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Oxygen permeation versus catalytic properties of bismuth-based oxide ion conductors used for propene oxidation in a catalytic dense membrane reactor

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Abstract

Dense membranes of Bi_2O_3–25% Er_2O_3 (BE25), BE25–Ag cermet, and $Bi_2V_{0.9}Co_{0.1}O_{5.35}$ (BICOVOX.10) were used to separate the two compartments of the so-called catalytic dense membrane reactor. The setup allows to measure the rate of permeation of dioxygen as well as the catalytic properties in oxidation of hydrocarbons. Higher oxygen permeation rates are observed on BE25 and BE25–Ag cermet than on BICOVOX.10 whereas the latter is more active for propene oxidation. The polarization of the membrane measured in situ during catalytic reaction shows that the overall oxygen transfer in BICOVOX.10 is enhanced and that permeation of dioxygen is not a key property in selective oxidation of hydrocarbons.

Keywords: BIMEVOX; Propene oxidation; Catalytic dense membrane reactor; CDMR

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1. Introduction

Bismuth-based oxides in general, and particularly BIMEVOX compounds synthesized at LCPS at the end of the eighties [1], exhibit high oxide ion conductivity at moderate temperature ($T = 500$–$1000\,K$). The BIMEVOX family is derived from $Bi_4V_2O_{11}$ by partial substitution of vanadium by another metal such as cobalt or copper and are described by the general formula: $Bi_2V_{1-x}Me_xO_{5.35}$. These materials are attractive for use as dense ceramic membranes in several applications, such as oxygen sensors, oxygen generators, solid oxide fuel cells or catalytic membranes.

Bismuth and vanadium ions are a priori active cations for the catalytic oxidation of hydrocarbons. Indeed, BIMEVOX materials have already been investigated in the catalytic coupling of methane and oxidative dehydrogenation of propane [2] and more recently in the oxidation of propene [3], as Bi is known to allow unsaturated hydrocarbons to form π-allylic intermediates at the surface of the catalyst [4].

In selective oxidation of hydrocarbons, the typical Mars and Van Krevelen redox mechanism may be decoupled by performing the two steps separately [5], so that conditions for each one can be optimized. This may be done by using a circulating bed reactor [6], a periodical feed reactor or a catalytic dense membrane reactor (CDMR) [7,8]. Basically, a CDMR is built on a dense membrane separating two compartments. One side of the membrane is fed with pure or diluted oxygen whereas the other is fed with the reactant diluted in a neutral carrier gas. In contrast to porous membranes across which oxygen diffuses as molecular dioxygen, the migration of oxygen anions O^{2-} through the dense oxide ion conducting membrane is expected to refill the oxygen vacancies created by the catalytic reaction. Membrane materials for use in a CDMR should thus exhibit both high oxygen conductivities and interesting catalytic properties for hydrocarbon activation and oxidation. Furthermore, the role of electronic conductivity is essential, as electrons must flow within the bulk of the membrane, in contrast to the case of fuel cells or oxygen generators in which an external circuit ensures the electroneutrality of the system.

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The aim of this paper is to measure oxygen permeation in bismuth-based oxide materials and use them as membrane for CDMR for propene oxidation in order to settle correlations between oxygen permeation and catalytic properties. Two Bi based oxide materials were selected: a δ-Bi_2O_3 form stabilized by erbia ($Bi_2O_3 + 25\%\,Er_2O_3$, BE25) and $Bi_2V_{0.9}Co_{0.1}O_{5.35}$ ($Bi_4V_2O_{11}$ with 10% of V substituted with Co, BICOVOX.10). These materials both exhibit a p-type electronic semiconductor behavior [9,10]. Bismuth-erbia membranes have been extensively studied by Bouwmeester et al. [11,12] who showed that the oxygen permeation could be strongly enhanced by addition of silver as electronic conductor. The catalytic behavior of such cermet membranes was also compared to that of BICOVOX.

2. Experimental

BICOVOX.10 and BE25 powders were synthesized from pure oxides (Bi_2O_3 99.9% pure, V_2O_5 99.6% pure, CoO min. 99% pure and Er_2O_3 99.9% pure) as already described elsewhere [1]. A silver cermet with BE25 (BE25–Ag) was also prepared by mixing BE25 powder with 40 vol.% silver powder (99.9% pure). Cylindrical pellets ($\varnothing = 15$ mm, $d = 1$–2 mm) were prepared by uniaxial followed by isostatic pressing (150–180 MPa). Each membrane was then sintered at 1023 K for BICOVOX.10 or 1173 K for BE25 and the BE25–Ag cermet. The relative density of such membranes is higher than 95%. In order to measure accurate oxygen permeation properties, both sides of the membranes were polished using a 4000 grit SiC paper. To characterize the

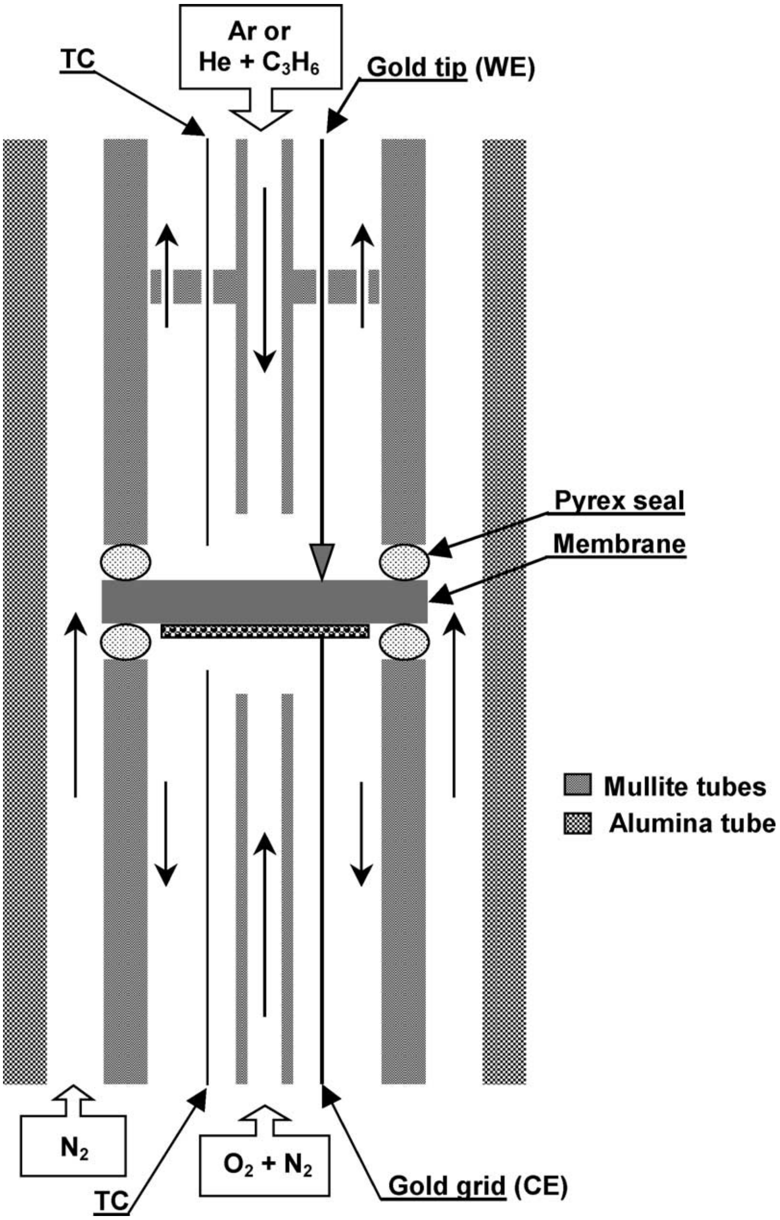

Fig. 1. Catalytic dense membrane reactor. TC: thermocouple; WE: working electrode; CE: counter electrode.

surface polarization, a gold grid was stuck on the oxygen rich side of the membrane, using a suspension of gold and cellulose in ethanol as fixing agent. The membrane was then annealed at 973 K in order to burn the cellulose and ensure the porosity of the metal layer.

The CDMR (Fig. 1) was based on the experimental setup described by Fouletier et al. [13]. The membrane was introduced in between two mullite tubes and sealed, by means of Pyrex rings at the operating temperature. The central mounting was inserted in a larger alumina tube in which nitrogen (99.996% pure) flowed in order to minimize the effect of the lateral wall of the membrane. Gases were supplied to each side of the membrane through mullite tubes, respectively, O_2 (99.90% pure) diluted in N_2 in the “high” oxygen pressure (HOP) side, and Ar (99.9990% pure) in the “low” oxygen pressure (LOP) side for oxygen permeation measurements. For catalytic activity measurements, He (99.99990% pure) and propene (99.6% pure) were fed to the LOP side instead of argon. In all cases the gases introduced in the LOP side contained about 0.5–1 ppm O_2 as impurity. Flow rates were adjusted using Brooks Sho-Rate flowmeters and switching valves allowed the measurement of the gas phase composition in the inlet and outlet of both sides of the membrane using an oxygen gauge (Setnag, JC48V) and/or an on-line quadrupole mass spectrometer (Pfeiffer, Omnistar Prisma 200).

Oxygen permeation fluxes were first measured at various temperatures and for various oxygen partial pressures at the HOP side. Then, the LOP side was fed with a mixture of propene in helium and the catalytic properties of these membranes were characterized by varying temperature and contact time. The polarization of the membrane surface was measured by following the electrical potential between two gold electrodes, the gold grid on the HOP side acting as counter electrode and a gold tip on the LOP side as working electrode (Fig. 1). This device allows to evaluate the activity of oxygen at the surface of the membrane and its evolution during catalytic reaction. A blank experiment without the gold electrode on BICOVOX.10 showed that it does not affect the catalytic activity of the membrane.

X-ray diffraction, scanning electron microscopy and XPS were used to examine the membranes before and after experiments.

3. Results

3.1. Oxygen permeation

Fig. 2 shows the oxygen permeation flux observed at equilibrium for all samples at various temperatures with air ($pO_2 = 21\%$) in the HOP side of the membrane. As expected, the oxygen flux through the cermet membrane is higher than those measured on pure ceramic BE25 membrane and on BICOVOX.10. The results obtained on both pure bismuth-erbia and cermet membranes are in very good agreement with those published by Bouwmeester et al. [11,12] which are reported in the same figure.

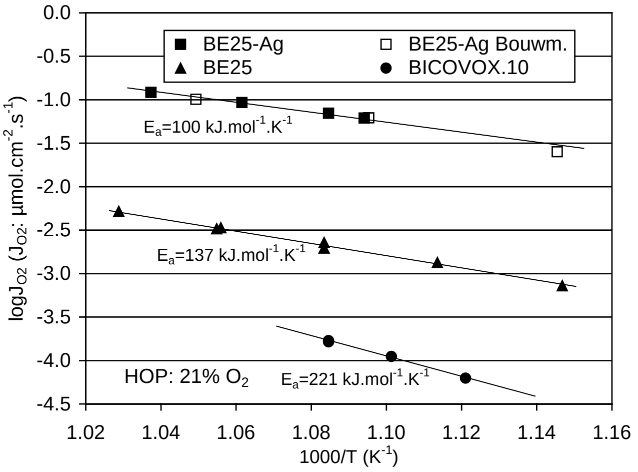

Fig. 2. Permeation flux of oxygen J_{O_2} vs. reciprocal temperature. Open symbols: values for BE25–Ag from [11,12].

3.2. Propene oxidation

Because oxygen permeation fluxes are higher in BE25–Ag cermet than in BE25, the catalytic activity measurements were performed mainly on the cermet and compared to the behavior of BICOVOX.10. The conversion of propene on BICOVOX.10 and BE25–Ag membranes as a function of temperature is reported in Fig. 3. In both cases the oxidation of propene is low (1–2 mol%) and produces mainly CO. However, by varying the temperature or the oxygen pressure in HOP, and according to conversion, significant amounts of hexadiene and/or acrolein (up to 10–20 mol%) were measured. On both membranes, the oxygen permeation flux is not affected by the catalytic reaction, as shown

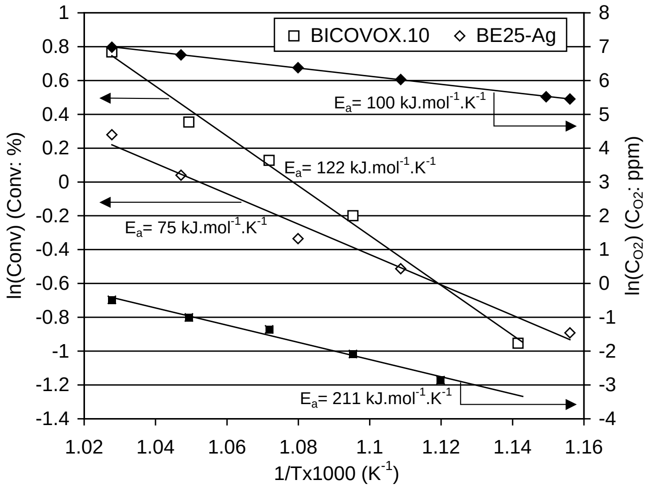

Fig. 3. Propene conversion (open symbols) and O_2 concentration (closed symbols) for BICOVOX.10 and BE25–Ag (total flow rate—LOP: 100 cm^3/min; HOP: 21% O_2; LOP: He + 1% C_3H_6).

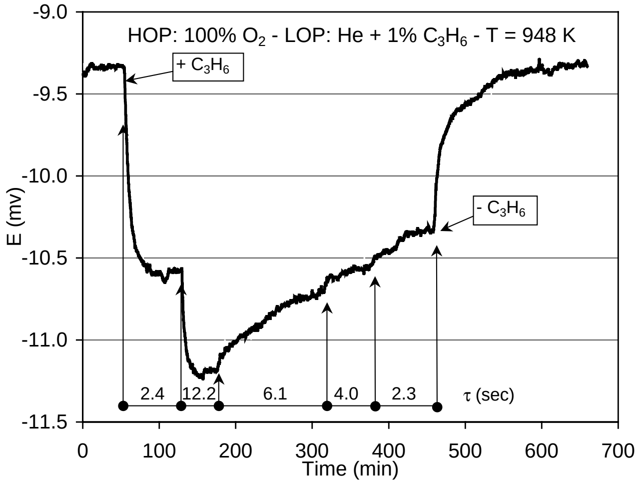

Fig. 4. Evolution with time and contact time τ of the potential measured between the counter electrode (CE) and the working electrode (WE) during catalytic oxidation of propene.

by the amounts of O_2 as well as by the activation energies which are similar to those obtained during permeation study (Fig. 2).

The BICOVOX.10 membrane is slightly more active than the cermet, even though the oxygen permeation through the latter is about three orders of magnitude higher. Indeed, very low oxygen contents (1–2 ppm) were measured in absence of propene in LOP, which cannot account for the total amount of CO and H_2O produced, as 1% of C_3H_6 converted would need up to 300 ppm O_2 in the same experimental conditions.

3.3. Surface polarization

The potential difference between the two faces of the membrane during catalytic test of BICOVOX.10 (100% O_2 in the HOP, $T = 948\,K$) is reported in Fig. 4. It can be seen that the polarization of the LOP side decreases (ΔE is more negative) when adding propene to the feed. This is emphasized when the contact time τ is increased by reducing the total flow in LOP, and that consequently conversion increases. The phenomenon is reversible when shutting off the propene since initial polarization values were recovered.

3.4. Characterization

SEM images showed that the particle size of the BICOVOX.10 grains slightly increased (from 5 to 20 μm in average) during the total experiment time on this sample which exceeded 1 month. However, no cracks could be observed on this membrane nor metallic spheres of Bi as sometimes encountered [8]. No significant evolution of the BICOVOX.10 surface composition was evidenced by XPS analysis, in particular concerning the Bi/V ratio.

4. Discussion

Oxygen permeation fluxes in such membranes are a function of the ratio of oxygen partial pressure between each side, the ionic conductivity, the electronic conductivity, the membrane thickness and the kinetics of transfer at the membrane surface. In the case of BE25 materials, oxygen fluxes were increased by at least one order of magnitude in the presence of silver indicating an electronic limitation in the case of the pure ceramic. Moreover, $^{18}O/^{16}O$ isotope exchange combined with secondary ion mass spectroscopy revealed that the kinetics of transfer are also increased for silver cermet, the transfer coefficient increasing from 2.9×10^{-8} cm/s for pure ceramic to 3.5×10^{-6} cm/s for BE25–40 vol.% Ag cermet [14]. The same experiments carried out on BIMEVOX materials showed very slow rate of oxygen transfer, with a transfer coefficient lower than 5×10^{-9} cm/s at 700 °C [15].

In all catalytic experiments the propene conversion is low (1–2 mol%), but such values are nevertheless significant because of the very small surface area of the membranes which were mirror-polished in order to determine accurate oxygen permeation properties. Based on the geometrical surface of the membrane and on a site density of 5×10^{14} sites cm^{-2}, one can estimate the turnover frequency of these membranes to be in the order of magnitude of 1–10 s^{-1} at 1% conversion**.** The total conversion can be greatly enhanced by developing dense membranes with higher surface areas in the LOP side, which is the matter of a forthcoming publication. The BICOVOX.10 membrane is slightly more active than BE25–Ag cermet one but the low oxygen fluxes measured in the absence of propene cannot account for the amount of hydrocarbon converted. This can be explained by the consumption of lattice oxygen and consequently by the reduction of the solid. However, in contrast to what is observed in a conventional fixed bed flow reactor [3], SEM, XPS and XRD analyses reveal no degradation of the material after experiments. If a decrease of the difference of potential at the surface membranes is observed when propene is fed in the LOP side, it comes back to its initial value when propene is turned off. This decrease of potential simply indicates a lowering in the oxygen surface activity in presence of propene. However, the difference of potential remains rather low—in the 10 mV range—indicating that the oxygen surface activity on this side remains high and is thus likely to protect the membrane against reduction. Indeed, if the membrane would have been at equilibrium with the gas phase, containing 3 ppm O_2 in LOP and 100% O_2 in HOP, a difference of potential of −259.5 mV (Nernst relation: $\Delta E = RT/4F \ln(p_{O_2}^{LPO}/p_{O_2}^{HPO})$) would have been expected. The high oxygen activity in the absence of propene and the overall enhancement of oxygen transfer—which is also reflected by the lower activation energy for propene oxidation (122 kJ mol^{-1} K^{-1}) as compared to oxygen permeation (211 kJ mol^{-1} K^{-1})—confirm that oxygen recombination is the rate-limiting step of the permeation process [15], and that propene provides an alternative pathway for oxygen removal from the surface.

5. Conclusions

The results obtained with BICOVOX.10 membrane show that materials exhibiting low oxygen permeation capacities can be used in catalysis provided the recombination of oxygen to dioxygen is the rate-limiting step of the process. Conversely, materials exhibiting high oxygen permeation properties, such as the BE25–Ag cermet, are not more interesting on a catalytic point of view as most of this oxygen is released to the gas phase and is not used selectively for the catalytic reaction. Contrary to other applications of these materials, the permeability to O_2 is not a key property to be related to catalysis. One can expect to considerably improve the conversion by developing higher surface areas at the LOP side of the membrane. On the other hand, the role of the Me dopant and that of the effect of the O_2 pressure in the HOP—which directly influences the oxygen activity at the LOP surface for such highly polarized materials—are worth to be investigated more deeply as they could lead to significant improvements of the selectivity. The possibility of modifying the O_2 pressure—thereby tuning the O^{2-} activity at the catalyst surface—independently from the hydrocarbon partial pressure without explosivity limitations (due to the very low O_2 pressure in the reaction compartment) opens new perspectives for the development of catalytic dense membrane reactors.

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