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Oxidative dehydrogenation of propane on catalytic membrane reactors

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Abstract

The oxidative dehydrogenation of propane (ODHP) has been studied in a catalytic membrane reactor using either an ODHP catalyst (V–Mg–O or Ni based) supported on commercial porous alumina membranes, or a V–Mg–O catalyst bed enclosed in a zeolite membrane. No significant membrane effects were found on the macro-and mesoporous V–Mg–O and Ni membranes. In contrast, the zeolite microporous membrane revealed to be an effective gas barrier, allowing a marked increase in propene yields at low C_3H_8/O_2 ratios under separate feeding configuration.

1. Introduction

The oxidative dehydrogenation of alkanes carried out at mild temperatures to produce useful olefins, offers a promising alternative to high temperature processes such as direct dehydrogenation and catalytic cracking. The oxidative dehydrogenation of propane (ODHP) has induced research interest over the last few years [1–5]. However, the main problem remains the release of heat produced by the total oxidation reactions leading to CO and CO_2.

Catalyst development aims at improving the selectivity of the partial oxidation products at the expenses of total oxidation products. Several researchers have developed mixed oxide catalysts for this reaction with V–Mg–O catalysts giving quite good performances at 500°C [1,2,4]. Nickel based catalysts have also been reported giving interesting yields for the oxidative coupling of methane [6], the oxidative dehydrogenation of ethane at low temperatures [7], and the oxidative dehydrogenation of propane [5].

From reaction engineering point of view, it would be desirable to develop a reactor where a controlled oxygen feeding would limit highly exothermic total combustion reactions. A membrane reactor with separate feed of hydrocarbons and oxygen might be a good candidate. Most commonly, the membrane operates as a separator of the reaction products of a catalysed reaction [8,9]. Applications of a membrane operating at the same time as a separator and as (or supporting) the catalyst are less numerous. Recent development and commercialisation of high quality ceramic porous membranes has induced material engineering on *catalytic porous membranes*. On the other hand, zeolite membranes which can theoretically act as a molecular sieve and effectively separate light gases from the heavier ones are under fast development [10]. Recently a new type of thermally stable composite silicalite–alumina membrane has been patented by our laboratory [11].

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The present work reports research concerning the ODHP carried out either with catalytic membranes, or with an inert membrane enclosing a fixed catalyst bed. Two different catalytic phases were used, oxide or metal based, giving two distinct approaches in catalytic membrane preparation, characterisation and catalytic activity testing.

2. Experimental

2.1. Catalytic membranes

Mixed oxide catalytic membranes consisted of an internal active layer of V–Mg–O catalyst deposited on a 200 nm α-alumina support (from S.C.T. Company). They were prepared by combining the 'slip-casting' and the sol–gel methods, consisting of a layer of MgO 'slip' followed by a layer of V_2O_5 gel. The membrane was calcinated at 700°C in order to incorporate the vanadium into the MgO lattice.

Nickel based catalytic membranes consisted of an internal active layer of NiO catalyst deposited on an alumina support. Two different methods were applied for the active phase deposition: (i) support–metal wet exchange using the ammonium complex of nickel nitrate as a precursor and, (ii) nickel impregnation of the support using a solution of nickel nitrate hexahydrate at a concentration of 2.65 M. The two resulting Ni membranes will be denominated Ni(ex) and Ni(im), respectively. The tubular alumina membrane used as carrier for the nickel membrane consisted of a 5 nm γ-alumina internal layer supported on an α-alumina support. The membranes were calcinated at 350°C under oxygen flow in order to stabilize the NiO particles on the alumina surface.

2.2. Membrane enclosed fixed bed reactor

In this system a non catalytic microporous zeolite membrane was used to enclose a fixed bed of an optimised 25V–Mg–O mixed oxide catalyst, thus forming a hybrid membrane reactor. The zeolite membrane consisted of a thin silicalite internal layer deposited in an alumina tubular substrate [11]. The 25V–Mg–O mixed oxide catalyst used to fill the inner compartment of the reactor was in the form of pellets. The catalyst was calcined following the same pattern as the corresponding V–Mg–O catalytic membrane.

2.3. Catalytic testing

After calcination, the above mentioned membranes were tested for the ODHP in a stainless steel membrane reactor designed to operate with two separated inlet flows. Two operating configurations were therefore tested: the separated feed configuration where propane was fed in the inner compartment and oxygen in the outer and, the co-feed configuration where both reactants were fed in the inner compartment. The reacting feed consisted of propane and oxygen diluted in helium. The feed ratio C_3H_8 to O_2 was varied between 1:0.66 and 1:8, the total flow rate of the feed between 20 and 150 ml/min and the reaction temperature between 300 and 600°C. A pressure difference ranging from -2.5 to $+2.5$ mbar for the macroporous, from -6.5 to $+6.5$ mbar for the mesoporous and from -150 to $+250$ mbar for the microporous membranes, was applied between the two compartments of the reactor.

The catalytic performances of the membrane systems were evaluated by the propene yield, given by the product of the propane conversion and the selectivity towards propene, calculated by summing the gas compositions at both outlets of the membrane reactor. The membrane separation effect was evaluated by comparing the molecular ratio of C_3H_8 to O_2 for each membrane compartment.

Finally, permeability measurements were performed before and after reaction in order to detect eventual defect creation or coke deposition during reaction.

3. Results

3.1. Membrane characterization before reaction

The change in nitrogen permeability as a function of the membrane internal pressure P_i is

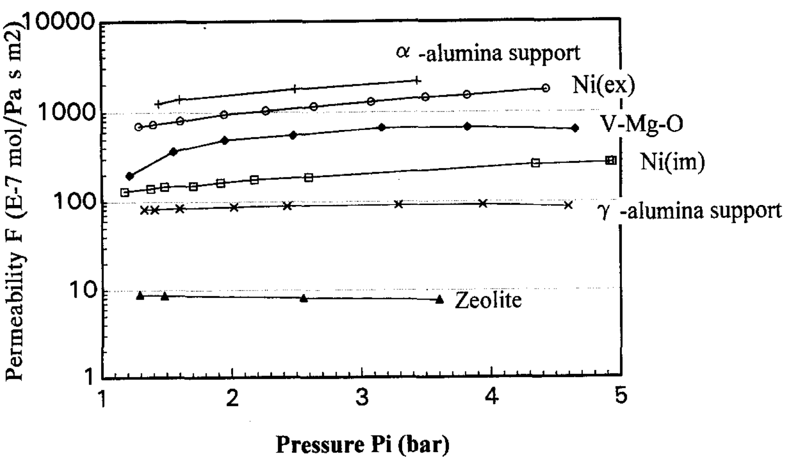

Fig. 1. Nitrogen permeability measurements of the catalytic membranes and their support at 30°C, after calcination and reaction.

reported in Fig. 1 for the catalytic membranes after calcination and reaction and for the corresponding supports.

V–Mg–O deposition on the α-alumina support slightly decreases the support permeability. In contrast, Ni deposition on the γ-alumina support tends to a marked increase of the support permeability depending on the used preparation method. The exchange method destroys the gamma alumina internal layer giving a macroporous catalytic membrane —Ni(ex) —, while the Ni membrane obtained by impregnation —Ni(im) —remains mesoporous. The zeolite membrane presents a much lower permeability (one order of magnitude) in accordance with its microporous porosity determined elsewhere [11].

3.2. *Catalytic performances and membrane separation effect*

Table 1 reports the catalytic performances of the various systems at given temperature and contact time. Close propane conversion levels have been selected in order to compare selectivities and yields. The corresponding intermembrane pressure gradients are also reported. The corresponding product distributions observed at both outlets of the membranes are reported in Table 2.

Catalytic V–Mg–O and Ni membranes

As can be seen in Table 1, the alumina supports exhibit non negligible activity under reaction conditions. The γ-alumina is more active than the α-alumina, probably due to its higher specific

Table 1
Catalytic performances of the V–Mg–O based and the Ni based membranes. Separate feeding

Membrane catalyst	Temperature (°C)	Catalytic performances (%)			Contact time τ (mg s/ml)	$\Delta P/P_{int}$ (mbar/bar) [a]
		X_{C3H8}	S_{C3H6}	Y_{C3H6}		
α-alumina support	550	3.2	65.5	2.1	–	–
γ-alumina support	400	3.1	18.9	0.6	–	–
Zeolite membrane	500	2.5	63.0	1.6	–	–
V–Mg–O based	600	9.8	47.8	4.7	1.021	−0.25/1.06
Ni based (ex)	360	10.3	37.1	3.8	0.400	−0.00/1.07
Ni based (im)	254	10.0	42.4	4.3	2.933	+3.50/1.08
V–Mg–O bed enclosed in zeolite membrane	500	9.7	76.2	7.4	11.125	+3.00/1.08

[a] Intermembrane pressure gradient: $\Delta P = P_{ext} - P_{int}$.

surface. However, the former shows a poor selectivity to propene (16.4%), probably because of its surface acidity. The higher selectivity to propene of the α-alumina could be related both to its low activity (3.2% C_3H_8 at 550°C) and milder acidity. The zeolite membrane is as selective as the α-alumina but exhibits a lower activity.

The temperatures needed for achieving around 10% C_3H_8 conversion with the catalytic membranes vary widely as a function of the catalyst. Thus, the Ni membranes give the same propane conversion as the V–Mg–O ones at approximately 250°C lower temperature. However, the Ni membranes tend to be less selective especially as temperature is increased.

In order to specify if these differences in catalytic performances were due to structural factors creating mass transport limitations, the effect of contact time on propene yields was studied for two reactor configurations: co-feeding and separate feeding (Fig. 2).

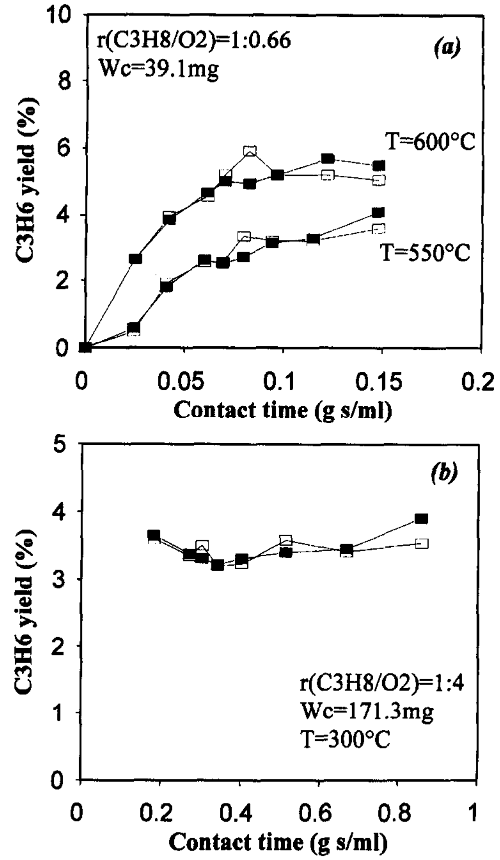

Fig. 2. Contact time effect on propene yields for (a) the V–Mg–O based and (b) the Ni based catalytic membranes. Separate feeding, ■; co-feeding, □.

It is observed for the V–Mg–O membrane that the propene yield slightly increases with contact time in the range of low contact time values, but tends to stabilize at higher contact times. This suggests a progressive transition from a catalytic to a diffusional regime. For both types of membrane, the reactor configuration does not induce any significant effect on the catalytic performances. This observation is in line with the distribution of products and the C_3H_8 to O_2 ratio which were found little different for the inner and outer compartment (Table 2). It is therefore obvious that the macroporous V–Mg–O and Ni(ex) membranes and the mesoporous Ni(im) membrane do not exhibit any significant separation effect between the two compartments.

Table 2
Product distribution and C_3H_8/O_2 ratio at the reactor outlets for the V–MgO and the Ni based membranes. Experimental conditions: (C_3H_8/O_2) ratio = 1:0.66, $P_{C_3H_8}$ = 0.02, reaction conditions see Table 1

Membrane catalyst	Reactor compartment	Product concentrations (Torr)							C_3H_8/O_2 ratio
		C_3H_8	O_2	C_3H_6	C_2H_4	CH_4	CO_2	CO	
V–Mg–O based	inner	14.6	7.6	0.83	0.15	0.05	1.55	0.64	1.92
	outer	15.5	7.9	0.84	0.17	0.06	1.92	0.64	1.96
Ni based (ex.)	inner	15.8	6.7	0.58	–	–	2.79	–	2.36
	outer	16.2	6.8	0.55	–	–	2.95	–	2.38
Ni based (im.)	inner	15.2	8.0	0.53	–	–	2.05	–	1.91
	outer	15.7	8.1	0.56	–	–	2.36	–	1.93
V–Mg–O bed enclosed	inner	30.1	2.4	2.05	0.04	0.08	1.05	0.61	12.40
in zeolite membrane	outer	5.0	18.1	0.45	0.04	0.02	0.24	0.15	0.28

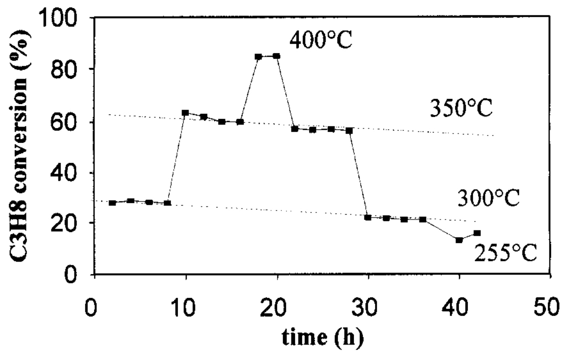

Fig. 3. Deactivation as a function of time at different temperatures for the Ni(im) catalytic membrane.

Finally, the membrane stability was studied for the catalytic membranes. The V–Mg–O membrane does not exhibit any deactivation, unlike the Ni membranes. Fig. 3 shows the deactivation profile observed during a catalytic run carried out at various temperatures over the Ni(im) membrane. A slow and weak deactivation is observed throughout the run (0.2% h^{-1}), independent of the temperature, and therefore of the conversion level. Similar profiles were observed for the Ni(ex) membrane. This behaviour excludes any ageing effect related to the conversion, such as carbon deposits and rather suggests a structural/textural ageing of the membrane. As nickel sintering is not likely in that temperature range, slow changes in the γ-alumina structure and/or texture could be considered.

V–Mg–O bed enclosed in a zeolite membrane

As can be seen in Table 1, the hybrid membrane reactor exhibited the highest selectivity (76.2%) and yield (7.4%) in propene at 500°C for a 10% conversion. Table 2 clearly indicates that, at variance with the previous catalytic membranes, the zeolite membrane acts as an effective gas barrier. A small amount of propane diffuses through the membrane ($P_{C_3H_8}$ outer = 5.0 Torr) and all the oxygen penetrating is consumed in the dehydrogenation reaction (P_{O_2} inner = 2.4 Torr). Thus, the product distributions and the ratios C_3H_8/O_2 are quite different for the inner and outer reactor compartments.

Table 3 illustrates the effect of the oxygen partial pressure on the catalytic performances of a V–Mg–O catalyst bed of 623 mg enclosed in the zeolite membrane. It is observed that there is a strong membrane effect by comparing the two separate feeding configurations. When oxygen is fed into the inner compartment, selectivity to propene is only 19.5% for a 7.2% propene conversion. When oxygen is fed into the outer compartment, selectivity is four times higher at similar propane conversion

Furthermore, it is obvious that the best propene yield ($Y_{C_3H_6}$ = 14.6%) is attained with the separate feeding configuration at high oxygen partial pressure (C_3H_8/O_2 = 1:8). This configuration gives a marked net increase in propene yield from 10.6 to 14.6%. However, at low oxygen partial pressure (C_3H_8/O_2 = 1:0.66), the best yield is obtained with the co-feeding configuration. A lack of oxygen in the catalytic zone could account for the low activity and therefore the low propene yield observed for separate feeding configuration at low oxygen pressure. It should be pointed out that

Table 3
Oxygen partial pressure effect on the hybrid membrane reactor performances for different configurations. Experimental conditions: T = 480°C, F = 56 ml/min, m_{cat} = 623 mg. $P_{C_3H_8}$ = 0.02

C_3H_8/O_2 ratio	Reactor configuration	Catalytic performances (%)				$\Delta P/P_{int}$ (mbar/bar) [a]
		X_{C3H8}	X_{O2}	S_{C3H6}	Y_{C3H6}	
1:0.66	O_2 inner	7.2	36.3	19.5	1.4	−5.75/1.07
	O_2 outer	6.7	14.2	79.3	5.3	+5.50/1.07
	Co-feed inner	27.0	98.4	43.2	11.6	−73.00/1.11
1:8	O_2 inner	10.9	8.2	20.0	2.2	−13.75/1.07
	O_2 outer	39.1	13.6	37.4	14.6	+9.25/1.06
	Co-feed inner	55.6	25.1	19.2	10.6	−79.25/1.11

[a] Intermembrane pressure gradient: $\Delta P = P_{ext} - P_{int}$.

propene selectivity in separate feeding configuration, when oxygen is fed at the outer compartment, is always twice as high as the selectivity obtained with the co-feeding configuration.

As a summary, this system is very sensitive to oxygen partial pressure variations and the membrane effect increases as oxygen concentration increases.

4. Conclusions

The catalytic performances of various membrane materials having macroporous, mesoporous and microporous structures have been evaluated and compared. Two different active phases were used: V–Mg–O or Ni based. They were either deposited on a membrane support to give a catalytic membrane, or used to fill the inner compartment of a hybrid zeolite membrane reactor.

Permeability measurements have been performed in order to characterize the membranes porous structure and surface defects. No serious surface defects have been observed. The V–Mg–O and the Ni(ex) catalytic membranes were found macroporous, the Ni(im) membrane mesoporous, and the zeolite membrane microporous.

The V–Mg–O based membranes were found less active but more selective than the nickel based membranes. Thus, the V–Mg–O membranes are active for the ODHP at temperatures above 500°C, while the Ni membranes just above 250°C.

Two reactor configurations, separate and co-feeding, were compared at various experimental conditions. The best performance was achieved with the zeolite hybrid reactor when separate feeding configuration was used at high oxygen partial pressures. Its microporous structure, confirmed by the permeability measurements, most probably accounts for these performances. Incontrast, the macro and mesoporous catalytic membranes gave similar results whatever the feeding configuration.

Therefore, the catalytic performances appear to be mostly controlled by the membrane porous structure. Macroporous and mesoporous membranes do not behave as effective gas barriers, while the microporous zeolite membrane displays highly promising separation properties.

Acknowledgements

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