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Mesoporous nickelsilicate membranes on porous alumina supports
I. Effect of nature and surface pretreatment of alumina supports on the catalytic membrane formation

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Abstract

Ordered mesoporous nickelsilicate catalytic membranes have successfully been synthesized on the surface of γ-alumina disk and α-alumina tube by dip coating and immersion. The surface of the supports was cleaned and chemically modified by a series of aqueous solutions. The resulting films and bulk materials have been characterized by XRD, N_2 adsorption–desorption, SEM and TEM. Gas permeation testing was carried out in a Wicke–Kallenbach cell to evaluate the separation properties of the synthesized membranes. The formation, morphology and permeation properties of the membranes have been correlated with the nature of the alumina supports, their surface treatment, and conditions of the hydrothermal synthesis. The lower permeance for oxygen molecules has been explained by a chemical effect. The different permeance between methane and propane through the membranes results most probably from the different diffusion constraints of the two molecules, i.e. a physical effect.

1. Introduction

M41S molecular sieves are recognized as materials with important potentials in various fields [1–4]. Their adsorption capacities and molecular sieve properties, combined with their potential catalytic performances, have attracted great interest in the synthesis of mesoporous MCM-41 membranes on various substrates. These inorganic membranes with well-defined pores, similar to the zeolite membranes [5–8], have very important and very promising applications with respect to separation, purification and catalysis.

Incorporation of transition metals into the MCM-41 network conducts to the catalytically active materials in the oxidation reactions with hydrogen peroxide [9–12]. Preparation of M^{n+}-MCM-41 molecular sieves by direct synthesis is the most common method reported [11–16]. However,

in general, transition-metal-containing MCM-41 molecular sieves are obtained in the powder form, and the synthesis method of these materials in the form of a thin layer needs to be developed.

The present paper deals with two important aspects related to the synthesis and properties of Ni-MCM-41 membranes: the sensitivity of the surface of alumina support to the pretreatment conditions and effects of the alumina surface pretreatment and hydrothermal treatment on the film morphology, structure, and molecular sieve properties. Two new methods for the synthesis of Ni-MCM-41 catalytic membranes on alumina disk or tube have been developed. The mesoporous membranes synthesized could be the efficient catalysts for oxidation of hydrocarbons.

2. Experimental

2.1. Membrane preparation

The synthesis of nickelsilicate membranes on alumina supports (disk and tube) was performed in three steps: 1)

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pre-treatment of the alumina supports, 2) preparation of the nickelsilicate gels and 3) formation of the membranes by hydrothermal synthesis in a stainless steel autoclave [17].

2.1.1. Pre-treatment of the alumina supports

γ-Alumina disk ($\varnothing = 28.5$ mm and 3 mm in thickness, 0.5 μm diameter of the pores and surface area of 186 m^2/g) and α- alumina tube (12.3 mm o.d. and 8 mm i.d. 0.2 μm diameter of the pores and surface area of 14.9 m^2/g) were cleaned in an ultrasonic bath containing a mixture of 2-propanol, ethanol, and water (1:2:2 volume ratio) acidified with HCl. To study the effects of surface functional groups on the membrane formation, the supports were wetted, from 0.5 to 12 h, with an aqueous solution of a single component such as NaOH, NH$_4$OH, and TMAOH or a mixture of NH$_4$OH + TMAOH, NH$_4$OH + CTMAB and TMAOH + H$_2$O$_2$. After wetting, the pretreated supports were dried 2 h at 373 K before further utilization.

2.1.2. Preparation of the nickelsilicate gel

Nickelsilicate gel with the molar composition of 1.00SiO$_2$:0.04 Ni^{2+}:0.48CTMAB:0.28Na$_2$O:2.70TMAOH: 196.00H$_2$O was obtained by mixing an aqueous solution of sodium silicate containing 25.5–28.5 wt.% of silica, Ni(CH$_3$COO)$_2$·4H$_2$O, cethyltrimethylammonium bromide (CTMAB), tetra-methylammonium hydroxide (25 wt.% TMAOH in water). The pH was modified to 10.5 by adjusting the amount of H$_2$SO$_4$ added and the gel was aged in air under ambient conditions for 2 days.

2.1.3. Preparation of the membranes

Two membrane preparation methods were used. Firstly, after loading the gels in autoclaves, the cleaned and pretreated alumina disks were immersed in the gels and one face of the disk was protected. For the α-alumina tubes, the gel was introduced into the tube. Secondly, a thin layer of the prepared gel was deposited on the top surface of the γ-alumina disk by dip coating. The thin layer of the gel coated on the alumina support was hydrothermally treated under vapor of the same gel in autoclave. The hydrothermal treatment was carried out, under static conditions, at 373 K for 5 days. After the hydrothermal treatment the supported films were washed with distilled water, cleaned in ultrasonic bath, dried at 373 K and calcined at 823 K.

2.2. Membrane characterization and gas permeation measurements

The starting supports and the membranes obtained were characterized by X-ray diffraction (Philips PW 170 diffractometer), N$_2$ adsorption–desorption (Tristar, Micromeritics), scanning electron microscopy (SEM, Philips XL-20 microscope), transmission electron microscopy (TEM, Philips Tecnai microscope) and porosimetry (Colter porosimeter). XRD and SEM measurements were directly made using supported membranes, while TEM and N$_2$

adsorption–desorption measurements were performed by using only the membrane part after a careful separation of membranes from the supports. The pore size distribution was determined by the BJH method using the adsorption branch of the isotherm.

Permeation of O$_2$, CH$_4$ and C$_3$H$_8$ through nickelsilicate membranes was investigated in thermostatted Wicke–Kallenbach cell at 295 K. The concentration of the permeated gas was determined by gas chromatography.

3. Results and discussion

3.1. Synthesis and characterization

The effect of pretreatment time and solution on the formation of nickelsilicate catalytically active membranes on the γ- and α-alumina supports was investigated.

3.1.1. Membranes formed on γ-alumina

The nucleation and binding of the ordered mesoporous layer on the surface are very sensitive to the pretreatment of the γ-alumina. γ-Alumina surface after pretreatment under the basic conditions contains a high concentration of O$^-$ and OH functional groups. This very active surface can adsorb a high amount of cations (NH$_4^+$, TMA$^+$, Na$^+$, and CTMA$^+$).

Membranes synthesized on γ-alumina, pretreated with different aqueous solutions, have various morphologies (Figs. 1 and 2). The homogeneous nickelsilicate membranes were obtained on γ-alumina treated with aqueous solution of TMAOH + H$_2$O$_2$ (Fig. 1a and b) and TMAOH if wetting time is shorter (Fig. 2a and b). Pretreatment with aqueous solution of NH$_4$OH (Fig. 1c and d) conducts to membranes with low uniformity and cracks. Membranes containing the zeolite or amorphous phases with very small particles (not shown here) were obtained after pretreatment with NaOH solution.

The dependence of the film thickness and morphology on the experimental conditions was evidenced for two types of nickelsilicate films obtained by hydrothermal treatment in gel or vapor atmosphere. Fig. 3 demonstrates the influence of the coating method and the atmosphere of the hydrothermal treatment on the surface morphology. These membranes were synthesized on γ-alumina pretreated with an aqueous solution of TMAOH. Fig. 3a shows a membrane obtained from a gel deposited on the support by dip coating and subjected to hydrothermal treatment in the vapor of the same gel present in the autoclave. The membrane shown in Fig. 3b was hydrothermally synthesized by immersion of the pretreated support in the gel. It is obvious that the membrane synthesized by dip coating is relatively homogeneous in spite of some roughness.

Our study shows a significant effect of time of the pretreatment on the morphology, thickness, and uniformity of the membrane surface. Increasing pretreatment time can increase the size of the particles, which results in the formation
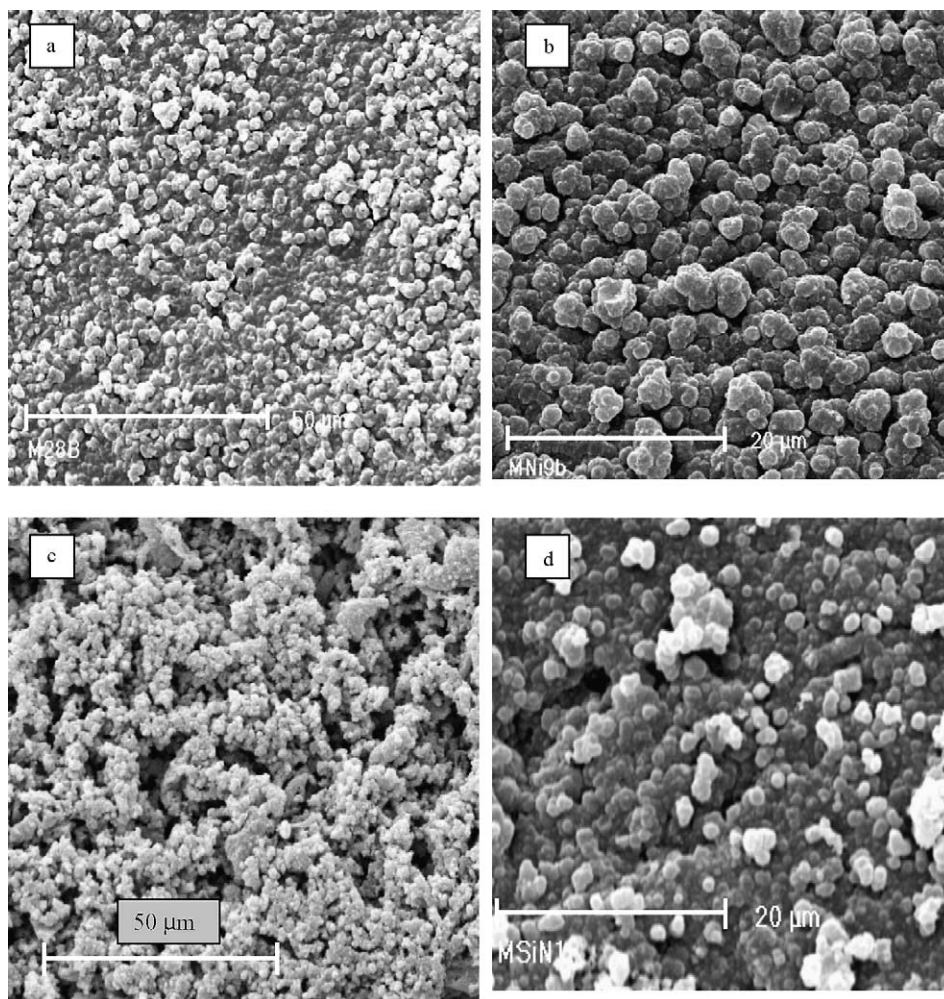
Fig. 1. SEM images of the nickelsilicate membranes synthesized on γ-alumina pretreated for (a) 2 h and (b) 12 h with aqueous solution of TMAOH + H_2O_2, and for (c) 2 h and (d) 12 h with aqueous solution of NH_4OH.

of the aggregates (Fig. 2c), leading to a less homogeneous membrane. SEM images of the membranes obtained by immersion of the support into nickelsilicate gel and hydrothermal treatment during 1, 2, 3, or 5 days show the formation of membrane only after 2–3 days. Thickness of the membranes synthesized for 5 days is very high, with a bad uniformity of the surface. The N_2 adsorption–desorption isotherms confirmed the presence of mesopores in the nickelsilicate membranes obtained by immersion into the gel of the γ-alumina support treated with aqueous solution of TMAOH + H_2O_2. The specific surface area is very high (850–950 m^2/g) and the pore size distribution is very narrow and centered at values of around 2.9 nm.

3.1.2. Membranes formed on α-alumina

The surface of α-alumina is not very sensitive to the variation in pretreatment. The same morphology was observed for all the membranes (Fig. 4). Typical features in these images are the small sized and homogeneously distributed particles on the substrate surface. Fig. 4d depicts a cross-section view of nickelsilicate membrane synthesized on α-alumina

pretreated with aqueous solution of TMAOH + H_2O_2. A difference in the particle size between the outer and inner layers of the film was observed for all the membranes (Fig. 4d). The particle size of outer layers is much smaller than that of the inner layers. Fig. 5 compares the particle morphology of a typical nickelsilicate membrane synthesized on α-alumina and of a typical highly ordered mesoporous nickelsilicate in powder form. No difference is observed. It is clear that nickelsilicate in membranes or in the powder form have the same morphology as reported in literature [12–20].

3.2. Structural characterizations

TEM image (Fig. 6) of the membrane synthesized on γ- and α-alumina supports exhibit a typical ordered mesoporous structure with a hexagonal channel array of pore systems. In Fig. 7 are presented XRD patterns of the membranes synthesized on γ-alumina pretreated with the mixture of TMAOH + H_2O_2, with NH_4OH and the nickelsilicate powder obtained in the same autoclave. One very intense reflection peak at around 2° (2θ) and two other reflection
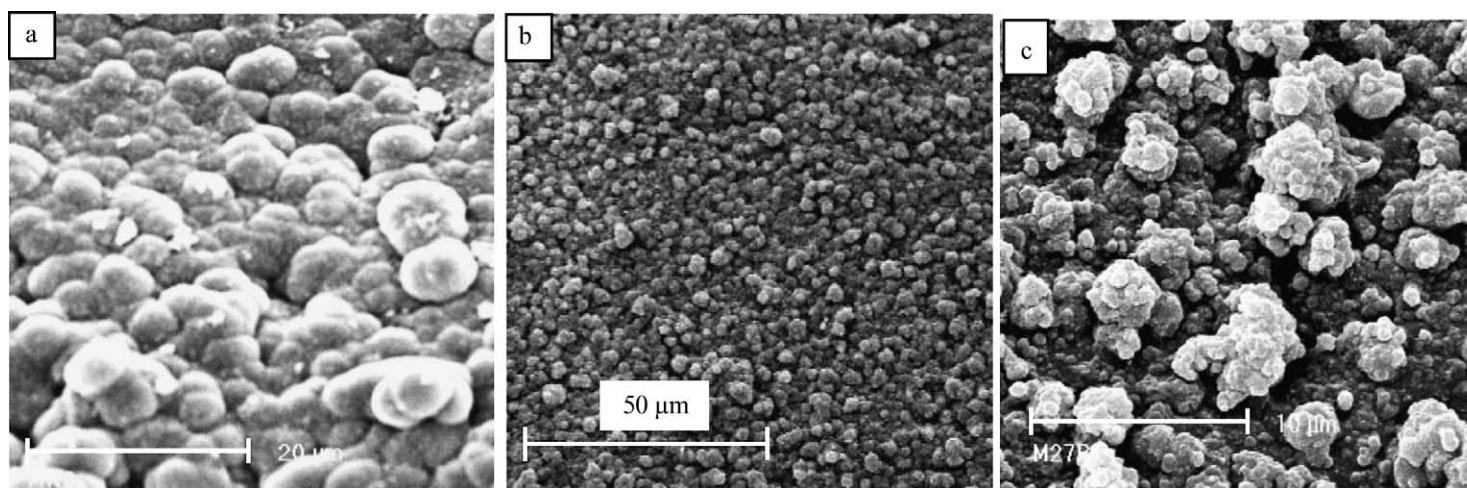
Fig. 2. SEM images of the nickelsilicate membranes synthesized on γ-alumina pretreated for (a) 0.5 h, (b) 2 h, and (c) 12 h with aqueous solutions of TMAOH.
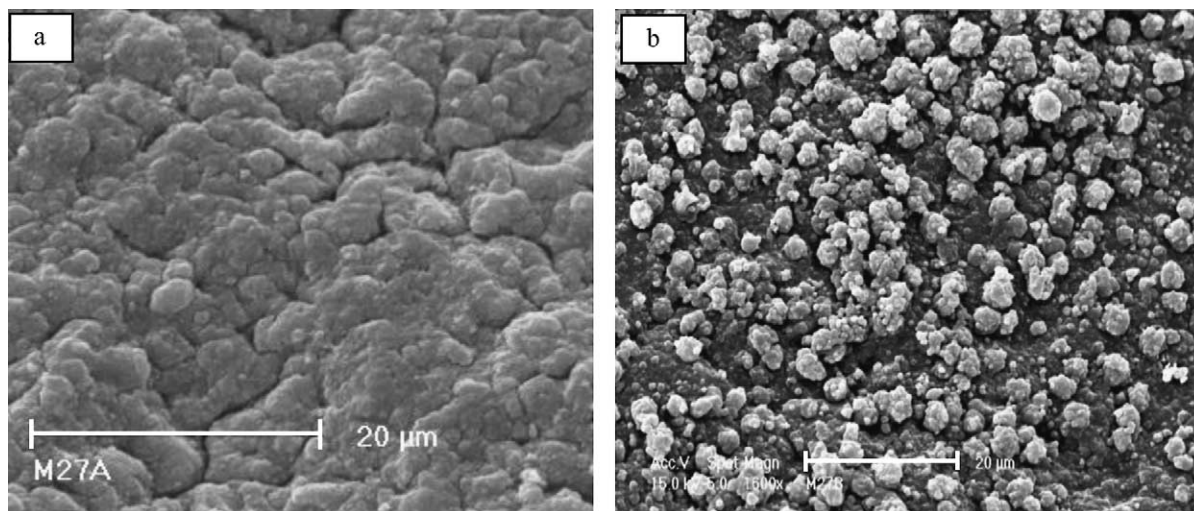
Fig. 3. SEM images of the membranes obtained by (a) dip coating and treatment in the vapor atmosphere and by (b) immersion and treatment in the gel.
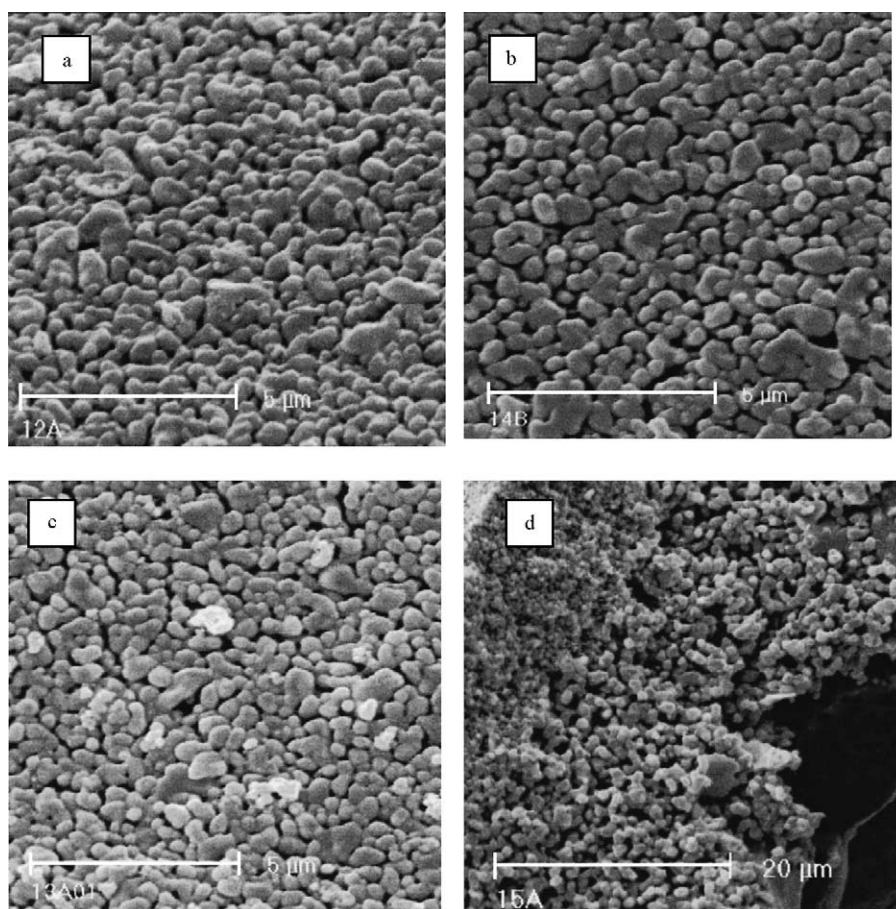

Fig. 4. SEM images of the membranes synthesized on α-alumina tubular support: (a) untreated; and pretreated with an aqueous solution of (b) NH_4OH, (c) $NaOH + H_2O_2$ and (d) $TMAOH + H_2O_2$.
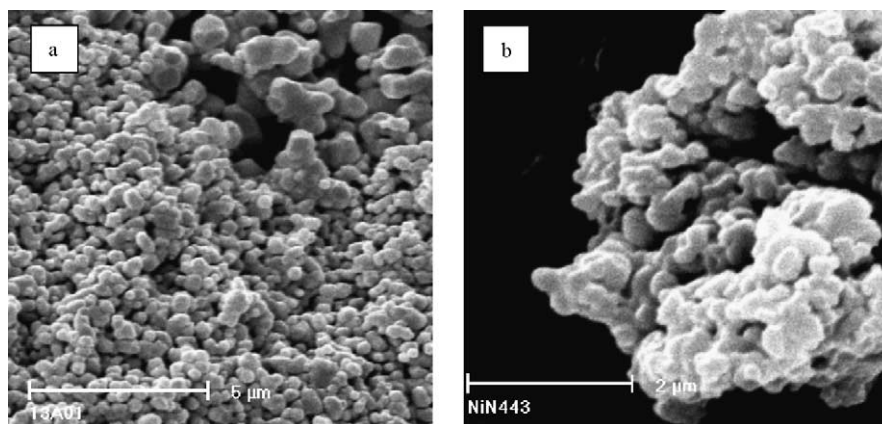
Fig. 5. SEM images of the sectional view of (a) nickelsilicate film synthesized on α-alumina pretreated with an aqueous solution of TMAOH + H_2O_2 and of (b) nickelsilicate powder obtained from the gel in autoclave.
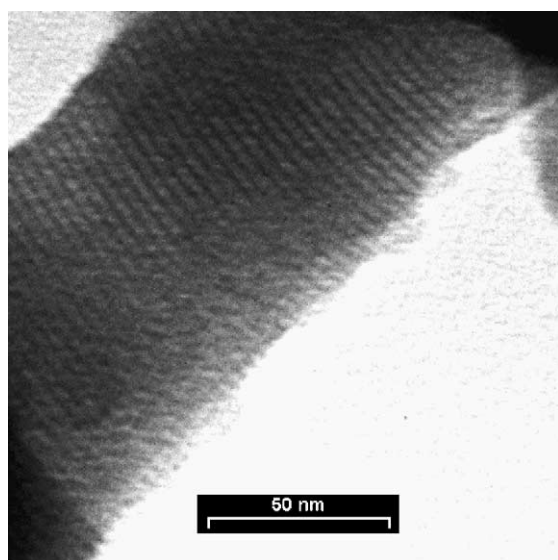

Fig. 6. TEM image of the nickelsilicate material of the membrane synthesized on γ-alumina pretreated in an aqueous solution of TMAOH + H_2O_2.

Fig. 7. XRD patterns of the nickelsilicate powder and membranes synthesized on γ-alumina pretreated in two different aqueous solutions.

XRD, N_2 adsorption–desorption, and SEM results confirm the MCM-41 structure of our membranes [12,13].

3.3. Gas permeation

The porous properties and quality of the as-synthesized membranes were evaluated by gas permeation. A variation of single-gas permeance with solution and time of pretreatment was observed (see Table 1). The permeance of methane and propane (Fig. 8) through the MS27 membrane

lines in the range of 3–5° (2θ) are present and characteristic of the mesoporous MCM-41-type structure. The intensity of all these peaks of membranes is less important compared with that of Ni-MCM-41 in powder form due to the difficulty in measurements. Nevertheless, all the TEM,
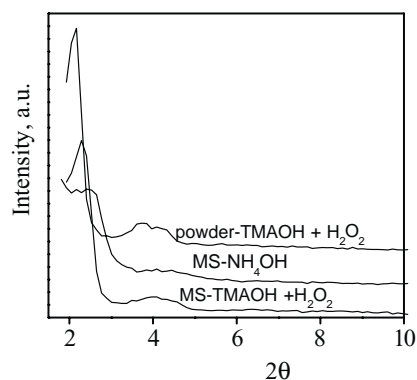
Table 1

Results of gas separation of the binary mixtures at 296 K by supported nickelsilicate membranes

ΔP (10^{-2} Pa)	Selectivity, CH_4/O_2			Selectivity, CH_4/C_3H_8			Selectivity, C_3H_8/O_2		
	MS9	MS27	MS28	MS9	MS27	MS28	MS9	MS27	MS28
0.6	81.7	165.8	41.7	4.2	2.2	2.6	19.4	76.5	16.1
3.3	107.7	224.0	57.9	3.6	2.1	6.8	30.1	104.4	8.5
4.3	109.1	120.3	53.3	3.2	2.9	6.3	34.0	41.5	8.5
6.1	84.7	122.6	51.3	3.3	2.7	6.5	25.5	45.0	7.9
7.8	71.0	98.1	42.8	2.3	2.1	5.3	31.2	46.2	8.1

MS9: synthesized on γ-alumina pretreated for 12 h with aqueous solution of TMAOH + H_2O_2; MS27: synthesized on γ-alumina pretreated for 2 h with aqueous solution of TMAOH; MS28: synthesized on γ-alumina pretreated for 2 h with aqueous solution of TMAOH + H_2O_2.
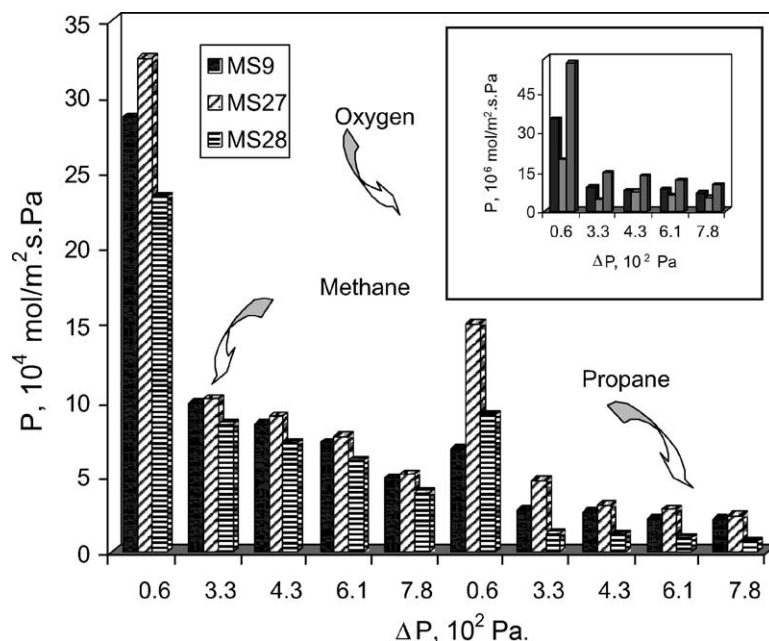
Fig. 8. Single-gas permeances at 296 K as a function of transmembrane pressure for three MS membranes (MS9, MS27, and MS28).

(synthesized on γ-alumina pretreated for 2 h with aqueous solution of TMAOH) is higher under any ΔP value in comparison with that of MS28 and MS9 membranes (synthesized on γ-alumina pretreated for 2 and 12 h, respectively, with aqueous solution of TMAOH + H_2O_2). However, the permeance of O_2 is the lowest for the MS27 membrane among the three membranes studied. It is evident that the pretreatment of the alumina surface influences the adsorption properties of the nickelsilicate surface. Permeance of oxygen is lower for the membranes pretreated with aqueous solution of TMAOH but higher for the membranes pretreated with aqueous solution of TMAOH + H_2O_2. Time of pretreatment of the γ-alumina support with TMAOH+H_2O_2

also influences the permeance of the hydrocarbons. Longer the wetting, the higher the permeance of hydrocarbons, but lower the permeance of oxygen. Nevertheless, in comparison with that of the hydrocarbons, the permeance of oxygen is quite low on these three membranes (Figs. 8 and 9), indicating a high affinity of these three membrane with oxygen molecules. This is most probably due to the possible interaction of oxygen molecules with the active Ni sites incorporated in the MCM-41 framework, reducing its permeance through the membranes. This is a chemical effect.

The influence of transmembrane pressure (ΔP) on the permeation through membranes was noted only for the lower values. The permeance decreases with increasing
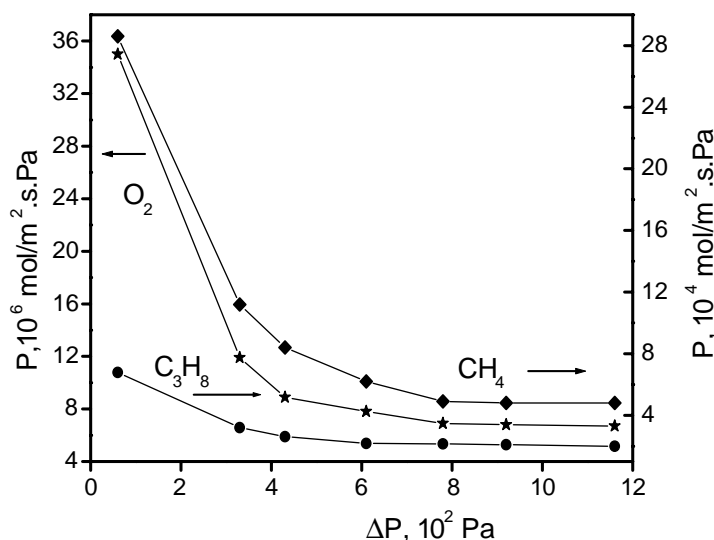

Fig. 9. Single-gas permeances at 296 K as a function of transmembrane pressure for the MS9 membrane.

ΔP values. The difference observed in the permeance of methane and propane seems to indicate a strong molecular size effect (Fig. 8) since methane molecules permeate more easily than propane molecules although propane molecule is only slightly larger than the methane molecule and the membranes used are mesoporous. This molecular size effect can most probably be attributed to the diffusion rate of these two molecules. It is obvious that methane molecules diffuse more quickly due to its smaller size. This behavior of membranes explains their potential for use in separation processes.

Although the change in single-gas permeances with different kinetic molecular diameter is a good indication of membrane quality, single-gas permeance cannot be correlated with separation selectivity because of competitive adsorption. Separation is possible by preferential adsorption, molecular sieving and differences in diffusion and flow rates. All these three membranes show a good selectivity of hydrocarbons/O_2; moreover, the MS27 membrane has the highest CH_4/O_2 and C_3H_8/O_2 selectivity because it has the lowest oxygen permeance.

4. Conclusions

Ni-MCM-41 catalytic membranes were prepared on pretreated γ- and α-alumina supports by two methods: dip coating and immersion. The structure, morphology, and permeation properties of nickelsilicate membranes synthesized on γ-alumina supports are very sensitive to the pretreatment of the substrate. The morphology of membranes observed on α- alumina supports is the same. The lower permeance of oxygen is explained by the interaction of oxygen molecules with Ni—which are catalytically active sites—incorporated in the mesoporous framework, while the difference in permeance between methane and propane is thought to be due to the different diffusion rates of these two molecules. The separation efficiency of hydrocarbons/oxygen is very high, indicating the potential use of these membranes in the separation processes.

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