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Limitations and potentials of oxygen transport dense and porous ceramic membranes for oxidation reactions

A. Julbe *, D. Farrusseng [1], C. Guizard [2]

Institut Européen des Membranes (UMR 5635 CNRS/UM2/ENSCM), CC 47, Place Eugène Bataillon, 34095 Montpellier cedex 05, France

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Abstract

This overview focuses on both dense and porous ceramic membranes for high temperature oxidation reactions, i.e. partial and total oxidations. Non-permselective porous membranes are efficient contactors for total oxidation of VOC or soot. They are also still attractive as oxygen distributors for the partial oxidation of long chain alkanes, although dense mixed conducting membranes are now on the way to be commercialized for methane involving reactions. By a proper selection of the ion conducting materials composition, structure and thickness, and by combining in a suitable way both dense and porous layers, the oxygen flux, performance and stability of dense ceramic membranes can be considerably improved. In view of the large number of material challenges and scientific approaches found in the literature, it is clearly difficult to be exhaustive. New developments in the field of advanced membranes constantly contribute to improve the potential of membrane reactors, through the development of new preparation methods, of optimized layer stacking and of new membrane materials with original or improved properties. After a rapid overview on both dense and porous membranes used for oxidation reactions, examples of the developments in the field of membrane materials, structures, architectures, synthesis methods and reactor designs are reported, coming from either our Institute or from the recent literature on both membrane reactors and SOFCs.

Keywords: Ceramic membranes; Membrane reactors; Oxidation reactions; Oxygen transport

1. Introduction

The concept of combining membranes and reactors is being explored in various configurations, which can be classified in three groups, regarding the role of the membrane in the process [1]. The membrane can act as an *extractor* (the removal of product(s) increases the conversion by shifting the reaction equilibrium), as a *distributor* (the controlled addition of reactant(s) along the reactor wall limits side reactions), or as an active *contactor* (the controlled diffusion of reactants to the catalyst can lead to an engineered catalytic reaction zone). In the two first cases the membrane has usually no catalytic properties and is combined, for example, with a fixed bed of catalyst placed on one membrane side [2].

In the active contactor mode, the membrane acts as a diffusion barrier and plays the role of a catalyst whereas separation properties are usually not required. The concept can be used with a forced flow-mode or with an opposing reactant mode. The forced flow contactor mode has been applied to the total oxidation of VOC [2].

The distributor mode is usually well adapted to limit consecutive and parallel deep oxidation reactions for partial oxidation, oxidative dehydrogenation of hydrocarbons and oxidative coupling of methane [2,3]. For these reactions, the local oxygen concentration at the catalytic site greatly influences both hydrocarbon conversion and product selectivity. Indeed strong oxidizing conditions promote the total combustion responsible for hot spots in the catalytic bed [2,3]. Using membrane supported concepts, oxygen can be dosed in a controlled manner so that the hydrocarbon–

* Corresponding author. Tel.: +33 4 67 14 91 42; fax: +33 4 67 14 91 19.
E-mail address: julbe@iemm.univ-montp2.fr (A. Julbe).
[1] Present address: Institut de Recherches sur la Catalyse (CNRS - UPR 5401) - 2, Avenue Albert Einstein, 69626 Villeurbanne cedex, France.
[2] Present address: Laboratoire de Synthèse et Fonctionnalisation des Céramiques, FRE 2770 CNRS/SAINT GOBAIN C.R.E.E. - 550, Avenue Alphonse Jauffret, BP 224-84306 Cavaillon cedex, France.

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oxygen ratio is tuned along the catalyst bed. Providing the kinetics of the oxidation reaction are known, an optimal oxygen partial pressure profile can be controlled along the reactor [2,3]. The derived ideal oxygen permeation profile allows the design of optimized membranes in terms of permeability or thickness gradients [2,3]. In addition, the oxygen–hydrocarbon feed separation helps to overcome flammability and explosion limits. It results in a greater catalytic activity while the controlled oxygen supply avoids the catalysts to be deactivated in reducing conditions. The concept of tuned oxygen supply has also a beneficial role in mitigating the temperature rise in the reactor [2], which is a key issue in alkane partial oxidation. The O_2 permselectivity of the membrane is also an important economic factor because air can be used instead of pure O_2. The extremely high permselectivity of dense ionic conducting ceramics, coupled with their ability to generate highly reactive/selective O^* species, explains their impressive development for these applications over the last 15 years [4]. However, due to the very poor conductivity/permeability of dense membranes below 800 °C, further improvements are still needed for applications in the range 400–700 °C, for which to date poorly permselective porous membranes have to be used [2,5].

A large number of recent review articles and books seeks to review literature and new developments on membrane reactors over the last 10 years [1–10]. Research directions that were previously considered promising have been recently reconsidered, and new ideas have emerged [9]. The present paper highlights several specific aspects in the field of membrane materials for high temperature oxidation reactions. New material developments constantly contribute to improve the potential of membrane reactors, through the implementation of new preparation methods, new shapes and new membrane materials with original or improved properties (composition, crystallographic structure, architecture, porous structure, reactivity, transport mechanisms, oxygen flux, permselectivity, long-term stability, ...). Recent developments in SOFCs, involving thin supported electrolyte films, with composition and porosity gradients (from the dense electrolyte to the electrodes) are also directly applicable to membrane reactors for partial oxidation reactions.

2. Dense membranes for oxidation reactions

Dense membranes (cf. Fig. 1a and b) are of particular interest for oxygen transport applications [4,11,12] because of their high permselectivity compared to porous membranes (cf. Fig. 1c). Oxygen ions are selectively transported through the non-porous ceramic membrane that is tight to other species. Different types of electrochemical membranes can be developed and in all cases the dissociation of an oxygen molecule must occur at the cathode side of the cell, usually the high oxygen partial pressure compartment, according to the interfacial reaction ($1/2\,O_2 + V_o^{\cdot\cdot} + 2e^- = O_o^x$), in which $V_o^{\cdot\cdot}$ is an oxygen vacancy [12]. After migration of the oxygen anions through the electrolyte, the reverse reaction must necessarily occur at the opposite (anodic) side in order to restore the O_2 molecule in the anodic gas phase. The way by which the electrons are transferred from the anode to the cathode determines the different membrane concepts [11]. The ion flux is driven either by an electrical field (cf. Fig. 1a) or by an oxygen pressure gradient (cf. Fig. 1b).

Most materials of interest to produce these membranes are based on fluorite (AO_2) or perovskite (ABO_3) related structures [11,12]. Dual phase membranes based on metal–ceramic combinations can also be used in the configuration of Fig. 1b [11]. Ion transport is via oxygen vacancies and the total flux of oxygen species is determined by both the bulk permeability and the reaction rate of molecular oxygen at the interface membrane/external gas phase. Many conducting oxides have a sufficient ionic conductivity to be used as oxygen distributors in oxidation reactions at temperatures higher than 700 °C. This is typically an adapted temperature range for CH_4 involving reactions (oxidative coupling or conversion to syngas) [13]. Two impressive US-DOE programs led by the two major American industrial gas companies (Air Products & Chemicals, and Praxair) have rapidly driven this "energy key-technology" to the prototype level [14]. If successful, this would be the first radically new reforming technology in over 3 decades.

A number of materials including perovskite derived structures have been identified as promising candidates to transport oxygen at relatively low temperature. Obviously

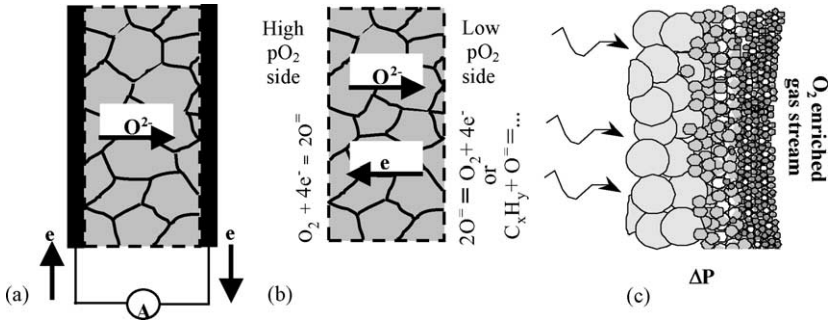

Fig. 1. Different membrane concepts for oxygen distribution in a reactor: (a) solid electrolyte cell (oxygen pump), (b) mixed ionic-electronic conductor (MIEC), (c) asymmetric porous membrane with a graded porosity.