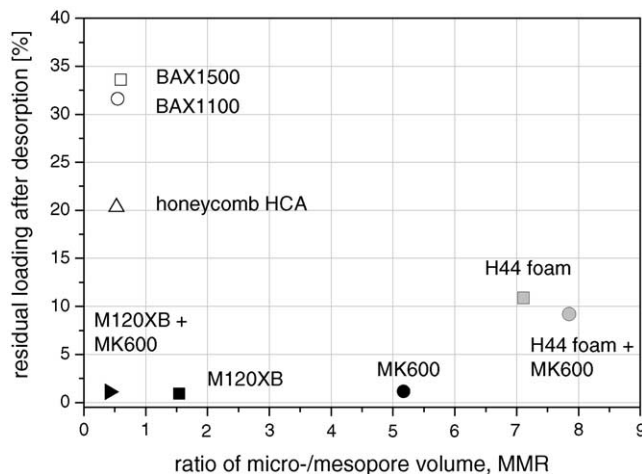


Fig. 7. Residual loading after desorption by forced air-flow for 14 h at 41 °C in relation to the ratio of micro- and mesopore volumes, MMR.

as it allows to control the vapour adsorption and desorption as desired in application. In case of the foamed ceramers a residual amount of adsorbed hydrocarbons remains. It can be concluded that for both the activated carbons and the ceramers the microstructural design must consider a suitable content of micro- and mesopores; of minor importance is the macroscopic design realising foams, honeycombs or pellets.

4. Conclusions

The newly developed ceramers can be designed in the total pore volume and in the pore size distribution in order to optimise the adsorption, desorption and the total remittance or release of hydrocarbons. It could be shown that the total amount of adsorbed hydrocarbons is in the same functional dependence on the total pore volume as it is the case for activated carbons. The very important advantage of the ceramers is the possibility to clean the adsorber totally from the adsorbed species whereas in case of activated carbon some vapour remains always trapped in the microstructure. Thus, the ceramers are especially usable for purposes where a controlled and total release of adsorbed species has to be realized.

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