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Solvothermal deposition and characterization of magnesium hydroxide nanostructures on zeolite crystals

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A methodology to engineer roughened inorganic nanostructures on zeolites by deposition and growth of metal hydroxides is reported. Pure-silica (PS) MFI and (aluminosilicate) LTA zeolite crystals are treated by solvothermal methods to deposit inorganic hydroxide (e.g., $Mg(OH)_2$) coatings with nanoscale roughened features on the crystal surfaces in a controlled manner. Detailed characterization of the surface-modified MFI crystals by nitrogen physisorption allows the quantification of the surface roughness of the $Mg(OH)_2$ nanostructures. Pore volume characterization shows that the nanostructure deposition has only a marginal effect on the porosity of the MFI. The surface-roughened zeolites are used to fabricate zeolite/polymer mixed matrix films with considerably improved interfacial adhesion properties. Solvothermal deposition of inorganic nanostructures is also demonstrated on zeolite LTA crystals, which present aluminosilicate surfaces. In this case, the intracrystalline sodium ions in LTA are partially substituted with magnesium ions from the reagent solution during treatment. The solvothermal treatment is thus modified to deposit smaller $Mg(OH)_2$ nanostructures, resulting in more roughened zeolite LTA surfaces. Our detailed characterization reveals that the surface-treated LTA crystals may be promising materials for applications in mixed matrix membranes.

1. Introduction

The fabrication of composite films and membranes is often an effective way to combine the advantages of two disparate materials and to minimize their drawbacks. For example, there has been increasing interest in composite membranes for a variety of chemical separation applications [1–4]. Membrane-based gas separation offers several advantages including ease of operation, lower energy requirements and lower operating costs over conventional gas separation processes [4]. Polymeric membranes have been utilized in commercial applications [5], and their mechanical properties and processability are attractive. However, existing polymeric membrane materials are limited by an inherent trade-off: an improvement in permeability is accompanied by a loss of selectivity, or vice versa [6,7]. Meanwhile, high-performance inorganic molecular sieve membranes have been developed using zeolites and other materials [8,9]. The accurate size and shape discrimination originating from the uniform nanopores in molecular sieve materials ensures superior selectivity. However, the cost of processing these inorganic membranes is significantly higher than that of polymeric membranes [8].

One promising way to achieve high separation performance is to incorporate molecular sieves into polymer membranes [4]. In this "mixed matrix membrane" concept, one can combine the easy processability and good mechanical properties of the polymer with the high separation performance of the molecular sieve. Many studies have demonstrated the high separation performance of mixed matrix membranes exhibiting performance beyond the intrinsic properties of polymers [4,10–12]. However, problems have arisen associated with the presence of poor interfacial morphologies between the inorganic fillers and polymers. Many researchers have demonstrated that adhesion problems occur at the polymer/zeolite interface [4]. The poor polymer/zeolite adhesion results in interfacial voids that are often visible in SEM images, and which are the major cause for deterioration in separation performance. Diffusing molecules take a non-selective and low-resistance path through the voids, bypassing the embedded molecular sieve.

Various methods for surface functionalization of zeolites have been investigated. Silane chemistry is one of the most well-studied methods to functionalize the surface of zeolites or silica for fabrication of composite materials. In general, the silane coupling agents used have two functional moieties: reactive surface groups such as alkoxides at one end, and a functional group intended to interact with the polymer at the other end. The coupling agents are anchored on the zeolite surface by condensation reactions

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between the silanol groups on the zeolite surface and the alkoxides in the silane reagent. By covalent (or other) bonding of the pendant functional group at the other end of the coupling agent with functional groups in polymer chains, the coupling process between inorganic fillers and polymers is accomplished. For example, silane coupling agents with amine functionalities can be used to fabricate mixed matrix membranes with poly(imide)s, since the pendant amine group can react with imide rings in the polymer to form covalent bonds [13]. In other studies, poly(imide)s with carboxylic acid groups were synthesized to generate chemical bonding with amine groups in silane coupling agents [14]. Adhesion between the zeolite and polymer can also be enhanced without chemical bonding between the coupling agent and polymer, for example by van der Waals or hydrogen bonding interactions [15,16]. However, Husain et al. reported that there can be non-selective gas permeation through gaps between the zeolite and polymer due to insufficient organic loading [15]. Similarly, enhancement of gas separation performance of mixed matrix membranes made with zeolite A and poly(sulfone) was not satisfactory when a silane coupling agent with amine functionality was used [16]. Consequently, methods other than silane chemistry may be desirable for polymer/inorganic sieve compatabilization.

Shu et al. reported that a "nano-whisker structure" could be created on the surface of zeolite A via a halide/Grignard route [11,17]. Highly roughened surfaces created by formation of $Mg(OH)_2$ nanocrystals on the zeolite surface provided enhanced interactions at the polymer/particle interface, via possible adsorption and interlocking of polymer chains in the whisker structure. The resultant mixed matrix membrane demonstrated significant improvement in gas separation performance. However, this method utilizes a complicated procedure and highly unstable reactants, and may not be cost effective. Thus, the development of rational methods to create such nanostructures, using more benign chemistry that is amenable to scale-up, would be highly attractive. $Mg(OH)_2$ crystals can be formed by reactions between a magnesium source, a base and water. There are several studies that demonstrate the formation of $Mg(OH)_2$ nanostructures via precipitation at moderate temperatures [18–21] or hydrothermal processes [22–25]. The type and concentration of both the magnesium source and base [18,19], reaction time [25], pH (in aqueous processes) [18,19,23] and reaction temperature [23] are important factors affecting crystallinity and morphology of resulting nanomaterials. It was reported that nano-needles or nano-rods could be obtained by the addition of a dispersant such as polyethylene glycol [21], surfactants and soluble proteins [20]. In these methods, $Mg(OH)_2$ crystals were formed rapidly via homogeneous precipitation. Meanwhile, it was also shown that well-defined $Mg(OH)_2$ nanorods could be created solvothermally with a non-aqueous solvent [25,26]. In this method, ethylenediamine acted as both reaction medium and base. Magnesium sources and a small amount of water were the other components of the reaction mixture. It was found that both the nature of the magnesium source and the ethylenediamine:water ratio were key factors affecting the resultant crystal morphology. For instance, nanorods could be formed from magnesium powder and $Mg(SO)_4$ but only platelets were obtained using $Mg(NO)_3$ as the metal source. A high ethylenediamine-to-water ratio was also essential to create nanoneedles or nanorods. Although the true role of ethylenediamine is unclear, the authors speculated that the selective interaction between the coordinating solvent (ethylenediamine) and surface ions (Mg^{2+}) slows the growth of specific lattice planes, resulting in one dimensional growth of nanocrystals.

To create nanostructured morphologies on zeolite surfaces based on the aforementioned methods, the synthesis conditions should be modified to allow the precipitation of inorganic crystals on the zeolite surface in a controlled manner, rather than precipitation in the solution independent of the zeolite surfaces. Thus, heterogeneous deposition, as well as heterogeneous nucleation and growth on the zeolite surface, are both desirable effects. Very recently, we reported a facile solvothermal method to deposit inorganic nanostructures on PS–MFI surfaces [27]. Enhanced gas separation performance was achieved with mixed matrix membranes containing surface modified PS–MFI due to improved polymer/zeolite adhesion. Specifically, mixed matrix membranes prepared by dispersing the functionalized zeolite in Ultem® and Matrimid® polymers showed dramatic increases in CO_2 throughput while maintaining high selectivity over CH_4. Furthermore, O_2 and N_2 permeation data elucidated the role of interface quality in determining the membrane properties. Here we report a detailed study of solvothermal methods to grow inorganic nanostructures on the surface of zeolites. Two zeolites with different surfaces, aluminosilicate zeolite LTA and PS–MFI, were used as model substrates. We demonstrate the tuning of the solvothermal surface modification chemistry to deposit a range of fine nanostructures, resulting in highly roughened zeolite surfaces. The structural properties of these modified zeolites relevant to their application in composite films are thoroughly investigated.

2. Experimental section

2.1. Materials

The following chemicals were commercially available and were used as received: tetraethylorthosilicate (TEOS, 98% Sigma–Aldrich), tetrapropylammonium hydroxide (TPAOH, 40% w/w aqueous solution, Alfa Aesar), tetrapropylammonium bromide (TPABr, 98%, Sigma–Aldrich), tetramethylammonium hydroxide (TMAOH, 25% in water, Sigma–Aldrich), ethylenediamine (EDA, 99%, Sigma–Aldrich), diethylenetriamine (DETA, 99%, Sigma–Aldrich), methylmagnesium bromide (3 M in ether, Sigma–Aldrich), 2-propanol (Sigma–Aldrich), dichloromethane (DCM, 99.5%, Sigma–Aldrich), toluene (99.8%, Sigma–Aldrich), colloidal silica (Ludox HS-30, Sigma–Aldrich), and aluminumisopropoxide ($Al(OiPr)_3$, 97%, Sigma–Aldrich), magnesium sulfate heptahydrate (Acros) and sodium chloride (Fisher Scientific).

2.2. Synthesis of zeolite MFI

Pure-silica MFI crystals were synthesized hydrothermally at 150 °C from TEOS/TPAOH/water solutions. The TEOS/TPAOH molar ratio was 1:0.36 or 1:0.24 and the water content was varied from 20 to 360 on a molar basis as part of a synthesis matrix that included variation in the reaction time (2–4 days). The general methodology otherwise followed that described in our previous work [28]. Large crystal MFI was also prepared using the method described in the literature [29]. The solution with molar ratio of $1TEOS{:}0.1TPABr{:}0.1NaOH{:}98H_2O$ was aged at 50 °C for 7 days and crystallized at 120 °C for 2 days. The zeolite particles were repeatedly centrifuged and washed with deionized water at least 5 times, and dried at 80 °C. Finally, calcination was performed at 550 °C for 8 h in air to remove the structure-directing agent from the zeolite pores.

2.3. Synthesis of zeolite LTA

LTA particles were synthesized hydrothermally based on the method published by Larlus et al. [30]. Colloidal silica (Ludox HS-30) and aluminum isopropoxide were used as silicon and aluminum sources, respectively and the structure directing agent was TMAOH. For 300 nm particle synthesis, clear precursor solution with molar ratio of $0.2NaOH{:}\ 1SiO_2{:}\ 1Al(OiPr)_3{:}\ 4TMAOH{:}170H_2O$ was prepared at room temperature and treated hydrothermally at