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Catalysis Today 25 (1995) 377-383

CATALYSIS TODAY

Catalytic membrane reactor for oxidative coupling of methane. Part II — Catalytic properties of LaOCl membranes

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Abstract

This work presents the potential of a LaOCl porous membrane reactor for the reaction of oxidative coupling of methane. The sol–gel method provided LaOCl membranes supported on alumina tubes which presented mesoporous texture. Actually, the severe operating conditions of this reaction caused textural instability which restricted any transport effects to the macroporous domain. However, despite moderate separation effects between methane and oxygen, beneficial effects of the membrane reactor have been observed, subject to surface composition, structural and feeding configuration requirements.

1. Introduction

Within the intense effort of research devoted to the oxidative coupling of methane (OCM) during the past decade, most of the promising areas of catalyst development have been thoroughly explored; however, the hydrocarbon yields obtained up to now still remain under the target that would make the process commercially feasible (around 30%). Together with catalyst development, reactor configuration has also been studied in order to optimize the C_2 yields achieved with the best catalysts. Due to the basic competition between the selective routes towards hydrocarbons and the unselective routes leading to the oxidation products, modes of contact which would minimize the oxygen concentration around the catalyst should favour the desired reaction at the expenses of the undesired ones. Thus reactors allowing a distributed feed of oxygen along a catalyst fixed or fluidized bed have been implemented [1–3]. Modelling studies have demonstrated the interest of this approach, but experimental results were found to depend on numerous operating parameters. Membrane reactors have also been explored as ultimate and continuous systems for oxygen distribution. For this case, a first option was to promote dense catalytic membranes allowing only ionic oxygen to permeate through the oxide layer in order to regenerate the catalytic surface. In spite of very high selectivities towards hydrocarbons, yields were proved to be severely limited by the rate of ionic oxygen diffusion [4]. A second option was to promote porous membranes which enable a controlled diffusion of molecular oxygen under the conditions of the OCM reaction. This concept was recently tested by comparing a co-fed fixed bed reactor to a fixed bed reactor with oxygen fed separately through a porous membrane [5,6]. Another way to implement this controlled oxygen distribution was to combine catalysis and separa-

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0920-5861/95/$09.50
SSDI 0920-5861(95)00088-7

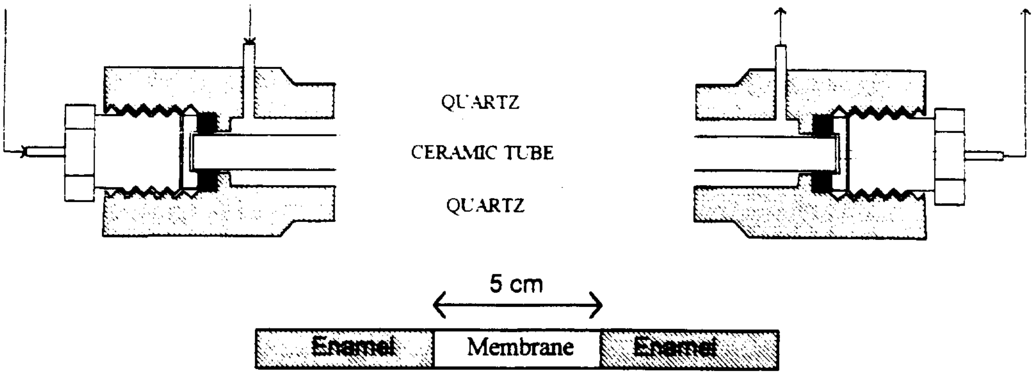


Fig. 1. Scheme of the membrane reactor and tubular membrane.

tion in the same porous zone by depositing the active phase on the porous membrane. This paper reports the catalytic results obtained with ceramic membranes based on lanthanum oxychloride deposited on porous alumina tubes by the sol–gel technique. Though lanthanum oxychloride was not the most active and selective lanthanum phase, this material was chosen due to its ability to be prepared by the sol–gel technique, as detailed in part I of this work [7].

2. Experimental

2.1. Materials

Two classes of materials were prepared, (i) test-membranes (3 cm tubes for catalytic testing in a conventional tubular reactor and characterisation) and (ii) membranes adapted to the membrane reactor (35 cm tubes for testing in a membrane reactor).

The morphological aspect of the prepared ceramic films was observed by scanning electron microscopy. The chemical composition was determined by X-ray and chemical analysis. The specific surface area and the pore diameter distributions of the membranes have been determined by N_2 adsorption/desorption method. Permeability measurements were carried out before and after reaction in the membrane reactor, at room temperature with nitrogen or at reaction temperature with helium, oxygen and methane.

2.2. Catalytic testing

Catalytic activities of 3 cm test-membrane samples were determined in a conventional quartz tubular reactor without separation effect. Conditions were: $CH_4/O_2/He$ (60/30/670 Torr), flow rate: 3.6 l/h and repeated heating/cooling cycles under reacting mixture were carried out to evaluate catalyst ageing.

The proper membrane reactor consisted of two cylindrical co-axial tubes, (i) one internal porous alumina tube (from SCT company), coated on the internal surface with a LaOCl layer deposited by the sol–gel method [7] and (ii) one external non porous quartz tube (Fig. 1). Two operating modes were applied: either co-feeding CH_4, O_2 and He or feeding separately He and CH_4 into the inner compartment and He and O_2 into the outer one, in order to study membrane separation effect. Conditions were: $CH_4/O_2/He$ (60/30/670 Torr), flow rate: 3.6 to 6.0 l/h at 750°C. The total pressure was measured at the entrance of the reactor and the differential pressure between the two compartments. Temperature gradients along the internal tube were limited by restricting the porous section to the homogeneous zone of the furnace, the tube ends being enamelled.

3. Results

3.1. Membrane characterization

Two types of membranes were studied: (i) LaOCl deposited on γ-alumina support presenting a mean pore diameter of 5 nm; and (ii) LaOCl deposited on α-alumina support presenting a mean pore diameter of 200 nm.

Effect of support

LaOCl membrane on 5 nm γ-alumina support.

After LaOCl deposition and calcination at 500°C, an homogeneous top layer (100 nm thick) was observed by SEM [7] (Part I). After calcination at 800°C, i.e., the temperature required for the OCM reaction, the top layer was completely infiltrated inside the γ-alumina layer. SEM/EDX analysis of the surface revealed much higher La/Cl atomic ratios (from 5.6 to 9.3) than expected from LaOCl stoichiometry (1.0), as well as very low La/Al ratios (around 0.05), whatever the enlargement considered. These results confirm the penetration of the lanthana phase into the γ-alu-

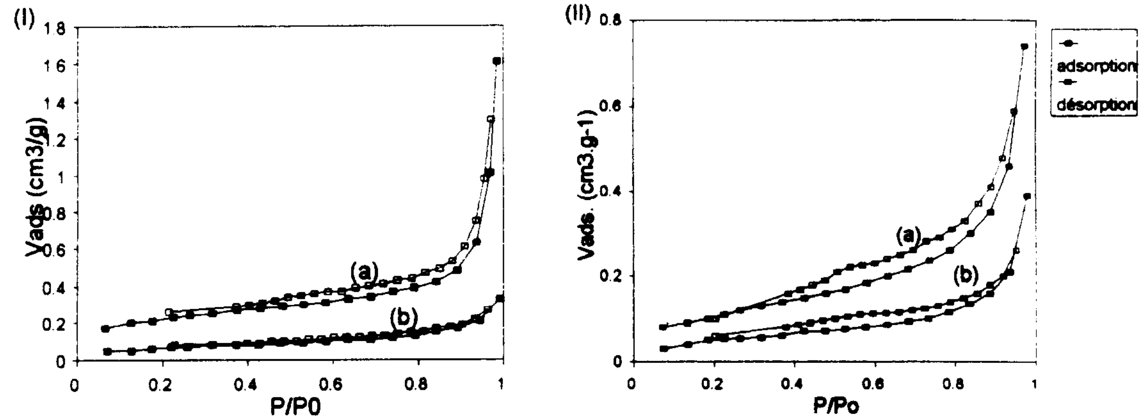


Fig. 2. N_2 adsorption/desorption isotherms of LaOCl membranes onto 200 nm support (I): SD, and (II): DD; after calcination (a) and after reaction (b).

Table 1
Surface area and porous volume of LaOCl membranes deposited on a 200 nm α-alumina support, after calcination and after OCM reaction

LaOCl membrane		S_{BET} ($m^2 \cdot g^{-1}$)	Porous volume ($cm^3 \cdot g^{-1}$)
SD on 200 nm support	After calcination at 500°C	0.80	1.15
	After calcination at 800°C	0.16	0.28
	After reaction at 750°C	0.22	0.21
DD on 200 nm support	After calcination at 800°C	0.41	0.6
	After reaction at 750°C	0.21	0.2

Table 2
N_2 permeability at room temperature and catalytic performances of LaOCl supported membranes

LaOCl membrane	N_2 permeability ($\times 10^7$ $mol \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$)		Feeding mode (%)	X_{CH4} (%)	X_{O2} (%)	$S_{C2}{}^+$ (%)	$Y_{C2}{}^+$
	Before reaction	After reaction					
SD on γ-Al_2O_3	50	nd	co-feed	27	77	13	3.4
			separated	28	89	14	3.8
SD on α-Al_2O_3	161	nd	co-feed	32	87	24	7.8
			separated	32	73	27	8.6
DD on α-Al_2O_3	145	584	co-feed	35	96	29	10.3
			separated	35	97	31	11.1
TD/INF on α-Al_2O_3	106	128	co-feed	31	94	20	6.3
			separated	32	96	21	6.6

Note: N_2 permeability is measured at $2 \cdot 10^5$ Pa.
nd: not determined.

mina layer, and suggest that some decomposition of the LaOCl precursor occurred during the heat treatment, likely due to solid/solid reaction with γ-alumina. This membrane was found to be mesoporous as indicated by its type IV isotherm [8] and *t*-plot [9], with a permeability corresponding to the one of the γ-alumina layer (see Table 2).

LaOCl membrane on 200 nm α-alumina support.

In order to avoid the solid/solid reaction observed with γ-alumina support, membranes were prepared with a 200 nm α-alumina support (more chemically inert), either with a single deposit of LaOCl (1 to 2 μm thickness, named SD) or with a second thin deposit (0.1 to 0.2 μm thickness) over the first one (named double deposit DD).

For both cases, chemical and SEM/EDX analyses revealed that the atomic ratio La/Cl was close to 1.0 for either the unreacted or the reacted membrane, as expected from the LaOCl stoichiometry. This indicates that the active phase deposited on this type of support remained chemically stable during calcination and catalytic run. A high La/Al ratio (12 to 25) was observed on the main part of the surface, confirming the formation of a LaOCl top layer, except on some cracked zones presenting much higher concentration of alumina.

Another type of membrane with a third deposition has also been prepared: the third layer was deposited on the DD material without plasticizer, leading to a deep penetration of the LaOCl phase into the membrane and support top layers. It is named infiltrated triple deposit or TD/INF (see Part I).

Effect of calcination and of reaction

The changes in N_2 adsorption/desorption isotherms after calcination and reaction and the corresponding BET area and porous volume are reported in Fig. 2 and Table 1, respectively.

After calcination at 500°C, the SD membrane on 200 nm α-alumina was found essentially mesoporous with a small fraction of microporosity. After calcination at 800°C, the surface area and porous volume decreased markedly, attesting deep morphological changes with a marked lost of mesoporosity. After reaction carried out at 750°C on the 800°C-precalcined membrane, only slight changes in the porous volume and surface area were detected (Table 1).

After calcination at 800°C, the DD membrane was still found mesoporous, suggesting some stabilization effect of the double deposit. However, after reaction at 750°C, the final state of the membrane was quite similar to the one of the SD membrane, i.e., sintered and much less mesoporous.

Another effect of the reaction, consistent with the previous observations, was the increase of the membrane permeability, depending on the membrane and on the number of catalytic runs (Table 2).

3.2. Catalytic performances

Effect of support

Significantly higher C_{2+} selectivity and yield were obtained with membranes deposited on 200 nm α-alumina in comparison with membranes deposited on 5 nm γ-alumina (Table 2).

Effect of permeability

No clear relation was observed between N_2 permeability measured at room temperature, catalytic selectivity and yield for the various membranes deposited on the same α-alumina support (Table 2). However, it can be noted interestingly that the best yield was obtained with the most permeable membrane (measured on the DD sample after numerous catalytic runs), while the TD/INF membrane, much less permeable, was found little selective. The permeability of each of the OCM reacting gases —methane, oxygen and helium — was measured at reaction temperature (710°C), as reported in Fig. 3. The ratio of permeabilities is compared to the ratio of the square roots of the molecular weights in Table 3.

As can be seen, the permeabilities decrease according to the molecular weight (Fig. 3) and a reasonable agreement is noted between the ratios of the permeabilities and the ratios of the square

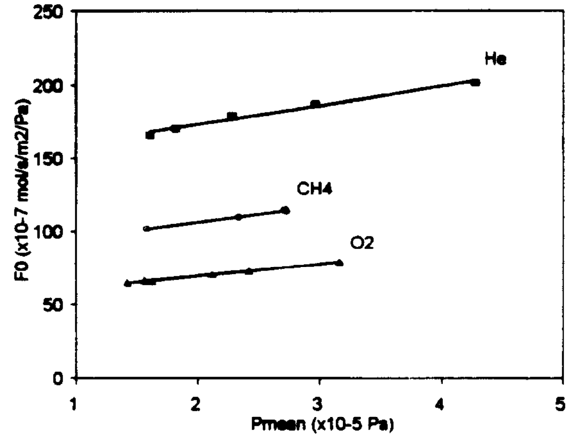


Fig. 3. Permeabilities of oxygen, methane and helium measured at 710°C on the LaOCl membrane deposited on 200 nm α-alumina support (DD).

Table 3
Ratios of gas permeabilities measured at 710°C, 1.6 atm compared to the ratios of molecular weight square roots

	He/CH_4	He/O_2	CH_4/O_2
Ratio of permeabilities	1.6	2.5	1.5
Ratio of molecular weight square roots	2.0	2.8	1.4

roots of the molecular weights (Table 3), as expected from gas diffusion under Knudsen regime. However, the slight deviations from a pure Knudsen regime which are observed in Table 3 suggest the contribution of other effects, such as gas/surface chemical interactions. Thus, some fast surface diffusion could favour the transport of methane and oxygen through the membrane by comparison with helium. Concerning the comparison between methane and oxygen, mechanistic studies carried out on lanthana catalysts [10] have clearly demonstrated that oxygen was strongly interacting with the catalytic surface through dissociative adsorption, while methane was only weakly interacting, without any surface accumulation. This could explain a slower diffusion of oxygen in comparison with methane.

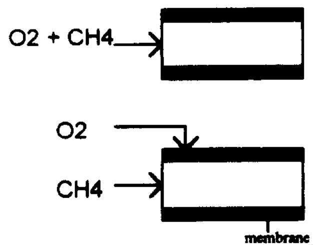
Effect of reactant feeding mode in the membrane reactor

The effect of reactant feeding mode is illustrated in Table 2. Whatever the membrane used (supported on 200 nm α- or on 5 nm γ-alumina tube), an increase of about 10% in the C_{2+} yield was observed when changing from co-feed to separated feed. Slight differences in gas concentration were also noted between the two reactor compartments, indicating concentration profiles through the pores. As schematically depicted in Fig. 4, under co-feed configuration, low CH_4/O_2 ratios were observed in the internal compartment, where the catalyst is located. In contrast, for a separated feed configuration, the highest methane concentration corresponded to the lowest oxygen concentration, leading to a high CH_4/O_2 ratio in the catalytic zone.

4. Discussion

Several factors were shown to play a significant role in the catalytic performances of LaOCl membrane reactors for the OCM reaction:

(i) Concerning the chemical composition of the active phase, it was observed that the use of γ-alumina as support top layer led to high surface concentrations of alumina after LaOCl deposition,



feeding mode	$(CH_4/O_2)_{int}$	$(CH_4/O_2)_{ext}$
cofeed	32.5	37.9
separated feed	**37.0**	33.3

Fig. 4. CH_4/O_2 ratios at reactor internal and external compartments according to the feeding mode.

as revealed by surface analysis. Alumina being a non selective material in OCM due to a too weak basicity [11], the poor catalytic performances observed with this membrane could therefore come from this surface enrichment. A first requirement for performing OCM membrane is therefore to avoid any solid/solid reaction between the selective LaOCl and the non selective Al_2O_3 phase of the support. The deposition (single or multiple) of LaOCl on the inert α-alumina support fulfils this requirement.

(ii) The structural properties of a membrane are well represented by its gas permeability which results from the average porosity but also from the small fraction of large pores and from membrane defects [12]. For the present case, it was observed, to our surprise, that the best catalytic results corresponded to the most permeable materials, for a given surface composition and whatever be the mode of reactant feeding (co-feed or separated feed). Note that the reverse effect would have been expected if proper separation effects had been achieved. Accordingly, if transport effects are unlikely, chemical effects have to be considered. The OCM reaction has been shown by several authors to be structure sensitive [10,13–15]. For similar materials such as lanthana catalysts, Lacombe et al. [10] have provided strong evidences that specific sites were responsible for the total oxidation, being low coordination atoms located on surface defects and crystallites edges. It was also shown that the specific concentration of such sites tended to decrease on sintered catalysts presenting lower surface area. For the present case of membrane reactors, the good performances of the most permeable membranes could therefore simply derive from a lower surface density of toxic sites leading to the total oxidation. Thus, a second requirement for efficient OCM catalytic membranes is to present a low surface area and a high permeability, at least in the present macroporous domain where transport effects are not dominant. As a matter of fact, recent results obtained from mathematical modelling of the present system [16] show that marked separation effects are achievable in the microporous domain; improvement in the membrane preparation and stability should therefore be considered as a prerequisite for actual gain in catalytic performances.

(iii) By examining the mode of reactant feeding in the membrane reactor, a slight but reproducible improvement of the C_{2+} yield (around 10%) was obtained by separating oxygen and methane at the membrane reactor inlet, rather than co-feeding the reactant gases. Besides, differences in concentration between the two compartments of the reactor have been observed. Owing to the mean pore size of the membranes and as confirmed by permeability measurements, the gas transport was shown to occur mostly by Knudsen diffusion. The observed concentration profiles could therefore derive from a slower diffusion of oxygen in comparison with methane, possibly also due to a stronger interaction of oxygen with the LaOCl surface. Accordingly, the best performances observed under separated feeding configuration could straightforwardly derive from higher CH_4/O_2 ratios in the catalytic zone. As a matter of fact, high CH_4/O_2 ratios are always favourable to C_2 production in the OCM reaction, as revealed by lower partial orders versus oxygen pressure for the selective route by comparison with the unselective one [17]. A third requirement for optimized performances is therefore to run the membrane reactor under separated feeding mode, in order to get advantage of concentration profiles.

5. Conclusions

The objective of this work was to explore the potential of a porous catalytic membrane reactor in the OCM reaction. The sol–gel method has provided LaOCl membranes which presented promising textural characteristics. Actually, the severe operating conditions applying for this reaction (from 650 to 800°C in the presence of water vapour) caused textural instability which led to a partial sintering of the LaOCl phase and restricted any transport effects to the macroporous domain. However, despite moderate Knudsen separation effects between methane and oxygen, beneficial effects of the membrane reactor have been observed, subject to surface composition, structural and feeding configuration requirements.

Acknowledgements

H.B. thanks CNPq for granting her scholarship. Part of this work was supported by EEC Joule I programme.

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