Short communication

Preparation of an MFI zeolite coating on activated carbon

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Abstract

A new and simple method for the preparation of MFI zeolite coated activated carbon is presented. Suitable nucleation sites for the growth of zeolites were introduced to the carbon by adding hydrophilic montmorillonite clay to the carbon substrate. A gas tight MFI zeolite coating was obtained on this modified substrate by hydrothermal growth.

Keywords: Zeolite; Membrane; Silicalite-1; ZSM-5; Activated carbon; PSA

1. Introduction

Research in the field of adsorptive gas separation partly focuses on the development of more selective adsorbents [1]. Also, the importance of selective carbon materials in catalysis was pointed out [2]. Currently, we are working on the development of coated adsorbents for pressure swing adsorption (PSA). For this new type of adsorbents, the selectivity is enhanced by a selective membrane which is applied to the outer surface of the adsorbent particles in the PSA column (Fig. 1). The enhanced selectivity for coated adsorbents has been shown elsewhere [3] by preliminary model calculations.

The use of a zeolite membrane is especially interesting for the following reasons:

- High selectivity [4–7];
- High permeability for smaller gas molecules

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Fig. 1. Coated adsorbent for PSA.

(e.g., H₂, CO₂, CH₄, C₁–C₄ linear hydrocarbons) which is important for the capacity of a PSA cycle:

- High thermal and chemical stability;
- The hydrothermal synthesis method for the zeolite membranes may be suitable for the coating of particles.

In PSA usually the expensive carbon molecular sieves must be used to obtain a proper separation. For coated adsorbents, however, a cheap, poorly selective microporous activated carbon can be used instead, provided that the membrane enhances the selectivity.

The growth of a zeolite membrane on a porous carbon fibre substrate was reported by Smith and co-workers [8] who pointed out that carbon is a superior support for the production of inorganic composite membranes. The production of fibres gives a very attractive alternative for the known low surface area tubular or flat sheet zeolite membranes [4–7,9–11]. In this light, the preparation of zeolite-coated activated carbon particles for the use as coated adsorbent in a PSA process is very interesting: It provides an alternative way for increasing the membrane surface without the need for producing large areas at once. The module building problems currently limiting the use of inorganic membranes are overcome in this way.

The present communication describes an alternative method for the growth of a silicalite-I membrane on activated carbon. In contrast with the methods of Smith and co-workers [8] who used surface oxidation or impregnation with silicon atoms to introduce nucleation sites (increase hydrophilicity) to the inert carbon surface, here the nucleation sites are not introduced by such a chemical modification but simply by the addition of strongly hydrophilic, finely dispersed, montmorillonite clay powder (containing Si, Al, Mg, O, H) to the activated carbon substrate [12]. The substrate has a tablet geometry to facilitate characterisation of the membrane by gas permeation measurements.

2. Experimental

The activated carbon tablets were prepared from a 50/50 (wt. wt.) mixture of NORIT RB-1 activated carbon powder and demineralised water. For the activated carbon a sieve fraction $<13\ \mu\text{m}$ was used and 10% (w/w) bentonite (basically montmorillonite clay [13], Sigma) powder was added to increase the hydrophilicity of the carbon. The montmorillonite also acts as a binder. The particle

size of the bentonite powder was 0.2–0.3 μm (Microtrac X100 particle analyser). In one batch of tablets, 5% glycerol was added to the water as a lubricant to reduce the surface roughness of the tablets.

The paste was pressed into tablets using a mould with a diameter of 20 mm at a pressure of 250 bar (calculated for the tablet area) for 10 min. The tablets had a thickness of 1.2 mm. After pressing, the residual water was removed by evaporation during a heat treatment of 20 K min to 473 K and the tablets were baked during a subsequent heat treatment of 10 K min to 1073 K (dwell time of 1 h). All heating was performed in a nitrogen atmosphere. During baking, first the surface hydration water (353–433 K) and subsequently structural hydroxyl water (823–973 K) are removed from the montmorillonite clay [13]. Also the glycerol, if any present, was removed partly by evaporation and partly by decomposition during heat treatment [14]. The pore size distribution of the tablets was determined by mercury intrusion using a Carlo Erba Strumentazione Series 200 Porosimeter. The total porosity was calculated from the density in mercury (Mettler AT 200 balance) and helium (Micromeritics AccuPyc 1330), respectively.

The zeolite layer was grown hydrothermally using a mother lye for the growth of MFI zeolite silicalite-I as reported in [15] of the following composition: 1.14 g sodium hydroxide (Merck), 81.45 g tetrapropylammonium hydroxide solution (Fluka Chemika), 17.38 g silicic acid (J.T. Baker). The synthesis was performed at 393 K for 70 h. The tablets were put on the bottom of the autoclave. Prior to zeolite growth, no additional surface layer was used to reduce the surface pore size of the activated carbon substrate. After the synthesis the tablets were washed excessively with water of 333 K and dried at 353 K for 24 h followed by evacuation at approximately 50 Pa for at least 16 h. To remove the template from the zeolite pores the tablets were heated to 823 K (25 K/h) for 3 h in air.

For characterisation of the membranes, SEM (JEOL JSM-35 CF scanning microscope), X-ray diffraction (Philips PW 1710 X-ray diffractometer) and carbon dioxide permeation measurements in a dead-end cell were used. The coated tablet was

mounted in the permeation equipment as represented in Fig. 2.

3. Results and discussion

Strong activated carbon tablets were obtained after baking. The average pore size as determined by mercury intrusion is approximately $0.4\ \mu\text{m}$. However, the largest pores to be covered had a minimum span of approximately $5\ \mu\text{m}$ radius as observed by SEM. The average total porosity was 65%. The use of glycerol prevented the tablet from sticking to the mould during preparation and thus resulted in a smoother surface. A SEM picture of the surface of an activated carbon tablet prepared with glycerol is shown in Fig. 3a.

After the hydrothermal synthesis had been finished it was observed with SEM that a continuous top-layer with a thickness of 5 to $20\ \mu\text{m}$ was formed on the activated carbon tablets (Fig. 3b and 3c). The X-ray diffraction pattern of pure silicalite-1 powder (an MFI zeolite) and a coated tablet show close agreement (Fig. 4a and 4b, respectively) indicating that the observed layer was a crystalline MFI zeolite layer (though the presence of gas tight non-crystalline material in the layer cannot be excluded completely). Since the montmorillonite binder in the activated carbon tablet contains aluminium, the MFI zeolite may have some aluminium content and is more ZSM-5 than pure silicalite-1. This is not detectable by X-ray

Fig. 2. Mounting of coated activated carbon tablet for gas permeation: 1 activated carbon tablet, 2 zeolite membrane layer, 3 epoxy resin sealing, 4 perforated stainless steel support, 5 support ring for removal from the cell, 6 inlet, 7 O-ring, 8 bolt.

Fig. 3. SEM images (15 kV) of (a) the surface of an activated carbon tablet prior to growth; (b) the surface of a MFI zeolite coated tablet and (c) a cross-section of an MFI zeolite coated tablet.

diffraction. The reference X-ray diffraction pattern of an activated carbon tablet prior to growth is shown in Fig. 4c. No layer was formed on the surface of montmorillonite-free activated carbon

Fig. 4. X-ray diffraction patterns for (a) pure silicalite-1 powder, (b) MFI zeolite layer on an activated carbon tablet, (c) activated carbon tablet prior to growth.

extrudate particles that were in the same synthesis for reference. For both tablets and extrudates also growth of zeolite in the macropores inside the tablet and on the back-side of the tablet was observed but those pores were not blocked.

To test the MFI zeolite layer for defects, carbon dioxide permeation was used prior to removal of the template molecules from the zeolite pores. No permeation could be observed. This is a strong indication that the activated carbon tablets with macropores up to approximately 2 μm pore radius were coated with a defect-free MFI zeolite layer. Since the hydrothermal growth of zeolites is not very shape-dependent, this method may also be suitable for the coating of activated carbon particles (provided they contain montmorillonite).

It is assumed that montmorillonite exposes a suitable surface for heterogeneous nucleation and growth of MFI zeolite. This is in line with the observed failing layer growth on tablets that were prepared with the glycerol lubricant. In that case

the montmorillonite surface may have become covered by carbonaceous decomposition products of glycerol that were formed during baking [14].

The assumption of montmorillonite acting as nucleation site is also in line with growth experiments on pure bentonite tablets. Well attached MFI zeolite layers were found on those bentonite tablets. Again surface growth failed when glycerol was used during the preparation of the bentonite tablets.

From the presence of zeolite crystals inside the macropores of both types of tablets it can be concluded that the presence of decomposition products in the mother lye does not inhibit the growth of MFI zeolite.

A suitable method for the removal of the template molecules from the zeolite pores still has to be developed. The heating of the MFI zeolite coated activated carbon tablet to 823 K in air resulted in destruction of the activated carbon and therefore cracking of the MFI zeolite layer. Probably, a lower temperature, e.g., 673 K and a reduced oxygen content will be more successful. However, under these mild oxidation conditions coke formation in the zeolite pores may occur [4], resulting in poor permeation properties.

4. Conclusion

The addition of suitable nucleation sites in the form of finely dispersed montmorillonite facilitates the growth of a defect-free MFI zeolite layer on the surface of the activated carbon.

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