ON STRUCTURE AND CATALYTIC ACTIVITY OF MEMBRANES OBTAINED FROM MCM-41 MOLECULAR SIEVES WITH TRANSITION METAL CATIONS

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abstract: Mesoporous Ni-MCM-41 mesoporous sieves powders and membranes have been synthesized. The resulting films and bulk materials have been characterized by XRD, N2 adsorption-desorption, SEM and TEM. The obtained materials were tested in oxidation of aromatic hydrocarbons with hydrogen peroxide. Comparative experiments of the membrane reactor and static reactor with the same catalyst (Ni-MCM-41) in power form showed higher reaction rates, the control of the feed of oxygen peroxide in the reaction side and a higher selectivity to styrene oxide.

1. Introduction

Nanostructured materials present advantages to facilitate a direct connection between the inorganic, organic and biological worlds. The ability to assemble and organize different components in a single material represents a very attractive direction for developing novel multifunctional materials presenting a wide range of novel properties [1]. Soft chemistry based processes (low temperature and pressure) offer new methods to obtain tailored nanostructyre materials. However, the resulting nanostructures, their degree of organization, and thus their properties certainly depend on the chemical nature of their organic and inorganic components, but they also rely on the synergy between these components [2]. The growth of soft chemistry derived inorganic or hybrid networks templated by organized surfactant assemblies, named structure directing agents allowed construction of a new family of nanostructured materials in the mesoscopic scale (2-100 nm). The mesoporous materials like MCM-41 were obtained by tailoring of silicate network with surfactant and opened new opportunities to develop catalysts systems for fine chemicals. Many efforts have been undertaken to geherate catalytic active sites in this material. Especially the preparation of redox catalysts by modification of silica-based MCM-41 material has been reported using transition metal oxides [4-6]. MCM-41 molecular sieves, with high surface area, porosity and a large number of silanol groups

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offer the possibility to graft the active species or to incorporate directly the metal ions inside the mesoporous framework by substitution of Si atoms in regular tetrahedral positions. Transition Ti, V, Mn, Fe, Co, Cr, Mo, Ni. Fe were introduced in meso-porous MCM-41 molecular sieves by direct synthesis [5-7]. The serious effort has been devoted to studying the catalytic properties of these so-called redox molecular sieves in the liquid phase oxidation of organic compounds [7-10]. In general, transitional metals-containing MCM-41 molecular sieves are obtained in powder form. Ordered mesoporous nickelsilicate membranes have successfully been synthesized on the surface of γ-alumina disk and α-alumina tube by dip coating and immersion [11]. The formation, morphology and permeation properties of the membranes have been correlated with nature of alumina supports, their surface treatment and conditions of the hydrothermal synthesis. The results show a strong effect of the pretreatment of the γ-alumina supports and hydrothermal treatment on the structure, morphology, uniformity, thickness, permeation and catalytic properties of the films [11,12]. The paper present the effects of structure and morphology of membranes on their permeability and catalytic properties. The membranes were synthesized by two different methods from a a gel with the same composition with Ni-MCM-41 powder.

2. Experimental

Ni-MCM-41 materials were synthesized by hydrothermal treatment using gel molar composition of 1.0 SiO_2: x Mn^+: 0.48 CTMAB: 0.28 Na_2O: 3.7 TMAOH: 196 H_2O (x= 0.02 for powder and 0.04 for membranes). The gel obtained was sealed into Teflon-lined steel autoclaves and heated 5 days at 373K. The solid products were recovered by filtration, washed and dried in air. The as-synthesized samples were calcined at 773K in a flow of N_2 followed by air. [9]. The synthesis of nickelsilicate membranes on alumina supports (disk) was performed in three steps: pre-treatment of the alumina supports, preparation of the nickelsilicate gels and finally formation of the membranes by hydrothermal synthesis in a stainless steel autoclave [13]. Two membrane preparation methods were used. Firstly, after loading the gels in autoclaves, the cleaned and pretreated alumina supports 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 alumina support was hydrothermally treated under vapor of the same gel in autoclave.

The membranes obtained and powders materials were characterized by X-ray diffraction, N_2 adsorption-desorption scanning electron microscopy and transmission electron microscopy. The reaction temperature and time varied from 297 to 343 K, 6 to 12 h respectively. The molecular sieves were tested in catalytic oxidation reactions of styrene and benzene with hydrogen peroxide. In the catalytic membrane reactor the molar ratio of hydrocarbon/acetonitrile/hydrogen peroxide was controlled by the permeability of the components through the membranes. Permeation measurements of the H_2O_2 and aromatic hydrocarbons were carried out in the reactor conditions.

3. Results

MCM-41 silicates with Ni isomorphously substituted into their structures were prepared as powder and membranes. These membranes were synthesized on pretreated γ-alumina support by two hydrothermal methods. The ordered mesoporous nickelsilicate membranes were obtained on γ-alumina treated with an aqueous solution of TMAOH+H_2O_2 (Fig. 1) or TMAOH.
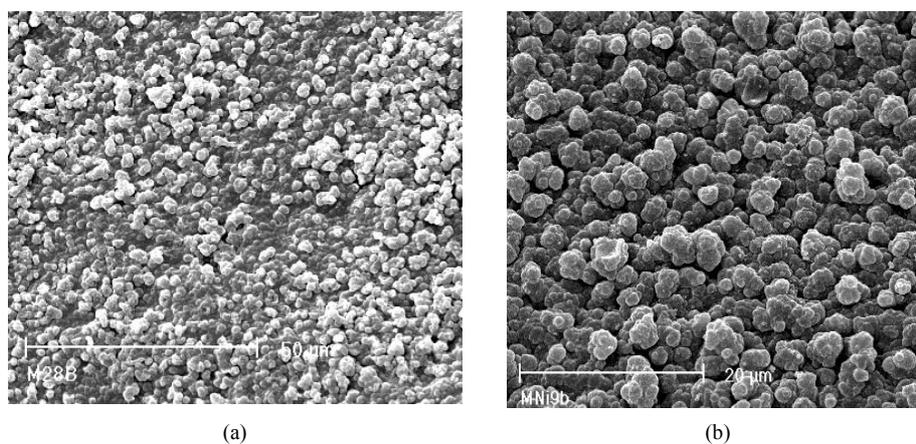

<div align="center">(a)   (b)</div>

Fig. 1 *SEM images of the nickelsilicate membranes synthesized on γ-alumina pretreated during 2 (a) and 12 h (b) with aqueous solution of TMAOH+H_2O_2.*

Membranes containing the zeolite with ordered crystals were obtained after hydrothermal treatment under autogeneous atmosphere of the aqueous ammonia solution. SEM images of these samples show the formation of hexagonal pillars perpendicular oriented on the surface. The ordered structure with hexagonal arrangement of channels of our materials was further confirmed by TEM for all the samples (Fig. 2). TEM images of the membrane syntheses on γ-alumina supports exhibit a typical ordered mesoporous structure with a hexagonal channel array of pore system.

The XRD patterns of calcined powder and membrane materials show diffraction lines characteristic of mesoporous materials with hexagonal arrangement of their cylindrical channels. This indicates that all the prepared catalysts have a structure comparable to that of Si-MCM-41 [14]. Ni-MCM-41 prepared as membrane gives a less well resolved XRD pattern.

The XRD patterns of Ni-MCM-41 membranes obtained on γ-alumina pretreated with NH_4OH aqueous solutin are also less well resolved. 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 are presented in Fig. 3. One very intense reflection peak at around 2° (2θ) and two other reflection lines is the range of 3-5° (2θ) are present and characteristic of mesoporous MCM-41 type structure. All the TEM, XRD and SEM results confirm the MCM-41 structure of our powders and membranes.
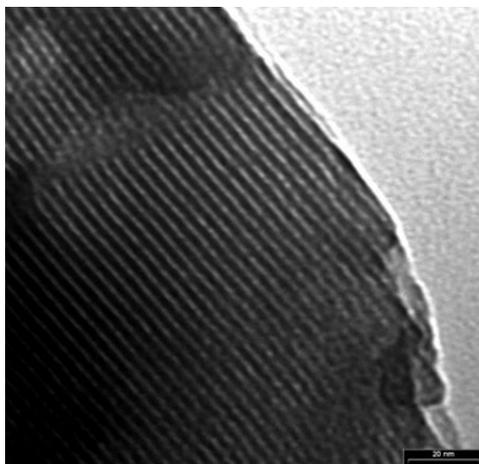
Fig. 2 *TEM images of Ni-MCM-41 material*

Thickness and uniformity of the membranes can be controlled by the time of the pretreatment and the hydrothermal treatment. 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 sizes of the particles and long time pretreatment (12 h) results in the formation of the aggregates. The N_2 adsorption-desorption isotherms and the porometry measurements confirmed the presence of mesopores in the nickelsilicate membranes obtained by immersion into the gel of the γ-alumina support treated with an aqueous solution of TMAOH+H_2O_2. The specific surface area is very high (850-950 m^2/g) and the very narrow distribution size centered at the values around 2.9 nm.
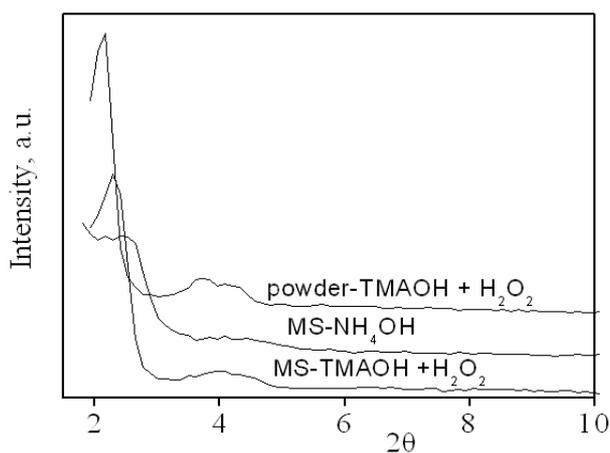

Fig. 3 *XRD patterns of Ni-MCM-41 powder and membrane*

The ordered mesoporous nickelsilicate powder or membranes synthesized on γ-alumina [11,12] were utilized in oxidation of benzene and styrene with H_2O_2 in the catalytic reactor. The catalytic oxidation reactions of styrene and benzene were performed, for powder, using

a 25 cm^3 glass flasks or Teflon lined autoclaves with magnetic stirring for 12 hr in a temperature range of 203-343K using an oil bath. In the membrane reactor the organic substrate and aqueous oxidant are contacted through the catalytic membrane.
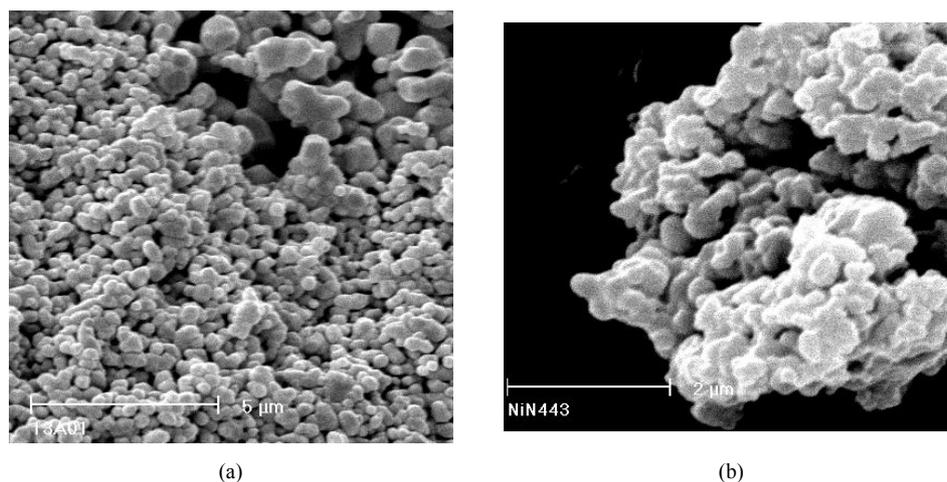

(a)   (b)

Fig. 4 *Morphology and structure of Ni-MCM-41 materials from the membrane* (a) *and powder* (b).

The variation of conversion and selectivity in the catalytic membrane reactor was correlated with conditions of the membrane synthesis and catalytic reaction. A comparison with conventional catalytic reactor for the oxidation in liquid phase is presented too. Morphology of powders and membranes with Ni-MCM-51 molecular sieves are spherical and similarly (Fig. 4).

In Fig. 5 the conversion of styrene and selectivity to epoxide are plotted against the reaction time. In the catalytic reactor with nickelsilicate membrane, the conversion of the aromatic hydrocarbons and rate in the first step of reaction increases and the oxidation of styrene is selective to epoxide.

The higher activity was obtained for the membranes synthesized on the γ-alumina pretreated 2 h with aqueous solution of TMAOH (MS27). Permeation of the hydrocarbons, in gas and liquid phase, is higher than that of the membranes synthesized on alumina pretreated with aqueous solution of TMAOH+H$_2$O$_2$ (MS9, MS28). These properties result from selective adsorption of the hydrocarbons in presence of air or aqueous solution.

A high activity and selectivity to epoxide and phenol were obtained on MS28 membrane. The pretreatment of the support in oxidative conditions conducts to formation of nickelsilicate membrane with very active sites in activation of H$_2$O$_2$. The high time of the pretreatment decreases the permeation and reactivity of the membranes (MS9). The conversion of aromatic hydrocarbons increases with temperature, time of the reactionand permeance of H$_2$O$_2$ until a permeance of 8.6 .10^{-6} mol/m^2.s. After this value effect of the permeance is insignificant. A higher conversion is maintained when the feed with H$_2$O$_2$ is constant and not very high.
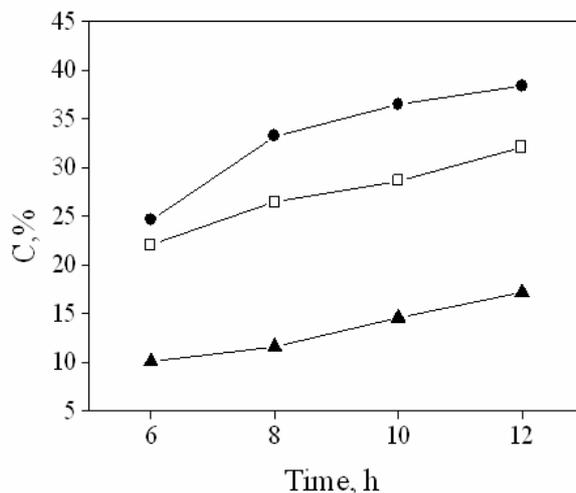
Fig. 5 *Variation of styrene conversion in time for various permeance values*
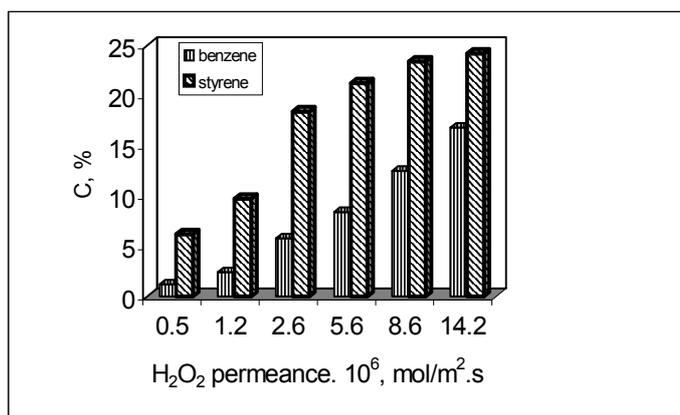

Fig. 6 *Conversion of styrene and benzene as a function of H2O2 permeance*
(MS-28, time-6 h)

The conversion of aromatic hydrocarbons increases with temperature, time of the reaction and permeance of H_2O_2 until a permeance of $8.6 \cdot 10^{-6}$ mol/m^2.s. After this value effect of the permeance is insignificant. A higher conversion is maintained when the feed with H_2O_2 is constant and not very high.

The conversion of styrene is higher in the membrane reactor compared with static reactor (Fig. 6). In oxidation of styrene with H_2O_2 on Me-MCM-41 catalysts (Me-transitional metals) the reaction rate is lower in the first 12 h of reaction [13]. Introduction of the H_2O_2 step by step increases significantly the rate of reaction in the first 10- 20 h. Comparatively with the normal non-separative reactor, the control of the H_2O_2 feed increases the conversion of hydrocarbon in the first hours, and the efficiency of the H_2O_2. In the membrane reactor the feed with H_2O_2 in the reaction side is controlled by the permeance

through membrane. A variation of the pressure in the feed room favours the control of the rate of the oxidation.

4. Conclusions

Nickelsilicate powder or membrane were obtained by structure directing agents network with using the surfactants. The obtained material is powder or membrane. The mesoporous molecular sieves were tested in a selective oxidation of styrene to benzaldehide, for powder or epoxide, for catalytic membranes and benzene to phenol. The membrane offers a very good possibility to the control of feed with hydrogen peroxide and to increase of the reaction rate in oxidation of the hydrocarbons and selectivity in oxidation of styrene to epoxide. The oxidation of styrene by means of a porous nickelsilicate membrane was carried out to give a high conversion in a lower reaction time compared with a normal non-separative reactor.

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