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Formation of clathrasil layers by secondary growth of DOH-type nuclei for gas separation applications

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ABSTRACT

Dodecasil 1H (D1H) possessing the zeolite framework type DOH is one of the all-silica zeolites and therefore offers high chemical, thermal and hydrothermal stability. D1H is a 6-ring clathrasil with small pore apertures of about 3 Å and may be able to selectively transport hydrogen or helium while rejecting other gasses such as CO_2. These properties make D1H an interesting microporous membrane material for precombustion applications. Moreover, it has been shown that D1H crystals can be prepared practically structure directing agent-free.

Prior to the attempt to prepare complete layers of D1H crystals, the general crystallisation behaviour of D1H was investigated. To obtain optimal crystallisation conditions a large number of synthesis experiments were performed aiming, in particular, at the preparation of pure material consisting of small and very thin crystals with a reduced number of organic molecules occupying the cage-like voids of the structure. The syntheses were performed in the system aminoadamantane/silica/ethylenediamine or ammonia/water and by systematically varying synthesis parameters like temperature, gel composition, aging of the synthesis mixture, seeding and the type of agitation during the synthesis run. In some additional runs aminoadamantane was replaced by other structure directing agents.

Moreover, the removal the organics filling the zeolite cages was studied by different approaches, including calcination at atmospheric pressure and by applying high pressure cycling and calcination of ball milled crystals. The obtained materials were then characterized by powder XRD, SEM, thermal analysis, chemical analysis and optical microscopy. Knowing favourable synthesis conditions, D1H layers have been prepared on a α-Al_2O_3 support by using secondary growth of small D1H nuclei.

1. Introduction

Global CO_2 emissions can be reduced by capture and storage. CO_2 capture in power plants can be performed by means of post-combustion, precombustion or oxyfuel concepts [1]. Many research groups studied zeolite membranes for the application of precombustion concept where H_2 is separated from other gasses (mainly CO_2) under harsh conditions such as the presence of CO, H_2S and water vapour at elevated temperatures. The requirements for these membranes are: high permeability in combination with acceptable separation factor, high mechanical, (hydro)thermal and chemical stability. Excellent reviews [2–5] discuss **MFI, FAU** and other zeolite type membranes where the dominant transport is determined by preferential sorption and not by molecular sieving due to size exclusion.

The most intensively studied zeolite membrane material is ZSM-5 (zeolite framework type **MFI**). So far, no **MFI**-type membranes with H_2/CO_2 permselecitivities significant higher than the Knudsen factor were achieved. The Knudsen factor is an expression of the difference in molecular masses of the transported species. The low permselectivity can be explained by the large pore aperture (0.51 × 0.55 nm) compared to 0.289 and 0.33 nm for H_2 and CO_2, respectively.

Known 8-ring zeolite type membranes are Zeolite A (framework type **LTA**) and deca-dodecasil 3R (DD3R) with framework type **DDR**. Guan et al. [6] prepared aluminosilicate LTA zeolite membranes with rather low permselectivities of 7.5 for H_2/N_2. Hedlund et al. [7,8] offered the opportunities of Zeolite A membranes by preparing ultra thin layers of 200 nm or less. The low H_2/CO_2 permselectivity of Zeolite A membranes can be explained by the possibility that both H_2 and CO_2 can enter the pores and by the fact that intercrystalline pores may be present as a result of poor poly-crystallisation.

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This drawback is less critical for pervaporation applications. Nowadays, the Japanese company NGK prepares commercially available membranes based on **LTA** and **DDR** type zeolites. 6-ring zeolites (e.g. a clathrasil of the DOH type) have pore apertures that might be large enough to let H_2 penetrate but reject larger gasses. To the best of our knowledge, no all-silica 6-ring zeolite membranes have been published with significant permselectivity to date.

Dodecasil 1H (D1H) [9] possessing the zeolite framework type **DOH** [10] is one of the all-silica zeolites and therefore offers high chemical, thermal and hydrothermal stability. D1H is a 6-ring clathrasil with a small pore aperture and might be able to selectively transport H_2 or He while rejecting other gasses such as CO and CO_2. These properties make D1H an interesting microporous membrane material for precombustion applications. It has been shown that D1H crystals can be prepared practically structure directing agent free [11–14] and might be accessible for He or H_2.

During crystal growth, D1H, DD3R and Sigma 2 (framework type **SGT**) are competing phases. DD3R and D1H can crystallize at temperatures in the range of 160–190 °C [15,16]. Generally, single phase D1H is formed at temperatures higher than 190 °C. Grebner et al. [11,17] and den Exter [15] attempted to remove the structure directing agent (SDA) 1-aminoadamantane (ADA) by means of calcination at temperatures higher than 700 °C. They were not able to remove the SDA completely. Grebner et al. [11,17] were able to synthesise D1H by secondary growth of SDA containing D1H nuclei using a gel composition without SDA. D1H have been prepared partly-SDA free in the past. This article describes (i) the optimization of the synthesis of small crystal D1H by systematically modifing the gel composition and crystallisation time, (ii) the preparation of quasi SDA-free D1H by post synthesis treatments and (iii) the D1H layer formation on porous supports by means of secondary growth of D1H nuclei.

2. Experimental

2.1. Dodecasil-1H synthesis

Gies et al. [18,19] synthesised D1H by dissolving aminoadamantane (ADA) or piperidine in a basic solution of ethylenediamine (EN) in water. Tetramethoxysilane (TMOS) was added drop wise to avoid fast hydrolysis and agglomerations. Grebner et al. [13] used NH_3 (33 wt% in water) as the base. Den Exter [15] reproduced the D1H synthesis of both Gies et al. [18,19] and Grebner et al. [11,17].

Here, the "EN synthesis route" using ethylenediamine (Aldrich) was performed by dissolving ADA (Aldrich) in an aqueous EN solution. TMOS (Aldrich) was added drop wise to produce gel compositions of $100SiO_2$:9–11ADA:70–267EN:3000–7400H_2O. Fifty milliliters Teflon liners were filled to 2/3 with this gel composition. Crystallisation was performed at 200 °C for 1–60 days in autoclaves. The "ammonia synthesis route" is similar but the aqueous solution of EN is replaced by 33% NH_3 (Aldrich). The crystallisation was performed statically or dynamically. Crystallisation agitation was either performed by rotating the autoclaves or by stirring the gel in the autoclave using a magnetic stirrer in combination with an oil bath.

2.2. Preparation of quasi SDA-free D1H by post synthesis treatments

The synthesised zeolitic products were washed with H_2O and ethanol. Subsequently several post synthesis treatments have been attempted to remove the structure directing agents (SDA) from the large [$5^{12}6^8$]-cages of D1H:

(A) calcination at 700–900 °C in air at ambient pressure. The heating time was varied between 5 h and 21 days with a heating and cooling ramp of 5–10 °C/min

(1) of as made-D1H crystals
(2) of D1H being ball milled to reduce the crystal size. The D1H crystals were ball milled for 4–72 h

(B) calcination in pressurised air: hot isostatic pressure (HIP) calcination was performed with a vacuum sinter oven of Engineered Pressure Systems International N.V. Belgium. The samples were calcined between 700 and 900 °C for 5 h. During this time the air pressure was varied between 1 and 200 MPa with a frequency between 1 and 10 times. All attempts to directly synthesise quasi-SDA-free D1H according to Grebner et al. [13] were unsuccessful.

2.3. Dodecasil-1H layer formation

D1H Zeolite layers were prepared on commercially available alumina disks (Inocermic GmbH Hermsdorf, Germany). A 0.5 wt% suspension of D1H nuclei in H_2O was spin-coated 3 times on the substrates with a Delta + 80 7 equipment of SÜSS Microtec. The seeded substrates were heated at 600 °C for 3 h with a heating and cooling rate of 1 °C/min. The seeded substrates were located horizontal at the bottom Teflon lined steel autoclave. A clear solution with a molar ratio of $100SiO_2$:11ADA:267EN:7400H_2O was added. Finally, the seeded substrates were subjected to hydrothermal crystal growth at 200 °C for 24–48 h.

The second attempt of D1H zeolite layer formation was carried out by depositing a suspension of 0.25 wt% D1H nuclei in H_2O on a substrate (Table 1). The seeds were dried at 200 °C prior to the hydrothermal step. A clear gel composition with a molar ratio of $100SiO_2$:5.9ADA:69EN:3500H_2O was added. The hydrothermal treatment was performed at 200 °C for 24 h. The zeolitic layers were washed with ethanol and H_2O and finally calcined at 700 °C for 5 h with a heating and cooling rate of 1 °C/min.

2.4. Characterisation

Powder X-ray diffraction measurements were done using a Siemens D500 diffractometer with monochromatised Cu Kα1-radiation. The crystallinity of the sample is calculated based on the ratio of the crystalline and amorphous area as displayed by the XRD pattern which was previously corrected by the background contribution. The total integrated area (intensity * 2Θ) of the XRD patterns is assumed to be an accumulation of background, amorphous and crystalline intensity in a selected XRD angle range, in this case selected from $10 < 2\Theta < 35°$. The relative crystallinity value contains an error of 12% as a result of sample preparation.

Table 1
Coating properties and molar ratio gel composition for the preparation of D1H membranes

Coating technique	Sample #	Nuclei Deposition steps	Gel composition SiO_2:ADA:EN:H_2O	Crystallisation	
				Temperature (°C)	Time (h)
Spin-coating, 600 °C	A	3	100:11:267:7400	200	48
Depositing, 200 °C	B	1	100:5.9:69:3500	200	24