

Synthesis and Characterization of Crystalline Indosilicates with the MFI Structure

G. Vorbeck,*† J. Jänchen,† B. Parltz,^a M. Schneider^b and R. Fricke^a

^a Centre of Heterogeneous Catalysis and ^b Centre of Inorganic Polymers Berlin-Adlershof, Rudower Chaussee 5, D-12484 Berlin, Germany

Crystalline MFI-type indosilicates containing indium ions in framework positions have been hydrothermally synthesized and characterized to exhibit rather weak acidity.

The isomorphous substitution of silicon atoms in zeolites and related molecular sieves by suitable trivalent elements has become a convenient procedure for modifying systematically their physical and chemical features, resulting in different adsorptive and catalytic properties.¹ Among those molecular sieves modified *e.g.* with aluminium, boron, gallium or iron those with the MFI structure are well characterized.²⁻⁴ However, very little has been published about MFI-type silicates modified with indium,⁵⁻⁸ although this metal is also a Group 13 element, suggesting similar adsorptive and catalytic effects of the corresponding indosilicates. Hence, in the present work a series of MFI-type indosilicates containing different amounts of indium was hydrothermally synthesized and characterized by several physicochemical and spectroscopic methods.

After careful preparation of the starting gels the syntheses were carried out under identical conditions. The detailed synthesis procedure in addition to the following treatments (ion exchange and calcination) to obtain the corresponding ammonium or acid forms, was described earlier⁹ using iron as the substitution metal. Additionally, a silicalite with an SiO₂:Al₂O₃ ratio of 1000 was prepared in the same way as a reference (Table 1).

According to the XRD pattern all samples are well crystallized and show the typical reflections of the MFI structure. Its largely pure formation is confirmed by the results of *n*-hexane adsorption. The values of the real micropore volume are fairly close to the theoretical value calculated for an ideal MFI structure (0.19 cm³ g⁻¹; Table 1). There is, however, a difference between those obtained earlier for analogous ferrisilicates⁹ and those for indosilicates with comparable Si:M ratios. This indicates a higher degree of non-framework species in the channels of the latter. Table 1 also shows the unit-cell volumes of the MFI-type indosilicates V_{uc} ; V_{uc} increases with the number of indium atoms per unit cell (In per uc)_Σ. If at least a part of the indium is incorporated into the framework such an increase should take place. This is due to the fact that, in fourfold coordination, In³⁺ has a larger ionic radius than silicon (0.62 Å *cf.* 0.26 Å).¹⁰ A second indication that part of indium is incorporated into the MFI framework was obtained from solid-state IR spectroscopy. With increasing indium content per unit cell, a clear shift of the wavenumber of the T-O-T lattice vibration ν_{T-O-T} towards lower values was observed (Table 1). An analogous shift for other MFI-type metallosilicates has been described previously.^{2,9}

The number of indium ions incorporated into the framework per unit cell was determined *via* the temperature

controlled decomposition of the ammonium forms of indosilicates. We estimated the relative number of indium ions incorporated by determining the relative amount of ammonia desorbed during decomposition. (It is well known that the introduction of one foreign trivalent ion into the zeolite framework generates in principle one Brønsted-acid bridged OH group in which the proton can be exchanged, for example, by an ammonium cation.) These values in connection with

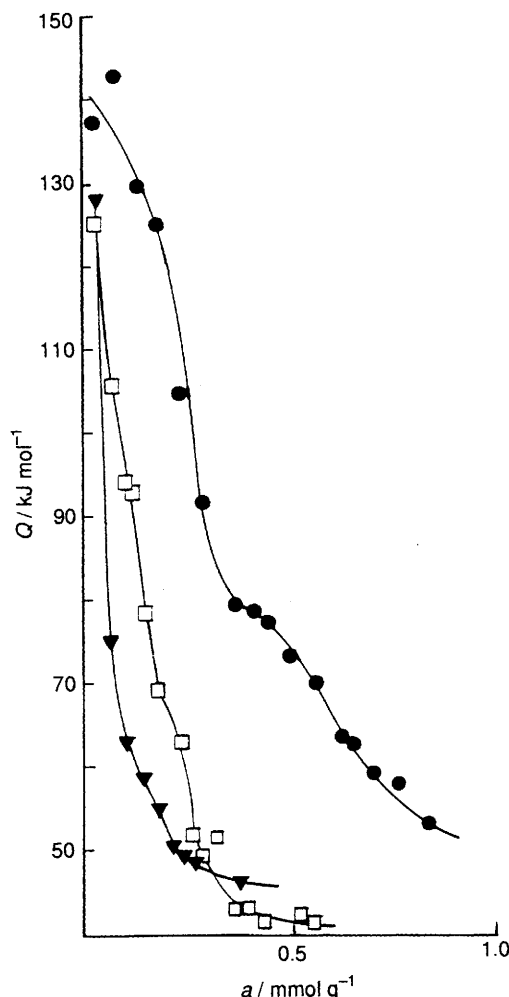


Fig. 1 Differential molar heats of adsorption of ammonia on silicalite at 423 K: (▼), InSil(67) (□) and ZSM-5 (50) (●)

Table 1 Sample composition and physicochemical characterization

Sample	(In per uc) _Σ	a^a /cm ³ g ⁻¹	V_{uc} /Å ³	ν_{T-O-T} /cm ⁻¹	C_{OH}^{TPD} /mmol g ⁻¹	(In per uc) _F	C_{IE}^b /mmol g ⁻¹	(In per uc) _F
InSil (67) ^c	2.78	0.170	5355	1102	0.20	1.2	0.06	0.4
InSil (80)	2.34	0.178	5350	1104	0.14	0.8	0.09	0.5
InSil (104)	1.81	0.172	5341	1104	0.11	0.6	0.05	0.3
silicalite	—	0.197	5342	1108	0.03	—	—	—

Σ, overall In content; F, framework.

^a Adsorption capacity for *n*-hexane ($p/p_s = 0.5$). ^b C_{IE} , Ammonium ion exchange capacity. ^c Values in brackets: SiO₂:In₂O₃ ratios (obtained *via* bulk chemical analysis).

chemical analysis data allow a quantitative estimate of the indium distribution between framework and non-framework positions. The results are summarized in Table 1. Thus, only 30–40% of the indium atoms are located in the framework. This is in contrast to analogous metallosilicates where the proportion of atoms which can be isomorphously substituted for silicon reaches 70% or more for comparable moduli. This demonstrates a markedly lower affinity of the silicate framework towards In^{3+} during the hydrothermal synthesis compared with ions such as Al^{3+} and Fe^{3+} .

As mentioned above, the relative amount of ammonia desorbed also conforms with the number of Brønsted-acid sites C_{OH} . Table 1 shows that an increase in the indium content leads to an enhancement in the number of these sites. In order to determine the acid strength distribution of the indosilicates, adsorption calorimetric measurements were performed. After activation of the sample in vacuum at 670 K for 16 h, ammonia as a probe molecule was adsorbed at 423 K. Fig. 1 shows the differential heats of sorption as a function of the ammonia loading for the sample HInSil (67). For comparison, the heat curves of the silicalite as a reference and of ZSM-5 are included. For ZSM-5 the amount of ammonia chemisorbed at medium and strong acid sites ($Q < 80 \text{ kJ mol}^{-1}$)¹¹ conforms, not unexpectedly, with the number of aluminium atoms per unit cell (1.9). Owing to aluminium impurities (0.02 wt%) a few very strong acid sites have been detected for the silicalite sample. For the indosilicate, the number of acid sites with a sorption heat between 80–110 kJ mol^{-1} differs significantly from that for the silicalite. The greater number of these rather weak acid sites is in agreement with the difference in the corresponding NH_4^+ ion-exchange capacities and with the values obtained from the temperature-controlled decomposition of the NH_4^+ forms of indosilicates (Table 1). This supports the assignment of these sites to Brønsted-acid centres, simultaneously confirming the partial incorporation of indium ions into the framework.

It was difficult to detect the IR vibration band of the corresponding OH groups. Apart from a small band at 3610 cm^{-1} , most likely due to the Al impurity, only a poorly developed shoulder at *ca.* 3638 cm^{-1} could be observed. This is probably due to the low thermal stability of the bridged OH groups in indosilicates. Thus, a re-exchange of the acid forms of indosilicates (obtained *via* calcination of the NH_4^+ forms at 670 K for 2 h) with an NH_4NO_3 solution, followed by a

redetermination of their NH_4^+ ion-exchange capacity, revealed a dramatic decrease in the concentration of Brønsted-acid sites and a consequently decrease in the amount of indium incorporated (Table 1).

In conclusion, it is possible to substitute indium for silicon isomorphously in the MFI framework, generating Brønsted 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 temperatures.

The authors are very grateful to Mrs E. Schreier and to Mrs E. Löffler, respectively, for the IR and DRIFT measurements.

Received, 5th July, 1993; Com. 3/03871H

Footnote

† Present address: Eindhoven University of Technology, Schuit Institute of Catalysis, The Netherlands.

References

- 1 J. C. Vedrine, *Stud. Surf. Sci. Catal.*, 1991, **69**, 25.
- 2 R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold Catalysis Series, Van Nostrand Reinhold, New York, 1989.
- 3 R. B. Borade, A. B. Halgeri and T. S. R. Prasada Rao, *New Developments in Zeolite Science Technology*, Proc. 7th Int. Zeol. Conf., Tokyo, 1986, ed. Y. Murakami, A. Jijima and J. W. Ward Kodansha, Ltd., Tokyo, Japan, p. 851.
- 4 S. A. Axon and J. Klinowski, *Stud. Surf. Sci. Catal.*, 1989, **52**, 113.
- 5 G. Wengui, L. Juan, L. Hongyuan, Y. Muliang and H. Jiehan, *Stud. Surf. Sci. Catal.*, 1985, **24**, 279.
- 6 K. G. Ione, L. A. Vastrikova and V. M. Mastikhin, *J. Mol. Catal.*, 1985, **31**, 355.
- 7 L. W. Zatorski, *Bull. Pol. Acad. Sci., Chem.*, 1987, **35**, 325.
- 8 K. Yamagishi, S. Namba and T. Yashima, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 949.
- 9 G. Vorbeck, M. Richter, R. Fricke, B. Parltitz, E. Schreier, K. Szulzewsky and B. Zibrowius, *Stud. Surf. Sci. Catal.*, 1991, **65**, 631.
- 10 *Structural Chemistry of Silicates*, ed. F. Liebau, Springer-Verlag, Berlin, 1985, p. 308.
- 11 U. Lohse, B. Parltitz and W. Patzelova, *J. Phys. Chem.*, 1989, **93**, 3677.