The First Redox Switchable Ceramic Membrane

David Farrusseng,* Anne Julbe, and Christian Guizard

Laboratoire des Matériaux et Procédés Membranaires
UMR 5635 CNRS-UMII-ENSCM
Ecole Nationale Supérieure de Chimie
8, rue de l'Ecole Normale
34296 Montpellier Cedex 5, France

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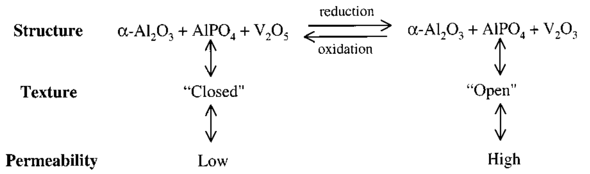
Liquid and solid membranes commonly use the molecular recognition function based on complexation properties between a carrier located in the membrane and guest molecules, or ions in liquid media to facilitate mass transport.[1] For biomembranes[2] and well-designed synthetic membranes,[3] the molecular recognition is directed by a redox function of the receptor leading to the concept of a redox-switchable membrane.

Here, we report a new type of redox switchable gas transport for an original porous ceramic membrane. Although supra molecular recognition is not involved in gas transport mechanisms for porous membranes, the permeability of this vanadium oxide-based membrane is directly controlled by its oxidation state. At low-oxidation state, the membrane permeability is high, whereas its permeability is much lower at high-oxidation states. We report here on the synthesis and characteristics of a composite V_2O_x−$AlPO_4$/α-Al_2O_3-supported membrane which, to the authors' knowledge, is the first example of a porous ceramic membrane able to control reversibly its permeability by its redox properties (Scheme 1). The structure−property relationships of the membrane are described and discussed in terms of morphological and textural transformations.

Scheme 1. Crystalline Structure, Porous Texture and Permeability Relationships



The composite V_2O_x−$AlPO_4$/α-Al_2O_3 membranes were prepared by infiltrating an organic sol derived from a vanadium alkoxide and a mixture of alkyl phosphates[4] in a tubular α-Al_2O_3 support.[5] After drying, the as-made membranes were calcined at 923 K in air for 2 h. Results from FESEM observations (Figure 1a) and Hg porosimetry measurements show that the inner porous α-Al_2O_3 layers of the support (∼60 μm) are almost completely filled by crystalline materials, yielding composite layers with a very low porosity. Nitrogen permeance studies[6] as a function of the transmembrane pressure and as a function of the temperature indicate that gas transport is governed by both Knudsen diffusion and viscous flow mechanisms. This behavior is typical for a porous texture containing both macro- and mesopores. Nitrogen sorption analysis confirmed the very low porosity of the as-prepared membrane (5×10^{-5}cm^3·g^{-1}) and a broad pore-size distribution (Figure 2a).

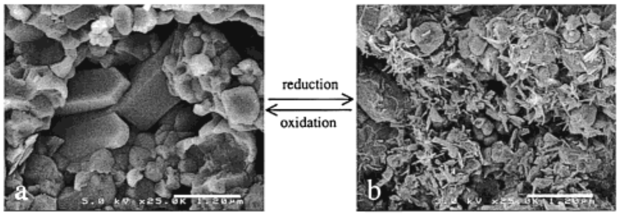


Figure 1. FESEM observations of the membrane cross-section after (a) an oxidizing treatment, (b) a reducing treatment.

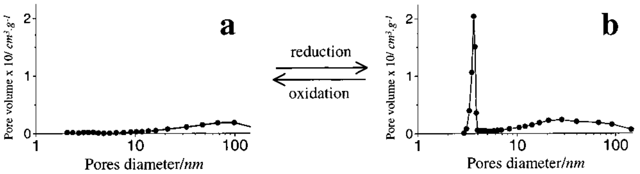


Figure 2. Pore-size distribution of the membrane, after (a) an oxidizing treatment, (b) a reducing treatment.

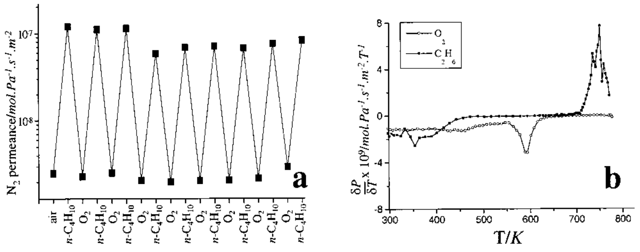


Figure 3. Effect of the redox conditions on the membrane permeance; (a) N_2 permeance evolution at 773 K during redox cycles, (b) TPO and TPR analyses from the O_2 and C_2H_6 permeance measurements, respectively.

The membrane N_2 permeance was measured at 773 K after successive reducing and oxidizing treatments at 773 K for 0.5 h under n-C_4H_{10} and O_2 flows respectively (Figure 3a). A permeance evolution was spontaneously observed when switching the permeating gas from N_2 to pure n-C_4H_{10} or pure O_2 at 773 K. The N_2 permeance drastically increases up to 10^{-7} mol·Pa^{-1}·s^{-1}·m^{-2} and decreases down to 2×10^{-9} mol·Pa^{-1}·s^{-1}·m^{-2} after reducing and oxidizing treatments, respectively. This permeation behavior is almost entirely reversible over the eight performed redox cycles. The average ratio between the N_2 permeance for the "reduced" and "oxidized" states of the membrane is about 30.

The evolution of the C_2H_6 and O_2 single gas permeances were measured as a function of the temperature after an oxidizing or reducing treatment, respectively (Figure 3b). Since the reducing or oxidizing gas permeates through the membrane, these temperature programmed permeation studies (TPP) reflect the membrane redox properties by means of temperature programmed

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* Author for correspondence: Institut de Recherches sur la Catalyse, CNRS, 2 avenue Albert Einstein, F-69626 Villeurbanne Cédex. E-mail: farrusseng@catalyse.univ-lyon1.fr.

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(3) Nabeschima, T.; Furusawa, H.; Yano, Y. *Angew. Chem., Int. Ed.* **1994**, *33*, 1750−1751.

(4) The vanadium alkoxide was prepared according to Livage, J.; Guzman, G.; Beteille, F. J.; Davidson, P. *J. Sol.-Gel Sci. Technol.* **1997**, *8*, 857−865. Detailed preparation procedure may be found elsewhere: Farrusseng, D.; Julbe, A.; Lopez, M.; Guizard, C. *Catal. Today* **2000**, *56*, 211−220.

(5) Commercial α-Al_2O_3 tubes supplied by SCT-France were used as supports. They consists of an inner, an intermediate and an external layer with 0.2, 0.8, and 10 μm mean pore sizes, respectively. The porosity for the three layers is 25% ± 1.

(6) The permeation experiments were carried out by using the Dead End method described elsewhere in van de Graaf, J.; Kapteijn, F.; Moulijn, J. A. *J. Membr. Sci.* **1998**, *144*, 87−104. The permeance ($\Pi = F/\Delta P$) is calculated from the measurements of the flow (F) by imposing a known transmembrane pressure (ΔP).

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reduction (TPR) and oxidation (TPO). The derivative of the C_2H_6 permeance curve versus temperature shows a broad positive peak centered at 750 K, indicating an increase in the permeance corresponding to the reduction step. The derivative of the O_2 permeance curve shows the oxidation occurs at 160 K lower. The results of TPP studies with various gases[7] were in good agreement with conventional TPR and TPO experiments measured by transient gravimetric analysis.[8] At 773 K, the completion of the oxidation process with pure O_2 is much faster than reduction under n-C_4H_{10} flow (4 and 25 min, respectively). Under steady-state conditions at 773 K, the ideal selectivities for H_2/O_2, C_2H_6/O_2, and n-C_4H_{10}/O_2 derived from the ratios of single gas permeances are 120.9, 34.0, and 14.3, respectively. These ideal selectivities between a reducing gas and O_2 at high temperature are much greater than those classically reported in the literature for porous ceramic membranes[9] and particularly higher than the Knudsen ideal selectivities (i.e., for H_2/O_2, C_2H_6/O_2, and n-C_4H_{10}/O_2 the Knudsen selectivities are 4.00, 1.03, and 0.74, respectively).

The crystalline structure and morphology, as well as the porous texture of the membrane material, were characterized during the redox treatments. Solid-state NMR (^{51}V, ^{31}P, ^{27}Al) and X-ray diffraction studies reveal that the material occluding the pores of the α-Al_2O_3 support consists of $AlPO_4$ and V_2O_5 crystallites after the oxidizing treatment, the latter transforms to V_2O_3 after the reducing treatment.[10] The structural changes during the reduction step induce a drastic modification of the vanadium oxide morphology, which transforms from a compact porous texture exhibiting elongated crystals, to platelets and small grains (Figure 1b). Nitrogen adsorption−desorption experiments performed on the reduced and oxidized membranes reveal that the reducing treatment: (i) generates a new family of mesopores with a narrow size distribution centered at 3 nm (Figure 2b), (ii) increases the specific surface area by a factor 2.5, and (iii) increases the porous volume by a factor 7. Similar results have been obtained with a V_2O_5 commercial powder,[11] thus confirming the role of the vanadium oxide redox properties on the membrane porous structure and permeance behavior. The membrane changes in crystalline structure and related textural transformations were found to be reversible (Figures 1 and 2).

When the vanadium is V^{V}, the low porosity of the oxidized membrane material partially hinders the gas transport, resulting in a decrease in permeance, the membrane is in the "closed" state. When the vanadium is V^{III}, the higher porosity of the reduced membrane material enhances gas transport, increasing its permeance; the membrane is in the "open" state. The membrane therefore exhibits specific chemomechanical property as its pore volume reversibly expands and contracts in response to an external input.[12] Although the $AlPO_4$ and α-Al_2O_3 materials do not play a role on the redox switchable property, they contribute to the overall transport resistance. The unusual ideal selectivities reported for the V_2O_5-based membrane do not result from a highly "selective" transport mechanism but from a porous texture modification of the membrane during mass transport. Since the permeance of the "open" membrane is 1−2 orders of magnitude higher than the permeance of the "closed" membrane, we may state that the reactivity of this V_2O_5-based composite membrane allows a redox-switchable permeance. Further studies reveal that the V_2O_5-based membrane is not only capable of "switch-on/off" effects but is also able to regulate continuously its permeance as a function of the redox characteristics of the gas phase. For example, the membrane adapts its permeance to the reducing/oxidizing strength of the gas or to the composition of an alkane/O_2 mixture (Figure 4).[13] This original composite membrane combines in a single unit a redox sensor effect and a gas valve function.

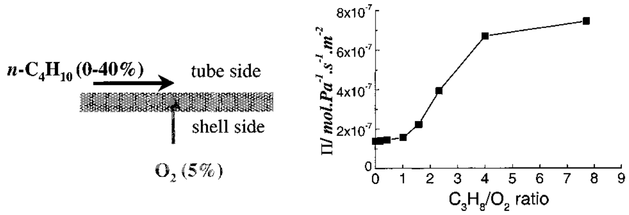

Figure 4. Evolution of the membrane permeance as a function of the C_3H_8/O_2 molar ratio.

On the basis of the original properties of this new V_2O_5-based composite membrane, we are investigating a new generation of membrane reactors called *chemical valve reactors* which are potentially able to auto-regulate the O_2 distribution in a reactor for the partial oxidation of alkane. Moreover, the high permeability discrepancies between the reduced/oxidized states of the membrane and its fast response to changes in the redox characteristics of the gas phase are attractive properties for potential application of the V_2O_5-based membrane as a sensor. We strongly believe that the new properties of this double-function membrane material could have attractive elements for the development of new membrane reactors, sensors, or O_2 absorption at high temperature.

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Supporting Information Available: Temperature programmed permeation and reduction plots and micrographs of vanadium oxide samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) O_2, H_2, C_2H_6, C_3H_8, and n-C_4H_{10}.

(8) Experimental description of the transient gravimetric analysis: Zeng, Y.; Lin, Y. S. *Solid State Ionics* **1998**, *110*, 209−211.

(9) For recent comparison with ideal selectivities of meso- and microporous ceramic membranes at high temperature: (a) Burggraaf, A. J. In *Transport and Separation Properties of Membranes with Gases and Vapors*; Burggraaf, A. J., Cot, L., Eds.; Elsevier: Amsterdam, 1996; Vol. 4, pp 330−434. (b) Hsieh, H. P. *Inorganic Membranes for Separation and Reaction*; Elsevier: Amsterdam, 1996; Vol. 3. (c) *Microporous Mesoporous Mat.* **2000**, *38* (entire volume). (d) Coronas, J.; Santamaria, *Sep. Purif. Methods* **1999**, *28*, 127−177.

(10) $AlPO_4$ orthorhombic, V_2O_5 orthorhombic ($d_{th} = 3.364$), and V_2O_3 monoclinic. Corresponding ICDD, PDF-2 files: no. 11−500, no. 41−1426, and no. 39−0774, respectively.

(11) Purchased from Rhodia-Prolabo.

(12) Reversible porous structure modifications by external stimulus were reported for polymeric membranes in: (a) Nishino, M.; Gong, J. P.; Osada, Y. *Bioseparation* **1998**, *7*, 269−280. (b) Mika, A. M.; Childs, R. F.; Dickson, J. M. *J. Membr. Sci.* **1999**, *153*, 45−56. (c) Nishi, S.; Kotaka, T. *Macromolecules* **1986**, *19*, 978−984. (d) Tsuji, T.; Otake, K.; Konno, M.; Saito, S. *J. Appl. Polym. Sci.* **1990**, *41*, 1351−1353. For a definition of "hemomichanical property", see: Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242−244.

(13) The shell side was fed with a O_2/He stream (5% O_2), while the tube side was fed with a C_3H_8/He stream in which the C_3H_8 concentration was varied from 0 to 40%. For both streams, the flow rates were fixed at 1.49×10^{-5} mol·s^{-1}. The transmembrane pressure was measured by a digital sensor at steady state after each modification in the C_3H_8 concentration.