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Bi₂V_{1-x}MexO_{5.5-y} (Me = Ta, Ni) Membranes for Selective Oxidation of C₁-C₃ Alkanes in a Catalytic Dense Membrane Reactor

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$\text{Bi}_2\text{V}_{1-x}\text{Me}_x\text{O}_{5.5-\delta}$ (Me = Ta, Ni) Membranes

for Selective Oxidation of C₁-C₃ Alkanes in a Catalytic Dense Membrane Reactor

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Abstract

Pure and Me-doped $\gamma\text{-Bi}_2\text{V}_{1-x}\text{Me}_x\text{O}_{5.5-\delta}$ (BIMEVOX) (Me = Ta, Ni) materials exhibit a transient behaviour during the oxidation of $\text{C}_1\text{-C}_3$ alkanes when shaped as dense membranes separating two compartments fed with diluted hydrocarbon and with air, respectively (catalytic dense membrane reactor). Alkenes are first produced at low conversion and CO and H_2 follow at higher conversion. The H_2/CO ratio increases up to values close to the stoichiometric ones and continues to increase after a peak of activity during which coke builds up. The same transient phenomena as initially observed happen after burning the coke by replacing diluted hydrocarbon by air. This in situ regeneration of the membrane means that the structure and integrity of the membranes have not been modified, as indeed shown by physicochemical analyses (XRD, SEM, XPS). The catalytic properties are mainly related to the presence of ME which affects the electronic conductivity of the materials. At variance with quite neutral BITAVOX, the behaviour of BINIVOX is close to that of BICOVOX which is also a p-type semiconductor. Only BINIVOX is able to oxidise methane (conversion ca. 22-25 mol%) to syngas at low temperature (650°C) in a quite steady manner.

Keywords: Catalytic dense membrane reactor, $\text{Bi}_2\text{V}_{1-x}\text{Me}_x\text{O}_{5.5-\delta}$, BIMEVOX, oxidation of $\text{C}_1\text{-C}_3$ alkanes, syngas

1. Introduction

Among other applications, catalytic dense membrane reactors are studied for increasing yields or checking purity of hydrogen or syngas production to be further used in Solid Oxide Fuel Cells or in Fischer-Tropsch synthesis. Dense membranes made up from oxides exhibiting mixed ionic and electronic properties (MIEC) are used. These properties make them suitable for the activation of methane to syngas, but also to C₂ hydrocarbons (oxidative coupling), as well as for the oxidative dehydrogenation of other light alkanes [1-5]. In the literature, large fluxes of permeating dioxygen through the membrane are generally considered as a necessary requirement for the targeted reaction. The permeating flux depends on both steps of reduction of O₂ on one side and oxidation of O²⁻ on the other (reaction) side, the rates of which are related to the electronic conductivity of the dense membrane. Very often a catalyst is added on both sides of the membrane to increase the rates of the O₂ reduction as well as of the reaction.

A decade ago, we investigated a catalytic membrane reactor for the selective oxidation of propene to hexadiene and benzene (oxidative dehydrodimerisation) on BiLaO membranes [6,7] after the pioneering work of Di Cosimo et al. [8]. As shown by Sokolovski et al. [9], lattice oxygen is the main specie involved in the reaction, although the participation of some radical-like specie could not be fully ruled out, so that the redox mechanism prevails. In our mind, the idea was to explore the influence of physically decoupling the redox mechanism on the catalytic properties. Such a decoupling may be a way of enhancing the selectivity, owing to the possible and separated optimisation of the operating conditions on each side (reaction and regeneration). More recently we have studied other Bi-based materials for the same reaction, like Bi₄V₂O₁₁ and its solid solutions Bi₂V_{1-x}Me_xO_{5.5-δ} (called by the BIMEVOX acronym), as powders in a fixed bed microreactor [10,11], as well as membranes in a catalytic dense membrane reactor (CDMR) [12,13]. The comparison of the performances showed that the materials behave similarly when the conversion of propene is small, but

that at higher conversion a transient state was observed during which syngas was formed in the case of the CDMR.

BIMEVOX oxides have the same structure as γ - $\text{Bi}_2\text{VO}_{5.5}$ [14]. Layers of bismuthyl groups ($\text{Bi}_2\text{O}_2^{2+}$) alternate with layers of vanadate groups containing oxygen vacancies which favour the mobility of oxygen specie. As compared to the high 2D-ionic conductivity exhibited at temperature as low as 600°C , the electronic conductivity is small and its n- or p-type depends on the ME dopant [15,16]. Such a low electronic conductivity is not favouring the semipermeability to oxygen because $\text{O}_2 + 4e \leftrightarrow \text{O}^{2-}$ become rate-limiting steps. Indeed, the measured oxygen fluxes JO_2 are $1.5\text{-}1.8 \cdot 10^{-4} \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ at 650°C on $\text{Bi}_2\text{V}_{1-x}\text{Me}_x\text{O}_{5.5-\delta}$ doped with Cu or Co ($x = 0.1$) or Ta ($x = 0.2$), compared with 10^{-2} for $\text{Bi}_{1.5}\text{Er}_{0.5}\text{O}_3$ at 680°C and with typically $1\text{-}8 \mu\text{mol}_{\text{O}_2}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ for the best MIEC [2,3,5]. BIMEVOX materials were proposed as electrolyte for Ceramic Oxygen Generator (COG) to deliver very pure oxygen gas from one (feeding) to another (delivering) side. Under imposed polarization, the material was found able to self convert reversibly and dynamically from electrolyte to electrode, which led to a new concept of COG based on a unique material [17]. Because of the well-known catalytic properties exhibited by bismuth as well as by vanadium in several mild oxidation reactions, we have examined the properties of BIMEVOX in the catalytic oxidation of propene using them as dense membranes in the CDMR. The results already obtained with Cu and Co membranes had shown that products of selective oxidation (acrolein, hexadiene, benzene) were formed, together with carbon monoxide [12,13]. As their surface was mirror-polished (to ensure tightness), the number of active sites was low and the maximum of conversion of propene was 2 to 2.5 mol% at steady state. Once the surface state was made rougher by depolishing, their behaviour in the oxidation of propene and of propane became time-dependent. In this paper we present the study of depolished $\text{Bi}_2\text{V}_{0.8}\text{Ta}_{0.2}\text{O}_{5.5}$, $\text{Bi}_2\text{Ni}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ and of γ - $\text{Bi}_4\text{V}_2\text{O}_{11}$ membranes, and the comparison of their properties in the oxidation of propane, ethane and methane with those of depolished $\text{Bi}_2\text{Me}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ (Me = Co, Cu).

2. Experimental

Powders of $\text{Bi}_2\text{Ta}_{0.2}\text{V}_{0.8}\text{O}_{5.5}$ (BITAVOX), $\text{Bi}_2\text{Ni}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ (BINIVOX) and of $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ (BIVOX) were prepared by solid state reaction between the constitutive oxides in stoichiometric proportions [14]. The disc membranes ($\varnothing = 15$ mm, $d = 1.5$ mm) obtained by isostatic followed by uniaxial pressing were sintered at 750°C (BIVOX and BINIVOX), or 875°C (BITAVOX). Their relative density after sintering was higher than 95%. After polishing with 4000 grit SiC paper (to get parallel surfaces and ensure tightness between the compartments), both sides were depolished using 220 grit SiC paper. The membrane was mounted between the two mullite tubes constituting the reactor and sealed at high temperature by means of pyrex rings. A gold grid electrode on O_2 reduction and a gold tip electrode on reaction sides were inserted to measure in situ the polarisation of the membrane. The gas phase composition at inlets and outlets of the two compartments of the CDMR was monitored using a mass spectrometer (Omnistar Pfeiffer) for catalytic reaction and an oxygen gauge (Setnag) for O_2 permeation [12,13]. According to our experimental protocole [12,13], the oxygen semipermeability was first measured at given temperatures by flowing air ($F = 50 \text{ cm}^3 \cdot \text{min}^{-1}$) in the High Oxygen partial Pressure (HOP) compartment and helium in the Low Oxygen partial Pressure (LOP) compartment ($F = 50 \text{ cm}^3 \cdot \text{min}^{-1}$), respectively. Then helium was replaced by diluted methane, ethane or propane (1% in He, $F = 50 \text{ cm}^3 \cdot \text{min}^{-1}$) in LOP. The contact time was kept at 2.3 s while temperature ($T = 550\text{-}700^\circ\text{C}$) was varied. Both surfaces (LOP and HOP) of the membranes were characterized by SEM, XRD and XPS before and after reaction.

3. Results and discussion

3.1. BITAVOX during propane oxidation

Fig. 1 shows that the conversion of propane on BITAVOX-220 plotted vs. time of reaction is not constant and decreases with temperature. A peak of activity, which exhibits two to three secondary maxima, is observed at ca. 4.0, 12.1 and 33.3 min at $T = 675, 650$ and 575°C , respectively. For a better description of the phenomena at 650°C (Figure 2), five stages (I to V) during which the conversion of propane but also the type and distribution of products differ, are identified. The first

stage (I) corresponds to the arrival of the reactant molecules into the reactor and lasts around 30-60 seconds. The conversion cannot be calculated because the reactant pressure at the inlet is not yet stable. Nevertheless the type and amounts of products of reaction are similar to those observed in stage II. In this second stage, the conversion of propane is low and constant (2-3 mol%) during 90 to 1400 s depending on T (Figure 1). At the highest temperature propane flowing onto the membrane reacts too fast for this step to be correctly seen. During this steady state, the products are those of oxidative dehydrogenation (ODH) accompanied by CO and few CO₂ molecules. Selectivities decrease along CO > C₃H₆ > C₂H₄, CH₄ > CO₂. The steady conversion and the distribution and amount of products were the same as when the surface of the BITAVOX membrane was less rough (depolished with 800 grit SiC paper) [18]. During stages III to V (Figure 2), the activity of BITAVOX increases strongly and then it decreases. The main reaction is the production of CO and hydrogen, the partial pressure of hydrogen following the same trend as the conversion. These phenomena indicate that the partial oxidation of propane to H₂ and CO has replaced the ODH of propane, as if different sites were now involved. The slope of conversion vs. time is 0.06 %·s⁻¹ during stage III and increases (0.12%·s⁻¹) during stage IV, and so does p_{H₂} (1.2 and 2.9 Pa·s⁻¹, respectively). Stage III is characterised by a constant H₂/CO ratio which amounts to ca. 1.5 (instead of 1.33 for stoichiometric production) for 300 s. During stage IV, p_{CO} decreases while p_{H₂} increases, and thus H₂/CO increases continuously up to 4.6. After the maximum of p_{H₂} at 58 mol% of conversion, both decrease (stage V) down to steady values. During the activity peak, a definite amount of oxygen is available for the production of 100-120 μmoles of CO (integration of the CO curve between 250 and 1300 s). That amount of oxygen cannot come by permeation since only 0.4 μmoles of O₂ would flow at 650°C in the absence of reaction. The oxygen species are those which are immediately available due to the high polarisation of the membrane [12,13,18], and/or coming by diffusion from HOP side. The overall amount of CO corresponds approximately to the reduction of 7-8 % (for V⁵⁺ → V⁴⁺) or 3.5-4 % of the total V content of the membrane (V⁵⁺ → V³⁺). Bismuth could also undergo reduction (e.g. Bi³⁺ → Bi⁺ → Bi⁰), but the presence of Bi⁰ has not been observed by any post-mortem method of analysis we used. When it was formed during experiments carried out on BIMEVOX powders in fixed bed reactors, metallic bismuth

was easily identified by XRD, SEM [10,11], and even with naked eyes inside the reactor in severe cases like with Bi-La-O catalysts in CDMR [8,9]. Nevertheless, it is possible that locally the surface restructures with formation of reduced bismuth when the oxygen delivery (from HOP) is not fast enough as compared to the rate of the reaction (in LOP). Because the gas phase becomes strongly reducing during the formation of CO and H₂, it could favour the formation of Bi⁰ which would be responsible for the strong increase of activity (stages III, IV). As a consequence, the slope of conversion and of pH₂ vs. time increase while pCO decreases (stage IV), and thus H₂/CO increases.

During stage V, the conversion decreases down to a steady value (10 mol%) which is close to that found at the beginning of stage II. The pressures of H₂ and of CO also reach steady values (pH₂ ≈ 300 Pa; pCO ≈ 30 Pa, H₂/CO ≈ 10), but carbon deposits are formed as confirmed by the carbon balance which is not satisfied. It is worthwhile to note that CO continues to be formed in the same amounts as at the beginning of stage II and at similar conversion of propane. This means that there are still enough oxidising sites regenerated by oxygen specie diffusion for the reaction to be run.

The latter assertion was verified by the following experiment. Propane/He in the LOP compartment was replaced by air at the same temperature (650°C) in order to burn the coke formed during stages IV and V. Fig. 3 shows that ten minutes are enough for the coke to be oxidised to CO₂. When in turn air is replaced by propane/He in LOP, the same successive reactions than formerly observed proceed (Fig. 4). The time for ODH of propane (stage I) is shorter, and the whole peak of activity lasts a little less (ca. 900 instead of 1300 s). The possibility of regeneration of the LOP surface has been checked with all depolished BIMEVOX membranes we studied [12,13,18]. Therefore, the surface of the membrane undergoes the same successive transformations, the “reversibility” of which is accounted for by chemical analyses showing that the LOP (as well as HOP) side of membranes has not changed. XRD showed that the structure of Bi₂V_{0.8}Ta_{0.2}O_{5.5} was retained, and no line that could belong to another oxide or to metallic bismuth could be seen. As in the case of BICOVOX after propene oxidation, the main change seen by SEM was a slight increase by 20% of the size of domains separated by grain boundaries. XPS analyses show that the measured Bi/V ratio does not change much after reaction (4.13 vs. 4.31, resp.) but that it is twice higher than the bulk stoichiometry, while very

little Ta is found on surface in both cases. As that kind of figure was observed also both BICUVOX and BICOVOX, the possible increase of Bi on surface caused by the high vacuum in the spectrometer is under study.

3.2. BINIVOX and BIVOX in propane oxidation

The behaviour of $\text{Bi}_2\text{V}_{0.9}\text{Ni}_{0.1}\text{O}_{5.35}$ (BINIVOX) depolished with 220 grit SiC paper during propane oxidation is close to that of BITAVOX, but the peaks of activity and of production of H_2 , CO occur sooner. At 650°C , the two maxima of conversion ($C = 58$ and 48 and mol%) that were seen at ca. 700 and 1000 s for BITAVOX (Fig. 2) are $C = 59$ and 40 mol% at ca. 200 and 350 s. The maximum pressure of products decreases along H_2 (1280) > CO (640) > CO_2 (500 Pa) at 250, 125, 80 s respectively. Apart from a temporary decrease at ca. 250 s (when pCO reaches a minimum while pH_2 begins to decrease) the H_2/CO ratio increases steadily, up to 18 at the final steady state. On the contrary, the conversion of propane on $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ (BIVOX) membrane is low (1.5 mol%) and steady. CO and C_3H_6 are the main oxydation products and selectivities decrease along CO (36) > C_3H_6 (32) > C_2H_4 (20) > CH_4 (8 mol%). Very little hydrogen is produced and water is the main H-containing molecule. BIVOX behaves like BITAVOX when its surface was smoother (depolished with 800 grit SiC paper) [13,18]. Therefore, apart from CO which was also found as a main product in the case of powdered BIMEVOX in fixed bed reactor, the ODH reaction is predominant when the conversion is low.

3.3. BITAVOX and BINIVOX in the oxidation of ethane and of methane

A similar evolution of the conversion of ethane as compared to that of propane is observed using BITAVOX and BINIVOX at 650°C . The phenomena are slowed down as expected from the lower reactivity of ethane. At first, the conversion of ethane on BITAVOX is low ($C = 2\text{-}10$ mol%) while ethylene (ODH) is produced, together with a small amount of CO_2 . Then it increases and reaches a maximum at $C = 50$ mol%, while the partial pressures decrease along $\text{H}_2 > \text{CO} > \text{CO}_2, \text{CH}_4$. Finally the conversion decreases to values below 10%, during which H_2 and coke are the major products.

Carbon monoxide is still produced in small amounts. It has already been noticed that the rate of CO production (in the same conditions: same temperature and air in HOP) does not depend on the nature of the alkane, as if the solid was delivering the same amount of oxygen [18]. During ethane oxidation, $H_2/CO = 1.8$ for a short time as compared to 1.5 for propane (both being slightly higher than the respective stoichiometric ratio), and later it levels off at 9 for 450 s (8 for 250 s with C_3H_8). Up to the maximum of conversion, H_2/CO increases steadily to values around 10-12 with formation of coke.

The behaviour of BINIVOX in the oxidation of ethane is closer to that of BICOVOX in the oxidation of propane than to that of BITAVOX. Two peaks of activity are shown at ca. 500 (C = 40 mol%) and 1150 s (C = 22 mol%) (Fig. 5). The production of H_2 is parallel to the conversion ($p_{H_2} = 710$ Pa at C = 40 mol%), while CO reaches a maximum ($p_{CO} = 300$ Pa) before that of hydrogen. The H_2/CO levels off at 1.8 at low conversion, then increases and reaches a second constant value at 3 (during the minimum of conversion at 850 s), and it increases again up to 7 while coke is formed (Figure 6).

BITAVOX is quite inactive when methane is fed at $650^\circ C$ (C < 0.5 mol%) and very little CO is produced. On the contrary BINIVOX is active and the maximum conversion of methane is 22-25 mol% at the same temperature. The production of CO and H_2 is quite steady ($H_2/CO = 2.5$ for 1000 s and 4.0 later).

3-4. Comparison with other BIMEVOX

The catalytic behaviour along time of depolished BITAVOX and BINIVOX during the oxidation of C_1 to C_3 alkanes is very close to that observed during the oxidation of C_3H_8 using depolished Cu and Co-doped BIMEVOX membranes. Although the same SiC paper was used to depolish all BIMEVOX membranes, the real state of the surface and particularly the number of active sites cannot be directly checked. However the trend is the same than in the case of mirror-polished [12], or of rougher surfaces already studied [13,19], in the oxidation of propane as well as of propene. During the experiments described here, which were carried out at the same temperature with propane in LOP and air in HOP compartments, respectively, several types of active sites seem to be successively formed.

At first the material displays few sites active (or many sites poorly active) in ODH and in the formation of CO (low conversion, ca. 2 mol%). These sites are active during the whole experiment, since they are still present during stage V besides those responsible for the formation of hydrogen, as well as after regeneration. These O^{2-} specie are directly available as shown by the strong polarisation of the membrane, and/or are easily replaced by means of oxygen diffusion. We assume that they are bonded to vanadium (5+) which is a metallic cation commonly used in ODH of alkanes (2-electrons reactions). Then another type of sites which are more active since conversion increases up to ca. 10 mol% shows up. This stage II, during which products of partial oxidation (syngas, 6e-reaction) are prevailing, goes on for a more (ME = Co, Ni) or less (ME = Cu, Ta) long time, depending on ME. Further on, there is a kind of run-away (stages III-IV, activity peak), the extent and duration of which again depend on ME. This is indirectly proven by the low activity of undoped $Bi_2VO_{5.5}$ (BIVOX) which is unable to yield syngas (no III-V stages) but is active for ODH. The production of CO in large amounts (as compared to that in stages I or II) besides hydrogen could be related to the presence of surface O^- specie as proposed for that type of reaction [1-3]. However the way these specie would form is unknown. All proceeds as if the rate of this 6e-reaction (LOP side) was too high as compared to the rate of oxygen delivery which in turn depends on the rate of reduction of molecular oxygen in HOP side. By studying the effect of pO_2 in HOP on the catalytic properties of BIMEVOX membranes in the oxidation of propane and of propene, we have already shown that a high pO_2 was stabilizing stage II (delaying III-IV) on Co and destabilizing stage II (advancing III-IV) on Cu-doped BIMEVOX [13,18,19], while it had quite no effect on BITAVOX [18,19]. It was assumed that the transient behaviour is induced by limitations of electronic conductivity, Co, Cu and Ta-BIMEVOX being p-, n-type and quite neutral electronic conductors, respectively. The behaviour of BINIVOX along time is close from that of BICOVOX by the presence of two maxima (stages III-IV), these maxima being slightly delayed when air in HOP is replaced by pure dioxygen [16]. The common point is the possibility for Ni, like Co, to be oxidised to the trivalent state (Ni^{3+}) and therefore, BINIVOX exhibits a low but p-type semiconductority..

4. Conclusion

Contrary to undoped bismuth vanadate $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ which exhibits steady properties, the catalytic oxidation of propane on depolished BITAVOX and BINIVOX membranes in a CDMR depends on the time of reaction. Several stages are identified. As a product of oxidative dehydrogenation, propene accompanied by CO and little CO₂ are steadily formed at low conversion, and later on syngas is obtained at higher conversions, before partial coking occurs. These phenomena can be reproduced after burning of the carbon, thereby demonstrating the good bulk stability of BIMEVOX materials for CDMR applications, even in strongly reducing atmospheres. The transient behaviour and the distribution of products are very close to those shown by BICUVOX and BICOVOX membranes, the main differences being first the time and duration of the various steps, and to a lesser extent the values of conversion and selectivities to products. BINIVOX behaves similarly to BICOVOX, both being p-type semiconductors. A similar but slowed down sequence of reactions is observed with ethane, which is first oxidatively dehydrogenated to ethylene and later partially oxidised to syngas. However, only BINIVOX is able to oxidise methane to syngas at 650°C, which is a low temperature for such a reaction. The steady conversion amounts to 22-25 mol% and H₂/CO is close to the stoichiometry with little production of coke. The way and reasons why the surface of the BIMEVOX materials is restructuring remain to be studied, as well as the means to stabilise their properties, either for the oxidative dehydrogenation of propane or ethane, or for syngas production.

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Figure captions

Fig. 1. Evolution of the conversion of C_3H_8 vs. time on BITAVOX membrane; $T = 575^\circ C, 650^\circ C, 675^\circ C$, LOP = 1% C_3H_8 in He.

Fig. 2. Evolution of the conversion of C_3H_8 and distribution of products vs. time using BITAVOX membrane; $T = 650^\circ C$, LOP = 1% C_3H_8 in He.

Fig. 3. Regeneration of BITAVOX membrane: Formation of CO_2 during oxidation of coke by feeding air in LOP compartment; $T = 650^\circ C$, LOP = 20% O_2 in He.

Fig. 4. Evolution of the conversion of C_3H_8 and distribution of products vs time using regenerated BITAVOX membrane; $T = 650^\circ C$, LOP = 1% C_3H_8 in He.

Fig. 5. Evolution of the conversion of C_2H_6 vs time on BINIVOX membrane; $T = 650^\circ C$, LOP = 1% C_2H_6 in He.

Fig. 6. Evolution of the conversion (top) and of H_2/CO ration vs time during oxidation of C_2H_6 (BITAVOX and BINIVOX), and of CH_4 (BINIVOX); $T = 650^\circ C$, LOP = 1% C_2H_6 or CH_4 in He.