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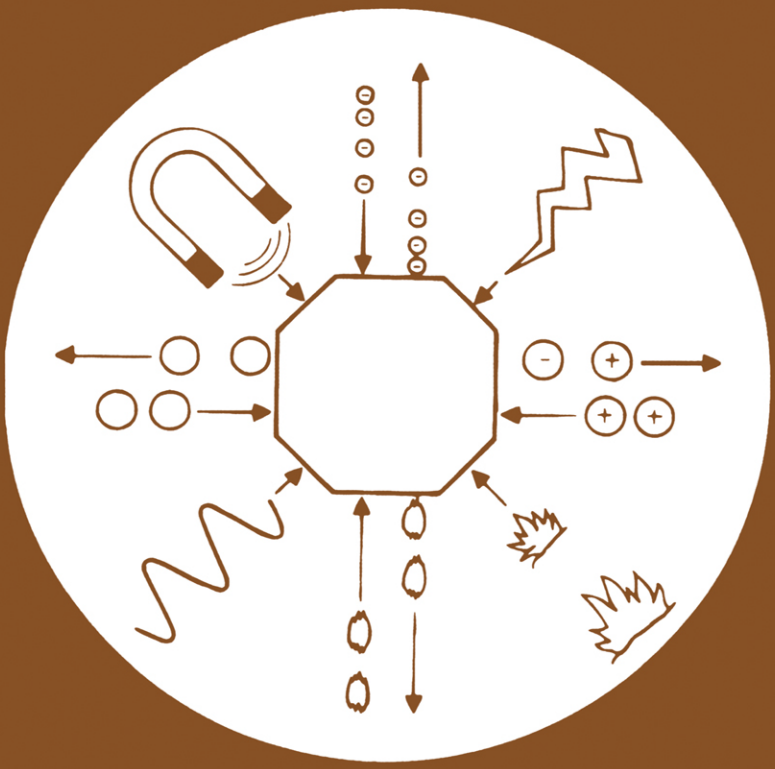

125

POROUS MATERIALS IN ENVIRONMENTALLY FRIENDLY PROCESSES

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(editors)

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POROUS MATERIALS IN ENVIRONMENTALLY FRIENDLY PROCESSES

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ENVIRONMENTAL APPLICATIONS

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Preface

To leave our planet liveable in the next millennium mankind is forced to find environmentally friendly ways in solving the problems of everyday life. Among others, technologies of producing chemicals, absolutely necessary for maintaining a comfortable life, have to be modified, in some instances fundamentally changed now, or in the very near future. We badly need zero emission chemical processes, either by increasing the selectivity to 100 per cent, or by enabling complete recycling of unnecessary or even harmful by-products, turning them into useful materials. This shift in paradigm calls for new reactions and since chemical production is largely based on catalytic processes, new catalysts. Developing new technologies requires strong and innovative fundamental research. In order to provide opportunity for crossfertilization the *Federation of European Zeolite Associations* decided to organise a conference, where researchers from academia as well as industry can meet, exchange ideas, show and discuss research efforts and results concerning the development of environmentally friendly processes and technologies.

Contributions of internationally renowned researchers are collected in this volume. The conference and thus the Proceedings is divided into two main parts. The first part contains works concerning the synthesis, modification and characterisation of zeolitic materials as catalyst candidates in environmentally friendly technologies. Works in the second part describe various applications starting from developing highly selective reactions for the fine chemical industry, through waste-water treatment to applying zeolite for formulating bacteria for pest control. Highly reputed scientists review the state-of-the-art at the beginning, thus, setting a high standard. The thorough work of the authors as well as the referees contributed to maintaining high quality.

Now, the editors are pleased to hand over this volume to the participants of the conference as well as the whole scientific community hoping that it will be an indispensable source-book of ideas for further works, thus serving the goal of preserving our planet for us and our successors.

THE EDITORS

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I. Kiricsi, G. Pál-Borbély, J.B. Nagy, H.G. Karge (Editors)
Porous Materials in Environmentally Friendly Processes
Studies in Surface Science and Catalysis, Vol. 125

Application of Zeolite Membranes, Films and Coatings

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Preparation methods of zeolite molecular sieve membranes and films with and without support were reviewed. Unsupported films have been prepared by in situ synthesis, casting of zeolite nanoparticles and solid state transformation, and supported films have been obtained by in situ synthesis, vapor-phase synthesis, secondary growth, casting of nanoparticles and their combinations or modifications. It is favorable to use supports to give mechanical strength to the zeolite films. In the film synthesis of AFI and MFI type zeolites on the substrates with flat, smooth and polished surfaces, the crystals tend to be oriented, and among the preparation procedures, secondary growth method, especially, secondary growth procedure using a surface modifier is apt to produce oriented zeolite films. The application of pulsed laser ablation and microwave heating to the synthesis of zeolite films is also effective for the densification and orientation.

In the separation of a mixture by the zeolite membranes, the selectivity is a function of the sorption and diffusion, and relative permeances can not be simply predicted on the basis of molecular size or shape alone. Generally the separation selectivity of a mixture does not reflect the single-component permeation ratio. In a mixture, the permeation of weakly adsorbing molecules often drop dramatically in the presence of strongly adsorbing molecules. Nature of zeolites, hydrophobicity or hydrophilicity, straightforwardly reflects the separation of aqueous mixtures, accordingly, in the pervaporation of the mixtures of an organic compound and water, an organic compound is selectively separated with hydrophobic MFI(Si) membranes, on the contrary, water is predominantly removed with hydrophilic LTA and FAU membranes. Permeation properties and separation performances of zeolite membranes are much affected by not only the properties of the membranes but also the operation conditions of the membranes.

Zeolite membranes are also useful for the optical resolution of racemic isomers. Zeolite films can be applied to chemical sensors with high selectivity and sensitivity by making use of the properties such as molecular sieving, hydrophobicity or hydrophilicity. Using zeolite membranes, disks and coatings, esterification, alkylation, synthesis of ether, conversion of methanol, deNOx reaction, hydrogenation and dehydrogenation have been carried out. In those reactions, it has been pointed out that zeolite membranes, disks and coatings show high performance or potential as the catalysts compared with conventional catalysts.

1. Introduction

Inorganic materials are generally much superior in thermal, mechanical and structural stability, and in chemical resistance to organic materials. In recent years, thus, the dramatic development of inorganic membranes, films and coatings has drawn much attention in view of promising applications in separation membranes, catalytic reactors, chemical sensors and opto-electronic devices. Especially, there is strong interest in zeolite membranes and films, because zeoiltes have pores with similar size to small molecules, ion exchange and solid acidity properties, in addition, show different affinities to hydrocarbon molecules depending on the

composition of elements constituting the frameworks. Here, I survey the work of zeolite membranes, films and coatings for the last decade.

2. Preparation

Zeolite membranes and films with and without support have been prepared in various manners, wet or dry, with or without seed, their combinations or modifications, etc.

2.1. Unsupported Film

Unsupported (self-supporting, self-standing) films can be obtained by traditional wet method (hydrothermal synthesis, that is, in situ synthesis) [1-9], casting of zeolite nanoparticles [10,11] and solid state transformation [12-14].

In the in situ synthesis, generally zeolite films are prepared firstly on substrates such as Teflon [1-5], cellulose molding [6], polyethylene [7], and then those substrates are removed by detaching or burning them. In this manner, unsupported films of silicalite, ZSM-5, SAPO and zeolite L have been obtained. These films generally consist of randomly and loosely packed crystals with irregular size, are fragile and have a lot of meso and macro pores, thus can not be used as the membranes for separation or catalytic reaction, although it has been reported that the strength and crystal packing of the film grown on the Teflon are improved, if the synthesis is carried out under a high gravity [15]. Dense films can be obtained without special procedures to remove the substrates, if a liquid surface stable chemically and physically under the synthesis conditions is used as the substrate. Actually, on a liquid mercury surface [8,9], a transparent or translucent film consisting of MFI crystals with uniform size was formed, the thickness was quite uniform for the whole area, and the crystallization rate and crystallinity were much higher than on the Teflon. Furthermore, on the mercury-touching side of the film, the crystals were densely packed to form smooth surface, and the ac faces of MFI crystals preferentially turned up, that is, the crystals were oriented. But, the mechanical strength of the film grown on the mercury surface was not enough, although the film showed a quite high selectivity of 52 for the single gas permeation of n-hexane/2,2-dimethylbutane.

A translucent film without support has been also obtained by casting of zeolite nanoclusters [10,11], in detail, slow evaporation of the water from a zeolite L nanosol placed in a petri dish whose surface was treated with wax. The film obtained is microcrack free and furthermore can be used as a seed sheet for secondary growth of the nanoclusters, but it is very fragile since zeolite clusters are not bonded together.

Thick zeolite films or plates without binder and support have been prepared by solid state transformation [12-14] in which a silica or silica/alumina gel and a layered compound mixed and intercalated with an organic amine, respectively, were shaped in disk form and then heated in a sealed system to be transformed into a zeolite disk. By this way, disks of silicalite, ZSM-5 and ZSM-11 can be obtained. The disks have enough mechanical strength to use as the membranes for separation or catalytic reaction, although they have a lot of meso and macro pores. This solid state transformation can be also useful for obtaining the substrates composed of zeolite crystals only.

2.2. Supported Film

Supported films have been widely and deeply investigated. There are various preparation procedures such as in situ synthesis [16-37], vapor-phase synthesis (dry-gel conversion) [29,38-41], secondary growth [10,11,29,42-46], casting of nanoparticles [47] and their combinations or modifications [29,48-53]. In the dry-gel conversion, sol (silica or silica-alumina) or sol containing an organic template is applied on a substrate by dip-coating, dried and treated with vapors of a template and steam to be transformed to a zeolite layer. In the secondary growth procedure, zeolite nanoparticles are layered or seeded on a substrate and grown to the continuous thin film by usual hydrothermal synthesis. In the modifications, surfaces of the substrates are treated in various manner prior to the film synthesis, as stated later. The substrates used in the film synthesis are varied in shape (plate, tube or honeycomb),

texture (porous or nonporous) and material (stainless steel, silver, gold, copper, alloy, ceramics, alumina, glass, quartz, silicon wafer, silicon nitride, etc.), and many types of zeolites such as MFI, FAU, FER, MOR, LTA, LTL, ANA, UTD-1, TS-1, AFI, SAPO-34 and FeAPO-5 have been manipulated to the thin films so far.

Using an elegant in situ synthesis [36] a bit different from the method stated above, a ZSM-5 layered mullite honeycomb was prepared quite recently. First, a honeycomb made up of clay and cellulose binder by extrusion forming was transformed to a sintered body composed of mullite and silica glass by heating it at 1650 °C. By hydrothermally treating the sintered honeycomb in alkaline solution containing an organic template, the mullite was turned to a porous mullite honeycomb framework by dissolving the silica into the solution, and the silica was transformed to ZSM-5 crystalline layer in situ to completely cover the surface of the honeycomb. This zeolite film showed good adhesion to the substrate and no cracks or pinholes even after it was heated at 900 °C for 60 h.

Besides films composed of single component zeolite crystals, a dense zeolite film consisting of mixed components, or mordenite, ZSM-5 and chabazite [37] has been synthesized onto the inner surface of a porous alumina tubular support by repeating the film synthesis four times. The composition of the gel used for the synthesis was initially optimized for the formation of mordenite. But, during the syntheses, part of the alumina support was dissolved and incorporated into the synthesis gel, and thus other compositions such as ZSM-5 and chabazite were possible.

In the secondary growth method, zeolite nanoparticles are seeded by different manners such as simple coating or adsorption, adsorption after the treatment of substrate surfaces with an organic modifier like a surfactant [29,48-53], and pulsed laser ablation [54,55]. As such modifiers, (3-mercaptopropyl)trimethylethoxysilane, 11-mercapto-1-undecanol phosphorylated, γ-mercaptopropyltrimethoxysilane, a cationic polymer and 3-amino-propyldimethylethoxysilane have been used. Roles of the modifiers are to link zeolite seeds and the substrate, and to balance or adjust their charges during the adsorption. By this type of modification, the zeolite crystals grown from the seeds tend to be oriented and be densely packed, actually the oriented films of $AlPO_4$-5, LTA and A zeolites have been obtained. In addition, this method can produce the ZSM-5 crystalline layer even in the absence of organic templates [50], although certain structure directing agent such as tetrapropylammonium hydroxide is generally essential for the zeolite film synthesis. By the pulsed laser ablation followed by hydrothermal synthesis, partially oriented films of the large-pore zeolite UTD-1 [54] have been obtained, and by the combination of pulsed laser ablation and vapor-phase synthesis, a thin films of FeAPO [55] was obtained.

Besides the laser ablation, the combination of microwave technique and the above synthesis procedures is also interesting [56-59]. In the hydrothermal synthesis of silicalite-1 crystals on a silicon support [56], the oriented film is obtained by microwave heating. On floating porous alumina anodized, vertically well-aligned $AlPO_4$-5 [57] and SAPO-5 [58] films are formed. Microwave heating induces the oriented growth of those crystallites along the c-axis in the channels of the alumina substrate and suppresses the heterogeneous nucleation outside the channels. In the film formation of $AlPO_4$-5 crystals on the quartz surface treated with an organic modifier [59], microwave heating contributes to improved control of both the synthesis of nanosized crystals and the preparation of very thin aluminophosphate film. Generally speaking, using microwave heating can drastically reduce the crystallization times.

Concerning supported films, it has been found so far that the film synthesis and the properties of the film formed are much affected by not only the preparation conditions but also the substrates. Surfaces having hydroxyl groups seem to be relatively preferable as the places for the formation of zeolite films, especially from the viewpoint of adhesion. Roughly speaking, flat, smooth and polished surfaces can contribute to the orientation of the zeolite crystals, and among the synthesis procedures, the secondary growth method tends to produce oriented films more or less. Interestingly, on the anodic alumina substrates, oriented growth of MFI [60] and AFI [61,62] crystals is apt to happen, that is, ZSM-5 crystals grow parallel to or perpendicular to the support, especially $AlPO_4$-5, $VAPO_4$-5 and $CoAPO_4$-5 crystals vertically

Table 1. Separation performance of supported zeolite membranes for single component gases and mixtures

Support	*Gases*	*Temperature (°C)*	*Selectivity(α)*	*Zeolite*	*References*
Alumina-T	(m) H_2/N_2	35-120	4.8	LTA(A)	63
Alumina-P	(s) H_2/N_2	50	11.2	SAPO-34	64
Alumina-T	(s) H_2/N_2	27	7.4	SAPO-34	65
Ceramics	(m) H_2/CH_4		15.5	MFI	17
Alumina-P	(s) H_2/CH_4	25	11.2	MFI(Si)	66
Alumina-P	(m) O_2/N_2	25	2	LTA(A)	67
Alumina-P	(m) C_2H_4/N_2	25	3.5	LTA(A)	67
Alumina-T	(m) CO_2/N_2	40	20-50	FAU(Y)	68,69
Alumina-T	(m) CO_2/N2	30	>100	FAU(Y)	70
Alumina-P	(s) CO_2/N_2	50	7.1	SAPO-34	64
Alumina-T	(s) CO_2/N_2	27	5.7	SAPO-34	65
Alumina-T	(s) CO_2/CH_4	27	19	SAPO-34	65
Alumina-T	(m) CO_2/CH_4	27	30	SAPO-34	65
Alumina-T	(m) H_2O/O_2	23	10	MOR/MFI/CHA	37
Alumina-T	(m) MeOH/H_2	100	>100	MFI	24
Alumina-T	(m) MeOH/CH_4	100	190	MFI	24
Alumina-T	(m) H_2/SF_6	310	13	MFI	71
SS-P	(m) n-butane/H_2	22	125	MFI(Si)	72
Alumina-P	(s) n-butane/i-butane	26	17	MFI	73
Alumina-T	(s) n-butane/i-butane	30-100	10-50	MFI	74
SS-P	(m) n-butane/i-butane	25	40	MFI	18
SS-P	(m) n-butane/i-butane	22-130	23-27	MFI(Si)	72
SS-P	(m) CH_4/i-octane	50	>300	MFI(Si)	72
Alumina-P	(m) n-butane/i-butane	200	10	MFI	75
Alumina-T	(m) n-butane/i-butane	225	57	MFI	76
Various	(m) n-hexane/2,2-dimethylbutane	49	17.2	MFI	5
Alumina-P	(m) n-hexane/2,2-dimethylbutane		>2000	MFI	75
Alumina-T	(m) n-octane/i-octane	140	40	MFI	77
Alumina-T	(m) n-heptane/i-octane	83	57	MFI	78
Alumina-T	(m) n-hexane/2,2-dimethylbutane	101	2580	MFI	76

Mullite-T	(m) benzene/n-hexane	65	7	FAU(Y)	79
Mullite-T	(m) benzene/cyclohexane	105	45	FAU(Y)	79
Alumina-T	(m) benzene/p-xylene	22	164	MOR	40
Alumina-P	(m) benzene/p-xylene	30	100	FER	41,40
Alumina-P	(m) cyclohexane/benzene	30	1.3	FER	41,40
Alumina-P	(m) p-xylene/m-xylene	room temp.	15	MFI	80
Alumina-P	(m) p-xylene/o-xylene	30	3.2	FER	41,40
Alumina-T	(s) p-xylene/o-xylene	107	12	MFI(Si)	81
Alumina-T	(m) p-xylene/o-xylene	107	~1	MFI(Si)	81
SS-P	(m) MeOH/H_2O	30	10	MFI(Si)	84
SS-P	(m) EtOH/H_2O	30	>60	MFI(Si)	82,83
SS-P	(m) 1-PrOH/H_2O	30	90	MFI(Si)	83
SS-P	(m) 2-PrOH/H_2O	30	>40	MFI(Si)	83
Ceramics-T	(m) H_2O/MeOH	50	2000	LTA(A)	85,79
Ceramics-T	(m) H_2O/EtOH	75	>10000	LTA(A)	85,86
Ceramics-T	(m) H_2O/EtOH	95	5000	LTA(A)	86,79
Ceramics-T	(m) H_2O/2-PrOH	75	10000	LTA(A)	79
Mullite-T	(m) H_2O/EtOH	75	410	FAU(X)	79
Mullite-T	(m) H_2O/EtOH	75	125	FAU(Y)	87,79
Alumina-T	(m) H_2O/PrOH	23	71	MOR/MFI/CHA	37
Ceramics-T	(m) H_2O/acetone	50	5600	LTA(A)	79
SS-T	(m) acetone/H_2O	room temp.	255	MFI(Si)	88
SS-P	(m) CH_3COOH/H_2O	30	2.6	MFI(Si)	89
Alumina-P	(m) CH_3COOH/H_2O	30	1	MFI(Si)	89
SS-T	(m) MEK/H_2O	34	70-146	MFI(Si)	90
Mullite-T	(m) MeOH/benzene	50	74	FAU(X)	79
Mullite-T	(m) EtOH/benzene	60	930	FAU(Y)	79
Alumina-T	(m) EtOH/MeOH	23	2.4	MFI	91
SS-P	(m) MeOH/MTBE	30	10	MFI(Si)	84
Mullite-T	(m) MeOH/MTBE	50	71	FAU(X)	79
Alumina-T	(m) MeOH/benzene	50	1400	FAU(Y)	87,79
Mullite-T	(m) EtOH/ETBE	50	1200	FAU(Y)	79

T: tube, P: plate, SS: stainless steel, (s): single component gas, (m): mixture

grow. AFI crystal nuclei seem to be unidirectionally deposited in cylindrical channels of anodic alumina and grow along the channel direction.

3. Separation

Zeolite films have been synthesized most for separation membranes. At present, unsupported zeolite films have big drawbacks in the mechanical strength and/or density and it is difficult to use them as the membranes, although their separation properties have been reported in a very few cases. Thus, separation data which have been obtained so far in gas or vapor permeation and pervaporation experiments were summarized only for the supported films prepared on porous substrates as shown in Table.

3.1. Small gases

In single gas component permeations, generally speaking, the permeation fluxes decrease with increasing molecular size. But, the situation changes a bit depending on the kinds of zeolites and gases. For example, SAPO-34 [64,65], Y zeolite [70] and silicalite [72] membranes show the permeance orders of $H_2 > CO_2 > N_2 > C_4H_{10}$ (or CH_4), $CO_2 > C_2H_6 > CH_4 > N_2$ and $CO_2 > CH_4 > C_2H_6 > H_2$, respectively. From the orders, it is easily understood that besides molecular sieving and difference in diffusivity, difference in adsorption is a key factor in separation. Accordingly, in many case, the separation selectivity of a mixture does not reflect the single-component permeation ratio. The permeation of weakly adsorbing molecules often drops dramatically in the presence of strongly adsorbing molecules. That is, stronger absorbing components suppress the permeation of weaker absorbing components leading to higher separation selectivities (see H_2O/O_2, $MeOH/H_2$, n-butane/H_2, etc., in Table).

The separation of carbon dioxide is interesting and important from the viewpoint of environment protection. The carbon dioxide permeations have been reported with MFI [72], FAU [68-70], SAPO-34 [64,65] membranes. Among the three membranes, FAU membrane shows the highest selectivity. The permeation properties of FAU membrane vary with the type of FAU (X or Y) and the cations exchanged, but are hardly affected by CO_2 concentration in the feed and heat-treatment of the membranes. The CO_2 permeances of the ion-exchanged membranes are in the order of $Li^+ \approx K^+ > Na^+ \approx Ba^{2+} > Ca^{2+} \approx Mg^{2+}$ and are not directly related to the radius of cations. The KY and LiY membranes show the highest and lowest CO_2/N_2 selectivity, respectively, and the NaY membrane is stable against exposure to air at 400 °C.

3.2. Pure Hydrocarbon Molecules

It is also clear that the separation selectivity is a function of the sorption and diffusion. In the mixtures of saturated hydrocarbon homologs, molecules with smaller size selectively permeate, thus in this case, the diffusivity of the molecules predominantly reflects the separation selectivity. In the separation for the mixtures of saturated and aromatic hydrocarbons, it is understood that the adsorption is a predominant factor. In the mixture of aromatic hydrocarbon homologs, both the adsorption and diffusion are recognized to play important roles for the separation. For the mixtures of hydrocarbon molecules having similar affinities to a zeolite, molecular sieving based on the size is also observed in some cases.

3.3. Oxygen Containing Molecules.

Nature of zeolites, hydrophobicity or hydrophilicity, straightforwardly reflects the separation of aqueous mixtures. As can be seen from Table, in the pervaporation of the mixtures of an organic compound and water, an organic compound is selectively separated with hydrophobic MFI(Si) zeolite (silicalite) membranes, on the contrary, water is predominantly removed with hydrophilic LTA, FAU and MOR/MFI/CHA membranes. Especially, by LTA membranes with smaller pore size, water can be separated in an extremely high selectivity or efficiency. The same trend can be observed for the separation of the organic mixtures containing benzene or an ether.

However, with MFI(Si) membrane supported on porous alumina, the selectivity of acetic acid to water is one, and acetic acid and water can not be separated different from the corresponding membrane supported on stainless steel. This is due to that, during the silicalite membrane synthesis, alumina is partly dissolved into the synthesis solution from the support and incorporated into the MFI framework to result in ZSM-5 which are more hydrophilic than silicalite expected [89]. This is very often observed in the silicalite film synthesis on alumina support.

Generally speaking, in the separation cases stated here, selective adsorption prior to diffusion is a governing factor for the separation [82,83,89,92].

As can be expected easily, permeation properties and separation performances of zeolite membranes are much affected by the structure and nature of zeolites, the quality and intrinsic properties of the membranes (thickness, shape, with and without cracks or pinholes, size and uniformity of the zeolite crystals [93]). Besides them, finally it should be emphasized that the operation conditions [94-97] of the membranes such as the separation mixture composition, temperature, pressure, the orientation of the membranes with respect to the feed side, with and without the use of a sweep gas, and the nature of a sweep gas, etc., much affect the permeation and separation.

4. Application

Besides separation, zeolite nanoporous layers also have been applied for the separation membranes of racemic isomers [98], highly selective sensors [29,48,55,99-101] and catalysts [102-112]. Furthermore, the potential of the application to optical devices [29,47,113-115] has been pointed out, although concrete effects in shaping of zeolite crystals to the film form are not observed yet.

4.1. Optical Resolution

The surface of unsupported ZSM-5 zeolite disk obtained by solid state transformation [12-14] was modified with 3,5-dinitrobenzoyl-L-aniline, then mounted in a tangential flow equipment, and used as the membrane for the optical resolution of racemic lactic acid [98]. When a solution containing racemic lactic acid was circulated on the one side of the membrane, L-lactic acid predominantly moved to the buffer solution of the opposite side.

4.2. Sensors

Thin films of FeAPO-5 molecular sieves deposited on TiN-coated silicon wafers using pulsed laser ablation followed by conventional gel and vapor phase transfer methods were employed as the dielectric phase in a capacitive type chemical sensor [55]. The FeAPO-5-based sensors exhibited significant changes in capacitance upon exposure to moisture. This type of sensor responded to moisture from breathing which makes it useful not only as a humidity sensor but as a respiration monitoring device.

When silicalite crystals were layered onto the gold electrodes of quartz crystal microbalances (QCM), the QCM showed selective response towards ethanol at low pressures (<1000 ppm) [29,99]. In the silicalite layers, uptake of molecules small enough to enter the silicalite pores can be 100 times greater than that of molecules with kinetic diameters bigger than the pores, and interference from water can be minimized through hydrophobicity of the silicalite molecular sieve. Similar QCM covered with a faujasite layer [100] can detect sulfur dioxide of 300 ppm even with the coexistence of oxygen of 22500 ppm at 150 °C.

Furthermore, zeolite coating of thin-film inter digital capacitor chips with gold electrodes using zeolite Na beta and H beta powdery crystals [101] has been investigated for the development of a sensor detecting ammonia in exhaust gases in the presence of water, and it was pointed out that the zeolite coating would open the opportunity to detect ammonia in low concentrations even in the presence of water.

4.3. Catalysts

Using zeolite membranes, disks and coatings, esterification [102], alkylation [103-107], synthesis of ether [106], conversion of methanol [108,109], deNOx reaction [106,110], hydrogenation [106,111] and dehydrogenation [112] have been carried out.

Vapor-permeation (VP) aided esterification [102] of oleic acid with ethanol and methanol was investigated at 110 °C using a laboratory module of zeolite membrane [85] with excellent VP performance for dehydration of organic liquids. The esterification was almost complete in a short time at the initial molar ratio 1.5 of alcohol to oleic acid. The reaction time, as for ethanol, was reduced by a factor of 1/3 as compared with the process performed under the atmospheric pressure using a laboratory module of polyimide hollow fiber. Here it should be pointed out that the zeolite membrane can be used at higher temperatures than organic membranes, in addition to the high permeability to water.

When H type of ZSM-5 disk stated above was fixed in a glass tube and used as a catalytic membrane for the alkylation of toluene with methanol [109-111], it showed outstanding performance. In the alkylation at 450 °C, the selectivity for the formation of p-xylene at the toluene conversion of 26.7% was 79.3% which is 5-10% higher than that obtained by the corresponding powdery catalyst [111]. Coatings of zeolite catalysts are expected to give a higher performance per volume of catalyst than the conventional zeolite catalysts from the viewpoint of catalyst utilization. Thus, zeolite beta coatings prepared on α-alumina beads by in situ synthesis [106,107] were tested for the transalkylation of benzene with diethylbenzene and the alkylation of benzene with ethylene, and compared in activity with the corresponding commercial bulk catalysts. In both reactions, the intrinsic activity of the beta coatings was similar to that of the commercial samples.

A zeolite beta coating [106] also has been used for the synthesis of ETBE from ethanol and isobutene. In the reaction carried out in an autoclave at 90 °C under autogeneous pressure, the selectivity for the formation of ETBE was as high as those of the corresponding powder and commercial catalysts. But, the turnover frequency of the coating was lower.

For the conversion of methanol to gasoline-range hydrocarbons, a ZSM-5 coating hydrothermally synthesized in situ on a cordierite ceramic honeycomb [108] was employed as a reactor. The new reactor could convert methanol to gasoline-range hydrocarbons with yields similar to those obtained in the conventional fixed and fluid bed reactors, and was intermediate in the product distribution between them. This new type of reactor was also found to offer advantages of both fixed and fluid bed reactors and have no problems of catalyst attrition or excessive pressure. Quite recently, it was reported that when a ZSM-5 membrane synthesized on a porous alumina tube by the secondary growth method is used as a catalytic membrane, it shows extremely pronounced performance for the conversion of methanol to lower olefins [109]. In the reaction at 400 °C, olefins were produced at higher selectivities of 80-90% over the wide range of the methanol conversions of 60-98%. By the way, in the case of the powdery crystals, the selectivity of olefins was only 7% at the conversion of 98%.

A stainless steel wire gauze coated with an in situ grown layer of ZSM-5 crystals (Cu-type) has been applied for the reduction of nitric acid with ammonia at 350 °C, and its high potential as the catalyst has been pointed out [106,110] as follows. The activity per atom of active metal is 30 times higher than for commercially used amorphous vanadia-titania/silica catalysts, thus, the activity per kg of catalyst packing can be increased to become significantly higher than the amorphous vanadia-titania/silica catalysts. At realistic deNOx conditions, the activity of the gauze catalyst toward reduction of nitric acid is over 100 times higher than toward oxidation of ammonia to nitric oxide, so the catalyst has a very high selectivity.

A titania-supported platinum catalyst covered with a silicalite layer [106,111] shows a high selectivity in the competitive hydrogenation of a linear and a dibranched alkene, and a good regioselectivity in the hydrogenation of long-chain alkenes. That is, in the competitive hydrogenation of 1-heptene and 3,3-dimethyl-1-butene at 100 °C, 1-heptene is exclusively converted to the saturated compound, and in the case of linear alkene regioisomers, an alkene with a terminal double bond is hydrogenated preferentially over an isomer with an internal double bond. It was found that the silicalite layer demonstrates shape- and regio-selective

effects in the hydrogenations. But, by coating the catalyst with silicalite, the activity decreases significantly. In the dehydrogenation, it was predicted recently that the application of a hybrid reactor equipped with ZSM-membrane for the conversion of ethylbenzene to styrene brings about an increase by 5-7% in the yield of styrene [112].

5. Conclusion

In the synthesis of zeolite membranes, films and coatings, there are many procedures such as in situ synthesis, casting of zeolite nanoparticles, solid state transformation, vapor-phase synthesis, secondary growth, and their combinations or modifications. According to the objectives and situation, a proper procedure should be chosen. In the separation of a mixture by the zeolite membranes, the selectivity is a function of the adsorption and diffusion, and much affected by not only the size and structure of zeolite pores and permeantes but also the properties of pores and permeantes such as hydrophobicity and hydrophilicity. The quality and operation conditions of the membranes are also important. These factors should be considered in the separation. For the application of the zeolite membranes, films and coatings to sensors and catalytic membranes, their high potential was recognized. Accordingly, there should be much hope for the future of zeolite membranes, films and coatings.

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Study of the influence of the silica source on the properties of silicate solutions and particulate properties of zeolite X

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It has been shown previously that zeolite synthesis results can be influenced by the silica source used. It also has been reported by several research groups recently that nanometer sized particulates were observed in the synthesis medium prior to the onset of zeolite crystallization. It has been conjectured that they may play a role in zeolite synthesis.

In this study the distinguishing features of four different silica sources were characterized by NMR, the molybdate method, synthesis results, and preliminary evaluation of quasi-elastic light scattering spectra.

The results suggest that differences in the silicate solutions stem from the presence of species larger than those detected by ^{29}Si-NMR methods, and that changes in some silicate solutions occur during room temperature aging, prior to mixing with the aluminate solution.

1. INTRODUCTION

Zeolite syntheses occur by the hydrothermal transformation of amorphous alumino-silicates into crystalline zeolites having unique microporosities. It is generally accepted that most zeolite syntheses occur by solution facilitated transformations, most commonly in basic media. It also is generally accepted that the transformations result from nucleation of a crystalline phase, or phases, followed by crystal growth by assimilation of alumino-silicates from the solution.

Two recent papers have demonstrated that the extent of nucleation of zeolites in solution can be a function of the source of silica selected for the experiments [1,2]. In those reports, the number of crystals of zeolites NaX and analcime was shown to depend strongly on the silica source with everything else held constant. In one report the concentrations of four impurities in the silica sources were shown to correlate with the extent of nucleation, but no specific impurity could be uniquely identified to play a role in zeolite nucleation.

Several research groups have reported observing nanometer-sized particulates in synthesis solutions both prior to the onset of crystallization and at the conclusion of the process [3-14]. The origin of these particulates and the role they play in zeolite nucleation has been the

subject of inquiry, but to date those questions have not been answered. Schoeman [11] suggested that the nanometer-sized particulates could be the site of nucleation, based on the observation that they appeared to be the same size as the growing crystals, when extrapolated back to the beginning of the syntheses. He also noted their presence throughout the synthesis. Gora, *et al* [12] reported observing the particulates in the silicate solution prior to mixing with the aluminate solution, and indicated that they persisted throughout the synthesis of zeolite NaA.

This study was undertaken to revisit the question of the reason why different silica sources influence the extent of nucleation of zeolite crystals in hydrothermal systems. In particular, the goal was to resolve whether there was something inherently different about basic silicate solutions produced from various silica sources, or whether the concentration of nano-particulates varied with silica sources.

2. EXPERIMENTAL

Containers of several silica sources used in a previous study [1] were still available in sufficient quantity to conduct experiments for this work. Silica samples were obtained from:

A. $Na_2SiO_3 \times 9H_2O$ Sodium metasilicate nonahydrate (Sigma)†

B. $Na_2SiO_3 \times 5H_2O$ Sodium metasilicate pentahydrate (Sigma)*

C. $Na_2SiO_3 \times 0H_2O$ Anhydrous sodium metasilicate (Eka)*

D. SiO_2 Silicic acid (Aldrich)*

† Not used in the previous study [1]. * The same batch as used in [1].

Appropriate amounts of water and sodium hydroxide were used to make sodium silicate solutions having the same compositions, which were:

$3.5\ Na_20 \times 3.5\ SiO_2 \times 227.2\ H_2O$.

Aluminum wire (99.999%) from one source was used to make the aluminate solution by dissolving it in an appropriate NaOH solution, resulting in a mole oxide composition of:

$1.26\ Na_2O \times Al_2O_3 \times 2.0\ TEA \times 227.2\ H_2O$,

where TEA represents triethanolamine which was added to stabilize the aluminate solution. All silicate and aluminate solutions were filtered through 0.2 μm polysulfone filtration membranes prior to use.
All synthesis solutions used had the composition:

$4.76\ Na_2O \bullet Al_2O_3 \bullet 3.5\ SiO_2 \bullet 454\ H_2O \bullet 2\ TEA$,

and were prepared by adding equal amounts of the two solutions noted above. This is a batch composition that produces zeolite NaX when heated in static sealed autoclaves at 115°C for 2-

6 hours, depending on the silica source used [1]. Syntheses were carried out using the four silicate solutions, and the common aluminate solution, both with freshly prepared silicate solutions and with silicate solutions aged for 44 days at room temperature.

^{29}Si-NMR was used to characterize the silicate anion distribution of the four silicate solutions, both freshly prepared and aged for 44 days at room temperature. The molybdate method [15] also was used to note primarily the presence of short chain silicate oligomers in freshly prepared and aged silicate solutions. The percent of silica remaining unreacted with molybdic acid as a function of time, measured by the absorbance at 400 nm, was plotted to determine the fraction of monomers of SiO_2, dimers, and higher oligomers.

3. RESULTS AND DISCUSSION

The first, and perhaps most obvious, test done on the four silicate solutions was to determine their silica concentration to verify that they were indeed the same. To within *ca.* 5% the concentrations of the unfiltered and the filtered silicate solutions were all the same, and as expected from the batch composition. Thus, there was no loss of silica due to filtration that contributed to unique solution properties.

Figure 1 shows the four ^{29}Si-NMR spectra obtained for the freshly prepared silicate solutions having the mole oxide composition described in the Experimental section. It appears from these four spectra that there were no significant differences in the silicate oligomer distributions in the freshly made silicate solutions. One might suggest that there were minor differences, perhaps sufficient to cause differences in subsequent syntheses, but this could not be argued with much confidence from these spectra.

Figure 2 shows the NMR spectra for the same four silicate solutions, but which were aged in sealed polypropylene containers at room temperature for 44 days. Again, one might suggest that there were subtle differences in minor peaks, but no significant differences were noted. Additionally, the spectra of all four of the aged solutions were almost identical to the corresponding spectra of the freshly prepared solutions. These observations suggest that there were no discernible changes in the silicate solutions over the aging period, at least none that could be determined by ^{29}Si-NMR. Furthermore, the variations in the properties of the silicate solutions that lead to different synthesis results were not determined by these NMR spectra; this conclusion is consistent with the preliminary tests reported previously [1]. These observations suggest that differences in the silicate solutions involved larger structures than could be observed by ^{29}Si-NMR, i.e., about 12 SiO_2 units.

Figure 3 shows plots of the ln(UR) vs. time, in seconds, where UR is the percent of unreacted silica remaining at time, t, and was computed from:

$$UR = \{1 - A(t)/A(eq)\}\ 100,$$

From the slopes of the curves of ln(UR) vs. time, it was determined that all four solutions contained approximately 51% dimeric species (-Si-O-Si-), and the remaining species were cyclic trimers and chain polymers. There seemed to be little difference in the molybdic acid reaction curves, except at long times, where the silica remaining was quite small.

Figure 4 shows the molybdate test results for the silicate solutions that were aged at room temperature for 44 days. It is noted that the results for the four silica sources were quite

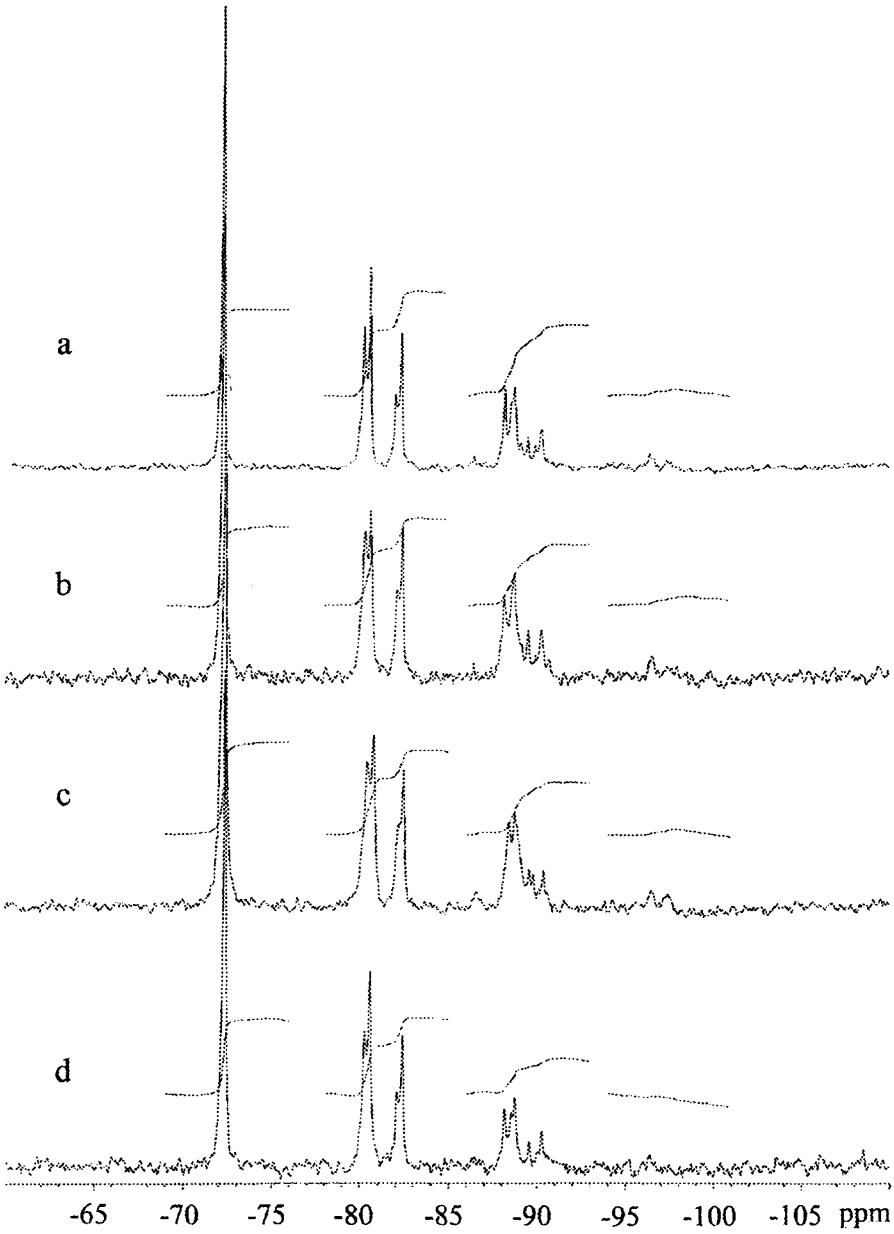

Figure 1. ^{29}Si NMR spectra of freshly prepared silicate solutions from the silica sources: (a) $Na_2SiO_3 \times 9H_2O$, (b) $Na_2SiO_3 \times 5H_2O$, (c) Na_2SiO_3 and (d) SiO_2.

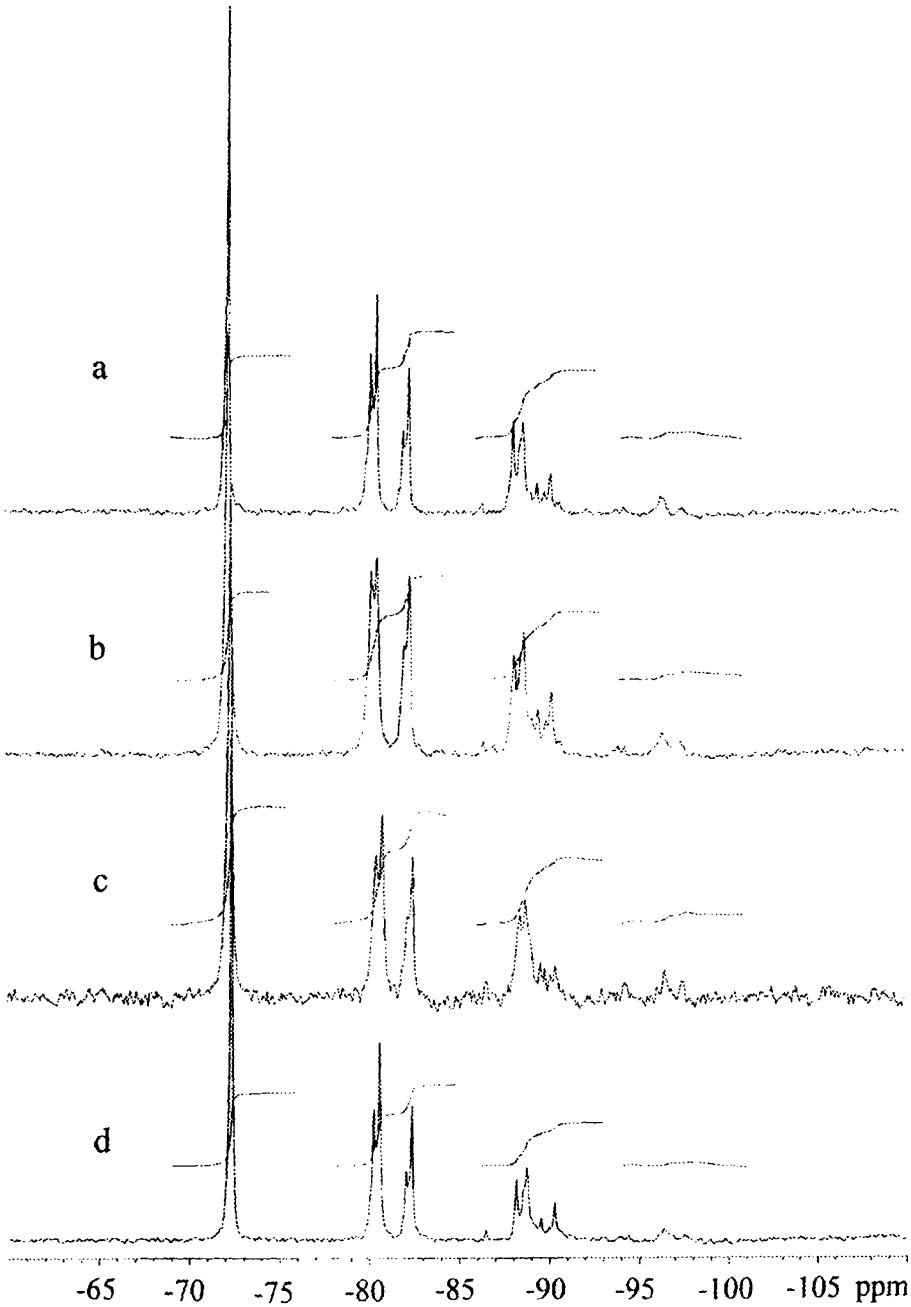

Figure 2. ^{29}Si NMR spectra of the aged prepared silicate solutions from the silica sources: (a) $Na_2SiO_3 \times 9H_2O$, (b) $Na_2SiO_3 \times 5\ H_2O$, (c) Na_2SiO_3 and (d) SiO_2.

different after aging for 44 days, and that the degree of polycondensation, DP, increased in the sequence: DP(silicic acid) < DP(anhydrous sodium metasilicate) < DP(sodium metasilicate pentahydrate) < DP(sodium metasilicate nonahydrate). That is, the degree of polycondensation increased with the number of waters of hydration incorporated in the structure of the initial silica source. There was not much difference in the DP of silicic acid and the anhydrous sodium metasilicate. It is interesting to note that the DP(aged sodium metasilicate pentahydrate) is about the same as the DP of the freshly prepared solutions, the DP(aged anhydrous sodium metasilicate) and DP(aged silicic acid) contained predominantly dimers and a lower percentage of higher oligomers than the freshly prepared silicate solutions, and that the DP(aged sodium metasilicate nonahydrate) increased during aging. It appears that some rearrangement of silicate anions among the larger species occurred during room temperature aging.

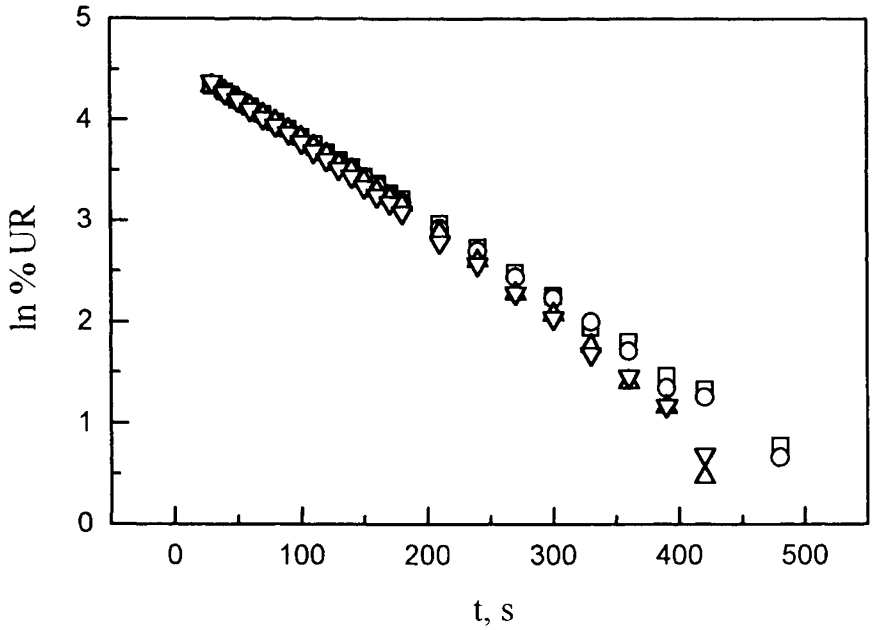

Figure 3. Logarithm, ln UR, of the percentage of SiO_2 unreacted with molybdic acid plotted as a function of the reaction time, t_R, of the molybdic acid with the silicate anions in the liquid phases of the freshly prepared silicate solutions from $Na_2SiO_3 \times 9\ H_2O$ (□), $Na_2SiO_3 \times 5\ H_2O$ (O), Na_2SiO_3 (△) and SiO_2 (▽).

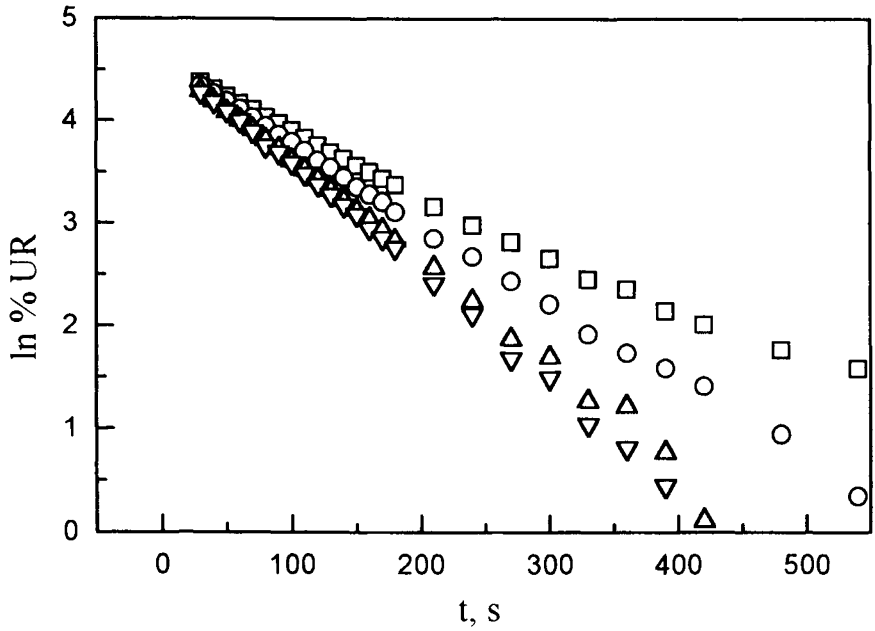

Figure 4. Logarithm, ln UR, of the percentage of SiO_2 unreacted with molybdic acid plotted as a function of the reaction time, t_R, of the molybdic acid with the silicate anions in the liquid phases of the aged silicate solutions from $Na_2SiO_3 \times 9\ H_2O$ (□), $Na_2SiO_3 \times 5\ H_2O$ (O), Na_2SiO_3 (△) and SiO_2 (▽).

4. CONCLUSIONS

Use of different silica sources significantly influences the crystallization pathway and particulate properties of zeolite X. Following the assumption that specific distributions of silicate species in silicate solutions are responsible for the observed effect, the distributions of silicate species in fresh and aged silicate solutions prepared from different sources were analyzed by ^{29}Si-NMR and molybdate methods. In contrast to insensitivity of distribution of silicate anions to a short time aging (for 1 day), an aging for 44 days considerably influences the distribution of silicate anions in silicate solutions. For instance, the degree of polycondensation (DP) in the aged silicate solutions increases in the sequence: DP(silicic acid) < DP(anhidrous sodium metasilicate) < DP(sodium metasilicate pentahydrate) < DP(sodium metasilicate nonahydrate). Hence, DP increases with increasing content of crystalline water in the silica source. Although the distribution of silicate anions (ca 50 % of

dimers and rest of cyclic trimers and higher chain polymers in silicate solutions is not markedly influenced by the silica source, one might suggest that even the minor differences, are perhaps sufficient to cause differences in subsequent syntheses, but this could not be argued with much confidence from these spectra. Hence, although the question about influence of the silica source on the crystallization pathway and particulate properties of the crystalline end products is still open, we believe that the question may be answered by further analyzes of the distribution of silicate species in both the silicate solutions and hydrogels prepared from these solutions.

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A method for the preparation of silicalite-1 microspheres

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Silicalite-1 containing microspheres were prepared by a new method based on the use of anion exchange resins as shape directing templates. The resins were hydrothermally treated in a synthesis solution yielding silicalite-1 at 100°C and finally removed by calcination. The resultant material consists of hard, solid and white spherical particles with a shape and size identical to the ion exchange resin used. Characterization of samples taken out after different times of treatment showed that an amorphous silica is formed at the beginning of the treatment. This amorphous silica shows structural changes with time parallel to which silicalite-1 starts to form. The crystallization reaction discontinues after a treatment time of about 48 h. A calcined sample obtained after 48 h contains a large amount of amorphous matter and the additional hydrothermal treatment does not substantially improve the crystallinity of the product. Silicalite-1 microspheres of a very high crystallinity were obtained by a two-step procedure using an initial treatment at 100°C followed by a secondary treatment at a higher temperature.

1. INTRODUCTION

Microporous materials are of great technological importance in areas such as catalysis, separation, ion exchange and sensing. Often, the practical application of these materials requires special shapes and sizes. A number of techniques exist for producing macrostructures in the form of pellets, extrudates, spherical particles and tablets. However, in the case of zeolites, most of the techniques use binders to increase the mechanical stability of the macrostructure desired. These binding additives decrease the efficiency of the zeolites.

Several methods have been developed to produce binderless zeolite materials. Self-bonded zeolite pellets have been prepared from very dense gels [1,2] as well as from natural products of volcanic origin [3]. A vapour-phase transport method has been used for the synthesis of defect free zeolite membranes of mordenite [4]. A method based on the transformation of kamenite intercalated with TPA and TBA cations for the preparation of silicalie-1 and silicalite-2 has been reported [5]. Later, based on the same method, ZSM-5 disks have been prepared by pre-shaping the kamenite-TPA-aluminoslicate mixture [6]. Pre-shaping of dry co-gels has also been used to obtain various shapes of TS-1 monoliths [7]. A new crystallization

method called the dry-gel conversion technique has recently been developed which allows the synthesis of zeolite BEA in the form of self-bonded pellets [8]. Furthermore, a novel honeycomb composite consisting of ZSM-5 and mullite has been prepared from a sintered kaolin honeycomb [9].

In all the examples given above, either self-bonded pellets were synthesized or raw materials were transformed to zeolites after being shaped. However, no methods have, to the best of our knowledge, been developed for the direct preparation of three-dimensional all-zeolite macrostructures using an organic shape-directing template. This paper reports such a procedure, exemplified by the preparation of silicalite-1 microshperes.

2. EXPERIMENTAL

A macroporous basic styrene-divinylbenzene ion exchange resin (Dowex MSA-1) with a bead size distribution in the range 0.3 - 1.2 mm and an ion exchange capacity of 3.5 meq/g was used in all experiments. A clear homogeneous solution with a molar composition 9TPAOH : $25SiO_2$: $480H_2O$: 100EtOH hydrolyzed for 12 hours on a gyrotary shaker prior to its use was employed. The starting mixture was prepared by mixing tetraethoxysilane (TEOS) (Merck, > 98%) with tetrapropylammonium hydroxide (TPAOH) (Sigma, 1.0 M aqueous solution) and distilled water [10]. Crystallization of a silicalite-resin composite material was realized by hydrothermal treatment of a mixture of the resin and the synthesis solution. In a base experiment, this treatment was carried out at 100°C in a polyethylene reactor submerged in an oil bath under reflux conditions. Samples were taken out after a treatment time of 0.5, 4, 10, 19, 24, 48, 87 and 504 hours. A series of experiments was also performed employing a two-step procedure using an initial treatment at 100°C followed by a secondary treatment at 165°C for different periods of time. In the latter case the entire treatment was performed in PTFE-lined stainless steel autoclaves. The synthesis solution/amount of the resin weight ratio was about 15 in all experiments. After the synthesis, the ion exchange beads were separated from the mother liquid and silicalite-1 crystallized in the bulk and treated in a 0.1 M ammonia solution in an ultrasonic bath for 15 min. Finally, the resin/silicalite-1 microspheres were washed three times by suspension in distilled water, filtered and dried at 60°C. To remove the ion exchange resin acting as a matrix in the preparation of the silicalite-1 beads the microspheres were calcined at 600°C for 5 hours, after heating to this temperature at a rate of 1°C/min.

X-ray diffraction (XRD) patterns were taken with a Siemens D5000 powder diffractometer using CuK_α radiation. A Philips XL 30 scanning electron microscope (SEM) equipped with a LaB_6 emission source was used for studies of the morphology of the samples. Raman analysis was performed with a Perkin Elmer PE 1700X NIR FT-Raman spectrometer equipped with a Nd YAG laser operating at 1064 nm. The spectra were collected at room temperature averaging 500 scans with a spectral resolution of 4 cm^{-1} using 1W power of the incident light. Specific surface areas were calculated with the BET equation using nitrogen adsorption data obtained with a Micromeritics ASAP 2010 surface area analyzer. Samples were outgassed at 300°C overnight prior to analysis. Calculations of the pore-size distribution were made by using the BJH-method (desorption isotherm). BET measurements were performed on the

calcined silicalite microspheres whereas before XRD and Raman analysis the calcined microspheres were ground into powder in an agate mortar.

3. RESULTS AND DISCUSSION

The samples obtained at 100°C were investigated by SEM prior to and after the hydrothermal treatment. No distinguishable changes in appearance were observed (for any sample) upon calcination. The calcined samples obtained consisted of very hard, solid, and white spherical particles. The particle size of the microspheres estimated from the SEM micrographs was within the range given for the starting ion exchange resin beads (Figure 1a-c). The primary particles building up the structure have a size of about 100 nm (Figure 1d), i.e. comparable to the pore size of macroporous ion exchange resin which is usually in the range 20-100 nm [11].

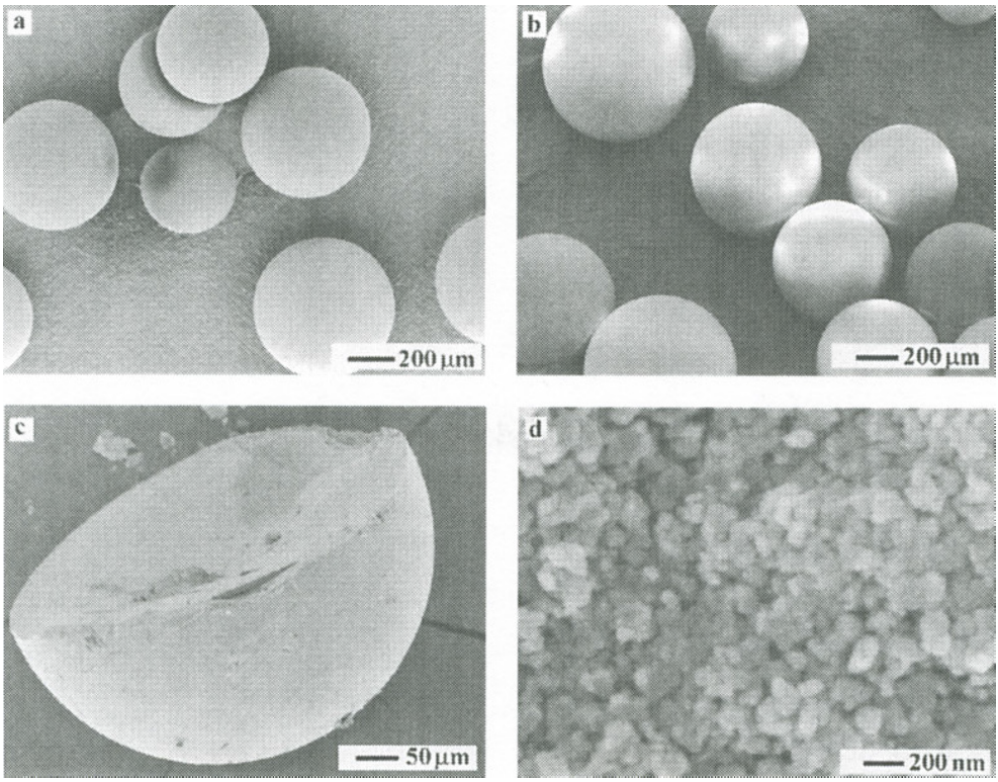

Figure 1. Scanning electron micrographs of: the starting ion exchange resin beads (a), microspheres obtained by treatment at 100°C for 48 h and subsequent calcination (b), a cross section of such a microspehere (c) and the nanosized particles building up that microsphere (d).

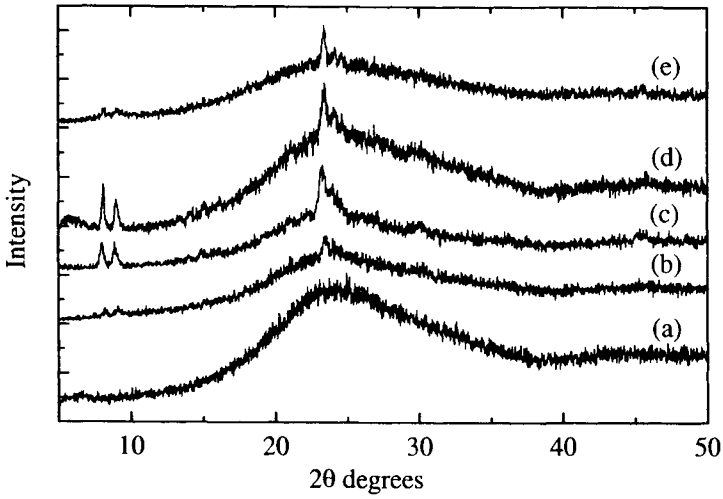

Figure 2. XRD patterns of calcined samples obtained after 19 (a), 24 (b), 48 (c), 87 (d) and 504 (e) hours of hydrothermal treatment at 100°C.

Figure 2 shows the XRD patterns of calcined samples obtained after hydrothermal treatment at 100°C for different periods of time. It can be seen that the sample obtained after 19 h of hydrothermal treatment was completely amorphous (Figure 2a). In the next sample (after 24 h, Figure 2b) silicalite-1 starts to form and the amount increase with increasing treatment time up to 48 h (Figure 2c). The XRD pattern of the sample obtained after 87 h shows an amount of silicalite-1 which is approximately the same as that in the previous sample but the amorphous halo is bigger (Figure 2d). Additional hydrothermal treatment (up to 504 hours, Figure 2e) does not seem to improve the crystallinity of the product.

Since the samples synthesized were either amorphous or contained a large amount of non-crystalline silicate phase, Raman spectroscopy was used for the further investigations. Figure 3 shows Raman spectra of the calcined samples obtained after 0.5, 24, 48, 87 and 504 h of hydrothermal treatment. The spectra were baseline corrected and normalized to the intensity of the peak at 495 cm^{-1}. The Raman spectrum of the calcined sample obtained after 0.5 h of hydrothermal treatment (Figure 3a) is typical of vitreous silica [12]. However, even at that stage, the structure of the amorphous silica is modified and partly destroyed which can be seen from the intensity ratio between the broad band at 445 cm^{-1} and the sharp peak at 495 cm^{-1} and also from the existence of the weak peak at about 970 cm^{-1}. These structural changes in the amorphous silica continue with crystallization time and are most probably due to the ordering of the TPA cations within the microsphere structure. Parallel to these changes silicalite-1 starts to form. In the spectrum of the sample obtained after 24 h of hydrothermal treatment a shoulder at 380 cm^{-1}, the location of the most intense peak in the Raman spectrum of silicalite-1, appears and is well pronounced in the spectrum of the next sample (obtained after 48 h) (Figure 3 b,c). If the Raman intensities at 380 and 495 cm^{-1} are used as a measure for the quantity of the crystalline and the amorphous phase, respectively, we can conclude that

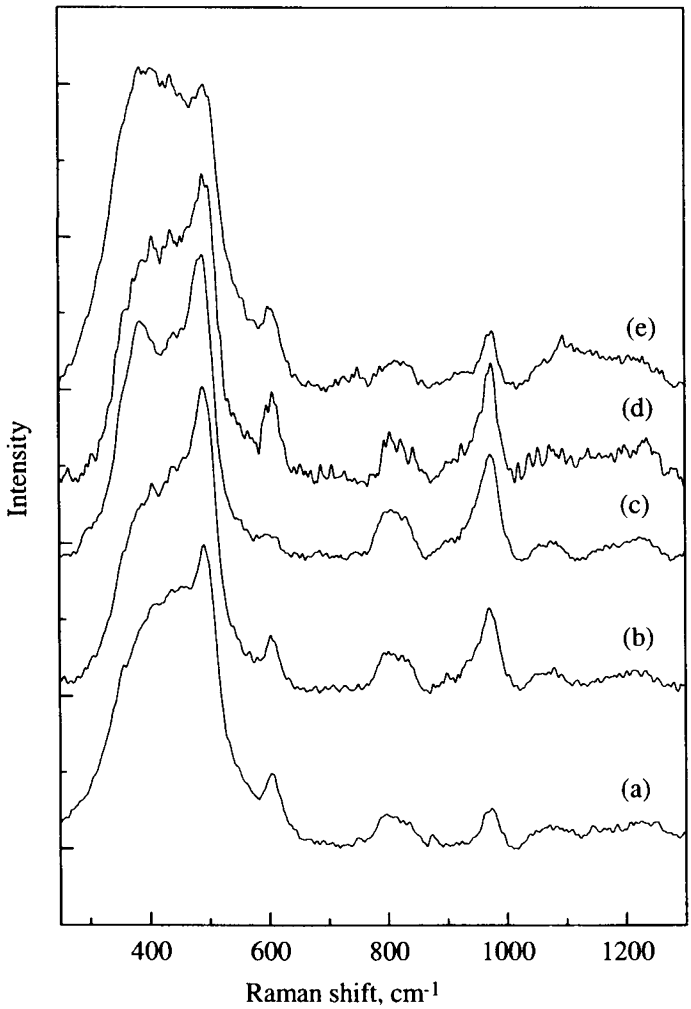

Figure 3. Raman spectra of calcined samples obtained after hydrothermal treatment at 100°C for 0.5 h (a), 48 h (b), 87 h (d) and 504 h (e).

the amount of silicalite-1 is approximately the same in the samples obtained after 48 and 87 hours (Figure 3 c,d). Upon further hydrothermal treatment up to 504 h the amount of silicalite-1 increases. However, the existence of a broad band from 380 to 460 cm^{-1} in the Raman spectrum of that sample indicates that the silicalite-1 is not well-crystallized (Figure 3e).

The calculated BET surface area of the samples obtained after 0.5, 4, 10, 19, 24, 48, 87 and 504 h of hydrothermal treatment at 100°C was 324, 930, 590, 505, 540, 468, 450 and 543 m^2/g, respectively. The variations in these values are not surprising regarding the approach used to prepare the samples. The method involves different steps and many factors might influence the pore structure of the final product. However, the calculated values are in

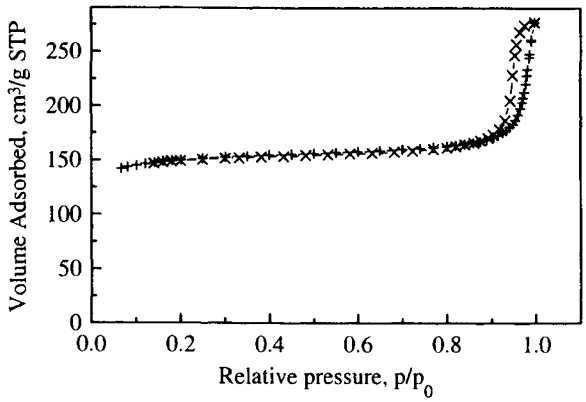

Figure 4. Adsorption isotherm for nitrogen at 77 K on a calcined sample obtained after 19 h of hydrothermal treatment at 100°C; + adsorption, x desorption.

agreement with the results obtained from the XRD and Raman spectroscopy and indicate that the main changes in the pore structure occur during the first hours of the hydrothermal treatment. Nevertheless, a remarkable observation is that although the samples obtained after 0.5 and 4 h are similar according to the Raman spectra, their surface areas are quite different (324 and 930 m^2/g, respectively).

The nitrogen adsorption measurements on the calcined samples from that series indicated the presence of both micro and mesopores. Langmuir type isotherms with identical, nearly horisontal, adsorption and desorption branches, typical for microporous material were obtained (Figure 4). However, at high relative pressures, a distinct hysteresis loop, indicative of mesopores can be seen. The shape of this hysteresis loop is of H1 type and it is often obtained with agglomerates of spheroidal particles of fairly uniform size [13]. The pore size distribution showed that the main part of the pore volume is found in micropores.

Silicalite-1 microspheres of higher crystallinity and even pure crystalline microspheres can be obtained by applying the two-step synthesis procedure. The initial treatment at 100°C is needed to obtain a self-bonded microporous body. The product obtained after the calcination of a sample treated entirely at a higher temperature (165°C) was rather a powder than microspheres. The secondary treatment at a higher temperature is important to complete the crystallization of the silicalite-1. However, because of the increased number of parameters influencing the final product, the reproducibility of this method is poor in comparison with the one-step synthesis at 100°C. Also, the microspheres of high crystallinity appear to be less mechanically stable. Figure 5a shows the XRD pattern of pure crystalline microspheres obtained by the two-step synthesis method and the corresponding Raman spectrum is shown in Figure 5b.

By varying the treatment times at the two different temperatures materials with different hardness, surface area and degree of crystallinity can be obtained. Various series of