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Electrochemical modification of the catalytic properties of composite membranes of substituted $Bi_4V_2O_{11}$ (BIMEVOX) for propane oxidation in a catalytic dense membrane reactor

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ABSTRACT

Dense BICOVOX membrane, bulk BICOVOX/Au cermet membrane and BICOVOX membrane with a BICOVOX/Au cermet on its surfaces are investigated in the partial oxidation of propane under open circuit voltage (OCV) and under electrical bias at 700 °C. The propane conversion remains in the range 10–12% whatever the conditions of polarisation. Mostly cracking products are observed. Hydrogen is the main product with a selectivity around 55–60%. At OCV, no product of oxidation is detected except water which can not be quantified. On the membrane with BICOVOX/Au cermet electrodes on surface, traces of CO are observed as well as a small increase of propylene content under anodic polarisation. This can be explained by partial oxidation and oxidative dehydrogenation of propane, respectively. An anodic polarisation leads to a decrease of hydrogen due to its oxidation into water. In contrast, an increase of the hydrogen content is observed under cathodic polarisation. The effects on the membrane are modest, but they show the possibility that such a system offers for modifying the catalytic properties of membrane materials in a CDMR.

1. Introduction

Selective hydrocarbon oxidation reactions on oxide catalysts proceed through the Mars and van Krevelen mechanism, according to which lattice oxygen is responsible for selective oxidation whereas more electrophilic adsorbed oxygen species lead to unselective products (CO, CO_2) [1]. As molecular oxygen is usually cofed along with the hydrocarbon, the selectivity cannot be optimised. By decoupling the two steps of the redox mechanism one expects to increase selectivity and to decrease carbon oxides production by lowering the oxygen partial pressure. The catalytic dense membrane reactor (CDMR) is one means to carry out this redox decoupling [2–4].

The principle of a CDMR is based on a mixed ionic electronic conductive dense ceramic membrane. The latter separates two compartments, one containing air or oxygen [high oxygen partial pressure (HOP)], the other containing the (diluted) hydrocarbon [low oxygen partial pressure (LOP)]. Because of the difference between the oxygen chemical potentials in HOP and in LOP, the oxide ions O^{2-} migrate from HOP to LOP and may react with hydrocarbons in LOP to yield oxidised products.

In order to be used in a CDMR, the membrane material must exhibit suitable catalytic properties and be stable in the reaction conditions, and it must be a good oxide ion conductor, and have sufficient electronic conductivity to balance O^{2-} migration.

BIMEVOX materials derive from the parent compound $Bi_4V_2O_{11}$ and are known for their high oxide ion conduction properties at intermediate temperatures, 400–700 °C [5]. BIMEVOX is an acronym used for $Bi_2V_{1-x}Me_xO_{5.5\pm\delta}$ composition. Numerous elements can be introduced the vanadium site, among these, Co, Ni, Cu, Ta, . . . In the past decade, they were tentatively developed as membranes for the electrically driven separation of oxygen from air. Current density up to 2 A cm^{-2} with 100% efficiency (1 A cm^{-2} corresponds to an oxygen flow of 3.5 cm^3 min^{-1}) could be applied without the need of any electrode material. The membrane was simply made up of a dense BIMEVOX electrolyte sandwiched between two gold grids, which were stuck on the surface by means of a porous layer of BIMEVOX [6,7]. Under open circuit voltage (OCV), that is with no electrical potential or current imposed, $^{18}O/^{16}O$ isotope exchange combined with secondary ion mass spectroscopy revealed that the rate of exchange of molecular oxygen at the membrane surface is very low [8]. In contrast, the

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kinetics of oxygen transfer was considerably increased when an electrical bias was applied to the membrane [9]. By in situ X-ray diffraction under electrical bias, the transfer at the surface was confirmed to be due to the partial reduction of vanadium (V) into vanadium (IV) under current polarisation [10].

Because bismuth and vanadium are a priori active cations for the catalytic oxidation of hydrocarbons, BIMEVOX were investigated as dense membranes in the CDMR for the oxidation of hydrocarbons.

In previous studies, the oxidation of propylene and propane has been investigated on BIMEVOX membranes with various surface roughnesses [11–14]. Owing to a low oxygen transfer coefficient at the surface, BIMEVOX membranes exhibit very low semi-permeability to oxygen [15]. In this work, the properties of a bulk BIMEVOX membrane are compared to a bulk cermet membrane composed of the same material mixed with gold in order to ensure a good electronic conductivity. Then, the possibility of modifying the catalytic properties through the application of an electrical bias [16,17] is investigated. For this purpose, electrodes composed of BIMEVOX/Au cermet have been deposited on both faces of the pure BIMEVOX membrane.

The cobalt substituted BIMEVOX (BICOVOX) has been chosen to study the oxidation of propane at OCV and under an electrical polarisation.

2. Experimental

2.1. Membrane preparation

$Bi_2V_{0.9}Co_{0.1}O_{5.35+\delta}$ powders were prepared by solid-state route and attrition milled as described in [18,19]. To prepare a membrane of pure BICOVOX, the powder was shaped into a disk pressed in a 20 mm diameter die at 1700 bars with an isostatic press. The membrane was then sintered at 750 °C for 1 h with heating and cooling rates of 5 °C min^{-1}. The cermets were prepared by mixing the attrited powder with a gold paste (90 wt% gold) in ethanol and 1% of cellulose using an ultrasonic bath, before evaporation of the ethanol at 40 °C. Two compositions were prepared, one containing 65/35 vol% of BICOVOX/Au, the other 30/70 vol% BICOVOX/Au. The 65/35 powder was used to prepare the bulk BICOVOX/Au membrane. This composition was chosen to get the electronic and ionic percolation. The cermet membrane was shaped and sintered in the same conditions as for the pure BICOVOX membrane. The BICOVOX membrane with cermet electrodes on surface was prepared as follows. The membrane was pre-sintered at 650 °C for 30 min with heating and cooling rate of 5 °C min^{-1}. For electrode deposition, an ink for serigraphy was prepared by mixing 75% of cermet powder with 25% of EC3 binder (mixture of terpenic alcohols and ethylcellulose terpineol, content >83%). A layer of each cermet composition was deposited on both membrane faces as shown in Fig. 1 (intermediate drying step at 60 °C between each deposition). The pre-sintered membranes were finally annealed at 750 °C by successive heating steps (up to 140 °C at 1 °C min^{-1}, up to 440 °C at 0.25 °C min^{-1}, and up to 750 °C at 5 °C min^{-1} heating rate) followed by cooling down to room temperature at 5 °C min^{-1} after a dwell at 750 °C for 1 h. After sintering, the diameter and thickness of the membrane were 16 and 1.5 mm, respectively. A cross-section of the cermet-covered membrane obtained by SEM is shown in Fig. 2 and reveals that the two porous cermet layers are 20 μm thick each.

2.2. The catalytic dense membrane reactor

The same reactor as described in [11] was used for this study. The membranes were placed in the reactor between two mullite tubes and sealed by means of pyrex glass o-rings. The study was carried out at 650 and 700 °C. The gas phase composition in the two compartments was monitored using a mass spectrometer (Omnistar Pfeiffer). Propane (1% in He, $F = 50\ cm^3\ min^{-1}$, contact time $t = 2.4$ s) was flowed in LOP and air was flowed in HOP at the same flowrate ($P = 1$ atm). For bulk BICOVOX membrane, the surface polarisation was determined by measuring the difference of electric potential between the two gold electrodes: a gold grid deposited on the HOP side of the membrane and a gold tip in contact with the LOP side. In the case of electrode-covered membranes, two gold wires were connected to the electrodes on both surfaces. The catalytic behaviour of the membranes in the oxidation of propane was first studied at OCV. In a second step, the electrodes were connected to an external circuit and electric potentials between −100 and +300 mV and currents up to 100 mA were applied.

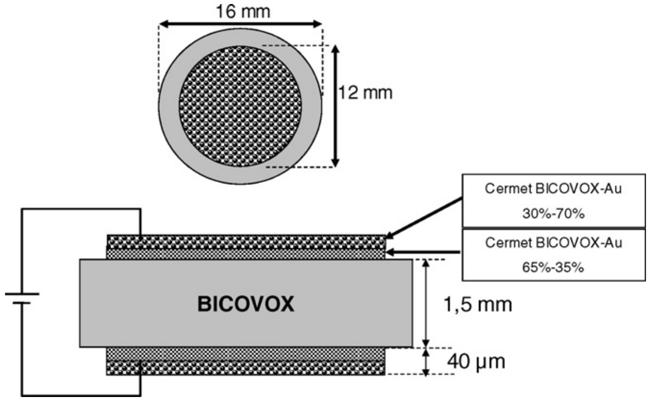

Fig. 1. A schematic of the BICOVOX membrane with two layers of cermet on both faces.

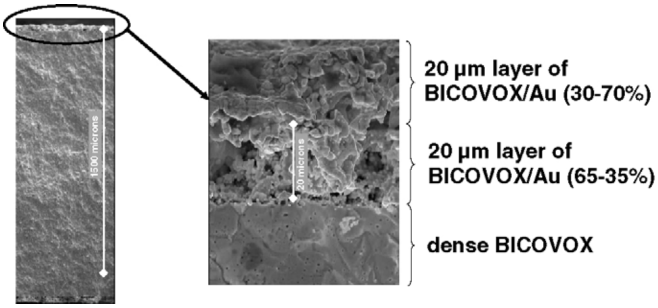

Fig. 2. Cross-section SEM images of BICOVOX membrane with BICOVOX/Au cermet electrodes after sintering.

3. Results and discussion

3.1. Catalytic behaviour under propane at OCV

Table 1 shows the results obtained for all membranes at OCV. A stationary regime was rapidly obtained, as shown in Fig. 3, and the conversion X of propane was very similar in all cases ($9 < X < 12$ mol% at 700 °C). Conversion rapidly falls to 1–2% at lower temperature (650 °C). A measurement made using a dense α-alumina disk in place of the membrane shows a similar conversion. One may thus conclude that the membrane does not contribute significantly to the activation of the hydrocarbon. This process probably occurs through thermal activation in the gas phase or by contact with the ceramic tubes of the reactor. Indeed, the reaction products are mostly due to cracking reaction

Table 1
Conversion and selectivity to products for membranes at OCV (700 °C, 1% C_3H_8/He in LOP, air in HOP)

Membrane	Temperature (°C)	Conversion (%)	S H_2 (%)	S propylene (%)	S methane (%)	S ethylene (%)
Pure BICOVOX	700	9.3	60	15	16	9
	650	1.7	64	15	14	7
Bulk BICOVOX/Au Cermet	700	9.2	49	23	17	11
	650	1.9	47	28	16	9
Alumina	700	9.9	57	20	14	9
BICOVOX with cermet electrodes (OCV)	700	12	58	17	17	8

(hydrogen, propylene, ethylene and methane), although some water is observed. One may not exclude the formation of coke although it was not observed when the reactor was opened after testing. With the bulk BICOVOX/Au cermet membrane the selectivity is slightly different from the other membranes. Less hydrogen is observed and more propylene is produced. In a previous study [15], it has been showed that this bulk cermet membrane exhibits the same oxygen permeation fluxes ($J_{O_2} = 5\text{–}6\,\mu\text{mol}\,\text{cm}^{-2}\,\text{s}^{-1}$) corresponding to approximately 1–2 Pa of O_2 in the LOP compartment in our experimental conditions. Thus, the enhancement of electronic conductivity does not contribute to the recombination of O^{2-} species to O_2. In reaction condition, it may nevertheless contribute to the migration of oxygen towards LOP which may react to produce water instead of recombining to O_2. This may explain the lower selectivity to H_2. As water cannot be quantified with this experimental setup, the extent of oxidative dehydrogenation cannot be determined. However it is certainly small as compared to cracking reactions when considering the amount of hydrogen produced.

With the pure BICOVOX membrane, the potential difference measured in the absence of propane is of $\Delta E_{\text{exp}} = -12$ mV (Fig. 4). With air in HOP ($p_{O_2} = 0.21 \times 10^5$ Pa), and assuming that the equivalent oxygen content in LOP is less than 10 ppm, from the Nernst equation a potential difference of $\Delta E_{\text{th}} = -233$ mV was expected between the two faces of the membrane. The experimental value shows that the system is far from equilibrium and that the LOP face of the membrane is strongly polarised. Upon introduction of propane, the potential difference decreased to $\Delta E_{\text{exp}} = -14$ mV (Fig. 4) and slowly it recovered its initial value when propane feed was stopped. The same behaviour was formerly observed in the case of propylene oxidation [11]. This strong polarisation is in good agreement with the low kinetics of exchange of oxygen molecules at the surface of the membrane. All proceeds as if the oxide ions (O^{2-}) were blocked close to the membrane surface. They may thus act as an oxygen reservoir available for oxidation of hydrocarbon molecules. However due to the small reactivity of the surface this reaction does not occur significantly and the oxide ion reservoir mainly contributes to keep the stability of the membrane. Indeed, even after several weeks of testing in various experimental conditions (temperature, HOP oxygen pressure, hydrocarbon pressure, . . .) all membranes proved to be very stable and showed no evidence of reduction or cracks.

3.2. Catalytic behaviour under propane under polarisation

With the aim to increase the amount of oxidation products, a polarisation was applied on the cermet-covered membrane. Whatever the polarisation, the conversion remained around 12%. To avoid any risk of bismuth reduction, the applied potential was limited to 300 mV. A cathodic polarisation of −100 mV was first applied, followed by an anodic polarisation of +300 mV. As Fig. 5 shows and compared with Fig. 3, the distribution of products is only slightly affected by the applied polarisation. The partial pressure of hydrogen increases under cathodic polarisation and decreases under an anodic polarisation. Traces of CO were observed under +300 mV. This is consistent with the fact that under positive polarisation the amount/reactivity of oxygen at the LOP side of the membrane should be increased.

A second experiment was performed in galvanostatic mode with an anodic polarisation. The current was increased by step of 10 mA from 20 mA up to 100 mA. An increase of the oxygen content in the gas phase with the current density was observed, the partial pressure of oxygen being 50 Pa at 100 mA in reaction conditions. The propane conversion remained almost constant during the whole experiment, $X \sim 12\%$. Fig. 6 shows the evolution of the selectivity to products with the current polarisation. Hydrogen decreases and CO increases as the current bias increases. A small increase of the selectivity to propylene and ethylene is also to be noticed.

The formation of CO and propylene can be accounted for by partial oxidation ($C_3H_8 + 3/2O_2 \rightarrow 3CO + H_2O$) and by the oxidative dehydrogenation of propane ($C_3H_8 + O_2 \rightarrow C_3H_6 + H_2O$),

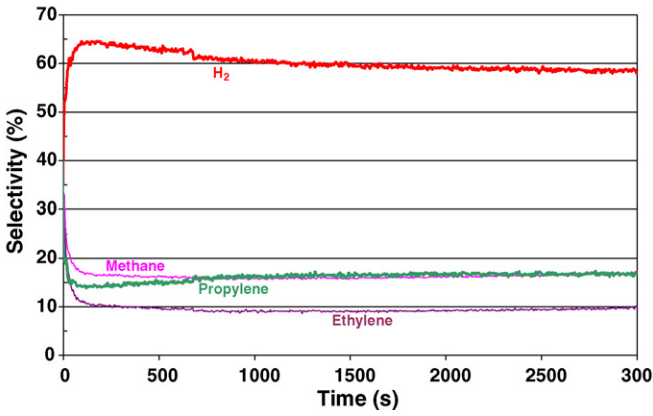

Fig. 3. Selectivity to products vs. time using a BICOVOX membrane covered with BICOVOX/Au cermet at OCV (700 °C, 1% C_3H_8/He in LOP, air in HOP).

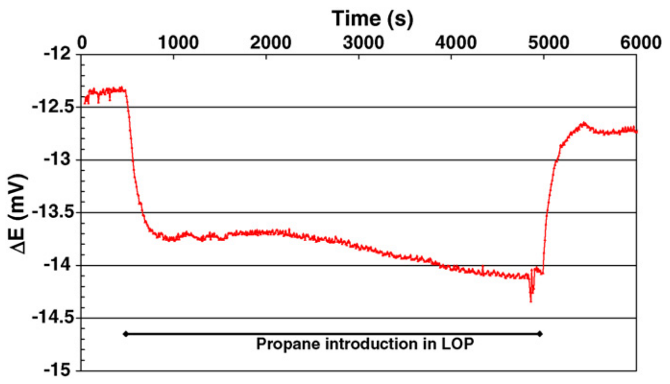

Fig. 4. Potential difference measured on bulk BICOVOX membrane as propane reaction occurs (700 °C, 1% C_3H_8/He in LOP, air in HOP).

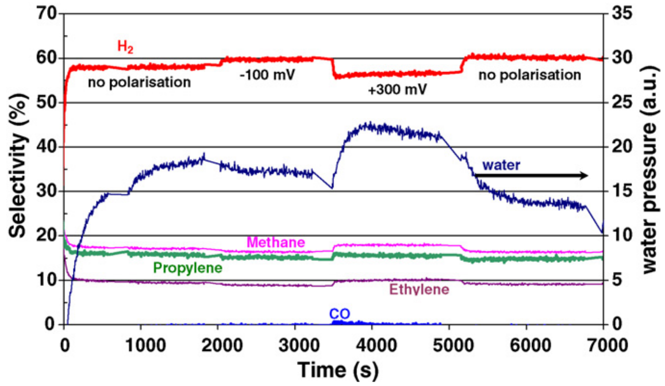

Fig. 5. Distribution of products and water pressure vs. time using a BICOVOX membrane with BICOVOX/Au cermet electrodes under OCV, and with cathodic (−100 mV) and anodic (+300 mV) polarisation (700 °C, 1% C_3H_8/He in LOP, air in HOP).

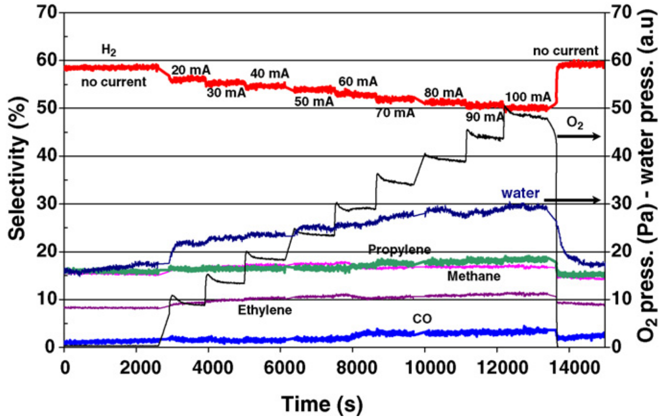

Fig. 6. Distribution of products, oxygen pressure and water pressure vs. time using a BICOVOX membrane with BICOVOX/Au cermet electrodes under OCV in galvanostatic mode (current from 0 to 100 mA) (700 °C, 1% C_3H_8/He in LOP, air in HOP).

respectively. However the CO amount and the C_3H_6 increase are very small and thermal cracking ($C_3H_8 \rightarrow C_3H_6 + H_2$, $C_3H_8 \rightarrow C_2H_4 + CH_4$) which account for the high selectivity to hydrogen is predominant.

For both experiments at imposed potential and in galvanostatic mode, the evolution of hydrogen content is easily explained by its oxidation into water when oxygen migration towards LOP is promoted (+300 mV potential) or forced (20–100 mA current). The trend of water pressure is indeed coherent with this interpretation (Figs. 5 and 6).

4. Conclusions

The conversion of propane on (i) pure BICOVOX, (ii) bulk BICOVOX/Au cermet and (iii) BICOVOX membrane with BICOVOX/Au cermet on its surface remained in the range 9–12% at 700 °C whatever the conditions of polarisation (under OCV or under an electrical bias). Furthermore, similar conversion was observed with a dense disk of alumina in place of the membrane indicating that the membrane does not contribute significantly to the activation of propane which, at this temperature, probably occurs in the gas phase and/or at the surface of the reactor ceramic tubes. This leads essentially to the formation of cracking products. The low contribution of the membranes may be explained by their low reactivity related to the very small surface area exposed. Indeed, conversion is the highest (12%) with the sample covered with the porous cermet electrodes. Hydrogen was the main product with a selectivity of 55–60% and no product of oxidation was detected except water. Traces of CO were observed under anodic polarisation and the small increase of propylene content can be explained by partial oxidation and oxidative dehydrogenation of propane. An anodic polarisation led to a decrease of the hydrogen content in the gas phase due to its oxidation into water and the reverse behaviour was observed under cathodic polarisation. However thermal cracking is predominant and the role of the BIMEVOX membrane in the catalytic process remains to be clarified. In particular it is not clear whether the oxygen flux promoted under polarisation generates O_2 which, in turn, reacts with H_2 from the gas phase, or if O^{2-} species react at the surface with adsorbed hydrocarbon. It may be noted however that selectivity changes are observed with BICOVOX/Au cermet as compared to BICOVOX whereas both membranes show the same (very low) O_2 permeation flux. This suggests that modifications of the surface properties indeed occur although they are difficult to put in evidence due to the cracking reactions. The effects are modest, but they show the possibility that such a system offers for modifying the catalytic properties of membrane materials in a CDMR. Further experiments will be performed at lower temperature. To achieve this, the catalytic activity of the membrane surface needs to be enhanced and the deposition of a catalyst on to the membrane surface will be considered.

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