Chemical Engineering Science 73 (2012) 116–122

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Preparation and characterization of ITQ-29/polysulfone mixed-matrix membranes for gas separation: Effect of zeolite composition and crystal size

Clara Casado-Coterillo [a],*, Jaime Soto [a], María T. Jimaré [a], Susana Valencia [b], Avelino Corma [b], Carlos Téllez [a], Joaquín Coronas [a]

[a] *Departmento de Ingeniería Química y Tecnologías del Medio Ambiente and Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, c/Mariano Esquillor s/n, 50018, Zaragoza, Spain*
[b] *Instituto de Tecnología Química, Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Av. de los Naranjos s/n, 46022, Valencia, Spain*

ARTICLE INFO

Article history:
Received 11 October 2011
Received in revised form
14 January 2012
Accepted 17 January 2012
Available online 25 January 2012

Keywords:
ITQ-29
LTA-type zeolite
Crystallization
Mixed matrix membranes
Gas separation
H_2 purification

ABSTRACT

This work concerns the preparation and characterization of ITQ-29 zeolite crystals with high Si/Ge ratio ($100-\infty$) and different particle size for obtaining mixed matrix membranes. The Si/Ge molar ratio and seeding content of the synthesis gel appeared to have an effect on the final crystal size, and particles of 2.5 μm were obtained for pure silica composition with good crystallinity. These were introduced, at 4, 8 and 12 wt% loadings, into a commercial polysulfone matrix to prepare mixed matrix membranes that showed promising results in the separation of H_2/CH_4 mixtures (highest H_2 permeability 21.9 Barrer and a separation factor of 118 for the 4 wt% ITQ-29/polysulfone membrane). The thermal treatment of the membranes and the type of solvent were also optimized to provide good interaction between the zeolite and the polymer, limiting aggregation of the particles in the matrix, and removing all residual solvent that hinders gas permeation performance.

1. Introduction

Zeolite A (LTA-type structure) is a small pore zeolite containing large cavities that generate a high void volume, widely used in industry as a shape-selective adsorbent, drying agent or cation exchanger in washing powders. Nevertheless, its performance as adsorbent is limited to water-free systems because of its extreme hydrophilicity, due to its low framework Si/Al ratio (Zhao et al., 2006). ITQ-29 was first presented in 2004 (Corma et al., 2004) as a zeolite with the same topological structure as zeolite A but a much higher Si/Al ratio (up to infinity, *i.e.* pure silica), using a bulky organic template obtained from the self-assembly of two identical organic cationic moieties through π–π type interactions. Since then, a few studies have been devoted to the fundamental understanding of the structure (Corma and Davis, 2004; Dorset et al., 2007) and the diffusion implications for adsorption kinetics and separations (Hedin et al., 2007, 2008; Palomino et al., 2009). Pure-silica ITQ-29 is a hydrophobic small-pore zeolite, which gives ITQ-29 the possibility of sieving and processing small organic molecules with high precision, even in the presence of water or other polar molecules (Corma et al., 2004). Pure silica zeolites have been prepared in the form of thin films on silicon wafers, and the study of the dielectric properties of these films confirmed the dependence of the performance properties of these materials not only on porosity but also on their structure (Hunt et al., 2010), as indicated by ring size, microporous volume and lattice symmetry (Sastre and Corma, 2006). Another research group reported the synthesis of ITQ-29 using different structure directing agents, and a variation of the morphology and size of the crystals down to 0.5 μm was observed by varying the gel composition and synthesis time (Huang and Caro, 2009; Huang et al., 2010). However, the Si/Ge ratio of the particles obtained in this way was as low as 2, making this zeolite unstable upon calcination, as it is well known that silicogermanates have limited framework stability in the presence of water or even when exposed to ambient moisture (Moliner et al., 2008; Gao et al., 2009).

Zeolite membranes with pores of molecular size can perform very well in many interesting applications, such as hydrogen separations from small gases (David et al., 2011). Al-free ITQ-29 has also been prepared as pure inorganic membranes by hydrothermal synthesis and tested on the permeation of N_2, CH_4 and propane (Tiscornia et al., 2008). In this case, the membrane was partially activated by ozonation at 200 °C, but not all the template was removed and the permeability and selectivity were not very high. Recently, ITQ-29 membranes have been prepared using Kryptofix 222 as SDA and activated by *in situ* O_2 flow at 300 °C before the permeation experiments (Huang and Caro, 2010). In

---

* Corresponding author. Tel.: +34 976 762471; fax: +34 976 76 1879.
E-mail address: casadoc@unican.es (C. Casado-Coterillo).

0009-2509/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2012.01.024

this case, a H_2/C_3H_8 separation factor of 127 was obtained. However, the removal of the large template, which is necessary to free the internal porosity of the ITQ-29 zeolite framework, still constitutes a major drawback in the preparation of defect-free membranes.

The particle size distribution in zeolite materials depends on several variables such as the composition of the synthesis gel, the crystallization time and the temperature (Cundy and Cox, 2003). The water content has been found to have a pronounced effect on the zeolite morphology (Larlus and Valtchev, 2004) and, recently, increasing water content in the synthesis gel of ITQ-29 has been reported to produce larger crystal sizes (Huang and Caro, 2009). The addition of seeds, *i.e.* previously prepared crystals, can modify the nucleation and particle size of zeolites, or zeolite-like materials such as TS-1 (Lu and Wang, 2006), ETS-10 (Casado et al., 2009) or JDF-L1 (Rubio et al., 2009). Small particle sizes (Zornoza et al., 2011) may find an application in the preparation of mixed matrix membranes (MMMs) for molecular separations, where the tiny crystalline particles can be homogeneously dispersed in the chosen polymer matrix, providing this with their intrinsic characteristics. These particles can have three effects on the membrane performance: (i) acting as molecular sieves, (ii) disrupting the polymeric structure increasing permeability and (iii) acting as a barrier, thereby reducing permeability. MMMs are, in principle, easier to prepare than pure inorganic membranes for gas separation.

Polysulfone is a glassy polymer that has been extensively studied for gas permeation and separation, because of its low permeability and comparatively high selectivity, which bring it close to Robeson's upperbound limit (Robeson, 2008). Hence, it is a commonly selected material for studying the effect of the incorporation of inorganic fillers in the transport properties of a polymer matrix (Ahn et al., 2008).

Zeolites were the first molecular sieves used as fillers. Numerous attempts have been reported to incorporate zeolite particles into polymer matrices for gas separation (Mahajan and Koros, 2000) because of their crystalline character with well-defined pore structures and shape selectivity properties. However, interfacial voids often exist between the zeolite and the polymer matrix. Therefore, the adhesion mechanism between zeolites and polymers has been studied (Lee et al., 2009) but its relationship with other factors such as solvent, residual stress and film formation conditions are not yet understood given the huge amount of combinations of materials available. Attempts to improve the interaction on the interphase zeolite–polymer have been carried out, from the modification of the surface of zeolite A before introducing the particles into a polymer matrix to the use of smaller zeolite crystal sizes, but even though gas permeability and selectivity seemed to increase a little, rigidification of the MMM was not avoided (Li et al., 2006). In addition, the priming protocol has already deemed necessary only for high particle loadings (Mahajan and Koros, 2000). The particle size of the zeolites added to the polymer also has an important role, since it has been reported that the smaller the particle size, the smaller is the zeolite loading into the polymer needed to reach the same value of gas permeability (Tantekin-Ersolmaz et al., 2000), even though filler aggregation might still be an issue to consider (Zornoza et al., 2009). Golemme et al. (2006) also studied the effect of particle size to introduce silicalite-1 particles inside a glassy polymer for gas separation, attempting to reduce the generation of voids between zeolite and polymer to obtain defect-free membranes.

In this work, the ITQ-29 particle size was varied as a function of synthesis conditions, such as the amount of seeding, water content, Si/Ge ratio and synthesis time. Si/Ge ratio was kept higher than 100 in order to work with an essentially pure silica zeolite. The smaller sized crystals were dispersed in a commercial polysulfone to produce dense MMMs for gas separation. The crystals and the membranes were characterized by XRD, SEM, TGA-DTA, DSC and N_2 adsorption/desorption. Membrane performance was validated in the separation of several equimolar gas mixtures, with the view of studying the transfer of the molecular sieving effect of ITQ-29 to the polymer matrix. Since this zeolite membrane has been proved particularly selective in the separation of hydrogen from hydrocarbons (Huang and Caro, 2010), which may be important in the application of membrane technology to processes such as steam reforming from methane (Ritter and Ebner, 2007), a special focus was accorded to H_2/CH_4 separation.

2. Experimental

2.1. ITQ-29 crystals

The ITQ-29 crystals were prepared using a procedure reported elsewhere (Corma et al., 2004). The molar composition of the synthesis gels was: $(1-x)\,SiO_2$: $x\,GeO_2$: 0.25 ROH : 0.25 TMAOH : 0.5 HF: $y \cdot H_2O$, being $x=0$–0.05 and $y=3$–12. In a typical synthesis of pure silica ITQ-29 particles, the gel was prepared by hydrolysis of the silica precursor, tetraethylorthosilicate, TEOS, (5.06 g) in an 0.50 M aqueous solution of 4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3.2.1-ij] quinolinium hydroxide, ROH, (12.15 g) and 25% tetramethylammonium hydroxide, TMAOH, (2.27 g) as structure directing agents, SDAs. The ROH was previously prepared by methylation and ion-exchange of a commercial organic precursor (julolidine 97%, Aldrich) to obtain the OH dilute template solution needed in the synthesis gel. The mixture was stirred until the ethanol formed during hydrolysis and the excess of water were evaporated and the desired gel composition was reached. Then, an aqueous solution of HF (48 wt%, Aldrich; 0.47 g) was added and the mixture was introduced into a Teflon-lined stainless steel autoclave and heated at 135 °C under static conditions. In this work, the effect of seeding on the crystal morphology and synthesis time was studied. For this purpose, gels of high silica content (Si/Ge$=$100 or ∞) were seeded by introducing different amounts (0.05–0.20 g) of previously prepared ITQ-29 particles. A summary of the synthesis conditions and results obtained for the ITQ-29 syntheses with different Si/Ge ratios is shown in Table 1. Synthesis time was varied from 3 to 10 days and the ratio of water content to (Si$+$Ge) was studied in the range from 3 to 12. After synthesis, the autoclave was removed from the oven and quenched under cold tap water to room temperature. The solid was thoroughly washed and filtered with

Table 1
ITQ-29 syntheses.

ID	H_2O/TO_2	Si/Ge	Seeding material, g	Time (days)	Crystal size (μm)[a]	% crystallinity[b]	a (Å)[c]
A	3	20	–	3	5.3 ± 1.5	86	11.8399
B	3	100	–	3	12.9 ± 1.1	78	11.8361
C	3	∞	A, 0.10	5	8.2 ± 2.5	95	11.8373
D	12	100	B, 0.05	7	2.5 ± 0.5	95	11.8334
E	3	∞	A, 0.20	3	2.9 ± 0.8	100	11.8311
F	5	∞	A, 0.10	10	5.5 ± 0.9	27	–

[a] Average value obtained from the measurement of more than 40 single crystals observed by SEM.

[b] The crystallinity percentage was calculated by comparing the maximum intensity of the XRD pattern of the samples with that of sample E.

[c] Calculated from the XRD of the samples using the Fullprof program (Rodríguez-Carvajal, 2001).