Modification of ceramic membranes by alcohol adsorption

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Abstract

This study aims at modifying ceramic membranes by means of alcohol chemisorption. Composite ceramic membranes with a skin layer of γ-alumina were used. First, the adsorption of several alcohol on powdered γ-alumina was investigated emphasizing the thermal stability of the adsorbed compounds. Later, a commercial γ-alumina membrane was modified by alcohol adsorption. The permeability of water and several organic compounds was obtained for both the non-modified and modified ceramic membrane. Also, its isoelectric point was determined. The results prove that all the alcohol were readily adsorbed on powdered γ-alumina not only physically but also chemically forming an alkoxide. The chemisorbed alcohol was stable up to 200°C. Beyond this temperature, the alkoxide breaks up releasing the alcohol although the alkoxide also can react yielding an olefin or ether. The ceramic membrane was also successfully modified by alcohol adsorption. The layer of chemisorbed alcohol imparts hydrophobic characteristics to the membrane surface, so water permeability decreases significantly. This cannot be merely explained by pore size reduction due to the adsorbed layer. Thermal treatment at 250°C recovered original permeability with only minor damage to the membrane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ceramic membrane; Membrane separation; Nanofiltration; Membrane modification; Alcohol adsorption; Isoelectric point

1. Introduction

Membrane-based separation processes have been progressively gaining acceptance in large-scale applications during the last decades. Nowadays, some membrane processes are more robust, efficient and economic than the conventional separation techniques [1,2]. Membrane processes could be often carried out under mild conditions that prevent the products from being damaged. Furthermore, the separation frequently takes place without phase change or addition of new products, which saves energy and overcomes further separations. Additionally, membrane separa-

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increasing its selectivity, altering the surface properties, preventing fouling, or simply changing the pore diameter. A popular method to implant chemically designed groups on ceramic surfaces is silylation using functionalised silanes [4,5]. If vinyl-functionalised silane is used, graft polymerisation can follow, which permits a desired polymer to grow [6]. Furthermore, in case of multifunctional silanes, polysilanes can be obtained [7]. Yet, other techniques have been developed to modify the characteristics of the membrane surface such as chemical vapour deposition (CVD) [8], phosphonation [7,9], or direct grafting of silicone oil [10].

Alumina can appear under several crystallographic (allotropic) forms, α- and γ-alumina being the most important. The well-known characteristics as adsorbent of the latter are due to its high surface area, around 200 m²/g, as well as the existence of acidic and basic sites on its surface. According the model developed for the γ-alumina by Peri [11], there exist five different hydroxyl groups with unequal characteristics due to their crystallographic environment and the interactions between neighbouring groups. A more recent model presented by Knözinger and Ratnasamy [14] assumes that the influence of near hydroxyl groups is negligible and differences in the surface hydroxyl groups come from different types of linking with the aluminium atoms.

The adsorption capacity of alumina is related to the hydroxyl groups on its surface. Usually, water occupies the active sites for adsorption because of its great affinity [13], thus avoiding other compounds to be adsorbed. Active centres can be activated by thermal treatment, which dehydrates the surface thus increasing the adsorption capacity of alumina. During this activation process, elimination of hydroxyl groups is assumed to take place in a random way. However, the exposure at high temperature decreases the surface area due to structural transformations [14,15], which could in turn reduce the specific adsorption capacity. Nevertheless, the existing models cannot yet, describe accurately the adsorption on alumina surface, especially, if organic compounds can react with the surface so, besides physisorption, chemisorption could take place. Consequently, obtaining of experimental data becomes essential.

The hydrophilic–hydrophobic characteristics of the membrane surface play a capital role in the separation. Preferential water adsorption on the membrane surface is encountered when the membrane is hydrophilic in nature, like ceramic membranes, and aqueous solutions of organic compounds are filtered. The modification of the membrane surface properties could completely change the affinity between the filtration medium and the dissolved species, the membrane performance being strongly affected. For instance, dramatic changes in the permeability of ceramic membranes have been observed when organic compounds were permeated through [16]. The change in the permeability was attributed to the chemisorption of organics on the membrane surface. For instance, as illustrated by Fig. 1, alcohol can chemisorb by reaction of its hydroxyl group with surface hydroxyl groups of the alumina, thus forming a stable alkoxide and releasing water. This mechanism has been proven for different normal and secondary alcohol [12,17–22].

The objective of this study is to demonstrate that alcohol effectively adsorb on alumina membranes in order to modify their characteristics. Thus, several normal and secondary alcohol were checked for adsorption on powdered alumina and later on alumina membranes. The hydraulic characteristics of non-modified and modified membranes were determined for different solvents. Also, the thermal stability of the adsorbed layer was checked and the feasibility of regenerating the virgin permeability was demonstrated. Finally, stability in acid or basic solutions was successfully tested and its isoelectric point was determined.

2. Experimental

2.1. Materials

High purity helium was used as carrier gas in the adsorption tests. Alumina used in adsorption tests was γ-Al2O3 (NORTON 6560) with a surface area of 207 m²/g, a porosity of 0.76 cm³/g and 8.1 nm of...
nominal pore diameter (according to the information given by the supplier). All the organic compounds were of analytical degree and used without further purification. Water used in permeability tests and solutions was obtained from a MilliQ equipment and had a conductivity below \(5.5 \times 10^{-2}\) \(\mu\)S.

The commercial membranes MEMBRALOX® IT1-70 were purchased from USF Spain S.A. This membrane is a composite element with a support made of \(\alpha\)-alumina internally coated with a thin layer of \(\gamma\)-alumina, which confers the nominal pore size. Theoretically, two identical membranes were used throughout the study; however, according to the technical information given by the supplier, one of the membranes had a pore size of 6.3 nm whereas the second one had 8.0 nm. Each element is 250 mm long and has 7.0 and 10.0 mm of internal and external diameter, respectively. The internal permeation area was calculated to be \(5.0 \times 10^{-3}\) m\(^2\).

### 2.2. Experimental set-up and procedures

Fig. 2 shows the apparatus used for adsorption–desorption of alcohol on \(\gamma\)-alumina. The carrier gas, helium coming from a high pressure cylinder, passes through two liquid traps containing the alcohol to be adsorbed. The stream saturated of alcohol then enters into the temperature programmed reactor (TPR) filled with 0.40 g of \(\gamma\)-alumina, where the alcohol adsorbs onto the alumina for 2 h at controlled temperature. Previously, the alumina was activated in the same reactor at 400°C for 8 h under pure helium in order to remove any adsorbed water. Desorption was conducted in the same reactor by increasing the temperature from 25 to 400°C at a heating rate of 5°C/min. The exiting stream is connected to a gas chromatograph (FISONS Instruments, model GC8000) coupled with a mass detector (FISONS Instruments, Model MD800). Data was acquired and subsequently processed to detect and identify the species desorbed.

Hydraulic permeability and isoelectric point studies were carried out using the experimental set-up shown in Fig. 3. A positive-displacement pump (ProMinent® Vario) allows working in a flow rate range from 0 to 500 ml/min and a maximum pressure of 10 bar. A pulse dampener (Dosapro Milton Roy ref. U002-A-16(V)1-A1) suppresses 95% of the pulses generated by this type of pump, yielding almost stationary flow. A metering valve placed at the outlet of the filtration module serves to fix the selected working pressure.

![Fig. 2: Apparatus for adsorption–desorption of alcohol on \(\gamma\)-alumina.](image-url)

Fig. 2: Apparatus for adsorption–desorption of alcohol on \(\gamma\)-alumina. (1) Cylinder of helium; (2) liquid traps containing alcohol; (3) reactor for adsorption and temperature programmed desorption; (4) gas chromatograph–mass spectrometer; and (5) data acquisition.
Both concentrate and permeate were recycled to the feed tank.

The permeability of the membrane was examined by measuring the solvent flow rate at transmembrane pressures ranging from 0.5 to 8.0 bar. After tests using alcohol, the membrane was regenerated by heating at 250°C for 1 h. The permeability constant, \( k \) (m²), was obtained by fitting the experimental data to the Darcy’s law as expressed by

\[
Q = \frac{k A \Delta P}{\mu L}
\]

where \( Q \) is the volumetric flow rate (m³/s), \( \Delta P \) the transmembrane pressure (Pa), \( A \) the internal area of the membrane (m²), \( L \) the thickness of the membrane (m) and \( \mu \) the viscosity of the fluid (Pa·s). A standard least square routine was applied for this purpose. The apparent pore diameter of the membrane after any treatment was calculated from the current and original water permeabilities, and the nominal pore diameter provided by the manufacturer assuming Poiseuille flow through the pores, which leads to

\[
d_{ap} = d_{oa} \left( \frac{k_{oa}}{k} \right)^{1/2}
\]

where \( d_{oa} \) and \( d_{ap} \) are, respectively, the original and apparent pore diameter as, \( k_{oa} \) and \( k \), respectively denote the original and current permeability constant for a selected solvent. In some cases, a normalised solvent permeability constant, \( k' \) (non-dimensional) is given by

\[
k' = \frac{k}{d^2}
\]

which was used in the discussion to take into account the change of pore size in different permeability tests.

Membranes were modified by alcohol adsorption following two different protocols. In any case, no previous activation step was performed as membrane heating at temperature around 400°C damages the membrane coating γ-alumina layer [16]. The first procedure, hereafter denoted as Procedure #1, was simply drying the membrane in an oven for 2 h after permeating some desired liquid alcohol. The temperature was set at 120°C, which helps the desorption of physisorbed alcohol as well as promotes chemisorption. In the second procedure, hereafter called Procedure #2, the modification was performed in gas phase. Thus, the membrane, filled inside with liquid alcohol, was located in the module and the two extremes were...
closed. This system was placed in an oven at controlled temperature. The permeate exit was connected to a vacuum pump. Thus, the liquid alcohol was forced to vaporise through the membrane pores. In the best conditions, the pressure was controlled at 50 kPa and the temperature was kept in the range 105–120 °C for 2 h.

The loss of hydraulic permeability shown by the modified membranes was reversed applying a thermal treatment. Thus, in order to recover the original permeability, the membrane was placed in an oven at 250 °C for 1 h. Beyond this temperature, any chemisorbed species is removed from the alumina surface either by desorption or by chemical reaction.

The isoelectric point was directly measured on the membrane adapting a procedure described in the literature [23]. With this goal, the system was operating in dead-end filtration mode. The initial pH of the feed was adjusted by adding HCl or NaOH with an ionic strength of 10^{-2} M. The transmembrane pressure was set at about 3 bar. The permeate was withdrawn and its pH was continuously measured until the value of the feed was reached.

3. Results and discussion

3.1. Alcohol adsorption on alumina powder

The feasibility of adsorbing alcohol onto γ-alumina, as well as the thermal stability of the adsorbed layer was first tested using alumina powder in the TPR. Alcohol adsorption was conducted in gas phase for several normal and secondary alcohol. Table 1 lists the normal alcohol tested, later used for modifying the membrane, and their corresponding normal boiling point and viscosity. Desorption tests prove that all the alcohol were readily chemisorbed. As expected, the desorbed species detected by mass spectroscopy were alcohol and also their main reaction products, such as ethers and olefins as well as water and other minor by-products. The physisorbed methanol or ethanol is removed at temperatures in the range 120–130 °C, fairly higher than their corresponding boiling point. However, alcohol was also found by mass spectroscopy at much higher temperatures, which is believed to be due to chemisorbed alcohol forming a stable alkoxide at temperatures below 250 °C. Beyond this temperature, chemisorbed alcohol can be removed by thermal breaking of its oxygen bond. However, alcohol molecules also can undergo dehydration giving olefins, if possible, or etherification yielding ethers. These species were detected for all the alcohol studied at temperatures above 200–250 °C. The detection of molecular alcohol at temperatures far away from its boiling point certainly proves that the alcohol is not merely physisorbed on the alumina surface.

It must be noted that chemisorbed normal alcohol are stable at temperatures up to 250 °C, whereas secondary alcohol desorbe earlier, at around 200 °C. This behaviour could be explained by steric effects appearing in the case of secondary alcohol, which make the alkoxide less stable. However, n-octanol behaves as secondary alcohol, which again could be related to its higher molecular volume. In turn, iso-amyl alcohol (3-methyl butanol) appears to show characteristic trends from normal alcohol. No rational explanation has been found in this case. On the other hand, physisorbed alcohol was undoubtedly identified only for the methanol and ethanol tests as its desorption occurred at low temperatures, 120–130 °C. The lack of physisorbed alcohol for the rest of alcohol could be attributed to its higher molecular volume, which could hinder the access to the pores. Thus, the amount of physisorbed alcohol could be very low. Anyway, the appearance of olefins and/or ethers during thermal treatment confirms that chemisorbed species do exist in all the cases. It must also be pointed out that, beyond 350 °C, no more desorbed species were detected by mass spectroscopy, which suggests that the alcohol is completely eliminated from the alumina surface.

3.2. Hydraulic characterisation of the membrane

The hydraulic permeability of the membrane for water, methanol, ethanol, n-propanol and n-octanol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Boiling point (°C)</th>
<th>Viscosity (× 10^{-3} Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>65.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Propanol</td>
<td>97.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Butanol</td>
<td>117.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Octanol</td>
<td>194.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>

* At 25 °C.
were determined in order to highlight the hydrophilic characteristics of the membrane. After each solvent test, the membrane was regenerated as described in the experimental section in order to remove any possible chemisorbed compound. The water permeability obtained after each regeneration was progressively increasing from $3.6 \times 10^{-17}$ to $7.0 \times 10^{-17}$ m$^2$, which indicates that the thermal treatment damages the membrane structure to some extent. Assuming that, the interaction between water and the pore surface was not changed by the regeneration procedure, the pore size estimated from Eq. (2) goes from the original 6.3 to 8.8 nm after the last regeneration. Therefore, the test-to-test change in pore size could invalidate the comparison of solvent permeabilities if this is just done in terms of permeability constants. To overcome this drawback, the comparison will be done in terms of normalised permeability constants as defined by Eq. (3), which only accounts for interactions between the solvent and the membrane material. Thus, as can be seen in Table 2, the normalised permeability constant for water is 0.91 whereas this parameter ranges from 0.39 to 0.53 for normal alcohol. Hence, as expected, the alumina membrane shows hydrophilic characteristics that facilitate the passage of water across the membrane. The similar values obtained for the alcohol, regardless of their molecular size, suggest that the permeation could be strongly influenced by the interactions between the alcohol functional groups and the hydroxylated surface of alumina. Only, the larger $n$-octanol shows a significantly lower permeability. This higher difficulty to permeate could be ascribed to the repulsion between the polar membrane surface and the non-polar alkyl chain of this alcohol. The size of the larger alcohol, $n$-octanol in its more extended form is about 1.2 nm (Chem 3D Plus$^\text{TM}$, version 3.1.2 for Molecular Modelling System of CSC Inc.) whereas the pore diameter was of 8.8 nm. This means that the majority of molecules of any alcohol cross the membrane without interacting with the hydrophilic membrane surface so, as encountered, the permeability constants are expected to be in the same range.

### 3.3. Performance of the modified membranes

The first set of modified membranes was obtained by Procedure #1, i.e. merely drying the treated membrane at 120°C for 2h, which was previously wetted with the desired alcohol. Then, the water permeability of the modified membrane was determined and compared with that of the virgin membrane. From the water permeability of the modified membrane, the apparent pore diameter, $d_p$ was calculated using Eq. (2) and then compared with that actual $d$, and also with that estimated $d_e$. The latter was calculated assuming a uniform and dense layer of alcohol adsorbed on the alumina surface, which would result in a reduction of pore diameter merely by physical reasons. The difference between the actual and the apparent pore diameter can be taken as a measure of the degree of modification reached. Table 3 lists the results obtained from modifications using methanol, ethanol, $n$-propanol and $n$-octanol. As proved by the values of $d_{ap}$, the modification of the membrane was evident.

### Table 2

Permeability of the unmodified membrane for different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$d_a$ (nm)</th>
<th>$k_b \times 10^{17}$ (m$^2$)</th>
<th>$k_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water$^a$</td>
<td>6.3</td>
<td>3.6</td>
<td>0.91</td>
</tr>
<tr>
<td>Water$^b$</td>
<td>7.4</td>
<td>5.1</td>
<td>0.91</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.6</td>
<td>2.6</td>
<td>0.46</td>
</tr>
<tr>
<td>Methanol</td>
<td>7.9</td>
<td>3.1</td>
<td>0.50</td>
</tr>
<tr>
<td>$n$-Propanol</td>
<td>8.4</td>
<td>3.7</td>
<td>0.53</td>
</tr>
<tr>
<td>$n$-Octanol</td>
<td>8.8</td>
<td>3.0</td>
<td>0.39</td>
</tr>
</tbody>
</table>

$^a$ Apparent pore diameter estimated from Eq. (2).

$^b$ Permeability constant estimated employing Eq. (1).

$^c$ Normalised permeability constant estimated employing Eq. (3).

$^d$ Membrane as received.

$^e$ Membrane after the first thermal treatment.

### Table 3

Water permeability constant, actual pore diameter and apparent pore diameter for membranes modified by alcohol adsorption using the Procedure #1

<table>
<thead>
<tr>
<th>Alcohol adsorbed</th>
<th>$k_b \times 10^{17}$ (m$^2$)</th>
<th>$d_a$ (nm)</th>
<th>$d_{ap}$ (nm)</th>
<th>$d_{es}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>5.4</td>
<td>7.9</td>
<td>7.7</td>
<td>7.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.7</td>
<td>7.6</td>
<td>5.4</td>
<td>6.9</td>
</tr>
<tr>
<td>$n$-Propanol</td>
<td>5.6</td>
<td>8.4</td>
<td>8.0</td>
<td>7.5</td>
</tr>
<tr>
<td>$n$-Octanol</td>
<td>6.2</td>
<td>8.8</td>
<td>8.3</td>
<td>6.7</td>
</tr>
</tbody>
</table>

$^a$ Calculated from the water permeability after membrane regeneration.

$^b$ Estimated from Eq. (2).

$^c$ Assuming an alcohol monolayer adsorbed on alumina surface.
only for ethanol and methanol since the differences observed for \(n\)-propanol and \(n\)-octanol fall within the experimental error, so unsuccessful modification must be accepted in practice. For ethanol, the apparent pore diameter is over 2 nm lower than the actual pore diameter. This difference cannot be only explained by a monolayer of adsorbed alcohol covering the pore. In this case, the expected reduction of the pore diameter should be of about 0.7 nm. This fact, suggests that the adsorbed alcohol changes the surface properties of the membrane, which turns from being hydrophilic to hydrophobic. This hydrophobicity is imparted by the alkyl chains and could explain the additional decrease in the water permeability. This also confirms that water permeability does not only depend on the pore diameter but also on the surface characteristics of the membrane. This effect sometimes has been expressed as an apparent viscosity with the purpose of calculating the permeate flux, which accounts for the interactions between the permeating liquid and the pore walls. A similar behaviour was observed for the methanol however, unlike ethanol, the modification procedure using methanol showed a poor repeatability, which makes it less reliable. Instead, repetitive tests using ethanol always gave significant differences between \(d\) and \(d_{\text{ap}}\), which move from 1.8 to 2.7 nm.

The failure in properly adsorbing alcohol other than ethanol was attributed to their intrinsic lower reactivity. As well, one can speculate that steric hindrances could also contribute to the apparent low reactivity for larger alcohol. However, the presence of adsorbed water on the alumina could also be enough for preventing the alcohol from reacting with the surface hydroxyl groups. Therefore, a second modification procedure, Procedure \#2, was checked using vacuum in the permeate side as the activation of alumina is preferably carried out under vacuum or using an inert gas carrier \[17,20,22,24\]. This procedure aimed at a double objective. The first goal was to force the alcohol to continuously pass through the pore during the reaction, which made the alcohol more available for reacting. The second aim was to remove adsorbed water, therefore leaving more adsorption sites free to react with the alcohol.

Table 4 summarises the results obtained from different alcohol using the second modification procedure. Unlike the Procedure \#1, it must be noted that a significant decrease of water permeability was detected for all the alcohol tested, which reveals that the modification was successful in all the cases. The differences between the apparent and the estimated pore diameter range from 0.8 to 2.6 nm, which is several times the length of the adsorbed alcohol. For subsequent tests, ethanol was selected as modifying agent as it showed the best repeatability features.

The stability against acids was checked by permeating several hours an acidic solution of the desired pH. Thus, the membrane modified with ethanol showed to be stable at acidic solutions down to pH equal to 1, using both hydrochloric or nitric acid, since no changes in permeability were found in any case. This would allow the use of the modified membranes in processes dealing with acidic solutions. As the degree of alumina surface covered by alcohol cannot be directly measured, the modification Procedure \#2 was repeatedly applied to the same membrane. After each modification, the membrane was tested for water permeability and stability in acid solutions. Obviously, no regeneration step was applied among modifications. Eight consecutive modifications were done until changes in the water permeability were no longer observed. Hence, the initial pore diameter was 13.3 nm and the final apparent diameter, i.e. after eight modifications, was calculated to be 7.9 nm. As expected, this indicates that the coverage of the alumina surface was not completed in a single modification step. As the coverage increases, the higher hydrophobicity of

<table>
<thead>
<tr>
<th>Alcohol adsorbed</th>
<th>(k \times 10^{17}) (m(^2))</th>
<th>(d_b) (nm)</th>
<th>(d_{\text{ap}}) (nm)</th>
<th>(d_{\text{es}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.6</td>
<td>10.7</td>
<td>7.9</td>
<td>10.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.1</td>
<td>12.9</td>
<td>10.7</td>
<td>12.2</td>
</tr>
<tr>
<td>(n)-Propanol</td>
<td>1.2</td>
<td>12.9</td>
<td>11.2</td>
<td>12.0</td>
</tr>
<tr>
<td>(i)-Propanol</td>
<td>1.2</td>
<td>12.9</td>
<td>11.2</td>
<td>12.2</td>
</tr>
<tr>
<td>(n)-Octanol</td>
<td>1.1</td>
<td>13.3</td>
<td>10.7</td>
<td>12.2</td>
</tr>
</tbody>
</table>

\(^a\) A new membrane was used for this set of tests, the nominal pore size being of 10.7 nm.

\(^b\) Calculated from the water permeability after membrane regeneration.

\(^c\) Estimated from Eq. (2).

\(^d\) Assuming an alcohol monolayer adsorbed on alumina surface.
the membrane reduces the water permeability, which confirms that the interaction between the aliphatic free chains of the alcohol and water plays a dominating role in the permeation process.

On the other hand, the modification did not change the isoelectric point of the membrane. Fig. 4 illustrates the change in the pH of a solution passing through the membrane for both non-modified and eight times modified cases. It is well-known that the surface of the γ-alumina has amphoteric properties due to its hydroxyl groups [23,25]. The isoelectric point of the membrane corresponds to a pH solution that does not vary the surface charge. Since during modification, replacing of hydroxyl groups for alkyl chains occurred, no change in the acid–base properties of the surface should be expected, which was experimentally proved as the isoelectric point is about 4.4 for both non-modified and modified membrane. This favourably agrees with previous investigations on a similar membrane [23]. However, the difference between the feeding pH and the permeating pH can be taken as a measure of the number of sites with acid–base capacity. This difference was considerably lower when a modified membrane was used, which means that the number of hydroxyl groups was highly reduced as a result of the alcohol adsorption. Thus, the acid (or base) consumed to equilibrate the membrane was over five times higher for a regenerated membrane than for the modified membrane, which could indicate that the surface coverage could be around 80%.

4. Conclusions

This study shows that alcohol can be readily linked to the alumina surface by covalent bonding. Whereas physisorbed alcohol can be easily removed by heating at 120°C, chemisorbed alcohol is stable at temperatures up to 250°C for normal alcohol. Beyond this temperature, the alcohol either desorbs, or undergoes a dehydration yielding the corresponding olefin or forms an ether. Above 350°C, mass spectroscopy analyses no longer detect desorbed species, which indicates that alumina surface has been cleaned.

In the virgin membrane, the permeability of water is almost twice that of the alcohol, which proves the hydrophilic nature of the membrane. All alcohol tested show minor differences in permeability regardless their molecular size. This suggests that the interaction between the surface hydroxyls of the membrane and the alcohol functional groups governs the permeation rather than the interaction with the aliphatic chain of the alcohol.

The modification of nanofiltration ceramic membranes was successfully achieved using different normal and branched alcohol and heating at 120°C under vacuum. In all cases, the reduction in water permeability was higher than expected by assuming a monolayer of adsorbed alcohol. This suggests that the chemisorbed alcohol imparts hydrophobic characteristics to the membrane enhancing the reduction in water permeability. Ethanol shows the best repeatability in the modification procedure. The layer of adsorbed ethanol was stable to acid attack in the range of pH tested, i.e. down to pH equal to 1. As expected, the isoelectric point of the membrane was not changed by the modification. The original water permeability of the membrane was recovered by heating at 250°C. This easy modification may have particular application for tailoring the membrane pore size or as an anti-fouling coating in aqueous separation processes.

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References