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Transient behaviour of dense catalytic membranes based on Cu- and Co-doped $Bi_4V_2O_{11}$ (BIMEVOX) in the oxidation of propene and propane

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Abstract

ME-doped γ-$Bi_4V_2O_{11}$ (BIMEVOX) oxides are highly oxide ion conducting materials and this property may be profitably used in selective oxidation of hydrocarbons. The catalytic properties of BICUVOX and BICOVOX when shaped as dense membranes displayed in catalytic dense membrane reactor are examined in the oxidation of propene and of propane. Mirror-polished BICUVOX and BICOVOX membranes studied previously were poorly active for propene oxidation because of a small number of active sites but showed an excellent stability and reproducibility (lasting more than one month) during which products of mild oxidation (acrolein, hexadiene) and CO were formed. Membranes with depolished surfaces exhibit high conversions of propene (up to 60 mol%), and also of propane (up to 20 mol%) but – contrary to mirror polished membranes – a complex transient behaviour is observed during which syngas production occurs. The membrane polarization followed by in-situ Solid Electrolyte Potentiometry shows that the oxygen reservoir is far higher than

expected on the reaction side which is separated (by the membrane) from the oxidising side where (diluted) oxygen is reduced to O^{2-} specie. The influence of oxygen partial pressure on the catalytic performance suggests that the electronic conductivity of the material is limiting the oxygen flux through the membrane, and thus is determining the catalytic properties and transient behaviours of depolished membranes.

Introduction

In selective oxidation of hydrocarbons during which the redox mechanism prevails, there is generally a competition between nucleophilic lattice O^{2-} oxygens considered as the selective agents and more electrophilic adsorbed oxygens which mostly lead to the formation of carbon oxides [1]. In usual fixed or fluidised bed reactors dioxygen is cofed with the hydrocarbon to regenerate the catalyst. If it is not cofed, one can expect an increase of selectivity for two reasons , (i) the direct gas phase oxidation of the hydrocarbon by gaseous O_2 cannot proceed, and (ii) electrophilic adsorbed specie cannot form after dissociation of O_2. The oxidation of n-butane to maleic anhydride in a circulating fluid bed reactor was the first industrial and successful case of decoupling of the redox mechanism [2, 3]. Among other means to decouple the redox steps either in space or in time, catalytic membrane reactors have already been proposed. The membrane may allow the extraction (of a product) or distribution (of a reactant, e.g. oxygen), or it may act as a contactor [4]. As a catalyst can be deposited onto a porous membrane, the latter is interesting in oxidation because the reactants may be separately fed on each side of the membrane allowing higher safety and higher selectivity. Another possibility, less common in selective oxidation, is to use a dense membrane which is intrinsically catalytic and exhibits as well oxide ionic and electronic conductivities [5, 6, 7]. Indeed, catalysts of mild oxidation behave as more or less good oxygen ion conductors although these properties are not often considered in catalytic oxidation [8a-b, 9]. In a

catalytic dense membrane reactor (CDMR), the membrane separates two compartments. The reactant side is fed by the (diluted) hydrocarbon (LOP, low oxygen partial pressure pO_2, or permeate side) and the oxidising side by diluted oxygen (HOP, high oxygen partial pressure, or retentate side). The driving force of oxide ion migration is the gradient of oxygen activity between the two compartments.

Oxidic materials based on the γ-$Bi_4V_2O_{11}$ structure in which V is partially substituted by a metallic cation, exhibit the highest oxide ion conductivities at moderate temperatures (623-873K) [10, 11]. For example, the ionic conductivity of γ-$Bi_4V_{1.8}Cu_{0.2}O_{10.7}$ is one hundred times that of yttria-doped zirconia at 873K. The BIMEVOX acronym has been accepted by the community because most cations of the periodic table can be used as ME dopants, thereby stabilising γ-$Bi_4V_2O_{11}$ down to room temperature. The catalytic properties of some BIMEVOX powders have been examined in the oxidative dehydrogenation of propane (ME = Zn, Cu) [12] and in the oxidative dimerisation of propene (Me = Cu, Co) [13, 14] in conventional fixed bed reactors. The catalytic behaviour of BICOVOX as dense membranes for the oxidation of propene in a CDMR has recently been examined [15]. As the surface of membranes was mirror-polished in order to get accurate measurements of oxygen permeation, the surface area was very low which explained why the conversion of propene was low (1-2 mol%). In the present paper, preliminary results obtained using Cu (BICUVOX) and Co (BICOVOX) doped γ-$Bi_4V_2O_{11}$ depolished membranes in the catalytic oxidation of propene and of propane in a CDMR are presented.

Experimental

Membranes of $Bi_4Cu_{0.2}V_{1.8}O_{10.7}$ (BICUVOX) and $Bi_4Co_{0.2}V_{1.8}O_{10.7}$ (BICOVOX) (∅ =15 mm, thickness 17 mm, relative density > 95% as compared with theoretical density) with two surface roughnesses (mirror-polished with 4000 SiC grit paper, further depolished by 200 SiC

grit paper) were prepared [15]. The membrane was sealed in between the two mullite tubes of the reactor by means of pyrex rings. Air or oxygen was flowed in the high oxygen partial pressure (HOP, retentate) side. The low oxygen partial pressure (LOP, permeate) side was fed with He (permeation mode), or with 1% propene or 1% propane in helium (both F = 50 $cm^3.mn^{-1}$) (reaction mode) at 823-1023K and P = 10^5 Pa. The CDMR assembly described in [15] allows combined studies of the solid catalyst (ionic conductivity, permeability, electronic polarisation) and of the catalytic reaction (activity, selectivity, etc.). The gas phase composition at inlets and outlets of the two compartments of the CDMR was monitored using a mass spectrometer (Omnistar Pfeiffer) for the catalytic reaction and an oxygen gauge (Setnag) for O_2 permeation. Gold electrodes were in contact of each side of the membrane and the difference of potential between these sides was in situ measured to follow the membrane polarisation (Solid Electrolyte Potentiometry, SEP). The standard protocole consisted first in the measurement of oxygen permeation fluxes. Then diluted propene or propane was flowed into LOP compartment and the catalytic properties were studied as well as SEP was performed. Parameters such as temperature (823-973 K), contact time (τ = 2-12 s), and oxygen pressure (pO_2 = 1-10^5 Pa) in HOP side of the membrane were varied. Pieces of membranes were characterized by X-ray diffraction (XRD), laser Raman spectroscopy (LRS), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) before and after reaction.

Results and discussion

Membranes with mirror-polished surfaces

As for BICOVOX membranes [15], low conversions of propene (up to 2.0 mol%, depending on temperature, contact time τ and propene partial pressure) were observed for the BICUVOX membrane with mirror-polished surface. For example, at 948K and τ = 6 s, conversion was

1.0 mol% and selectivities ranged as CO = 70, hexadiene = 15, acrolein = 12, benzene = 3 mol%. These figures were similar to those obtained with BICOVOX except that no CO_2 was present. If a 100 mol% selectivity to CO is supposed, 600 ppm of oxygen are necessary to convert 100 ppm of propene to $3CO + 3H_2O$. These oxygens could be provided by permeation. However, the JO_2 flux measured after flowing helium in LOP instead of diluted propene is very low (e.g. $JO_2 = 3.10^{-4}$-3.10^{-5} $\mu mol.cm^{-2}s^{-1}$ for BICOVOX at 873-953K), producing only 1-2 ppm O_2 in LOP in the same experimental conditions [15]. Indeed, most of the conductivity is due to oxide ions (transference number $t_i \approx 1$) and few electrons are available to ensure the dissociation of O_2 as well as the recombination of O^{2-} according to $O_2 \Leftrightarrow O^{2-} + 4e$, as confirmed by $^{18}O/^{16}O$ isotope exchange combined with SIMS [16]. On the contrary, the polarisation of the membrane remained high during all experiments, which means that the thermodynamic activity of oxygen at the surface in LOP is far higher than supposed. Indeed, calculations by the Nernst equation show that E = -10.5 mV measured by SEP gives $pO_2 = 0.13.10^5$ Pa, instead of 0.3 Pa observed experimentaly. In other words, the oxygen O^{2-} reservoir in LOP is larger than expected, and the oxidation of propene provides an alternative pathway for oxygen extraction in place of the recombination of O^{2-} to O_2.

The stability of the membrane was remarkable during the whole experiments which lasted up to one month. The characterisation of the membrane by XRD, SEM, LRS and XPS showed that the LOP, as well as the HOP surfaces remained unchanged.

Membranes with depolished surfaces

Depolished BICUVOX membranes give far higher values of propene conversion. However, their activity is not stable and decreases with time (Fig. 1). In the first 10 minutes, the propene conversion reaches 60-55 mol% while CO and H_2 are the main products. Then it decreases and is stabilised at 25 mol% after 1 h. Most of this residual conversion can be accounted for coke and H_2 formation. After coke burning and membrane regeneration (by feeding air

instead of propene in LOP), the oxidation of propane was performed in similar conditions of contact time and of partial pressures. A complex transient behaviour was observed. Initially, the activity is stable, the conversion of propane being at ca. 12.5 mol% (Fig. 2). Carbon monoxide, H_2, and little propene and CO_2 are the major products. The formation of small amounts of CH_4 and C_2H_4 observed all along the experiment may come from cracking. A two-fold increase of activity is then suddenly observed while the only products are CO, H_2 and water. Finally, the propane conversion returns to its initial value and remains stable for hours. Coke is still formed but in lower amounts than in the case of propene oxidation. Even in such conditions, the amount of oxygen contained in the reaction products (e.g.: at t = 1500 s, pCO = 700 ppm and pH_2O ~ 300 ppm) is far higher than that generated by permeation of O_2 through the membrane in the absence of propane (pO_2 in LOP < 10 ppm). The evolution of the H_2/CO ratio (Fig. 3) shows two distinct values (1.7 and 3.1) which reflect a change of the active state of the membrane surface. This change may depend on, (i) the nature of surface oxygen specie, (ii) the modification of the surface structure, or (iii) of the bulk structure. The nature of surface oxygen specie may change from nucleophilic O^{2-} to electrophilic O^- (or O_2^{2-}). Once the first nucleophilic O^{2-} are used to oxidise the hydrocarbon molecules, the diffusion of other O^{2-} from bulk ensures their replacement on surface. The prominent reaction being the oxidation of hydrocarbon by V^{5+}(-O), there is little chance that such electrophilic specie form, e.g. by the redox reaction V^{5+}-$O^{2-} \rightarrow V^{4+}$-$O^-$. The two other hypotheses rest on the relative contribution of surface reactions and of oxygen diffusion through the membrane.

When repeating the experiment with pure dioxygen in HOP side instead of air, the initial conversion increases up to 16% (Fig. 3), and the transient response is accelerated. Furthermore, a third phenomenon characterised by a higher H_2/CO ratio (H_2/CO = 5) appears at t = 540 s. However, the final conversion is not significantly affected by pO_2 in HOP (air or pure O_2) as it amounts to 10 mol% in both cases.

The BICOVOX membrane (Fig. 4) shows a similar transient behaviour, with an initial propane conversion of 10%, and three active states generating H_2/CO ratios of 2.1, 3.7 and 8-10 respectively. In contrast to BICUVOX, the increase of pO_2 in HOP (O_2 instead of air) does not significantly affect the initial propane conversion, and the transient phenomena are considerably slowed down.

For both BICUVOX and BICOVOX membranes, and despite the low oxygen partial pressure in LOP, SEP showed that the difference of potential between the two faces of the membrane remained high (ΔE = -1 to –15 mV) with respect to the Nernst equilibrium potential of -208 and -241 mV for HOP = 21% or 100% p_{atm}, respectively (calculated at 973K with LOP = 10 ppm O_2). Typically, negative potentials of several hundreds of mV with respect to air are needed for the reduction of the materials [17], which are far below those measured experimentally. These strong polarisations confirm the good bulk stability of the materials, even in the strongly reducing conditions of the catalytic reaction. This is in agreement with the high O^{2-} conductivity of these materials and it suggests that the rate limiting step of the overall process involve surface phenomena and/or electronic conductivity [8, 9].

The opposite behaviour of BICUVOX and BICOVOX membranes when increasing pO_2 in HOP could be explained by the different electron conductivity they exhibit, which is important for the O_2 reduction step. On the one hand, BICUVOX is a n-type semiconductor [18] and its electron conductivity is lowered by increasing oxygen partial pressure. It follows that the oxygen flux towards LOP surface should decrease upon increase of pO_2 in HOP. This could explain the acceleration of the transformation of the active surface yielding more coke and thus exhibiting more cracking properties. On the other hand, BICOVOX being a p-type semiconductor [18], its electron conductivity is thus enhanced by increasing pO_2, thereby stabilizing the more oxidized state of the surface and slowing down the transient coking phenomena.

Conclusions

The relatively high activity of depolished membranes for propene and propane oxidation in a catalytic dense membrane reactor confirms that the low conversions measured with mirror polished materials were due to the limited number of active sites. When more active sites are available (depolished membranes) for propene to be oxidized, the catalytic properties of BICUVOX and BICOVOX are modified and the steady production of mild oxidation products accompanying CO is replaced by a transient behaviour during which syngas is obtained. An even more complex transient behaviour is observed during propane oxidation. The respective amounts of H_2, CO and coke vary with time and, although the contribution of gas phase reactions may be significant at the operated temperatures, they seem to mostly depend on the chemical state of the active surface. Initial catalytic properties may be of interest for CO-H_2 synthesis (H_2/CO = 1.7 and 2.1 for BICUVOX and BICOVOX respectively), while little coke is formed, but also later on since regeneration is possible. The oxygen partial pressure in the HOP compartment significantly affects the evolution of the transient response with opposite effects according to the nature of the membrane. The influence of the membrane polarisation and of the oxygen partial pressure suggests that electron conductivity may be the limiting factor of the overall catalytic process. This opens the way for an optimisation of the catalytic reactor by improving the electronic conductivity in order to stabilize the most efficient active state of the membrane.

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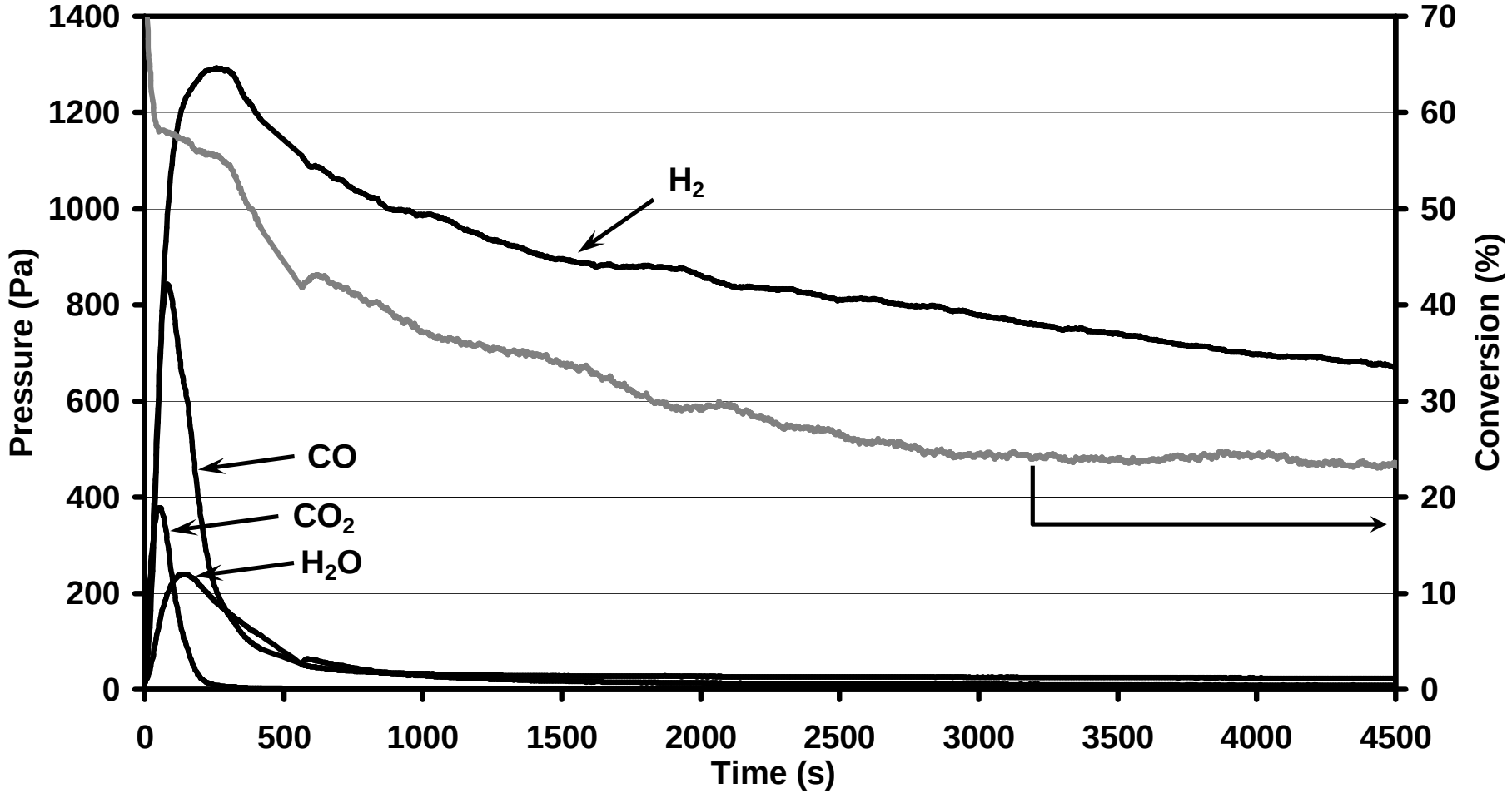
Figure Captions

Figure 1: Propene oxidation vs time on stream on unpolished BICUVOX membrane (T = 923K, HOP = Air, F = 50cc.min^{-1}, $pC_3H_6 = 10^3$ Pa)

Figure 2: Propane oxidation vs time on stream on unpolished BICUVOX membrane (T = 973K, HOP = Air, F = 50 cc.min^{-1}, $pC_3H_8 = 10^3$ Pa)

Figure 3: Propane conversion and H_2/CO ratio vs time on stream on unpolished BICUVOX membrane for HOP = Air and O_2 (T = 973K, F = 50cc.min^{-1}, $pC_3H_8 = 10^3$ Pa)

Figure 4: Propane conversion and H_2/CO ratio vs time on stream on unpolished BICOVOX membrane for HOP = Air and O_2 (T = 973K, F = 50 cc.min^{-1}, $pC_3H_8 = 10^3$ Pa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1200
1000
800
600
400
200
0
Pressure (Pa)
70
60
50
40
30
20
10
0
Conversion (%)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Time (s)
H2
CO
CO2
H2O

Figure 1

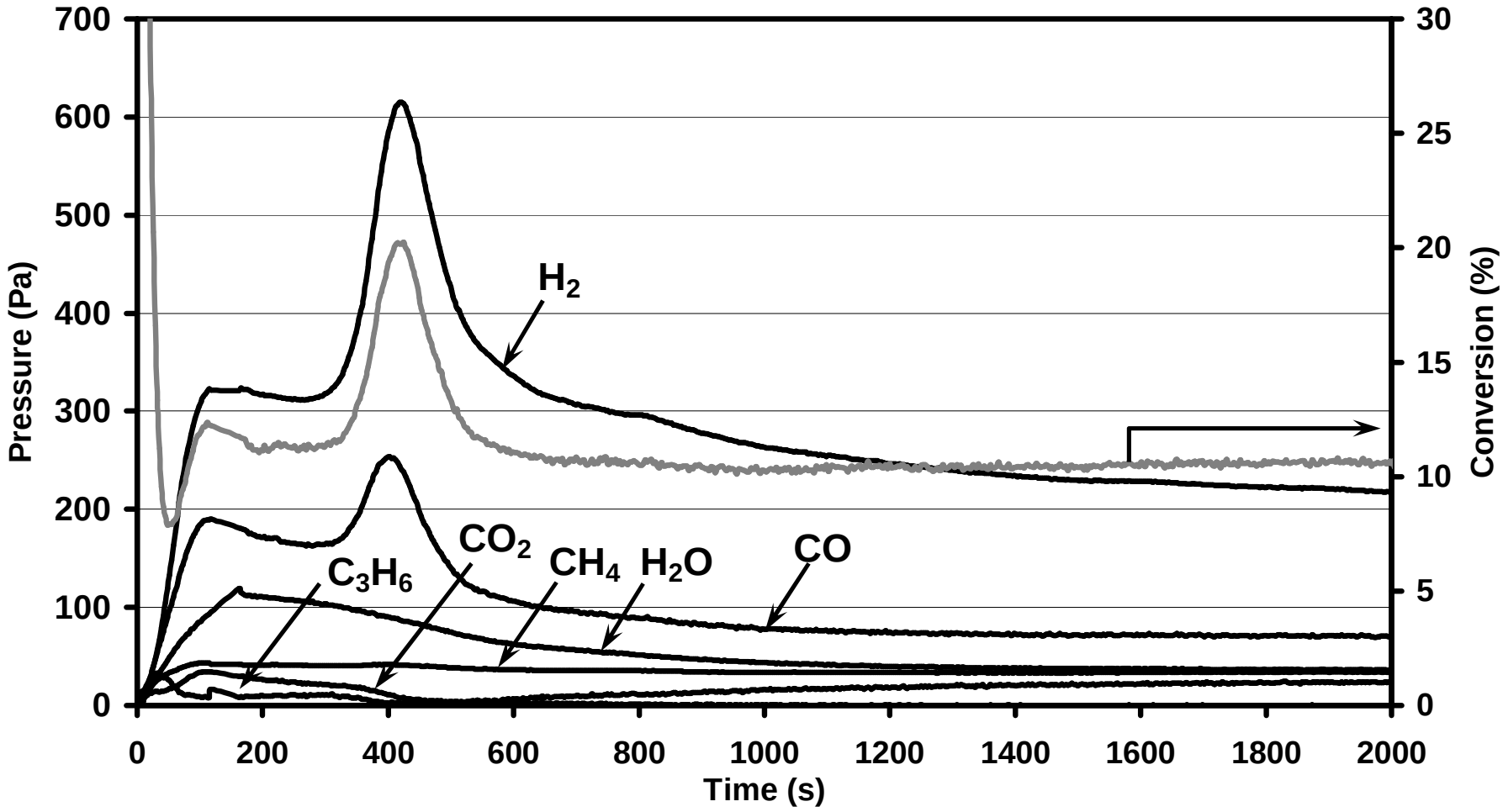
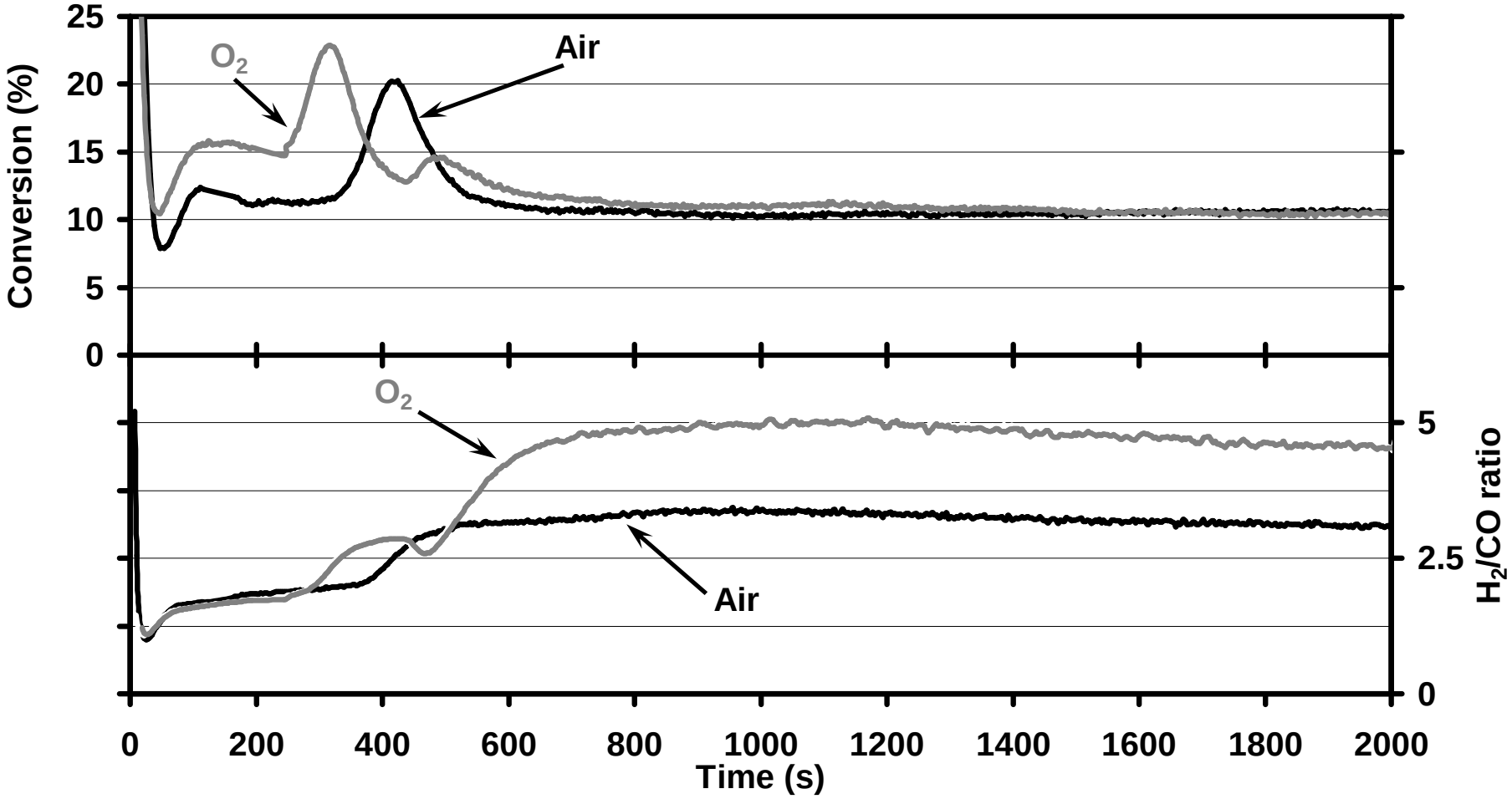

Pressure (Pa)
Conversion (%)
Time (s)
H2
CO2
CH4
H2O
CO
C3H6
0
100
200
300
400
500
600
700
0
5
10
15
20
25
30
0
200
400
600
800
1000
1200
1400
1600
1800
2000

Figure 2


Conversion (%)
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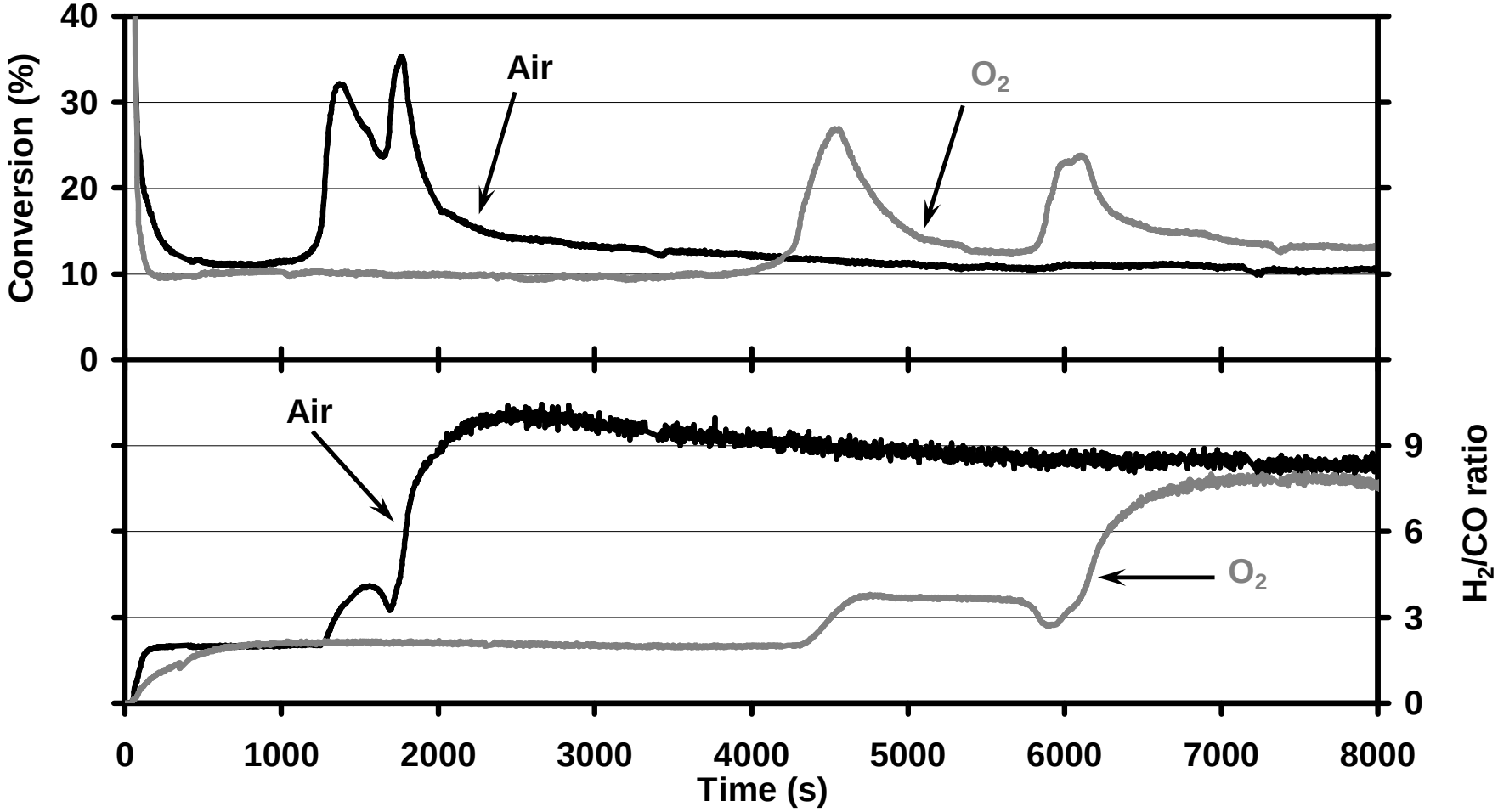
20
15
10
5
0
O2
Air
O2
Air
5
2.5
0
H2/CO ratio
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time (s)

Figure 3


Conversion (%)
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30
20
10
0
Air
O2
Air
O2
9
6
3
0
H2/CO ratio
0
1000
2000
3000
4000
5000
6000
7000
8000
Time (s)

Figure 4