Oxidative Dehydrogenation of Alkanes using Oxygen-Permeable Membrane Reactor

Rui-qiang Yan*, Wei Liu‡, Chun-lin Song‡‡

a. Department of Materials Engineering, Taizhou University, Taizhou 318000, China
b. Faculty of Materials and Energy, Southwest University, Chongqing 400715, China
c. CAS Key Lab Mat Energy Convers, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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The oxidative dehydrogenation (ODH) reactions of ethane and propane were investigated in a catalytic membrane reactor, incorporating oxygen-permeable membranes based upon La2Ni0.9V0.1O4+δ or Ba0.5Sr0.5Co0.8Fe0.2O3−δ. As a compromise between the occurrence of a measureable oxygen flux and excessive homogenous gas phase reactions, the measurements were conducted at an intermediate temperature, either at 550 or 650 °C. The results show the dominating role of the oxygen flux across the membrane and available sites at the membrane surface in primary activation of the alkane and, hence, in achieving high alkane conversions. The experimental data of ODH of propane and ethane on both membrane materials can be reconciled on the basis of Mars-van Krevelen mechanism, in which the alkane reacts with lattice oxygen on the membrane surface to produce the corresponding olefin. It is further demonstrated that the oxygen concentration in the gas phase and on the membrane surface is crucial for determining the olefin selectivity.

Key words: Oxidative dehydrogenation, Membrane reactor, Oxygen-permeable membrane
**Ionic-electronic conducting membrane, endowed with suitable catalytic properties or modified with a suitable catalyst, is employed. The membrane facilitates a continuous and controlled flux of oxide ions to the permeate side exposed to the alkane feed, as illustrated in Fig.1 [17, 19]. The oxygens arrive at the surface via solid-state diffusion exclusively. Accumulation of oxygen in the gas phase can be avoided by matching the oxygen flux through the membrane with the rate of consumption of oxygen by the selective oxidation reaction at the immediate membrane surface.**

Wang et al. [17] reported selectivity of 80.1% towards ethylene at ethane conversion of 84.2%, using a catalytic membrane reactor made of Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF), at 800 °C, whereas selectivity and conversion of 53.7% and 83.6%, respectively, were obtained using BSCF powder in a conventional fixed-bed reactor. When propane was used as a reactant, selectivity of 23.9% towards propylene at conversion of 71.8% was obtained at 750 °C [19]. In a similar study of ODH of ethane to ethylene, Rebeilleau-Dassonneville et al. [16] observed substantial formation of hydrogen as a by-product, indicating that the reaction significantly proceeds via gas phase dehydrogenation. It is required to clarify the role of the membrane, where it should be noted that both selectivity and yield are found to be enhanced by application of a surface catalyst at the permeate side of the BSCF membrane [16].

In this work, we explored the mechanism of oxidative dehydrogenation of alkanes in the oxygen-permeable membrane reactor. Catalytic membrane reactors, made of either La0.9Ni0.1V1−xO3+x (LNV10) or BSCF, were exploited for ODH of propane and ethane. The influence of the catalytic membrane on the ODH reaction was studied. As a compromise between a measurable oxygen flux and occurrence and extent of the gas phase reactions, the measurements were conducted at an intermediate temperature, either 550 or 650 °C, to minimize the extent of the gas phase reaction.

**II. EXPERIMENTS**

**A. Membrane preparation and characterization**

Powders of LNV10 and BSCF were prepared by thermal decomposition of precursor complexes derived from a mixed solution, containing the corresponding metal ions in the appropriate stoichiometry, using ethylenediaminetetraacetic (EDTA) as complexing agent. The vanadium-containing solution was prepared by dissolving V2O5 in diluted HNO3. Metal nitrates were used for preparing the other solutions. The powders obtained were calcined in air for 10 h, at 1050 and 950 °C for LNV10 and BSCF, respectively. After calcination, the powder was ball-milled in acetone for 5 h. Phase purity of the powders was checked by X-ray diffraction, using a Philips PANalytical PW1830 diffractometer. Powders of LNV10 were pressed into either green tubes or discs via cold isostatic pressing at 400 MPa, and subsequently sintered in air at 1420 °C for 10 h, using heating and cooling rates of 3 °C/min. Similarly, BSCF powders were pressed into discs and sintered at 1220 °C. The relative density of the dense ceramics was higher than 95%. Surface of the membranes were carefully polished by hand using 240-mesh SiC grinding paper.

Oxygen permeation through the LNV10 disc membrane (0.97 mm thickness) was measured in the range of 575–700 °C. Soda lime silicate glass (AR-glass) rings were used for sealing of the disc into the reactor. After sealing, synthetic air and high purity helium were fed to opposite sides of the membrane at flow rates of 100 and 10 mL/min, respectively. The effluent gas was analyzed by on line gas chromatography (Varian CP 4900 equipped with molecular sieve 5A PLOT and PorapLOT Q columns). The gas chromatograph was calibrated using standard gas mixtures (O2, N2 balanced with He). Oxygen leakage, due to imperfect sealing, was evaluated by measuring the nitrogen concentration in the effluent gas. Permeation data were corrected for oxygen leakage, using the corresponding nitrogen concentration. Corrections were less than 1% of the total oxygen concentration in the effluent gas.

**B. Catalytic experiments**

ODH of propane was studied, at 650 °C, using a tubular LNV10 membrane reactor of length 33 mm, and with outside and inside diameters of 6 and 4.1 mm, respectively. A gas mixture of oxygen balanced with nitrogen (~100 mL/min), having oxygen partial pressures in the range of 0.1–0.8 atm, was fed to the feed side, while 10% propane balanced with helium (~10 mL/min) was fed to the reaction (permeate) side of the LNV10 membrane. Similarly, studies of ODH of ethane and propane, using BSCF disc membranes, were conducted, at either 550 or 650 °C. The thickness of the membranes varied between 0.8 and 1.0 mm, while the effective membrane area at the reaction side was about ~0.8 cm2. For ODH of propane, 10% propane balanced with helium (~10 mL/min) was swept along the reaction side, feeding nitrogen (~100 mL/min) on the opposite side of the membrane. Next, the nitrogen was diluted with...
oxygen (∼100 mL/min) to give oxygen partial pressures in the range of 0.02–0.4 atm. Prior to experiment, the membrane was pre-equilibrated for 5 h, using nitrogen (∼100 mL/min) and helium (∼10 mL/min) as sweep gases along both sides of the membrane. For ODH of ethane, oxygen balanced with nitrogen (∼100 mL/min), having an oxygen partial pressure of 0.1–0.8 atm, was fed to the feed side, while diluted ethane (∼10 mL/min), in the range of 24%–76% in helium, was fed to the reaction side of the BSCF membrane.

To investigate thermal cracking and/or dehydrogenation of the alkanes in the gas phase, experiments were carried out, using either a quartz tube or discs, replacing tubular and planar membranes, respectively, and keeping all other conditions similar to those as used in the membrane reactor experiments. These experiments, referred to as blank experiments, were carried out both in the absence and presence of gaseous oxygen.

Reactor effluents were analyzed using online gas chromatography, as specified above. All reactant gases passed through an ice-bath condenser before injection into the gas chromatograph. The absence of nitrogen in the effluents was taken as evidence that no leakage occurred through the membrane or glass seal.

Conversions and selectivities were calculated based on the carbon balance [19]. The conversion was calculated from the following equation:

\[ C = 1 - \frac{nY_{C_nH_{2n+2}}}{\sum m_i Y_i} \]  

where \( m_i \) and \( Y_i \) are the number of carbon atoms and molar fraction of the \( i \)-th carbon-containing product, respectively. The selectivity towards the \( i \)-th carbon-containing product was calculated from

\[ S_i = \frac{m_i Y_i}{\sum m_i Y_i - nY_{C_nH_{2n+2}}} \]  

For all catalytic tests, the carbon balance was within 100%±1%.

III. RESULTS AND DISCUSSION

A. Characterization of membrane materials

The XRD powder diffraction pattern of LNV10 is presented in Fig. 2. Like that of its parent La\(_2\)NiO\(_4\), the pattern of LNV10 can be indexed on the basis of a tetragonal unit cell, with cell parameters \( a=3.873(2) \) Å and \( c=12.659(2) \) Å. The diffraction pattern of BSCF (not shown) could be indexed on the basis of a simple cubic perovskite structure. In both cases, no evidence was found for the presence of phase impurities or second phase formation.

Figure 3 shows oxygen permeation measurements results of LNV10 in this work, results for BSCF reported in Ref.[20] are also shown for comparison. From these data it is apparent that, at the moderate temperatures covered experimentally, oxygen transport in LNV10 is much lower than in BSCF. A value of 164 kJ/mol was calculated for the activation energy for oxygen permeation through LNV10.

B. ODH of propane using catalytic membrane reactors

Quantitative reaction products observed when propane passed through the tubular LNV10 membrane reactor were \( \text{H}_2 \), \( \text{CH}_4 \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_6 \) and \( \text{C}_3\text{H}_6 \). Figure 4 shows the distribution of products, at 650 °C, while maintaining \( P_{O_2} \) of 0.8 atm at the feed side of the membrane. Also shown in the figure are the corresponding data from pyrolysis experiments in an empty reactor (referred to as blank experiments). It
is clear that under the conditions of the experiments there is a significant contribution from gas phase reactions. Besides H₂O, combustion products CO₂ are formed when oxygen is fed to propane via the LNV10 membrane.

In Fig. 5(a), the product concentrations are plotted against the oxygen flux. The latter was varied by maintaining different oxygen partial pressures, in the range of 0.1–0.8 atm, at the feed side of the membrane during the experiments. The results show that the oxygen concentration at the reaction side remains virtually zero, while the formation of all products, including H₂O and CO₂, increases with increasing the oxygen flux.

As shown in Fig. 5(b), the conversion of propane increases concomitantly from 6.3% to 7.8%, without a significant change in the propylene selectivity. In the range of the experiments, the latter slightly decreases from 51.8% to 49.5%. The emerging picture is that, at given experimental conditions, amongst which the absence of a catalyst is considered important, molecular oxygen acts as a scavenger of free radicals. Compared to the data from pyrolysis experiments, addition of oxygen to the propane stream is found to lower propane conversion. The conversion is further lowered upon increasing the oxygen concentration in the gas phase, as can be judged from the data presented in Table I. Under the conditions of the experiments with O₂, the oxygen consumption by gas phase reactions is limited. As seen in Fig. 6., free, i.e., unreacted, oxygen can still be detected, while only limited oxygen is traced back in the form of CO₂, but none in the form of H₂O. The situation alters when oxygen is supplied to the propane stream via the BSCF membrane. Although free oxygen can still be detected in the gas phase, significantly enhanced conversion to olefins (C₂H₄, C₃H₆) is found.

The data shown in Fig. 6 emphasize on the catalytic conditions, amongst which the absence of a catalyst is considered important, molecular oxygen acts as a scavenger of free radicals. Compared to the data from pyrolysis experiments, addition of oxygen to the propane stream is found to lower propane conversion. The conversion is further lowered upon increasing the oxygen concentration in the gas phase, as can be judged from the data presented in Table I. Under the conditions of the experiments with O₂, the oxygen consumption by gas phase reactions is limited. As seen in Fig. 6., free, i.e., unreacted, oxygen can still be detected, while only limited oxygen is traced back in the form of CO₂, but none in the form of H₂O. The situation alters when oxygen is supplied to the propane stream via the BSCF membrane. Although free oxygen can still be detected in the gas phase, significantly enhanced conversion to olefins (C₂H₄, C₃H₆) is found.

The data shown in Fig. 6 emphasize on the catalytic
role of BSCF in the dehydrogenation of propane. It is assumed that propyl radicals are generated at the BSCF surface involving a mechanism in which lattice oxygen is responsible for \(\text{C-H} \) bond activation, and one which is consistent with a Mars-van Krevelen redox mechanism [6]. The propyl radical is desorbed as olefin with concomitant formation of \( \text{H}_2\text{O} \). The presence of reaction products \( \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \), however, indicates that under the conditions of the experiments gas phase reactions are active. The enhanced formation of \( \text{CO}_2 \), relative to the blank experiments in an empty reactor, \( i.e. \) in the presence of oxygen, suggests that \( \text{CO}_2 \) is essentially formed at the BSCF surface. Increasing the oxygen flux, by maintaining a higher oxygen partial pressure at the feed side of the BSCF membrane in a series of experiments, from \( p_{\text{O}_2}=0.02 \text{ atm} \) to \( p_{\text{O}_2}=0.40 \text{ atm} \), as shown in Fig.7, increases production of \( \text{CO}_2 \), but lowers conversion of propane. The propylene selectivity is only slightly reduced. It thus emerges that the membrane-assisted catalytic conversion of propane is an interplay between operating constraints (like the number of sites at the surface, residence time, feed concentrations, \( etc. \)), the oxygen flux, and the occurrence and extent of homogenous gas phase reactions. A distinct oxygen flux is required to achieve the desired conversion of the alkane into the corresponding olefin. A too high oxygen flux, however, leads to (i) unselective weakly-bonded adsorbed oxygen species, oxidizing alkyl radicals at the catalytic membrane surface, thereby producing \( \text{CO}_2 \), and (ii) increases the concentration of gaseous oxygen, limiting the extent of the gas phase reactions.

C. ODH of ethane using the BSCF catalytic membrane reactor

The catalytic performance of the BSCF membrane reactor was conducted, at 650 °C, in ODH of ethane. Typical results obtained upon passing 40.5% ethane, balanced with helium, through the reactor, while maintaining \( p_{\text{O}_2}=0.8 \text{ atm} \) at the feed side of the BSCF membrane, are shown in Fig.8.

Quantifiable reaction products at the exit of the reactor were \( \text{H}_2 \), \( \text{CH}_4 \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and \( \text{C}_2\text{H}_4 \). Under the conditions of the experiments, ethane conversion was 6.09% with ethylene selectivity of 87.7%. Results of thermal pyrolysis experiments (blank experiments) carried out in an empty reactor are shown in Table II.

TABLE I Conversion and \( \text{C}_3\text{H}_6 \) selectivity in thermal pyrolysis and ODH of propane, at 550 °C, performed in an empty quartz reactor without or with different content of \( \text{O}_2 \).

<table>
<thead>
<tr>
<th>Inlet gas composition</th>
<th>Conversion/%</th>
<th>Selectivity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%( \text{C}_3\text{H}_8 )/He</td>
<td>0.25</td>
<td>61.4</td>
</tr>
<tr>
<td>0.035%( \text{O}_2 )/8.64%( \text{C}_3\text{H}_8 )/He</td>
<td>0.21</td>
<td>59.5</td>
</tr>
<tr>
<td>0.070%( \text{O}_2 )/7.20%( \text{C}_3\text{H}_8 )/He</td>
<td>0.15</td>
<td>63.6</td>
</tr>
</tbody>
</table>

FIG. 6 Product distribution in ODH of propane, at 550 °C, from experiments using the BSCF membrane reactor. Reactant side: 10%\( \text{C}_3\text{H}_8 \) (10 mL/min), feed side: \( p_{\text{O}_2}=0.05 \text{ atm} \). Also shown are corresponding data of thermal pyrolysis experiments (blank, without \( \text{O}_2 \)) and ODH of propane (blank, with \( \text{O}_2 \)), at 550 °C, performed in an empty quartz reactor.

FIG. 7 Catalytic performance of the BSCF membrane reactor in ODH of propane, at 550 °C, as a function of the oxygen permeation flux. (a) Product distribution and (b) conversion and propylene selectivity. Reactant side: 10%\( \text{C}_3\text{H}_8 \) (10 mL/min).
FIG. 8 Product distribution in ODH of ethane, at 650 °C, from experiments using the BSCF membrane reactor. Reactant side: 40.5% C₂H₆ (10 mL/min), feed side: \( p_{O_2} = 0.80 \) atm.

TABLE II Conversion and C₂H₄ selectivity derived from ethane pyrolysis experiments with different feed concentration of C₂H₆, at 650 °C, performed in an empty quartz reactor.

<table>
<thead>
<tr>
<th>C₂H₆/%</th>
<th>Conversion/%</th>
<th>C₂H₄ selectivity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.3</td>
<td>0.42</td>
<td>99.6</td>
</tr>
<tr>
<td>42.9</td>
<td>0.41</td>
<td>99.5</td>
</tr>
<tr>
<td>61.6</td>
<td>0.39</td>
<td>99.5</td>
</tr>
<tr>
<td>81.0</td>
<td>0.37</td>
<td>99.4</td>
</tr>
</tbody>
</table>

It is seen that the corresponding ethylene selectivities are close to 100%, albeit that these are at low ethane conversions in the range of 0.37%–0.42%, obtained using different feed concentrations of ethane (Table II). In accord with the data presented in Fig.9, ethane conversion is found to increase pronouncedly if oxygen is fed via the BSCF membrane to the reaction side where the ethane is passed. The loss in ethylene selectivity observed in the membrane experiment, relative to that obtained during thermal pyrolysis in the empty reactor, is explained by the fact that the oxygen flux exceeds the rate of oxygen consumption by the catalytic reaction at the membrane surface. The presence of weakly adsorbed oxygen species in conjunction with gas phase oxygen lowers the overall ethylene selectivity. It is also confirmed by the results from measurements, in which either the inlet concentration of ethane was varied, i.e., at constant \( p_{O_2} \) at the feed side of the BSCF membrane, as listed in Table III, or those in which the \( p_{O_2} \) at the feed side of the BSCF membrane was varied, i.e., at constant inlet concentration of ethane, as shown in Fig.9. Both data sets demonstrate that the ethylene selectivity increases when the oxygen flux and rate of oxygen consumption by the catalytic reaction are better in balance.

On the whole, the oxygen concentration both in the gas phase and on the surface of the catalyst membrane is crucial for determining the selectivity for ODH of ethane and propane.

FIG. 9 Catalytic performance of the BSCF membrane reactor in ODH of ethane, at 650 °C, as a function of the oxygen permeation flux. (a) Product distribution and (b) conversion and ethylene selectivity. Reactant side: 73.9% C₂H₆ (10 mL/min). Oxygen partial pressures maintained at the feed side of the membrane are indicated in the figures.

TABLE III Catalytic performance of the BSCF membrane reactor in ODH of ethane, at 650 °C, using different inlet concentrations of ethane (10 mL/min). Feed side: \( p_{O_2} = 0.80 \) atm. Also given are the gas phase oxygen concentrations measured at the reaction side of the membrane.

<table>
<thead>
<tr>
<th>C₂H₆/%</th>
<th>Conversion/%</th>
<th>Selectivity/%</th>
<th>( O_2/% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.3</td>
<td>3.48</td>
<td>78.8</td>
<td>1.18</td>
</tr>
<tr>
<td>40.5</td>
<td>6.09</td>
<td>87.7</td>
<td>0.32</td>
</tr>
<tr>
<td>57.2</td>
<td>5.31</td>
<td>90.1</td>
<td>0.17</td>
</tr>
<tr>
<td>73.9</td>
<td>4.40</td>
<td>91.5</td>
<td>0.11</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

In summary, the results show the dominating role of the oxygen flux across the membrane and available sites at the membrane surface in primary activation of the alkane and, hence, in achieving high alkane conversions. The results of ODH of propane and ethane on

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both membrane materials used in this work can be reconciled on the basis of Mars-van Krevelen type of kinetics, in which the alkane reacts with lattice oxygen on the membrane surface to produce the corresponding olefin. As expected, the oxygen concentration in the gas phase and the presence of weakly-bonded oxygen species on the membrane surface are crucial for determining the residual olefin selectivity. The latter emphasize on the paramount importance to carefully match the oxygen flux with the rate of olefin production at the surface of the membrane.

V. ACKNOWLEDGMENTS

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