SYNTHESIS OF A CERAMIC ZEOLITE MEMBRANE BY MEANS OF A DIP-COATING TECHNIQUE

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ABSTRACT

The preparation of a composite ceramic membrane consisting of large silicalite (MFI-type) crystals, embedded in a ceramic matrix is reported. The dip-coating technique employing a boehmite sol, has been used to investigate the applicability of dip-coating in a direct membrane preparation procedure.

INTRODUCTION

In the development of ceramic membranes for gas separation, selectivities are expected to be improved by decreasing the pore diameter of the separating layer. Well-defined crystalline microporous materials like zeolites provide for sufficiently small and uniform pores. In addition, zeolites are stable up to sufficiently high temperatures to be used within ceramic membranes.

Different preparation procedures for ceramic zeolite membranes have been suggested [1,2]. A new preparation route starts from a monolayer of relatively large zeolite crystals (silicalite/ZSM-5 type), which are uniquely oriented on a macroporous support. In between the zeolite crystals a gas tight matrix is to be deposited to ensure that mass transport exclusively occurs through the zeolite micropores [3]. Selective deposition besides the zeolite crystals is favourable, as this may lead to a direct and easy preparation of a ceramic membrane with molecular sieve characteristics [4].

Here we report on the dip-coating of a boehmite sol, formerly used to prepare high temperature gas separation membranes showing Knudsen selectivity [5,6]. The resulting γ -alumina film is not gas tight, but demonstrates that the dip-coating technique can be favourably applied in the preparation of the present ceramic zeolite membrane. The effect of crystal shape and size as well as of zeolite coverage of the macroporous support on the dip-coating process has been studied.

EXPERIMENTAL

Relatively large silicalite crystals were prepared according to Chamami and Sand [7] (prisms), and Lermer [8] (cubes). The crystals were washed with water and ethanol and subsequently calcined at 500°C (heating rate 1°C/min). Table 1 gives an overview of the dimensions of the two crystal forms.

Table 1: Silicalite crystal dimensions

prisms (Sand-synthesis)	
a (μm)	35
b (μm)	30
c (μm)	170
cubes (Lermer-synthesis)	
a (μm)	100 - 250
b (μm)	50 - 150
c (μm)	200 - 350

Figure 1: Silicalite crystal forms and corresponding pore structure

Some 300 silicalite prismatic crystals of equal shape and size were oriented as a monolayer on top of two-layer α -alumina plate-shaped supports [9]. Some large cubic shaped crystals of silicalite were selected and positioned on similar supports. Prior to dip-coating, some adherence of the zeolite crystals to the support was required. This was achieved by absorption of water into the support and successively drying at 50°C.

Dip-coating experiments were performed with a boehmite (γ -Al₂O₃) sol [6], and a similar sol to which glycerol (1% by volume) was added. All substrates were dipped for 6 seconds (optimal dipping time) into the boehmite sol. A careful calcining procedure was required involving drying at 35°C for at least 24 hours, subsequently heating to 100°C (25°C/h), and finally heating to 500°C (100°C/h).

RESULTS

The dip-coating experiments with the Boehmite sol resulted in severely cracked films, for both prismatic and cubic shaped crystals. Reference films (appr. 3 μm in thickness) on substrates without zeolite crystals remained crack-free. Crack formation was strongly reduced when glycerol was added to the standard sol. Around separate crystals cracking mainly occurred at the sharp corners of the crystals (Figure 2).

Figure 2: Limited crack formation in the case of 1% glycerol added.

In Figure 3 it is shown that no deposition has occurred underneath the zeolite crystals, due to the slight adherence of the crystals to the microfiltration layer. The γ -alumina top layer is not connected to the zeolite crystal as a result of severe shrinkage of the film during heat treatment.

Figure 3: Silicalite crystal on top of a two-layer α -alumina support, on which a thin γ -alumina film is deposited. The γ -alumina film is not connected to the silicalite crystal, due to shrinkage during heat treatment.

Chemical analysis by means of EDAX did not reveal any deposition on top of the prismatic crystals. According to the chemical analysis, some deposition had occurred on top of the much larger cubic shaped crystals, which could not be observed by SEM. As the zeolite coverage increases, severe cracking occurs. The good adhesion of the dipping solution to the zeolite surface results, however, in a homogeneous deposition besides the zeolite crystals. The initially formed cracks could not be repaired by a second dipping procedure. After the second treatment some deposition on top of the zeolite prisms can be observed (Figure 4).

DISCUSSION

Due to the presence of silicalite crystals on top of the two-layer α -alumina support, the calcining procedure for the γ -alumina film becomes more critical. The addition of glycerol improves the mechanical stability of the deposited film. Glycerol may act as a (temporary) cross-linking agent, or as a drying control chemical agent. Other binders, like polyvinyl alcohol or penta erythritol, may lead to the preparation of fully crack-free composite films. Cracking is limited to sharp corners for separate crystals, but becomes more severe for higher zeolite coverages.

The adhesion behaviour of the applied boehmite sol resulted in a homogeneous film over the macroporous support. Some adherence of the zeolite crystals to the macroporous support is required to avoid deposition in between the crystals and the macroporous support. The incorporation of even smaller crystals than the applied silicalite prisms will be favourable, as (1) probably no deposition on top of the zeolite crystals will occur, (2) smaller crystals are expected to diminish cracking upon calcining, and (3) the layer

thickness decreases.

The deposited γ -alumina film is not gas tight. It has however been shown that the dip-coating process can be used successfully using low melting glaze suspensions [4]. As the glaze deposit consists of relatively large particles, it does not suffer from shrinkage problems. In addition, due to the occurrence of a melting phase at high temperature, a thermostable system results up to temperatures near the melting temperature of the glaze. Therefore, the optimal chemical composition of the dipping solution should be similar to low temperature glazes, to which some binder is added to avoid severe cracking.

Figure 4: Cracked film remains after second dip-coating; some deposition is visible on top of the silicalite crystals.

CONCLUSION

Within the present preparation procedure of ceramic zeolite membranes, the dip-coating technique can be applied to realize selective deposition of matrix material besides the zeolite crystals. The addition of a polyol significantly reduces the crack formation. The chemical composition of the dipping solution should be similar to low temperature glazes in order to produce a gas tight matrix at sufficiently low temperature.

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