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Characteristics and performance in the oxidative dehydrogenation of propane of MFI and V-MFI zeolite membranes

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Abstract

Original V-MFI zeolite membranes in/on alumina tubes have been prepared, characterized and tested for the oxidative dehydrogenation of propane. The morphological and textural characteristics of the V-MFI membrane were found to be very similar to those of V-free MFI membranes. The insertion of vanadium species has been checked by elemental analysis, XRD, FTIR and ESR. The single gas permeance studies showed that both MFI and V-MFI membranes were free of macrodefects and provided an activated transport for both C_3H_8 and O_2 above 400°C, with a Knudsen-like permselectivity. Both MFI and V-MFI membranes were found to produce propene with about 40% selectivity but with higher O_2 and C_3H_8 conversions for the V-MFI. In the studied conditions, between 550 and 650°C, the oxygen distributor configuration was not found to improve the reactor performance compared to the flow-through one. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Membrane reactor; Zeolite membranes; V-MF1 membranes; Oxidative dehydrogenation of propane

1. Introduction

Among the large research effort devoted to the oxidative dehydrogenation of alkanes, the potential use of membrane reactors appears to be of particular interest for (i) controlling the oxygen feeding to limit the highly exothermic total combustion [1,2] and (ii) improving the contact between the reactant and the catalyst. Zeolite membranes are thermally stable and well adapted to high temperature applications [3] since they can be used as separators only and/or as active contactors if they are catalytically active. Molecular sieves catalysts are also widely studied for selective oxidation reactions [4,5]. Immobilizing transition metal ions in zeolites by ion exchange or by incorporation into the lattice leads to stable, isolated and well defined redox active catalytic sites. Since the industrial applications of titanium silicalite, other redox molecular sieves are developed currently. Based on the catalytic properties of vanadium oxides for selective oxidations, the insertion of vanadium in MFI and MEL structures is widely investigated [4,6–11]. The present study reports preliminary data obtained for the preparation and characterization of supported V-MFI membranes by in situ insertion of V species during the hydrothermal treatment. The catalytic performance of both MFI and V-MFI membrane reactors are compared for the reaction of oxidative dehydrogenation of propane (ODHP).

2. Experimental

2.1. Synthesis of V-MFI composite membranes

The V-MFI membranes were prepared according to the method already reported for MFI membranes

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[12]. A sol ($VOSO_4/SiO_2$/TPAOH/H_2O) was treated at 185°C in contact with an α-alumina support (enameled tubes 15 cm long, T1-70, from US Filter-SCT). The tubes have a three layers asymmetric structure with mean pore sizes of 10 μm (external layer), 0.8 μm (intermediate layer) and 0.2 μm (internal layer). The molar ratio Si/V in the starting sol was 40 and the pH was about 13.5. After synthesis the template was eliminated by a thermal treatment in air at 600°C for 2 h. Vanadium-free-MFI membranes were also prepared (without $VOSO_4$ in the starting sol) and characterized for comparison. The hydrothermal treatment and consecutive thermal treatment resulted typically in an increase of about 5 wt.% for the support. The weight of zeolite in the studied MFI and V-MFI membranes (15 cm long) was 1.1 g.

2.2. Membrane characterizations

The vanadium species contained in a scrapped V-MFI membrane were investigated by elemental analysis, FTIR, ESR and XRD. The morphology and texture of MFI and V-MFI membranes were studied by SEM, mercury porosimetry and N_2 adsorption–desorption. For the single gas permeance studies, membranes were sealed in a stainless steel module using graphite o-rings and outgassed overnight at 450°C under N_2 before each test. During gas permeation measurements, one end of the membrane tube was closed and the internal pressure was varied between 1.5 and 4 bars at room temperature. The pressure in the permeate side (outside part of the tube) was the atmospheric pressure. No sweep gas was used. During the measurements as a function of temperature the transmembrane pressure was fixed to 500 mbar by a pressure regulator equipped with a pressure sensor. The membrane permeance for a given temperature was measured after stabilization of the flow rate. Single gas permeances were measured as a function of transmembrane pressure (from 0.5 to 3 bars) for N_2 and of temperature (from room temperature to 500°C) for O_2, CO_2 and C_3H_8. The measured permeances varied in the range $(1–5) \times 10^{-7}$ mol/(m^2 s Pa) with a maximum error of ±2%.

2.3. Catalytic tests

After calcination and single gas permeance studies, the above mentioned membranes were tested for ODHP in a stainless steel membrane reactor designed to operate with two separated inlet flows. Two operating configurations were tested: (i) the separate feed configuration (oxygen distributor) where propane is fed in the inner compartment and oxygen in the outer and (ii) the cofeed configuration (flow-through contactor) where both reactants are fed in the inner compartment. In the oxygen distributor configuration the exit was in the inner compartment and in the flow-through configuration, the exit was in the outer compartment. The reactant feed composition was typically 3 or 6% C_3H_8 and X% O_2 in He, with X varying from 0 to 12% with a total flow rate varying from 36 to 52 ml/min in the temperature range 550–650°C. A transmembrane pressure ($\Delta P = P_{\text{int}} - P_{\text{ext}}$) ranging from −0.1 to +0.5 bar was applied between the two compartments of the reactor. The propene yield (product of the propane conversion by the propene selectivity) was calculated from the gas analysis at the inlet and outlet parts of the reactor by gas chromatography. Permeability measurements were performed before and after reaction up to 650°C in order to detect eventual defects or coke deposition.

3. Results and discussions

3.1. Characterization of the zeolite membranes

A typical atomic ratio Si/V = 160 was found for the scrapped V-MFI membrane, representing the mean surface composition. The possible incorporation of aluminum from the support during the hydrothermal synthesis would induce a variation of the vanadium insertion (quantity and nature) from the support interface to the outer part of the membrane. The presence of the vanadium precursor in the starting sol did not seem to influence the growth of MFI crystals (quantity, morphology, location in the support and crystalline phase). The characteristics of the V-MFI membrane were found similar to those of the MFI one.

3.1.1. Morphology and porous structure of the V-MFI/α-Al_2O_3 composite membrane

As observed by SEM (Fig. 1), the zeolite crystals have grown both on the inner layer of the support and inside the pores. An external layer of non-connected

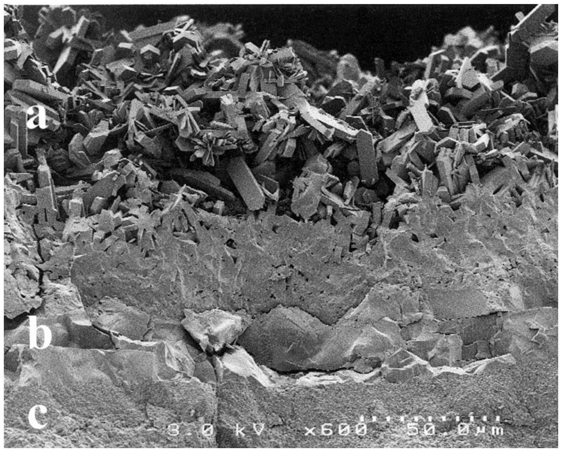

Fig. 1. FESEM cross-section image of a supported MFI zeolite membrane.

zeolite crystals (region a) has grown on a layer of connected zeolite crystals (region b) which is firmly stuck to the support (region c). The pores of the two internal layers of the support (0.2 and 0.8 µm pore sizes) were almost totally filled with zeolite (Fig. 2). The grains of the external layer (10 µm pore sizes) were only partially covered with zeolite crystals.

These observations were in good accordance with the mercury porosimetry analysis of the support before and after synthesis. As shown in Fig. 3, the large 10 µm pores were still present after synthesis but the two families of pores centered on 0.2 and 0.8 µm were largely modified and occluded by zeolite crystals. The N_2 adsorption–desorption isotherms of the scrapped zeolite were comparable to those obtained with a commercial MFI zeolite powder (Na-ZSM5 Uetikon).

3.1.2. Location and type of vanadium species in the V-MFI membrane

The location of the V ions either in the zeolite framework or randomly distributed within the pores and/or anchored to the crystal surface has been discussed in the literature on vanadium zeolite powders [4,7–9].

The cell parameters of the synthesized V-MFI crystals, calculated from the X-ray diffraction patterns [13], are presented in Table 1. Compared to the result obtained for MFI, a slight increase of the cell parameters c, β and consequently of the cell volume was noticed, which may indicate the insertion of vanadium species in the zeolite structure [14,15]. Furthermore FTIR spectra revealed a small absorption at 963 cm^{-1} characteristic of V–O–Si bonding [4].

Although the presence of polymeric vanadium species is not excluded, the hyperfine structure observed at room temperature in the ESR spectrum of the as-synthesized V-MFI membrane (Fig. 4a) reflected a very high dispersion of V^{4+} species. The ESR signal parameters were close to those reported by different authors for V^{4+} species in a distorted square pyramidal coordination [4]. After calcination at 600°C, the ESR spectra disappeared (Fig. 4b) indicating the oxidation of V^{4+} to V^{5+} species. Reduction of the calcined sample in H_2/Ar mixture at 500°C restored the ESR spectra and demonstrated a reversible V^{5+}/V^{4+} transformation. Some isolated V^{5+} species were consequently accessible to gas molecules and may act as active selective sites for ODHP as mentioned in [4].

3.2. Single gas permeances through the MFI and V-MFI membranes

The N_2 permeance of MFI and V-MFI membranes was measured at room temperature as a function of transmembrane pressure. The absence of viscous-flow when the transmembrane pressure was increased from 0.5 to 3 bars indicated that the membranes were free of macrodefects (>50 nm). The N_2 permeance of the MFI membrane was not modified after ODHP catalytic tests up to 650°C, although it decreased by 10% for the V-MFI membrane. This could result from some V-MFI membrane coking during the ODHP reaction [18].

The O_2, C_3H_8 and CO_2 permeances of MFI and V-MFI membranes were measured after the ODHP tests as a function of temperature in the range $(1–3) \times 10^{-7}$ mol/(m^2 s Pa) (Fig. 5). These data were typical of MFI membranes of relatively good quality [3,16]. The corresponding main transport mechanisms are tentatively schematized in Fig. 6. The O_2 and CO_2 permeances correspond to BCD curves between room temperature and 500°C. An ABCD curve was observed for C_3H_8. At high temperature (400–500°C) the measured activation energies for C_3H_8 and O_2 transport were about 11 kJ/mol for the MFI membrane, in good agreement with the activation energies reported in [17] for gas translation diffusion at high

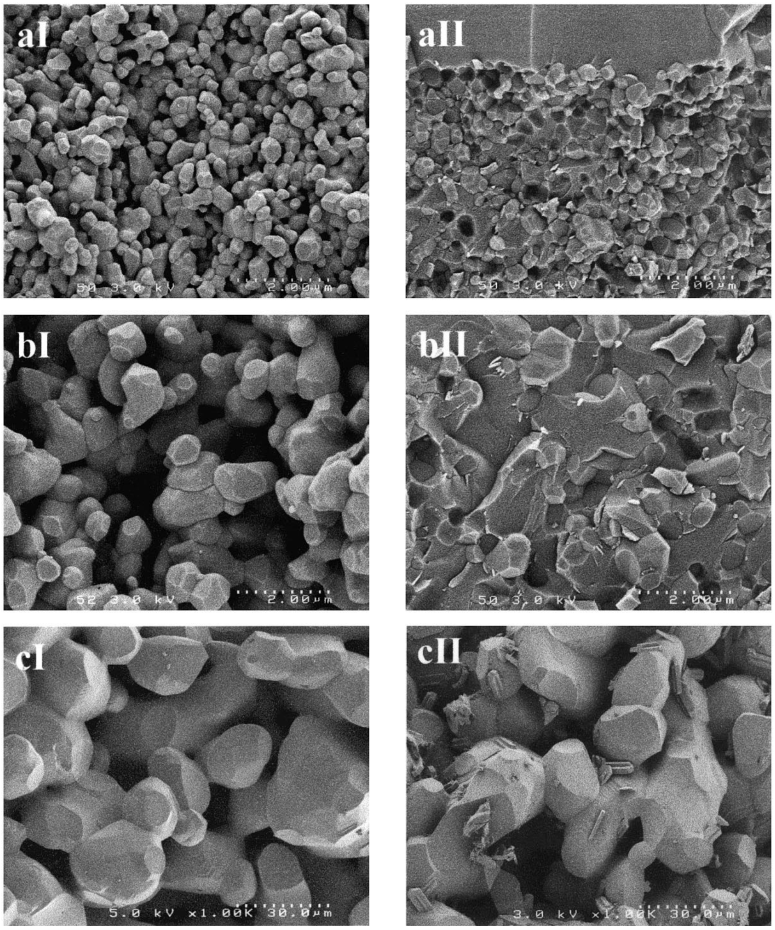

Fig. 2. FESEM cross-section images of the SCT support: (a) inner layer, (b) intermediate layer, (c) external layer before (I) and after (II) zeolite synthesis.

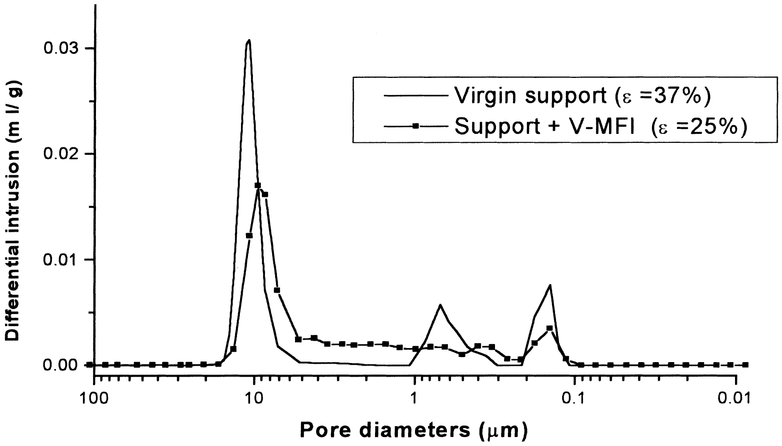

Fig. 3. Pore size distributions of the support before and after zeolite synthesis (mercury porosimetry).

Table 1
Values of cell parameters (from XRD) for V-MFI and MFI scrapped from alumina support after the firing treatment at 600°C[a]

Cell parameter	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Volume (Å^3)
MFI zeolite	19.877 (±0.005)	20.103 (±0.005)	13.365 (±0.003)	90.59 (±0.03)	5340 (±4)
V-MFI zeolite	19.876 (±0.003)	20.104 (±0.003)	13.373 (±0.002)	90.63 (±0.02)	5343 (±2)

[a] Estimated standard deviations are indicated in brackets.

temperature in MFI membranes. In the case of V-MFI membrane, lower activation energies were measured for O_2 (around 8 kJ/mol), indicating a lower membrane quality (larger number of microdefects). As shown in Fig. 5, the C_3H_8 and CO_2 permeance curves still show an influence of adsorption at 400°C and it was meaningless to measure the activation energy between 400 and 500°C.

At 500°C, the ratio of permeances (or ideal selectivity) $\alpha(O_2/C_3H_8)$ is 1.09 and 1.13 for MFI and V-MFI membranes, respectively. In good agreement with a gas transport mechanism by translation diffusion these values concerning gases with comparable activation energies are close to the Knudsen ratio: $\alpha_{\mathrm{Knudsen}}(O_2/C_3H_8) = 1.17$. A separation test with an O_2/C_3H_8 mixture (50/50) showed that the V-MFI membrane permeance selectivity varied from 0.77 at 25°C up to 0.96 at 200°C. No test was performed at higher temperature because of the reaction between the two gases. It may be assumed however that at 500°C the membrane selectivity for the mixture is identical to the one obtained for single gases (i.e. <1.17).

3.3. MFI and V-MFI membranes reactivity for ODHP

3.3.1. Effect of the O_2 content

The reactor was configured as a flow-through contactor, i.e. fed in the tube side (3% C_3H_8 and 0–12% O_2 in He) with a total flow rate of 45 ml/min, at 550°C, internal pressure 1.7 bar and transmembrane pressure 0.4 bar. The catalytic data are reported in Figs. 7 and 8 for MFI and V-MFI membranes, respectively.

Whatever the O_2 concentration, higher oxygen and propane conversions were achieved with the V-MFI with respect to the MFI membranes. Furthermore, a higher propene selectivity was obtained with the V-MFI membrane for low oxygen content ($<1\%$). However, by increasing the O_2 content from 1 to 12%, the propene selectivity decreased from 50 to 20% for the V-MFI membrane, while it remained around 50% for the MFI one. The largest propene yield (7%) was obtained with the V-MFI membrane with 1% O_2 in the feed. A higher oxygen content (6% O_2) was necessary to reach the same yield with the MFI membrane. In the absence of oxygen, propene

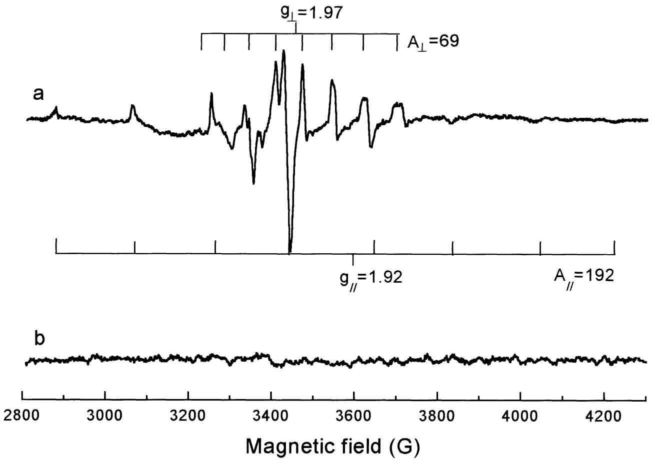

Fig. 4. ESR spectra at room temperature of (a) as-synthesized V-MFI membrane scrapped off the support, (b) V-MFI membrane scrapped off the support and treated in air at 600°C.

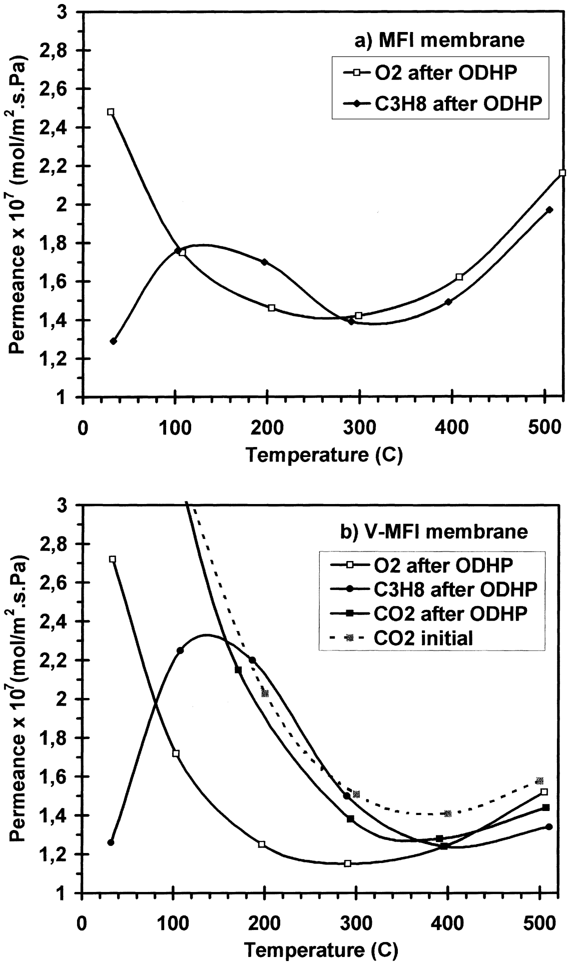

Fig. 5. Single gas permeances as a function of temperature ($\Delta P = 500$ mbar) (a) O_2 and C_3H_8 through the MFI membrane after the catalytic tests at 650°C, (b) CO_2, O_2 and C_3H_8 through the V-MFI membrane after the catalytic tests at 650°C; CO_2 permeance before the catalytic tests.

yields of 4% (with a selectivity of 85%) and 2.6% (with 73% selectivity) were obtained with the V-MFI and MFI membranes, respectively.

The observed activity of the MFI membrane which should be theoretically inactive may be related to acidic sites probably created after aluminum dissolution from the support during the hydrothermal synthesis (high pH) and leading to a kind of H-ZSM-5 membrane. Within this assumption, a mechanism involving radical formation on Lewis acid sites could be considered. In this case, a propyl radical formed

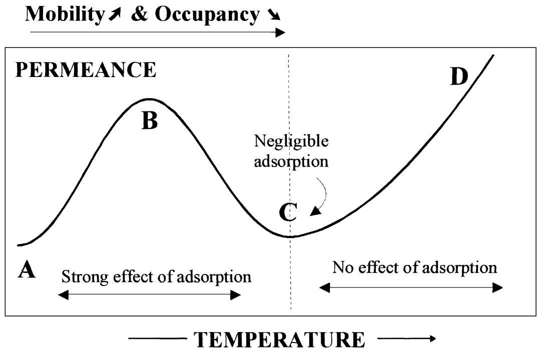

Fig. 6. Schematic evolution with temperature of single gas permeance through MFI membranes. ABC: activated configuration diffusion, AB: mobility of adsorbed species increases and occupancy decreases, B: the increase in mobility cannot compensate the decrease in occupancy, C: adsorption is negligible, CD: activated transport through micropores (gas translation diffusion).

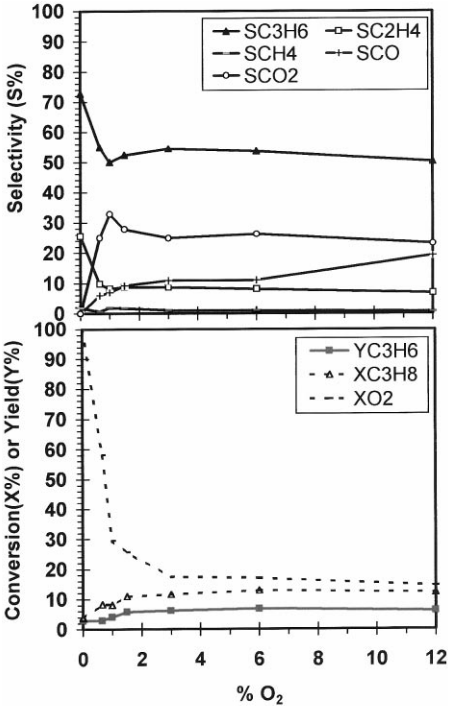

Fig. 7. C_3H_6, C_2H_6, C_2H_4, CH_4, CO, CO_2 selectivities; C_3H_8 and O_2 conversions and C_3H_6 yield for the MFI membrane as a function of the oxygen content in the feed (3% C_3H_8 and 0–12% O_2 in He), for a temperature of 550°C and flow-through contactor configuration with total flow rate: 45 ml/min, $P_{int} = 1.7$ bar and $\Delta P = 0.4$ bar.

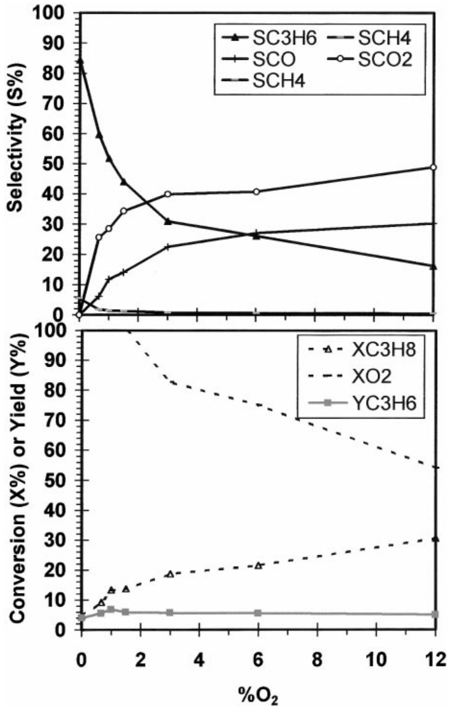

Fig. 8. C_3H_6, C_2H_6, C_2H_4, CH_4, CO, CO_2 selectivities; C_3H_8 and O_2 conversions and propene yield for the V-MFI membrane as a function of the oxygen content in the feed (3% C_3H_8 and 0–12% O_2 in He), for a temperature of 550°C and flow-through contactor configuration with total flow rate: 45 ml/min, $P_{\mathrm{int}} = 1.7$ bar and $\Delta P = 0.4$ bar.

on an Al□ site could either be dehydrogenated into propene by H abstraction on a second lattice oxygen or reacting with an electrophilic oxygen radical O^-, similarly activated on lattice vacancy, to be step-wise oxidized into CO_x [19]. Another possibility, favored at high temperature, would be to consider that the formed alkyl radical may desorb from the surface and react with gaseous oxygen to form propene and chain propagation radicals like $OH^{\cdot}$. In addition to these radical induced processes, a cracking reaction on these acid sites (via carbenium ions) could also account for the formation of C_1–C_2 molecules, independently of the oxygen pressure as observed in Fig. 7.

In addition to these acid sites arising from the hydrothermal synthesis, the V-MFI membrane also contains vanadyl Lewis acid sites, able to activate propane and oxygen according to a redox process [11]. The presence of these sites could explain the higher oxygen and propane conversions observed on V-MFI membrane. When the oxygen concentration increases above 1%, the V sites in the V-MFI membrane would favor the formation of electrophilic oxygen adspecies leading to total oxidation products (CO and CO_2). This is not observed with the MFI membrane.

The ODHP catalytic performance of the V-MFI membrane is compared in Table 2 to data reported for V-silicalite powder with $SiO_2/V_2O_3 = 545$ [11]. In spite of different experimental conditions, a three times lower propene selectivity is obtained with the V-MFI membrane at comparable propane conversion and temperature. The V-MFI membrane might contain a higher quantity of extra-lattice non-selective vanadium species compared to the V-MFI powder reported in [11] which has been treated with an ammonium acetate solution. The low selectivity obtained with the V-MFI membrane could also be related to a larger amount of aluminum than in the V-MFI zeolite studied in [11]. Experiments are currently performed with other supports in order to avoid the insertion of disturbing foreign species.

Table 2
Catalytic performance of V-silicalite powders reported in [11] ($SiO_2/V_2O_3 = 545$ for flow reactor with 2.8% C_3H_8, 8.4% O_2 or N_2O in He, 4.2 g of catalyst, total flow rate = 51 ml/min) and of the studied V-MFI membrane ($SiO_2/V_2O_3 = 320$ for flow-through membrane reactor with 6% C_3H_8, 12% O_2 in He, 1.1 g of catalyst, total flow rate = 45 ml/min)

Material	V-silicalite powder [11]			V-MFI membrane
oxidative gas	O_2	O_2	N_2O	O_2
Temperature	400 (°C)	540 (°C)	400 (°C)	550°C
C_3H_8 conversion	8%	28%	45%	30.6%
C_3H_6 selectivity	84%	64%	76%	16.2%
C_3H_6 yield	6.7%	18%	34%	5.0%

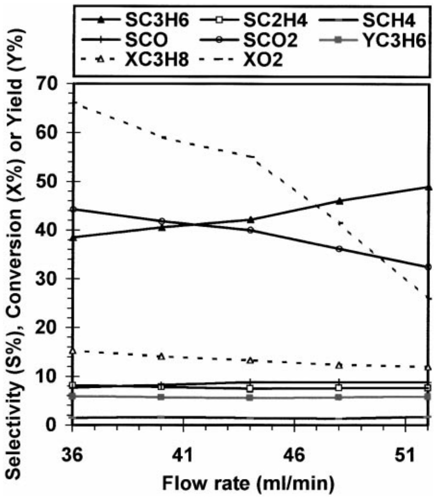

Fig. 9. C_3H_6, C_2H_6, C_2H_4, CH_4, CO, CO_2 selectivities; C_3H_8 and O_2 conversions and propene yield for the MFI membrane as a function of the total flow rate with flow-through contactor configuration for feed composition of 6% C_3H_8 and 1% O_2 in He at temperature 550°C.

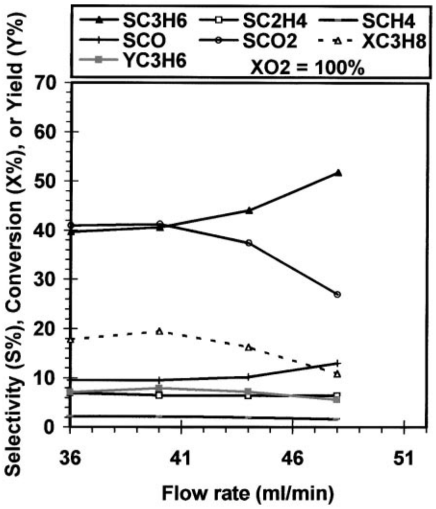

Fig. 10. C_3H_6, C_2H_6, C_2H_4, CH_4, CO, CO_2 selectivities; C_3H_8 conversion and propene yield for the V-MFI membrane as a function of the total flow rate. The O_2 conversion was always 100% with flow-through contactor configuration for feed composition 6% C_3H_8 and 1% O_2 in He at temperature 550°C.

The observation reported in [11] that the conversion increased and the selectivity decreased when the molar ratio SiO_2/V_2O_3 decreased is in good agreement with the relative performance obtained for MFI and V-MFI membranes.

3.3.2. *Influence of contact time*

The effect of contact time in the flow-through contactor configuration was studied at 550°C with 6% C_3H_8 and 1% O_2 in He by varying the total flow rate from 36 to 52 ml/min (Figs. 9 and 10, Table 3). As expected, with both membranes a decrease in C_3 conversion and an increase in propene selectivity was observed when the flow rate was increased, i.e. the contact time was decreased. Note that however the oxygen conversion was always 100% for the V-MFI membrane. For the MFI membrane, the maximum propene yields at 550°C were obtained with the highest and lowest flow rate (36 or 52 ml/min) whereas for the V-MFI membrane the maximum yield corresponded to a low flow rate (40 ml/min). The effect of contact time on the V-MFI membrane performance was no more observed at 650°C (no change in selectivity and conversion with the flow rate), indicating that at this temperature the gas phase mechanism tends to become prominent.

Table 3
Comparison of MFI and V-MFI membrane performance in flow-through contactor configuration at 550°C with 6% C_3H_8 and 1% O_2 in He, total flow rate = 36 or 40 ml/min[a]

Membrane/flow rate (ml/min)	XC_3H_8	XO_2	SC_3H_6	SC_2H_6	SC_2H_4	SCH_4	SCO	SCO_2	YC_3H_6	$\Delta P/P_{int}$ (mbar)
MFI/36	15.3	66.1	38.5	0.0	8.1	1.4	7.7	44.2	5.9	297/1650
V-MFI/36	17.8	100	39.7	0.6	7.0	2.2	9.5	41.0	7.1	290/1720
MFI/40	14.1	59.1	40.6	0.0	7.8	1.6	8.2	41.8	5.7	220/1666
V-MFI/40	19.5	100	40.6	0.0	6.5	2.2	9.5	41.3	7.9	320/1710

[a] Transmembrane and internal pressures are indicated in the last column ($\Delta P = P_{int} - P_{ext}$).

Table 4
V-MFI membrane reactor: evolution of propane conversion, product selectivity and propene yield as a function of temperature with two reactor configurations (oxygen distributor and flow-through contactor)[a]

Temperature (°C)	Conversion (X%), selectivity (S%) and yield (Y%)								Pressure (mbar)
	XC_3H_8	SC_3H_6	SC_2H_6	SC_2H_4	SCH_4	SCO	SCO_2	YC_3H_6	$\Delta P/P_{\mathrm{int}}$
Oxygen distributor (OD)									
555	10.2	40.6	0.4	8.6	2.6	10.1	37.8	4.1	−165/1720
579	14.7	39.7	0.8	11.4	4.5	8.1	35.4	5.9	−153/1730
604	11.7	42.6	1.2	15.4	6.5	8	26.4	5	−151/1650
628	14.7	42.5	1.8	20.1	9.6	6.5	19.6	6.2	−143/1690
650	19.8	43	0	26.4	11.3	4.9	14.4	8.5	−137/1650
Flow-through contactor (FT)									
555	13.8	52.2	0	6.4	1.6	11.7	28.2	7.2	410/1730
575	11.1	52	0	9	2.4	7.7	28.9	5.8	392/1710
603	12.7	52.5	0.4	12.3	3.9	7.1	23.8	6.7	374/1690
629	15.4	49.1	0.8	17.2	9.2	5.9	17.7	7.6	356/1680
654	21.1	47.5	1.3	23.8	10.3	5	12.1	10	339/1660

[a] Transmembrane and internal pressures are indicated in the last column ($\Delta P = P_{\mathrm{int}} - P_{\mathrm{ext}}$). Feed conditions: 6% C_3H_8 and 1% O_2 in He. Total flow rate: 45 ml/min.

3.3.3. *Influence of temperature and of reactor configuration*

The ODHP data for the V-MFI membrane between 550 and 650°C are reported in Fig. 11 and Table 4, both for the flow-through contactor and oxygen distributor configurations. The increasing contribution of the homogeneous gas phase reaction above 550°C may explain the stability of the propene selectivity and the increasing propane conversion with temperature. In all cases the oxygen conversion was 100%. Under the studied conditions, the flow-through contactor always gave the highest propene selectivity and yield, the conversion being also slightly higher in this configuration compared to the oxygen distributor configuration.

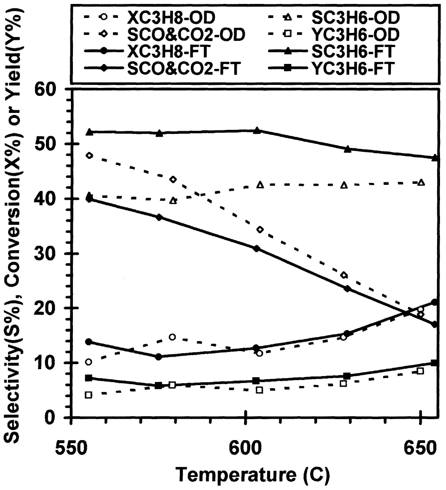

Fig. 11. C_3H_8 conversion, CO_x selectivity, C_3H_6 selectivity and yield between 550 and 650°C with a V-MFI membrane reactor in flow-through contactor (FT) or oxygen distributor (OD) configuration for feed composition: 6% C_3H_8 and 1% O_2 in He and total flow rate: 45 ml/min.

The zeolite membrane is not permselective to the reaction gases (possible retrodiffusion of both C_3 and O_2 species) and the gas transport mechanisms in such a zeolite membrane are not affected by pressure. Due to the fact that the propane conversion was similar in both cases and that the oxygen consumption was total, the same quantity of propane is expected to diffuse through the catalytic membrane in both configurations. The difference in selectivity could then be attributed to the residence time in the membrane of the primarily formed propene which could be further oxidized into CO_x. A higher residence time in the case of the oxygen distributor configuration, which is plausible due to counter flow effects, would explain the observed lower selectivity. It would be worthwhile to compare these results with those obtained with a similar membrane providing a viscous-flow transport contribution. Indeed in this case the permeance is a function of pressure and the flow rate and retrodiffusion of species might be controlled by pressure.

4. Conclusion

V-MFI membranes synthesized in/on a porous α-alumina support were found to present structural characteristics very similar to those obtained for V-MFI powders: well dispersed V^{4+} species and vanadium inserted in the zeolite framework. These V-MFI membranes presented the same morphology of the zeolite phase as compared to MFI membranes.

Single gas transport through the V-MFI and MFI membranes was controlled by adsorption, configuration diffusion and gas translation diffusion, as expected for such zeolite membranes. The O_2/C_3H_8 permselectivity of the membranes was comparable to the Knudsen selectivity at 500°C.

Both MFI and V-MFI membranes were found active for the ODHP at 550°C, but behaved differently according to the O_2 partial pressure leading to slightly better propene yield for the V-MFI. Acid sites related to some aluminum insertion during the hydrothermal synthesis are likely to be responsible for the MFI membrane activity. The vanadyl sites present in the V-MFI would contribute to the improved performances of this membrane. The oxygen distributor configuration was not found to improve the V-MFI performance in the flow-through configuration, possibly due to back mixing and residence time effects. However, in spite of the very low vanadium content in this V-MFI membrane, a promising propene yield up to 8% was obtained at 550°C with a selectivity in the range 40–50%.

Both MFI and V-MFI membranes were thermally stable for cycles between 500 and 650°C in ODHP conditions (i.e. in the presence of water). Indeed the initial permeance and catalytic performance were restored after 200 h ODHP test. The direct insertion of a very low vanadium content during the formation of the silica rich zeolite framework lead to stable V-MFI/α-Al_2O_3 composite membranes. In such membranes the vanadium active sites does not seem to migrate or alter the zeolite framework in ODHP conditions.

Further improvements of the V-MFI membrane material composition (elimination of aluminum and polymeric V species) as well as a modification of the oxidative gas reactivity (N_2O instead of O_2) will be attempted to improve the catalytic performance of these original and stable membranes.

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