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Catalytic membrane reactor for oxidative coupling of methane. Part 1: preparation and characterisation of LaOCl membranes

P. Chanaud [a], A. Julbe [a,*], A. Larbot [a], C. Guizard [a], L. Cot [a], H. Borges [b], A. Giroir Fendler [b], C. Mirodatos [b]

[a] *Laboratoire des Matériaux et des Procédés Membranaires (CNRS UMR 9987), Ecole Nationale Supérieure de Chimie, 8 Rue de L'Ecole Normale, 34053 Montpellier Cedex 1, France*

[b] *Institut de Recherche sur la Catalyse (CNRS), 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*

Abstract

The sol–gel process was investigated in order to prepare LaOCl inorganic membranes on commercial alumina tubular supports which were catalytically active for the oxidative coupling of methane. The preparation of LaOCl meso and microporous membranes is described on the basis of the fundamental phenomena occurring during the sol preparation and thermal treatment. Membranes were synthesised from $LaCl_3$ precursor in aqueous media. Important parameters, mastering the sol formation and consequently the final material textural characteristics, were the molar ratio [acetate]/La], $[NH_3]/[La]$ and the total concentration of lanthanum in the sol. Without any acetate addition, turbid sols were obtained leading at 800°C to mesoporous membranes. The effect of acetate ions is shown to be of prime importance in order to limit the polycondensation reactions in the sol and to prepare microporous materials. Under these conditions, quite dense membranes were obtained at 200°C due to lanthanum acetate polymerisation. The formation of carbonates and their decomposition at 600°C explain the maximum microporosity observed at this temperature. When these membranes were treated at 800°C, the microporous volume decreased.

1. Introduction

The interest shown in lanthanide compounds for catalytic applications and especially for methane activation is widely recognized [1]. Of the lanthanide compounds lanthanum oxychloride is an interesting candidate [2,3] because it is much more stable in air than lanthanum oxide. Of the possible configurations of catalytic membrane reactors for the oxidative coupling of the methane reaction, an attractive approach is the use of a catalytically active membrane able to fulfil both the reaction and separation functions. Indeed the potentialities of this kind of reactor should allow an increase in the C_2 reaction yield currently limited by a parasitic oxidation reaction. The concept implies the preparation of a crack-free reactive LaOCl membrane with a porous texture adapted to the reaction conditions and able to have a separative effect between O_2 and the products of the reaction. Furthermore the membrane has to be stable (catalytic activity and texture) at the reaction temperature: 750°C. To prepare such a membrane, the flexibility of the sol–gel process has proven useful [4,5]. The results presented here are based on the very first promising one gathered in Ref. [5]. In this first part of the work, we will focus on a detailed description of the mechanisms involved during the sol–gel process and consecutive thermal treatments of precursors leading to

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[*] Corresponding author.

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the preparation of homogeneous LaOCl membranes with specific porous textures.

2. Experimental procedure

2.1. Sol preparation

The sol formation was carried out under stirring by rapidly adding a desired amount of dilute ammonia (1.00 M) to an aqueous solution containing lanthanum chloride (Fluka) and a defined volume of an ammonium acetate solution. Three parameters are pointed out which control the sol formation: the molar ratio $CH_3COO^-/La^{3+}=A$, the molar ratio $NH_3/La^{3+}=B$ and the total lanthanum concentration C in the sol.

2.2. Membrane preparation

In order to perform a thin film deposition from the previous sols, a binder/plasticizer must be used to control the rheology of sols, the thickness of the cast films and their behaviour during the drying and firing treatments. The copolymer Rhodoviol 25/140 (Rhône – Poulenc) which contains polyvinylic alcohol and polyvinylacetate was found to fulfil these functions. Crack-free membranes were obtained with a 2.4 wt.-% concentration of Rhodoviol in the sols. Depending on their composition, sols were slip-cast onto different porous alumina tubular multilayered supports (supplied by SCT-US Filter): an α-alumina support which presents a 200-nm pore diameter inner layer and a γ-alumina support which corresponds to the previous one coated with a γ-alumina layer. Sols corresponding to $A=0$ were deposited directly on the α-alumina supports. The resulting gelled cast films were then dried at 110°C under N_2 and heat treated at 800°C for 5 hours (heating rate 2°C/min); crack-free LaOCl mesoporous membranes result from this procedure. Sols corresponding to $A\neq0$ were either cast on the previous LaOCl layer or on the γ-alumina support. This last support was pre-treated at 800°C before use in order to stabilise the pore diameters between 5 and 6 nm. After gel drying and firing a second type of LaOCl membrane, with a fine texture, was obtained.

3. Results and discussion

3.1. From solution to sol

3.1.1. Behaviour of lanthanum salts in aqueous media ($A=0$)

The first step of this sol–gel process is the solvation of lanthanum ions. From the literature, the hydration number of La^{3+} is 9 in aqueous concentrated solutions [6] and 12 in infinite dilute solutions [7]. Formation of the sol is then carried out by the addition of the ammonium solution to the lanthanum chloride solution and can be explained on the basis of hydrolysis and condensation reactions. The hydrolysis of lanthanum ions occurs simply by successive departure of protons from the hydrated ions. When the pH increases additional protons are lost from the coordinated water, resulting in the formation of successive basic ions. The corresponding reactions can be written as follows, by omitting the coordinated water:

$$La^{3+}+H_2O \rightleftharpoons [La(OH)]^{2+}+H^+ \quad (\mathrm{Log}K_1=-8.5) \tag{1}$$

$$[La(OH)]^{2+}+H_2O \rightleftharpoons [La(OH)_2]^{+}+H^+ \quad (\mathrm{Log}K_2=-8.7) \tag{2}$$

$$[La(OH)_2]^{+}+H_2O \rightleftharpoons [La(OH)_3]+H^+ \quad (\mathrm{Log}K_3=-8.7) \tag{3}$$

$$[La(OH)_3]+H_2O \rightleftharpoons [La(OH)_4]^{-}+H^+ \quad (\mathrm{Log}K_4=-11.0) \tag{4}$$

The equilibrium constants K_i [8] allow the calculation of distribution diagrams of lanthanum

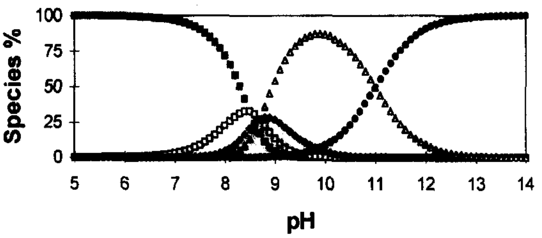

Fig. 1. Distribution of lanthanum species as a function of pH ($A = 0$), (■) La^{3+}, (□) $[La(OH)]^{2+}$, (◆) $[La(OH)_2]^+$, (△) $[La(OH)_3]$, (○) $[La(OH)_4]^-$.

species (in %) as a function of pH (Fig. 1) by mean of the following equation:

$$[La(OH)_n^{(3-n)+}] = 100.10^{(n \cdot pH + \Sigma_{i=1}^{i=n} \log_{10} K_i)} / \left(1 + \sum_{n=1}^{n=4} 10^{(n \cdot pH + \Sigma_{i=1}^{i=n} \log_{10} K_i)}\right) \quad (5)$$

From Fig. 1, one can say that hydrolysis begins when pH is greater than 6 and two basic species, $[La(OH)]^{2+}$ and $[La(OH)_2]^+$, predominate in a short pH range around 8.5. Hydroxide precipitates completely around pH = 10 but must be slightly soluble in strong basic medium because of the existence of $[La(OH)_4]^-$. This kind of graph (Fig. 1) is mainly valid in dilute solutions. In more concentrated solutions a condensation phenomenon, fed by the basic species, takes place and leads to polynuclear species. According to our experiments, the sol formation occurs through this condensation process in the pH range (7–8.5), *pH range of the two basic species as predicted in Fig. 1*. This kind of turbid sol has been used to synthesise mesoporous membranes on α-alumina supports.

3.1.2. Effect of acetate ions ($A \neq 0$)

In the presence of acetate ions, four kinds of lanthanum acetate complexes can be found in the literature [9]. The equilibrium constants for the formation of $[La(Ac)_n]^{(3-n)+}$ are respectively $\text{Log}\beta_n = 2.0, 3.3, 3.0$ and 2.9 for $n = 1, 2, 3$ and 4. By considering these complexes and the four previous hydroxide complexes we can obtain the following function where $pAc = -\log_{10}[CH_3COO^-]_{free}$ and $[CH_3COO^-]_{free}$ is the free acetate ion concentration:

$$[La^{3+}] = 100/\left(1 + \sum_{n=1}^{n=4} 10^{(n \cdot pH \Sigma_{i=1}^{i=n} \log_{10} K_i)} + \sum_{m=1}^{m=4} 10^{\log_{10}\beta_m - m \cdot pAc)}\right) \quad (6)$$

This function represents the variation in percentage of $[La^{3+}]$ with pH and pAc (Fig. 2). The La^{3+} concentration decreases from 100% to 0% when pH increases from 6 to 9 (basic ions formation) or when pAc decreases from 4 to 0 (acetate ions formation). When increasing pH, basic ions are formed which create the sol, and by decreasing pAc, acetate ions form complexes with lanthanum.

In the sol formation range, CH_3COO^- and OH^- are *competitive ligands* toward lanthanum. Acetate ions limit the polycondensation reactions in the sol by complexing lanthanum and lead to sols with low turbidity and to coatings with finer texture. The existence of lanthanum acetate complexes has been confirmed by infrared analysis and ^{13}C-NMR. From the results, we can consider a bidentate chelate coordination mode of acetate ions with lanthanum in the sol [10].

3.2. Sol–gel transition

During the drying step (110°C under N_2 atmosphere) translucent gels can be obtained from sols with $A = 1$. FT-IR analysis revealed a split of the $-CO_2-$-stretching vibrations corresponding to a polymeric coordination mode of acetate. Polymerically coordinated acetates involve both La–

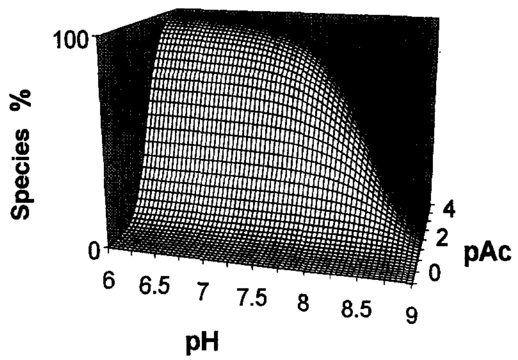

Fig. 2. Distribution of La^{3+} species as a function of pH and pAc.

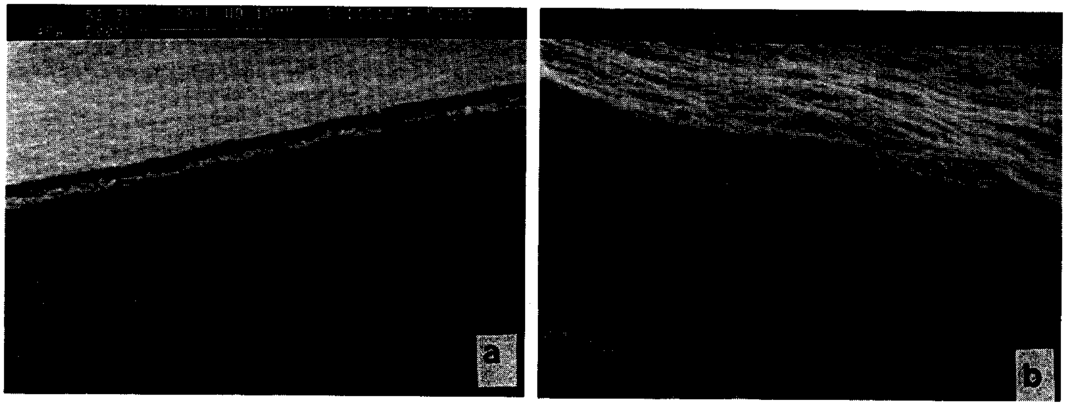

Fig. 3. (a) A LaOCl microporous membrane on a γ-alumina support. (b) A double LaOCl membrane on a α-alumina porous support.

O and La–O–La coordinations which induce a split of the two stretching vibrations as in anhydrous $LaAc_3$ [11]. This polymerization phenomenon allows the formation of quite dense coatings at low temperature.

3.3. *From gel to membrane*

Thermal analysis (TDA, TGA), X-ray diffraction and FT-IR spectroscopy enabled the different phenomena occurring during the heat treatment to be followed. The thermal behaviour of the different gels was compared to several recorded reference ($LaCl_3 \cdot 7H_20$, $La(Ac)_3 \cdot 1.5H_2O$, $La(OH)_3 \cdot xH_2O$, NH_4Cl and CH_3COONH_4) and to literature data [12–15]. The gel dehydration can occur up to 200°C. Free ammonium acetate presents a liquefaction point at 114°C and seems to be completely decomposed around 175°C. The binder decomposition occurs at 160–200°C and generates carbonate species. The phenomena linked to ammonium chloride departure are quite seldom (283°C and 325°C) and allowed us to estimate the quantity of 'free' chlorides in the gel. Above 350°C, hydroxides and acetates are decomposed respectively in oxides and carbonates. The LaOCl crystallisation (ASTM 34-1494) occurs around 450°C (430°C in the case of $LaCl_3 \cdot 7H_20$) while the chloride excess is liberated. The carbonate decomposition can be observed up to 600°C. In the case of pure lanthanum acetate hydrate, a crystallisation of a $La_2O_2CO_3$ phase (ASTM 23-322) is observed at 437°C and the carbonates liberate the lanthanum oxide surface at 808°C.

The model described earlier does not take into account the effect of chloride ions known as potential ligands toward lanthanum and its basic species [16–18]. Gel thermal analysis allowed to distinguish between two kinds of chloride. 'Free' chlorides are liberated as NH_4Cl in the first step of the heat treatment and 'bonded' ones are liberated at higher temperatures, above 400°C. For $A = 1$ xerogel we found 0.9 mole of NH_4Cl liberated per mole of lanthanum, i.e. a ratio of 2.1 'bonded' chlorides per lanthanum. If we assume that all the lanthanum species involved in the model carry chloride ions in order to be electronically neutral, we found a 1.8 ratio of 'bonded' chloride per lanthanum. This kind of model is useful to study the sol formation and confirms that hydroxide, acetate and also chloride ions are competitive ligands toward lanthanum in the pH range of the sol formation.

3.3.1. *Microporous LaOCl membrane on γ-alumina support*

By controlling the drying step and the firing treatment, homogeneous LaOCl membranes were obtained at 500°C on γ-alumina supports as shown in Fig. 3a. The thickness of this type of LaOCl membrane is around 100 nm. This membrane made from $A = 1$ sol presents only a microporous texture, i.e. pore diameters less that 2 nm. If this membrane is heat treated at a higher temperature a morphological modification starts just above

600°C, due to the high reactivity of the γ-alumina phase. Moreover, a $LaAlO_3$ phase (ASTM 34-22) can be pointed out at 1000°C by X-ray diffraction and explains the chemical reactivity between the γ-Al_2O_3 and LaOCl phases. This reactivity might be responsible for the membrane textural instability at high temperatures.

3.3.2. Mesoporous and microporous LaOCl membranes on α-alumina supports

In order to avoid the problems encountered when depositing LaOCl on a γ-alumina support, an α-alumina support was used. First a LaOCl mesoporous membrane was synthesised on this support before deposition of the microporous layer. Fig. 3b gives an example of such a double membrane.

The mesoporous LaOCl membrane was obtained from a turbid sol without acetate ion ($A=0$), in which the polycondensation levels were not limited. The effect of the sintering cycle on the membrane pore sizes was studied by N_2 adsorption–desorption at 77°K using the BJH model. This mesoporous membrane has a mean pore diameter around 20 nm at 500°C which increases up to 40 nm at 800°C. The corresponding pore volumes estimated on unsupported companion samples are 0.15 cm^3/g at 500°C and 0.05 cm^3/g at 800°C. As shown in Fig. 3b the membrane thickness is typically 1.5 μm.

Nitrogen adsorption studies revealed that the second membrane (made from $A=1$ sol) deposited on the mesoporous LaOCl one was almost dense at 200°C. This is due to the low polycondensation level of species in the sol and to acetate polymerisation during the drying step. At 400°C the LaOCl membrane is essentially microporous. Above 400°C, the membrane pore volume increases drastically due to the transformation of acetates into carbonates which open the pore structure. The microporous volume is at a maximum at 600°C (end of carbonate decomposition) and the hydraulic pore radius distribution is centered on 5.5 Å. Above 600°C the microporous volume decreases due to membrane sintering and a mesoporous texture appears. Quantitative data about membrane pore volume are not mentioned in this case because it has been impossible to prepare unsupported samples thin enough to avoid the crystallisation of ammonium chloride. Consequently measurements have only been performed on supported membranes.

In order to repair possible defects and decrease the microporous volume and pore size of the membrane, a third kind of LaOCl membrane was prepared. For this purpose a very fluid sol ($A=1$, $B=0$, no PVA) was infiltrated in the double LaOCl membrane (microporous on mesoporous) previously described. The corresponding thermally treated membrane is called an 'infiltrated membrane'.

3.3.3. Cations doped LaOCl materials

Because the sol–gel process starts from a homogeneous solution, homogeneous materials with improved performances can be obtained. Several cations (Li^+, Sr^{2+}, Ca^{2+} and Ba^{2+}) were used in order to increase the catalytic activity of the LaOCl membranes. For a molar ratio cation/LaOCl up to 4%, the textural properties of mesoporous and/or microporous LaOCl membranes are not greatly modified while their catalytic properties are changed [19]. Moreover, this technique of cation incorporation is accurate. Chemical analysis has revealed that the cation/lanthanum ratio is kept unchanged during the process. It remains the same from the sol to the final material.

4. Conclusions

The steps of LaOCl membrane synthesis have been studied in order to better understand the relationship between the properties of the sol and the textural characteristics of the final material. The sol formation can be explained by mean of the existence of several lanthanum species in solution. By monitoring the experimental parameters, sols are obtained with different properties allowing the formation of mesoporous or microporous supported LaOCl membranes after an adapted thermal treatment (above 600°C, microporous membranes tend progressively to become mesoporous). The catalytic performances of these membranes, for the oxidative coupling of methane, are developed in Part II of this work [20].

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