Mixed conducting materials for partial oxidation of hydrocarbons

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Thermodynamic calculations with additional conditions for the conservation of carbon and hydrogen were used to predict the gas composition obtained by partial oxidation of methane as a function of oxygen partial pressure and temperature; this was used to assess the stability and oxygen permeability requirements of mixed conducting membrane materials proposed for this purpose. A re-examination of known mixed conductors shows that most materials with highest permeability still fail to fulfill the requirements of stability under reducing conditions. Other materials possess sufficient stability but their oxygen permeability is insufficient. Different approaches were thus used to attempt to overcome those limitations, including changes in composition in the A and B site positions of ABO3 perovskites, and tests of materials with different structure types. Promising results were obtained mainly for some materials with perovskite or related KNiF3-type structures. Limited stability of the most promising materials shows that one should rely mainly on kinetic limitations in the permeate side to protect the mixed conductor from severe reducing conditions.

1. INTRODUCTION

The main methods proposed to convert hydrocarbons to a mixture of hydrogen and carbon monoxide (syngas), have been steam reforming and partial oxidation by means of mesoporous membranes, mixed conductors with high electrochemical oxygen permeability, or ionic conductors working under short circuited conditions or assisted by an external applied field. The mixed conducting membranes possess interesting advantages relative to endothermic steam reforming, or electrically assisted partial oxidation. In addition to high oxygen permeability the mixed conductor must meet other requirements of catalytic activity, stability under wide ranges of chemical potential and in the presence of CO2 steam, SO2 etc., and low thermal and chemical expansion under larger gradients of oxygen chemical potential.

A relatively wide range of mixed conductors has been studied for these membrane reactors [1-17], including single phase and composite materials consisting of a metallic conductor and a good ionic conductor. This concept is widely discarded because these composite materials are either based on noble metals of prohibitive cost, or fail to meet the required stability (e.g.Ag/Bi(FeO3)) or oxidation resistance conditions. The emphasis has thus been on mixed conducting ceramics, mainly single phase [1-16], and occasionally 2-phase ceramic/ceramic composites [17]. Perovskite materials SrLaCoO3 [3-5] and SrLaFeO3 possess the highest permeability, limited stability, and excessive thermal and chemical expansion. Other mixed conductors are based on perovskite materials with higher stability (e.g. gallates [6,10] and titanates [7-9]) with mixed valent additives. Some LaNiO2-based materials combine good permeability and relatively low thermal expansion [12-16].

2. SIMULATION OF LIMITING WORKING CONDITIONS IN MEMBRANE REACTORS

The chemical stability requirements of mixed conducting materials can be estimated by predicting the equilibrium gas phase composition expected under typical conditions of methane partial oxidation, in which case:

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 \]

\[ \text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2 \]

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O} \]

Methane cracking, CH4→C+2H2, is mainly catalysed by metallic surfaces, and one thus assumes that this is entirely suppressed on all ceramic membranes.

Limiting conditions were estimated by combining the equilibrium constants of reactions 1, 2, 3, with additional relations for the conservation of relevant elements (C and H). One thus obtained the following dependence of the fraction of methane converted \( \alpha \), and gas composition on the oxygen partial pressure \( P_{\text{O}_2} \):

\[ \alpha(\varepsilon+\mathbf{a})^2/[1+2(\varepsilon+\mathbf{a})] = K_0(p_{\text{O}_2})^2[1+K_1(p_{\text{O}_2})^2][1+K_2(p_{\text{O}_2})^2] \]
been used to prepare powders of a variety of materials with perovskite, materials with specific permeability of the order of $10^{-10}$ to $10^{-9}$ mol.cm$^{-1}$.s$^{-1}$ or even lower. This must be combined with surface modification or application of suitable catalysts when the membrane thickness is smaller than the critical value, i.e. L<k/D.

3. EXPERIMENTAL METHODS

Standard powder reactions and the glycine-nitrate method have been used to prepare powders of a variety of materials with perovskite, K$_2$NiF$_4$ and other structure types, as described in detail elsewhere.

$$[H_2] = \left[\frac{[w_{-2}+2\alpha]}{(1+z+w_{-2}+2\alpha)}\right] / \left[1 + \left[K_2(pO_2)^{1/2}\right]\right]$$  \hspace{1cm} (5)

$$[CO] = \left[\frac{\alpha/(1+z+w_{-2}+2\alpha)}{1 + \left[K_2(pO_2)^{1/2}\right]}\right]$$  \hspace{1cm} (6)

$$[CO_2] = \left[\frac{\alpha/(1+z+w_{-2}+2\alpha)}{1 + \left[K_2(pO_2)^{1/2}\right]}\right]$$  \hspace{1cm} (7)

$$[H_2O] = \left[\frac{(w_{-2}+2\alpha)}{(1+z+w_{-2}+2\alpha)}\right] / \left[1 + \left[K_2(pO_2)^{1/2}\right]\right].$$  \hspace{1cm} (8)

A balance of oxygen is also needed to establish the relevant relations between the permeability of the membrane material, and working conditions. This can be illustrated on assuming an ideal continuous stirred reactor with supply of an oxygen flux density j through mixed conducting walls of area A. Under steady state regime:

$$2A_j = C_o[CO]_i + 2[CO]_o + [H_2O] - Q_v[H_2O].$$  \hspace{1cm} (9)

where $C_o$ is the gas concentration and $Q_v$ is the volume flow rate at the inlet. The flux density supplied by the mixed conducting wall is a function of the gradient of oxygen chemical potential. If process is controlled by mixed conduction [3,7]:

$$j = \frac{\sigma_{amb}RT.4F}{L} \ln\left[pO_2/pO_2^{amb}\right]$$.  \hspace{1cm} (10)

where $\sigma_{amb}$ is the specific oxygen permeability, $\sigma_{amb}$ is the ambipolar conductivity of the mixed conducting material, R is the ideal gas constant, T is absolute temperature, F is the Faraday constant, $[pO_2]$ and $[pO_2]^{amb}$ are the values of oxygen partial pressure in the feed and permeate sides, and L is the membrane thickness. In this case, $\sigma_{amb}$ is independent of thickness. On the contrary, surface exchange control yields values of j independent of the membrane thickness, whereas $\sigma_{amb}$ increases with thickness. Changes both in j and $\sigma_{amb}$ with membrane thickness indicate mixed control, which occurs when the thickness of the membrane is close to a critical value $L_c$, k being a surface exchange coefficient and D the diffusion coefficient [4].

A numerical method was used to solve Eqs. 4 through 10, and a typical example is shown in Fig.1, to illustrate the severe stability and permeability requirements to be met by mixed conducting membrane materials. The fractions of hydrogen and CO typically reach maxima at $pO_2$ close to $10^{-10}$ atm and then decrease for more oxidising conditions, yielding CO$_2$ and H$_2$O. These stability requirements are excessive for mixed conducting materials based on LaCo$_{3}$ [3-5]. Other materials (e.g. (La,Sr)(MnO$_3$) are stable but possess insufficient permeability.

The permeability requirements can be accounted for by a dimensionless parameter $J^* = \sigma_{amb}RT.4F \ln\left[pO_2/pO_2^{amb}\right] L^{-1}$ which combines the effects of specific permeability, mass flow rate at the inlet, and geometric parameters of the mixed conducting wall, i.e. area and thickness. At 1173 K the highest combined fractions of H$_2$ and CO are attained for $J^* = 0.009$. Under these conditions, a reactor with membrane thickness of about 1 mm should be able to process about 6.4 kg of methane per hour and per square meter if the specific oxygen permeability reaches 10$^{-8}$ mol.cm$^{-1}$.s$^{-1}$; this is comparable to the highest permeability for the most promising materials. Unfortunately, this range was observed only for materials with relatively poor stability, and the results obtained for more stable materials are lower by 1 to 2 orders of magnitude. A change from self-supported thick membranes to thinner membranes with a porous support is thus probably needed to be able to use materials with specific permeability of the order of 10$^{-9}$ to 10$^{-8}$ mol.cm$^{-1}$.s$^{-1}$ or even lower. This must be combined with surface modification or application of suitable catalysts when the membrane thickness is smaller than the critical value, i.e. L<k/D.

![Fig1 Predictions of fraction of methane converted, gas composition and permeability requirements versus oxygen partial pressure, assuming equilibrium conditions.](image)

![Fig2 Stability limits of representative mixed conducting materials at 1173K, under reducing conditions predicted with data reported in references [19] and [20]. The dashed line represents conditions required to attain the highest fractions of CO and H$_2$ by partial oxidation of methane.](image)

4. PERMEABILITY AND CHEMICAL STABILITY REQUIREMENTS

The most promising mixed conducting materials possess perovskite or K$_2$NiF$_4$ structure types, and contain one or a combination of transition elements Fe, Co, Ni or Cu. Sr(Fe,Co)O$_3$ materials possess the highest specific permeability (about 10$^{-7}$ mol.cm$^{-1}$.s$^{-1}$) but are unstable [21], due to a perovskite to brownmillerite phase change. The stability of LaCoO$_3$ is also insufficient, as reported in [19,20], and shown in Fig.2. The stability limits of LaFeO$_3$ and LaMnO$_3$ [19] are suitable (Fig.2). Suitable compositions changes enhance the permeability, especially for (La,Sr)FeO$_{x+y}$ (from about 10$^{-10}$ mol.cm$^{-1}$.s$^{-1}$ to 10$^{-8}$ mol.}
5. ROLE OF SURFACE EXCHANGE KINETICS

One may also seek changes in design to obtain less harmful conditions for the mixed conducting materials. For example, a porous inert layer may provide both the required mechanical strength for relatively thin membranes, and also a diffusion barrier, thus rendering the stability requirements much less demanding. Kinetics may also contribute to bridge the gap between the reducing conditions inside the membrane reactor and the stability range of mixed conductors. The required changes might be related to surface processes at the permeate side of the mixed conducting membrane, and/or deviations from equilibrium in the gas phase, when partial oxidation (Eq.1) becomes somewhat sluggish. Significantly higher oxygen chemical potential is then needed to attain high values of methane conversion. Unfortunately, this is likely to yield further oxidation of CO to CO₂ and/or H₂ to H₂O.

Results obtained for La₃NiO₅-based materials indicate that their permeability is controlled by surface exchange at temperatures below about 1073 K, with mixed control at higher temperatures. Mixed control was also often found for perovskite materials. In these cases, one may not attain the required results by lowering the membrane thickness below its critical value, and should instead focus on surface modifications, either by adding catalysts, or depositing a porous layer of the same material with high specific surface area (Fig.5).

Surface exchange limitations are not restricted to the feed side of the membrane, and have been reported also for the permeate side. In this case, surface exchange limitations in the permeate side might even play a useful role, by providing kinetic protection from very reducing atmospheres. This possibility was demonstrated by testing La₃Ni₁ₓCoₓO₅₋ₓ under air/10%H₂-90%N₂ for 250 hours, at 973 K and La₃Sr₁₋ₓCaₓO₅₋ₓ under air/50%CH₄-50%He gradient, at 1123-1223 K, for 200 hours (Fig.6). The kinetic stabilization was confirmed by

\[ 2 \text{CuO} + \text{CO}_2 \rightarrow 2 \text{Cu} + \text{CO}_3^{2-} \]
post-mortem SEM analysis. Though these preliminary tests confirmed the potential applicability of mixed conducting membranes, suitable catalysts may be needed to increase the conversion of methane and the selectivity of CO and H₂.

6. CONCLUSIONS

The characteristics of known mixed conductors are still somewhat insufficient to be used as membranes for partial oxidation of hydrocarbons, mainly due to either poor stability or insufficient permeability. However, the present understanding of the effects of composition on transport properties and stability of candidate materials still allows one to expect further improvements. In addition, one may select operation conditions or optimised membrane designs providing kinetic stabilisation, thus bridging the gap between the stability of mixed conducting membrane materials and the actual conditions inside the membrane reactor. Suitable models for the reactor operation conditions must be revised to take into account that kinetic limitations cause significant shifts from predicted equilibrium conditions.

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