Hydrothermal synthesis and characterization of indium containing beta zeolite

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Abstract

The hydrothermal synthesis of indium containing beta zeolite has been reported. The efficiency of the synthesis depends mainly on the concentration of indium, synthesis temperature, and pH of the gel. Beta indium has been synthesized in a range of different SiO_2/In_2O_3 ratios using tetraethylammonium ion as a template. For SiO_2/In_2O_3 ratio around 40, beta indium was obtained as a pure phase with a good yield. The product was contaminated with ZSM-5 in case of low In_2O_3 content. If the synthesis is carried out at higher temperatures the possibility of the formation of ZSM-5 increases, whereas lowering the temperature takes longer, about 10–14 days. Upon calcination to remove the organic template, some demetallation occurs which lowers the crystallinity. Indium species present in the beta zeolite framework were characterized by IR NMR. The extra framework indium species probably exist in a cationic state. The catalytic activity of the sample was tested by the benzoylation reaction of naphthalene. © 1998 Elsevier Science B.V.

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1. Introduction

Zeolites, more generally speaking zeotypes, have shown outstanding potential to act as selective catalysts in chemical and petrochemical processes [1,2]. This success is based on the ability to fine tune both structural and chemical parameters to produce an adequate environment for given catalytic processes to occur.

In this context, isomorphous substitution of Al^{3+} by trivalent metal ions in zeolite has become a convenient procedure for modifying systematically their physical and chemical features. This results in different adsorptive and catalytic properties [3]. Generally the substitution of metal ions in zeolite takes place during hydrothermal synthesis or the post-synthesis step. The metal ion may stay in the framework or in the intra-framework cavities as metal oxide or counter ions. Pentasil type gallosilicate and galloalumino silicate zeolite

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were found to be very active in the aromatization of light alkane [4–8]. However, very little has been published about MFI type silicate and phosphate modified with indium, although this metal is also a Group 13 element, as Ga. suggesting similar adsorption and catalytic properties of the corresponding indosilicates.

We report here the crystallization of a large pore beta zeolite by the substitution of indium in place of aluminium, as well as some relevant physicochemical properties of the material.

2. Experimental

2.1. Synthesis

Synthesis mixtures were prepared by using the following reagents: tetraethylorthosilicate (TEOS), tetraethylammonium hydroxide (TEAOH), indium chloride and deionized water. All the chemicals were procured from Aldrich.

In a typical synthesis procedure TEAOH was added slowly to the TEOS with stirring. Then a solution of indium salt was added to the mixture with vigorous stirring. Finally, the mixture was stirred to homogeneity (4 h). The pH of the mixture was maintained the same as that of beta aluminium (12.35–12.6). After this the resulting gels were introduced into a PTFE-lined stainless steel autoclave. Gels of different chemical compositions were prepared (Table 1). The reaction mixture was treated hydrothermally for 10–14 days at 140 C under static condition. After quenching the autoclaves in cold water, the samples were centrifuged at 10 000 rpm, washed and dried at 353 K

overnight. A portion of the solids was calcined in air at 823 K.

2.2. Characterization

The chemical composition of the calcined sample was obtained from the ICP-AES. X-ray powder diffraction (XRD) patterns of the sample were recorded on a Rigaku D MaxIIIVC X-ray diffractometer using nickel filtered Cu Kα ($\lambda = 1.5406$ Å). Crystallinity was determined by measuring the intensity of the peaks appearing at $2\theta = 22.4$. Sample 2 with the most intense peak giving 100% crystallinity was taken as reference. Scanning electron microscopy was performed on a Hitachi S-800 scanning electron microscope. FTIR spectra in the framework region (1300–400 cm^{-1}) were recorded on a Perkin-Elmer model spectrum 1000 using KBr pellets. Thermal analysis was performed on the air dried sample using a computer assisted instrument Varian INOVA 500 NMR spectrometer with CPIMS probe for the NMR study.

3. Results and discussion

3.1. XRD and SEM

Reaction mixtures of different chemical composition were prepared and processed under the same crystalline conditions. A summary of initial gel composition is shown in Table 1. The X-ray powder diffraction pattern of as-synthesized beta [SiIn] and beta [SiAl] is shown in Fig. 1. The XRD pattern of beta aluminium is characterized by a combination of sharp and broad reflections

Table 1
Gel composition and crystallinity of phase formed during the synthesis of [SiIn] beta zeolite at 413 K (140 C)

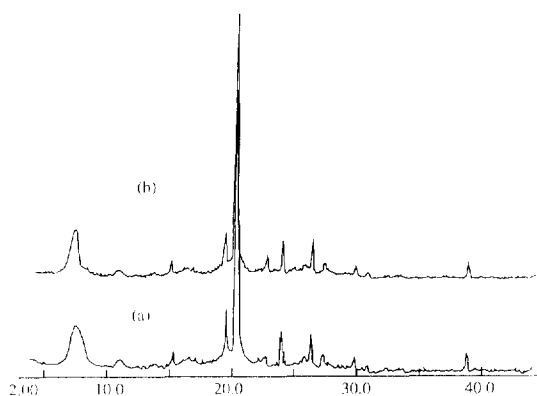| Sample	Gel composition SiO$_2$/In$_2$O$_3$	SiO$_2$/Al$_2$O$_3$	R SiO$_2$	H$_2$O/SiO$_2$	Time (days)	Zeolite phase	Crystallinity (%)
1	40		0.52	21	10	beta	100
2	60		0.52	21	10	beta	90
3	100		0.52	21	14	beta + ZSM-5	75
4	200		0.52	21	14	beta + ZSM-5	55
5	400		0.52	21	14	ZSM-5	
6		40	0.52	21	4	beta	100

Fig. 1. X-ray diffraction pattern of sample 2: (a) beta [SiAl]; (b) beta [SiIn].

[9]. It was observed that there were some changes in the intensities of these peaks with the variation of the ratio Si/In. The coincidence of the position of the lines and intensities with those given in Ref. [9] allowed us to identify the product as crystalline beta [SiIn].

The scanning electron micrograph of beta [SiIn] is shown in Fig. 2. These beta indium samples appear under the scanning microscope as small uniform cuboid shaped crystals of size 0.15–0.35 μm. The change of the ratio Si/In does not have any appreciable effect on the shape and size of the beta crystal.

3.2. FTIR spectroscopy

The high crystallinity of these samples can be ascertained from their framework IR spectra (1300–400 cm^{-1}) as shown in Fig. 3. The band positions were compared with those of the beta [SiAl] and results are summarized in Table 2. This shows that in the 500–650 cm^{-1} region a sharp band was observed which is typical of beta zeolite. The band at 1104 cm^{-1} observed as well for MFI [In] was representative of framework In (OSi)$_4$ entities [10]. With increase in indium content, a clear shift of the wavenumbers of the T–O–T lattice vibration towards lower values was observed. An analogous shift for other metallosilicates has been described previously. The above results indicate that a part of the indium was incorporated into the framework. This was in
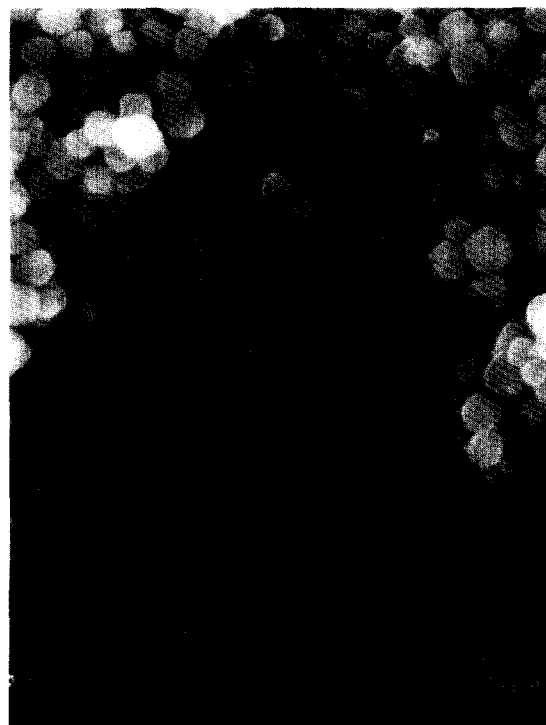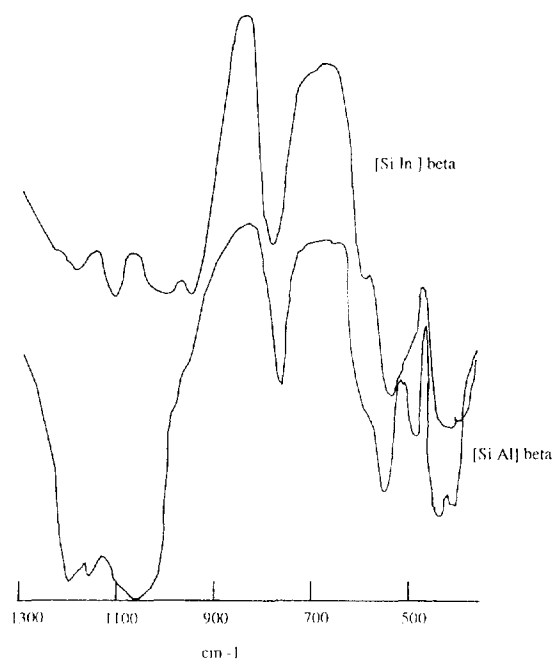

Fig. 2. Scanning electron micrograph of beta [SiIn].

Fig. 3. The infrared spectra of [SiIn] beta zeolite.

Table 2
Framework IR vibration frequencies (v, cm^{-1})

beta [SiAl]	beta [SiIn]
1220	1200
1172	1169
	1104
1084	1069
988	953
782	800
615 (sh)	622
572	566
480	462

contrast to analogous metallosilicates where the proportion of the atoms which can largely be substituted for silicon reaches a higher value. Thus isomorphous substitution (In for Al) has a greater influence on the O–H stretching frequency.

3.3. Thermal analysis

The weight and energy change during the thermal decomposition of the as-synthesized sample are shown in Fig. 4. The DTA/TG analysis of the sample was carried out in a flow of dry air under the following conditions: sample taken 10 mg, rate of heating 10°C/min, sample pan Pt, ref. alpha alumina. Two distinct zones of exothermic weight loss were seen in the DTA/TG curve with peak maxima at 297.4 and 431.0°C. A very small shoulder-like exothermic peak appeared between these two peaks. Perez-Pariente et al. [9] reported three exothermic weight losses at 220–350, 350–500, 500–700°C respectively, in the decomposition of a
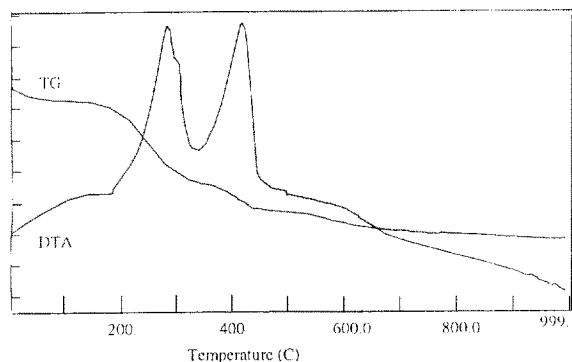
TEA beta zeolite. On the basis of assignment made earlier, the first two exothermic losses to the removal of occluded TEAOH and TEA$^+$ cations associated with the indium species which act as a framework charge compensating cation [11] respectively. The exothermic weight loss in the 500–700°C range was attributed to the oxidative decomposition of the organic material occluded in the zeolite. The results obtained in the present study are similar to those of Ref. [9], which confirms the incorporation of indium species in the beta framework.

3.4. ^{115}In NMR

The ^{115}In NMR spectrum of as-synthesized and calcined beta [SiIn] is shown in Fig. 5. The spectrum exhibits a narrow central line at around 236 ppm. Such a shift is characteristic of the indium atom in the tetrahedral position [12]. After calcination the intensity of the peak decreased. Considering this fact, one can easily predict that during calcination some demetallation has occurred, or the coordination of indium species may be transferred to a lower symmetry region which is very difficult to predict due to instrumental reasons. Because of the absence of the amorphous material in the XRD pattern of [SiIn] beta zeolite, and only tetrahedral indium at ~236 ppm appearing in the NMR spectra, the incorporated
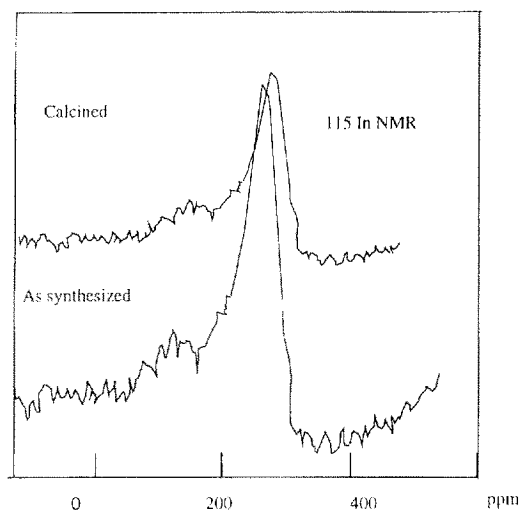

Fig. 4. Thermal analysis curve of as-synthesized beta [SiIn].

Fig. 5. The ^{115}In NMR spectra of beta [SiIn].

Table 3
Benzoylation of naphthalene using beta [SiIn]

Catalyst	Yield			
	BOC	1 BN	2 BN	1 BN 2 BN
beta [SiAl]	30.3	76.2	23.8	0.31
beta [SiIn]	25.4	78.0	22.0	0.28
AlCl₃	28.4	84.4	15.6	0.18

BOC = benzoyl chloride, 1 BN = 1 benzoyl naphthalene, 2 BN = 2 benzoyl naphthalene, 1 BN/2 BN = ratio of 1 benzoylnaphthalene to 2 benzoyl naphthalene.

indium atom in the as-synthesized beta [SiIn] may thus reside solely in the framework.

3.5. Catalysis

The benzoylation of naphthalene has turned out to be an appropriate reaction to characterize the catalytic properties of large pore zeolite. The results are given in Table 3. The results indicate that the conversion of benzoyl chloride and selectivity for 2-benzoylnaphthalene were greater than those for AlCl₃. This performance is attributed to its acidic property and three-dimensional 12-membered ring large pore structure. Blank experiments carried out in the absence of catalyst did not reveal any measurable conversion. Catalytic reactions were performed in a three-necked flask (capacity 50 ml) fitted with a condenser, gas supply tube and a septum (for the collection of product). 0.023 mol of naphthalene. 0.011 mol of benzoyl chloride and 1 g of catalyst were taken into the flask and heated in an oil bath to the reaction temperature (70°C) under stirring. Samples were collected periodically and analysed with a gas chromatograph equipped with 50 m × 0.2 mm capillary column with methyl silicone gum. Product distribution was done by comparison with authentic samples and GC mass spectroscopy. It has been found that the sensitivity towards this reaction is better than for aluminium chloride.

4. Conclusion

An essentially aluminium free indium containing BEA molecular sieves has been synthesized for the first time by unseeded hydrothermal synthesis at 140°C using TEA as templating agent. The synthesized samples were characterized by IR NMR methods. IR indicates the presence of indium in the framework position, and NMR results confirm the tetrahedral position of indium atom in the framework. One of the acid catalysed reactions was performed on the beta [SiIn] obtained by the described procedure, which shows some reactivity greater than that obtained by any other method. for example physical mixing, atom planting, as described previously [13]. So, it is possible to substitute indium for silicon isomorphously in the BEA framework generating Brønsted acid sites with rather weak acid strength. However, their thermal stability seems to be low owing to the tendency of indium to leave the framework at higher pretreatment temperature, which needs further study.

Acknowledgement

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