ELSEVIER

Catalysis Today 56 (2000) 247–252

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Vanadium-based catalytic membrane reactors for the oxidative dehydrogenation of propane

M.J. Alfonso, M. Menéndez, J. Santamaría *

Department of Chemical and Environmental Engineering, Faculty of Science, University of Zaragoza, 50009 Zaragoza, Spain

Abstract

Several catalytic membranes have been studied, with different loadings and radial distribution of the catalytic material. Two types of catalytic membranes have been prepared on top of alumina supports: (a) V/MgO membranes, where MgO was deposited in the support pores before impregnation with V, and (b) V/Al_2O_3 membranes, where the alumina supports were impregnated with a boehmite sol before V deposition. In both cases the introduction of V was carried only from the internal side of the porous tube, and using short impregnation times, in order to obtain a radial distribution of active material.

The membranes prepared have been tested under reaction conditions, giving yields to propene of up to 15%. It was found that the best V/MgO membranes are more selective but less active than the best V/Al_2O_3 membranes. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic membrane reactors; Vanadium supported catalysts; Oxidative dehydrogenation

1. Introduction

The use of membranes with catalytic activity is perhaps the most direct way to integrate a membrane in a catalytic reactor. As opposed to inert membrane reactors (IMRs), where the membrane does not participate in the reaction directly, but it is used to add or remove certain species from the reactor, in catalytic membrane reactors (CMRs) the reaction takes place directly on the membrane. This requires that the membrane material has intrinsic catalytic activity or that it is modified by the addition of active components. Several methods have been described for the preparation of catalytic membranes (e.g. [1–5]), including in situ reaction, chemical vapour deposition (CVD), sol–gel techniques, impregnation, and ion-exchange.

Several authors [7–10] have studied the use of catalytic membranes as a way to avoid the mixing of reactants, when reactants are fed to different sides of the membrane. This operation method is possible for fast reactions, that can easily become mass-transfer controlled. On the other hand, the possibility of using a CMR to improve the yield to valuable intermediate products was studied theoretically by several authors [11,12] using the following reaction scheme:

$$A + \nu B \rightarrow \nu_{R1} R \quad \text{(desired)} \quad r_1 = k_1 P_A^{n_1} P_B^{n_2}$$

$$A + \nu_{R2} R \rightarrow \nu_P P \quad \text{(undesired)} \quad r_2 = k_2 P_A^{m_1} P_B^{m_2}$$

Harold et al. [11,12] showed that, if the apparent reaction order with respect to A for the desired reaction is smaller than for the reaction where P is produced ($n_1 < m_1$), then significant yield improvements could be obtained by using a CMR with a segregated feed. The above reaction scheme is representative of many selective oxidations, and thus the concept has a wide

---

* Corresponding author. Fax: +34-976-762142.
E-mail address: iqcatal@posta.unizar.es (J. Santamaría).

PII: S0920-5861(99)00282-5

applicability. To achieve this improvement component A (oxygen) must be supplied from the support side and reactant B from the active layer side; furthermore the thickness of the active layer must be small compared with the total thickness of the membrane. In this way the diffusion across the inactive support layer results in a lower partial pressure of component A in the active layer, increasing the selectivity to the desired product.

The concept of lowering the oxygen partial pressure in selective oxidations has been experimentally demonstrated for several reactions (e.g. [6,13]) using IMRs. In this case, oxygen was distributed through the inert membrane to a fixed bed of catalyst. However, only limited success has so far been experimentally achieved using CMRs. The present work tries to design the CMR as outlined above. Instead of following the usual approach, i.e. a thin catalytic layer onto the surface of a membrane with negligible support resistance, in this case two zones with similar porosity and permeability were created, with the active component deposited only in the inner zone. This approach has two potential advantages: first, the inactive zone provides the diffusional resistance needed for a decreased oxygen concentration; second, the thicker active zone is present, with enough active material to achieve reasonable conversions.

2. Experimental

2.1. Membrane preparation

The starting material was in all cases a tubular α-Al_2O_3 microfiltration membrane (SCT), with 10 μm pores. This material was modified as in the following sections.

2.1.1. Preparation of V/MgO membranes

First, MgO was deposited inside the pores of the support. To this end the tube was impregnated at room temperature with saturated solutions of $Mg(NO_3)_2$ in water. The membrane was dried at 110°C and then calcined at 650°C. This procedure was repeated until a weight increase around 10% was obtained. In order to impregnate vanadium the tube was first immersed in deionized water and then the inside was filled with a saturated solution of NH_4VO_3. Preliminary experiments were carried out with both V/MgO and V/Al_2O_3 membranes to determine the impregnation time necessary for the V front to reach half of the membrane thickness. After impregnation the tube was dried at 110°C and calcined at 600°C. This procedure was repeated until a V_2O_5 load around 10–20% (relative to the amount of magnesium oxide) was obtained, which correspond to a V_2O_5 concentration in the active phase close the optimum load [14–18]. Actual values of V concentration are shown in Table 1.

2.1.2. Preparation of V/Al_2O_3 membranes

A boehmite sol was filtered through the initial membrane. After drying and calcination at 650°C a γ-alumina deposits formed in the pores of the starting material. This procedure was repeated until no more weight gain was observed, which corresponded to approximately 9 wt.% of γ-alumina relative to the total membrane weight. Vanadium was then added by the same method as for V/MgO membranes, although the V load was smaller in order to achieve a concentration in the active zones of 3–5% by weight, the interval recommended in the literature. The actual values are given in Table 1.

2.2. Reaction system

The reaction system has been described elsewhere [6]. Propane was fed to the tube side and a premixed stream of He and O_2 permeated from the shell side. The exit gases were directed to an on-line gas chromatograph for analysis. Carbon mass balance closures for the experiments in this work were always better than 5%, and usually better than 3%.

2.3. Membrane characterization

Two methods were employed to assess the radial distribution of V. By reducing in H_2 atmosphere at 700°C, metallic vanadium was formed, that can be observed visually. As can be seen in Fig. 1, V was deposited preferentially in the inner side, extending to about half of the membrane thickness. The second method involved measurements of V profiles using EDX which was in good agreement with the above observations (Fig. 1b).

Table 1
Characteristics of membranes

Membrane[a]	Support[b]	Composition[c] (wt.%)			Permeation flow (cm^3/(min bar cm^2))
		MgO	V_2O_5	γ-Al_2O_3	
$5V/Al_2O_3$	UF membrane (4 nm)	No	2.5	9	$16.5+3.6P_m$
20V/MgO	UF membrane (20 nm)	10.5	10.3	No	$28.2+9.9P_m$
40V/MgO	UF membrane (20 nm)	9	22.3	No	$57+64.3P_m$

[a] The number before "V" indicates the nominal V content in the active layer, as V_2O_5; i.e. 20V/MgO would correspond to 20% of V_2O_5 in the catalytic layer where V is located.

[b] The pore size of the UF thin layer is given between parenthesis.

[c] The percentage of V_2O_5 is referred to the total material added to the original membrane: $V_2O_5+(MgO)+(\gamma\text{-}Al_2O_3)$, while those of MgO and γ-Al_2O_3 refer to the total membrane weight: (MgO + support) or (γ-Al_2O_3 + support).

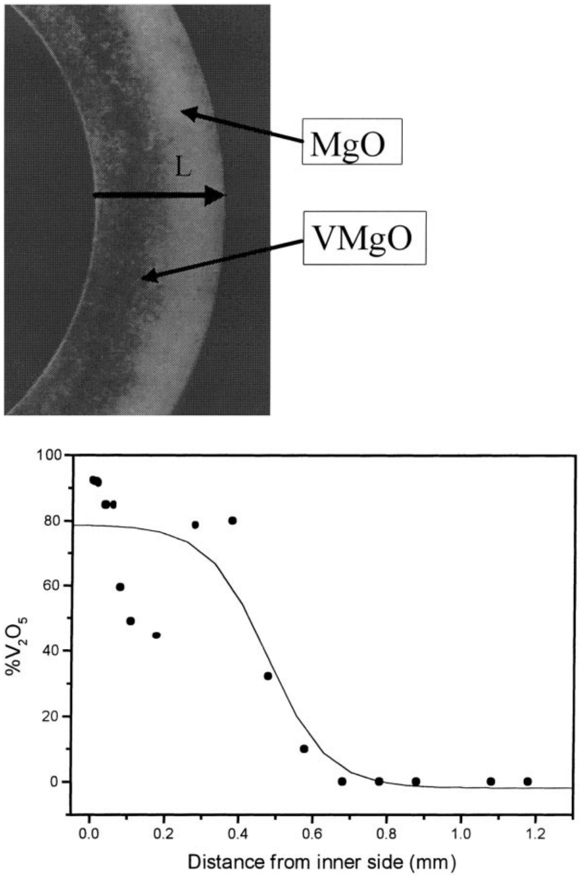

Fig. 1. (a) Optical photograph of a cut of the 40V/MgO membrane after reduction in hydrogen. The darker zone corresponds to a greater concentration of V, whereas in the clearer zone only MgO is filling the pores of the membrane. (b) V_2O_5 profile across the membrane radius, as obtained from SEM-EDX measurements. V_2O_5 % refers to the weight of V_2O_5 with respect to the weight of V_2O_5 plus MgO in the membrane.

The permeation data (N_2, ambient temperature) were fitted to

$$Q = A + BP_m$$

where P_m is the mean pressure, Q the permeation flux (cm^3/(cm^2 min bar)) and A and B measure the relative Knudsen and Laminar contributions to the total flow. The back-permeation, i.e. the diffusion of propane from the tube side to the shell side against the total pressure gradient, was also measured at the reaction temperature. In these experiments a mixture of He and N_2 (used instead of O_2 to avoid reaction) was fed to the tube side, and propane to the shell side.

3. Results and discussion

The permeation results in Table 1 indicate that higher permeation fluxes were obtained with the V/MgO membranes, were the relative contribution from the laminar term was also higher. Regarding back-permeation, in the experiments with the $5V/Al_2O_3$ membrane, with a larger Knudsen contribution, significant back-permeation was observed, e.g. with a He flow of 140 cm^3/min, and a propane flow of 20 cm^3/min, the steady state concentration of propane the shell side reached the 6% level. On the contrary with the 40V/MgO the propane concentration in the shell side was not measurable even with values of the He flow down to 75 cm^3/min. This results from the larger contribution of the laminar term with V/MgO membranes, where the convective flux towards the tube side prevents the back-permeation of propane.

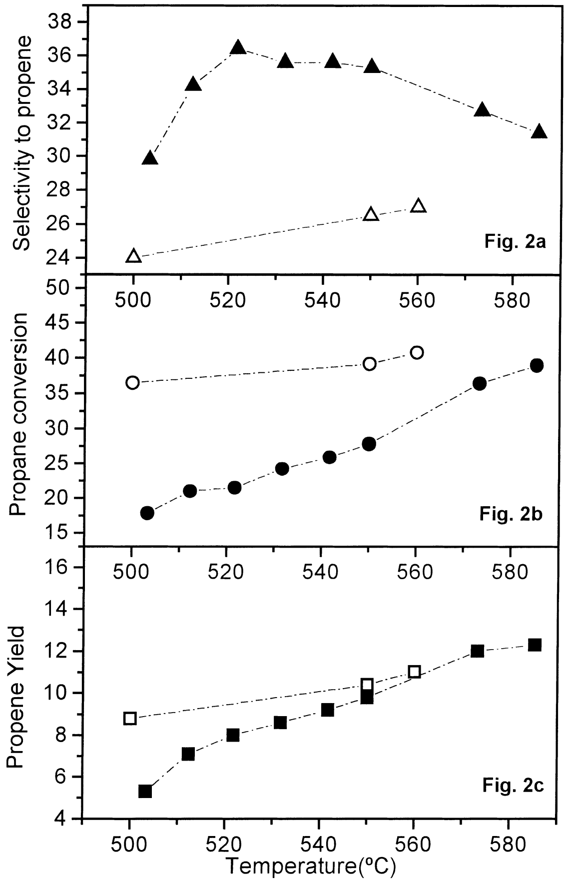

Fig. 2. (a) Selectivity to propene, (b) propane conversion and (c) yield to propene vs. reaction temperature, for 40V/MgO and 5V/Al_2O_3 membranes. For 40V/MgO (full symbols), the total flow rate was 4.15 N ml/(min cm^2) and the propane/oxygen/inert ratio was 8/8/84. For 5V/Al_2O_3 (open symbols) the total flow rate was 3 N ml/(min cm^2) and the propane/oxygen/inert ratio was 8/8/84.

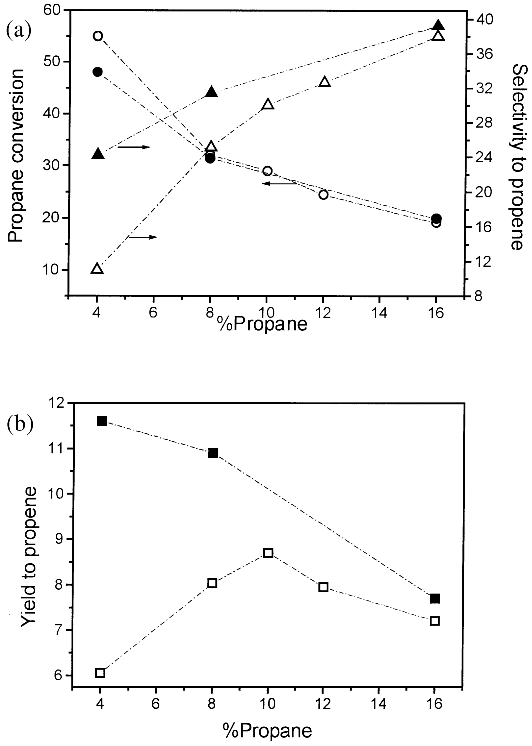

Fig. 3. (a) Propane conversion and selectivity to propene and (b) yield to propene vs. percentage of propane in the feed, for 40V/MgO (full symbols) and 5V/Al_2O_3 (open symbols) membranes. For 40V/MgO the temperature was 585°C and the total flow rate was 8.1 N ml/(min cm^2). For 5V/Al_2O_3 the temperature was 500°C and the total flow rate was 6 N ml/(min cm^2).

Fig. 2 shows the variation of propane conversion and of the selectivity and yield to propene obtained with the 5V/Al_2O_3 and 40V/MgO membranes as a function of temperature. It can be seen that the 5V/Al_2O_3 membrane is more active than the 40V/MgO, but clearly less selective in the 500–560°C temperature interval. It is interesting to observe that in this case the selectivity initially increases with temperature for both membranes. This is in agreement with kinetic experiments carried out in our laboratory (not shown), which indicated that the apparent activation energy for the selective reaction (oxidative dehydrogenation) is higher than for deep oxidation, and therefore an increase in temperature favours the selectivity. However, above a certain temperature the selectivity decreases, a consequence of the trade-off between conversion and selectivity, i.e. commonly observed in series–parallel reaction networks with an intermediate valuable product. Finally, Fig. 2c shows that in spite of its lower selectivity, the yield to propene obtained with the V/Al_2O_3 membrane was higher up to at least 560°C, due to the higher conversion attained on this membrane.

Fig. 3 compares the performance of 5V/Al_2O_3 and 40V/MgO membranes in experiments with a fixed oxygen input, and variable propane flow rate. In order to obtain comparable conversions, a higher temperature was employed for the lower activity V/MgO membranes. While the conversion obtained on both membranes is very similar over most of the range of propane concentrations investigated, the selectivity

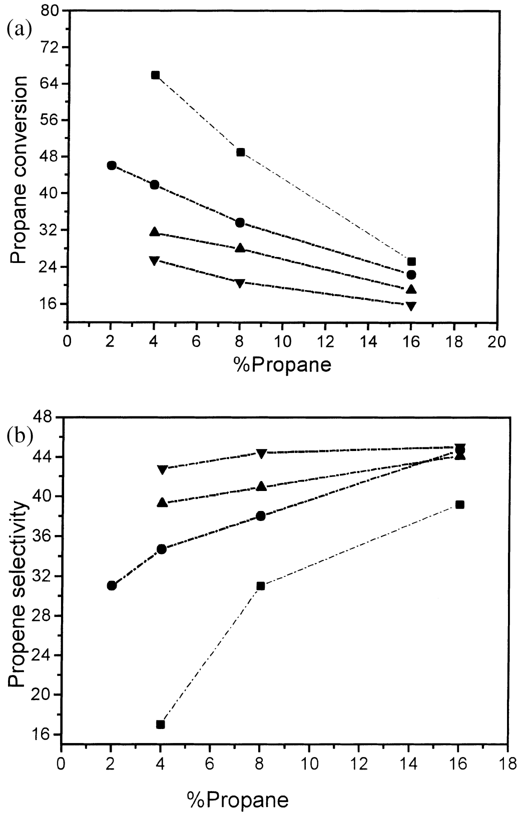

Fig. 4. (a) Propane conversion and (b) selectivity to propene vs. percentage of propane in the feed for several flow rates; 20V/MgO membrane ■; 1.25 N ml/(min cm^2), ●; 5 N ml/(min cm^2), ▲; 7.5 N ml/(min cm^2), ▼; 10 N ml/(min cm^2). Temperature = 585°C.

was always higher for the V/MgO membrane, which resulted in higher yields throughout the range of concentrations investigated. Furthermore, a maximum in the yield to propene was obtained with the 5V/Al_2O_3 membrane for a propane fraction around 10%. This maximum was not observed for 40V/MgO.

The effect of the V load was studied with the higher selectivity membrane (V/MgO), using lower concentrations of Vanadium. Fig. 4 shows the results obtained with the 20V/MgO membrane. The comparison of the conversion and selectivity with the data for 40V/MgO in Fig. 3 reveals that, while the conversion level for the same flow rate was similar, the selectivity is higher for the 20V/MgO membrane, in which yields exceeding 15% were obtained. This is in agreement with previous literature reports [14–18] stating that a V/MgO catalyst with a V_2O_5 content around 20–25% by weight provides the maximum selectivity.

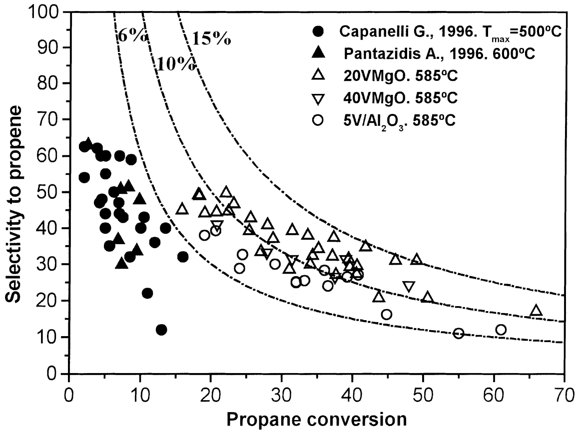

Fig. 5. Comparison of the results obtained in this work with previously published data.

Finally, a comparison between the results obtained in this work and those described in the previous literature on catalytic membranes for oxidative dehydrogenation of propane is shown in Fig. 5. It is clear that the yield to propene obtained is higher than in previously published works. In fact, the highest values of yield obtained in this work (ca. 15%) are close to the best yields reported with fixed bed reactors, in which the amount of catalyst is considerably higher. The main difference between the membranes used in this work and those of Capanelli and Carosini [19] and Pantazidis [20] in addition to the thickness of the active region, is the existence of a support layer with its pores partially plugged with MgO or Al_2O_3. This provides the diffusion resistance necessary to lower the partial pressure of oxygen in the active area.

4. Conclusions

Catalytic active membranes which are active and selective for the oxidative dehydrogenation of propane can be prepared by impregnation. The radial distribution of the active component can be controlled by using an impregnation procedure involving multiple short-time impregnation steps. The yields to propene obtained with membranes that combine the appropriate V loading in the active layer with a diffusion layer of sufficient resistance are significantly higher than those previously reported with catalytic membrane reactors for this system. Although these yields are still somewhat smaller than those achieved with the IMR [21], further improvement can be expected by optimizing the radial distribution of the active material and the permeation resistance of the support layer.

Acknowledgements

This work has been carried out with financial suppot from the European Commission, Project JOE3-CT95-0022.

References

[1] V.T. Zaspalis, W. van Praag, K. Keizer, J.G. van Ommen, J.R.H. Ross, A.J. Burggraaf, Appl. Catal. 74 (1991) 205.

[2] A.M. Champagnie, T.T. Tsotsis, R.G. Minet, I.A. Webster, Chem. Eng. Sci. 45 (1990) 2423.

[3] M.P. Pina, S. Irusta, M. Menéndez, J. Santamaría, R. Hughes, N. Boag, Ind. Eng. Chem. Res. 36 (1997) 4557.

[4] D. Farrusseng, A. Julbe, D. Cot, C. Guizard, S. Mota, J.C. Volta, Proceedings of the Third International Conference on Catalysis in Membrane Reactors, Copenhagen, 8–10 September 1998.

[5] K.L. Yeung, R. Aravind, R.J.X. Zawada, J. Szegner, G. Gao, A. Varma, Chem. Eng. Sci. 49 (1994) 4823.

[6] M.J. Alfonso, A. Julbe, D. Farruseng, M. Menéndez, J. Santamaría, Chem. Eng. Sci. 54 (1999) 1265.

[7] G. Saracco, J.W. Veldsink, G.F. Versteeg, W.P.M. van Swaaij, Chem. Eng. Sci. 50 (1995) 2005–2015.

[8] G. Saracco, J.W. Veldsink, G.F. Versteeg, W.P.M. van Swaaij, Chem. Eng. Sci. 50 (1995) 2833–2842.

[9] H.J. Sloot, C.A. Smolders, W.P.M. van Swaaij, G.F. Versteeg, AIChE J. 38 (1992) 887–900.

[10] J.W. Veldsink, R.M.J. van Damme, G.F. versteed, W.P.M. van Swaaij, Chem. Eng. Sci. 47 (1992) 2939–2944.

[11] M.P. Harold, V.T. Zaspalis, K. Keizer, A.J. Burgraaf, Chem. Eng. Sci. 48 (1993) 2705–2726.

[12] M.P. Harold, C. Lee, Chem. Eng. Sci. 52 (1997) 1923–1940.

[13] C. Téllez, M. Menéndez, J. Santamaría, AIChE J. 43 (1997) 777–784.

[14] M.A. Chaar, D. Patel, H.H. Kung, J. Catal. 109 (1988) 463–467.

[15] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, J. Catal. 148 (1994) 56–67.

[16] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, Catal. Lett. 23 (1994) 321–337.

[17] D.S.H. Sam, V. Soenen, J.C. Volta, J. Catal. 123 (1990) 417–435.

[18] A. Corma, J.M. Lopez Nieto, N. Paredes, A. Dejoz, I. Vazquez, Stud. Surf. Sci. Catal. 82 (1994) 113–120.

[19] G. Capanelli, E. Carosini, Chem. Eng. Sci. 51 (1996) 1817–1826.

[20] A. Pantazidis, Doctoral Thesis, Lyon, France, 1996.

[21] R. Ramos, M. Menéndez, J. Santamaría, Catal. Today 56 (2000) 239.