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## Organic solvent nanofiltration with Grignard functionalised ceramic nanofiltration membranes

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## ABSTRACT

In this paper the use of functionalised ceramic nanofiltration membranes in solvent filtration is described. The membranes were grafted using a novel method for surface modification based on Grignard chemistry. Commercially available 1 nm TiO<sub>2</sub> membranes were differently functionalised with a series of alkyl groups (methyl, pentyl, octyl, dodecyl) in order to generate a more hydrophobic membrane surface.

The properties of the modified membranes were examined by physico-chemical characterisation (contact angle measurements, micro-ATR/FTIR-spectroscopy) in addition to performance characterisation (flux measurements for solvents ranging from highly polar to non-polar, next to polyethylene glycol retentions in water and polystyrene retentions in acetone). All observations for modified membranes are consistent with the assumed partial replacement of the OH-groups on the membrane surface and the consequent amphiphilic character of the modified membrane surface.

The retentions of modified and unmodified membranes in acetone confirm the recent findings in organic solvent nanofiltration (OSN): an increase in the hydrophobicity of the membrane leads to an increase in the retentions.

A comparison with reference polymeric membranes shows that the newly developed membranes are a good alternative, having the advantage of the absence of effects of swelling. This new grafting technique for ceramic membranes allows to further explore solvent–membrane–solute interactions in OSN in a controlled way without the extra complexity of swelling.

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## 1. Introduction

Nanofiltration in non-aqueous media, denoted as organic solvent nanofiltration (OSN) is a recent membrane process, which can replace traditional separation systems in the chemical, pharmaceutical and biotechnology industry where solvents are used in production [1,2]. An increasing number of successful applications has been reported in catalysis [3], the petrochemical industry [4] and the pharmaceutical industry [5–8]. These applications include recovery of solvents (e.g., toluene) from dewaxed lube oil filtrates, solvent exchange, recovery of organometallic complexes from various organic solvents, separation of phase transfer catalysts from toluene, deacidification of vegetable oils and concentration and purification of pharmaceuticals [5,10]. Many of these applications demand process stability, low

requirements for preliminary treatment and a minimum need for support and maintenance.

Despite their enhanced chemical stability and their frequent use in applications, specifically developed solvent resistant polymeric membranes tend to swell and may crack or delaminate in some organic solvents, which reduces their potential for applications, especially in aggressive solvents [11]. Therefore, ceramic nanofiltration membranes characterised by a very high chemical, thermal and mechanical stability, combined with good separation characteristics and long lifetime, are thought a possible solution; they are applied where polymeric or other inorganic membranes cannot be used [12,13]. Most of the existing ceramic nanofiltration membranes are made of metal oxides such as alumina, zirconia, or titania [14]. Due to the presence of hydroxyl groups on the surface, these membranes have a hydrophilic nature and therefore a naturally high flux of water through the pores is characteristic [15–17]. However, in non-polar organic solvents, they are less applicable due to the low solvent fluxes induced by the hydrophilic character [4,18]. Improvement of

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the non-polar solvent fluxes can be achieved by grafting the top layer with hydrophobic groups (e.g., by silanation). Some examples of grafting techniques (silanation and phosphonic acid grafting) used for the hydrophobic modification of ceramic membranes have been reported in the literature [19,20,21,22]. Other papers describe the application of such modified membranes in membrane distillation [23], gas separation [24,22] or pervaporation [25,26].

Recently we developed a new grafting method for ceramic membrane hydrophobisation or other functionalisation based on Grignard chemistry [27,28]. The result of this method is a unique direct, covalent bonding of the aimed functional group (R) to the metal (M, with M=Al, Zr or Ti) of the metal oxide matrix, M–R, as will be explained in Section 2.1.1. This bond is much less sensitive to re-hydroxylation compared to the bonds via oxygen and an hetero element realized in the state-of-the-art techniques (M–O–Si–R for silanation, M–O–R for alcohol etherification or M–O–P–R for phosphonic acid grafting, although this last one is much more stable than the other two) [29]. Moreover, the Grignard grafting is compatible with many functional groups and therefore opens perspectives to tuneable membrane surfaces, fit for separations on the basis of affinity. Indeed, as now clear in the state-of-the-art of organic solvent nanofiltration, affinity effects between all three important actors (i.e., solvent, solute and membrane) determine the observed performance of all membranes in this process (Fig. 1).

In this work the performance of Grignard modified ceramic nanofiltration membranes is described, showing their unique behaviour in solvent nanofiltration. Grafting was carried out on commercially available 1 nm TiO<sub>2</sub> membranes, with linear alkyl groups for membrane hydrophobisation. In particular, linear alkyl groups with increasing length, i.e., *n*-methyl (C<sub>1</sub>), *n*-pentyl (*n*-C<sub>5</sub>), *n*-octyl (*n*-C<sub>8</sub>) and *n*-dodecyl (*n*-C<sub>12</sub>), have been grafted on

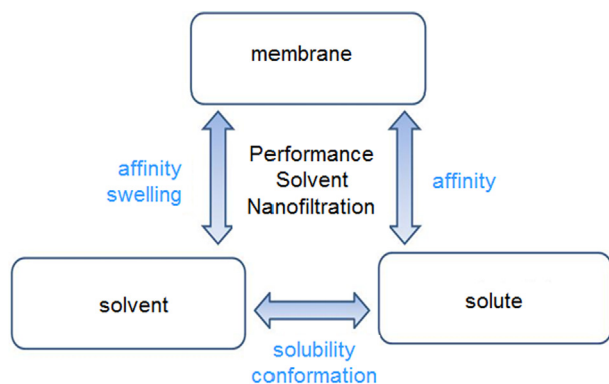


Fig. 1. Membrane-solvent-solute interaction in OSN.

1 nm TiO<sub>2</sub> membranes. This article describes the physico-chemical characterisation (contact angle and micro-ATR/FTIR) and the performance (pure solvent permeability and retentions in selected solvent/solute mixtures) of these innovative membranes.

## 2. Materials and methods

### 2.1. Membranes

#### 2.1.1. Grignard functionalised membranes

Small-scale asymmetric tubular 1 nm TiO<sub>2</sub> membranes (length 12 cm, outer diameter 1 cm, inner diameter 0.7 cm, and top layer thickness of about 50 nm [48] purchased from Inopor, Veilsdorf, Germany) were functionalised by grafting *n*-alkyl groups onto the membrane surface using appropriate organometallic Grignard reagents [Fig. 2]. Several series of membranes (modifications from C<sub>1</sub> to C<sub>12</sub>) were prepared for this study: one series for the permeability measurements and MWCO measurements, and one series for the retention measurements in acetone.

The details of the grafting procedure can be found elsewhere [27]. In general, the procedure can be described as follows. The membranes were first properly pretreated to remove the adsorbed water layer on the membrane surface. The membranes were then submerged for 48 h into a reaction mixture of Grignard reagent in diethyl ether. The reaction was carried out under sufficiently dry atmosphere at room temperature. In order to provide sufficient contact with the complete pore surface of the membranes, the reaction mixture was stirred and shaken, or filtered through the membrane. MgBr-salts, formed as side products of the reaction are washed out of the pores by a proper washing procedure [28]. After washing, the membranes were dried at 60 °C and vacuum to remove the washing water. The washing also removes any loosely bonded molecules so that after washing only covalently bonded groups remain on the surface. The efficiency of the washing was proven on Grignard modified powders by EPMA measurements showing the absence of any Mg for well-washed powder [28].

For efficient characterisation, 1 and 2 cm pieces of 1 nm TiO<sub>2</sub> membranes have been grafted simultaneously with the 12 cm membranes. Washing was similar as for the full membranes. The small pieces were used for physico-chemical characterisation, while the entire membranes were used in performance testing.

#### 2.1.2. Reference membranes

To compare the results of the modified membranes and have a better understanding of their separation behaviour, the fluxes and solute retentions of two polymeric membranes, Starmem240 and Duramem300, in addition to the unmodified 1 nm TiO<sub>2</sub>

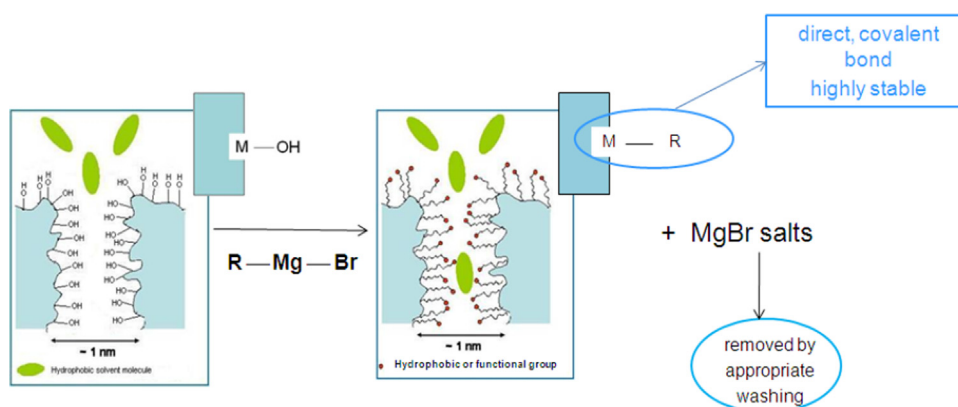


Fig. 2. Grignard modification of ceramic membranes [27,28].

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