

Long-distance Transfer of Indium into Large HZSM-5 Crystals

Vladislav Kanazirev,^a Valentin Valtchev^b and Mikhail P. Tarassov^b

^a Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

^b Institute of Applied Mineralogy, Bulgarian Academy of Sciences, 1000 Sofia, Bulgaria

Long-distance transfer and uniform distribution of indium in large crystals of a HZSM-5 zeolite occur when powdered In_2O_3 and HZSM-5 are loosely mixed and then subjected to hydrogen reduction at a temperature as low as 623 K.

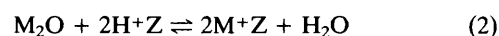
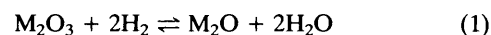
Gallium attracts nowadays great attention as a key component of ZSM-5 based zeolite catalysts for the aromatization of light alkanes.¹⁻⁴ Recently hydrogen or hydrocarbon reduction was found to be a crucial step in the formation of the active state of Ga-containing zeolites.^{5,6} Hydrogen reduction of mechanically mixed Ga_2O_3 and HZSM-5, for example, causes a process of depletion of the Ga_2O_3 crystalline phase and a transfer of cationic gallium species, probably Ga^+ , into the zeolite.^{7,8}

In the present work we have observed that, in the presence of hydrogen, indium can be introduced into HZSM-5 much more easily than gallium even in the case of large zeolite crystals and at a rather low reduction temperature.

Large ZSM-5 crystals were prepared in a 10 cm³ Teflon-lined stainless-steel autoclave without stirring. The batch composition of the initial gel was 31 Na_2O :40 NPr_4OH : Al_2O_3 :7 SiO_2 :3268 H_2O . The crystallization was carried out at 453 K for 120 h. The product obtained was washed and air-dried according to common procedures. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) showed the product consisted of large ZSM-5 (100–200 μm) and analcime (50–80 μm) crystals. The solid product was then converted in a H-form *via* template decomposition involving NH_4^+ exchange and thermal treatment. The final sample (32 mg) was placed in the crucible of a SETARAM92 microbalance and loosely mixed with 5 mg In_2O_3 (American Smelting and Refining Co). The mixture was subjected to temperature programmed reduction (TPR) in a H_2 -Ar flow and the final temperature of 623 K was maintained for 2 h. Several specimens consisting of a single zeolite monocrystal imbedded into epoxy resin tablets were examined on a PHILIPS 515 SEM equipped with an EDAX 9100/70 system. The XRD patterns of the monocrystals examined were identical with the patterns of the non-modified ZSM-5 material. Twenty EDAX analyses performed on five different tablets showed a content of indium ranging from 2.81 to 3.66 wt% with an average of 3.21 wt%. Values within this range were also obtained using specimens which had been polished prior to the EDAX measurements. Fig. 1 shows the micrograph of an 140 \times 50 \times 50 μm monocrystal which has been polished about 15 μm (one third) down from the surface. Over 80 microanalyses were performed in small steps throughout the crystal. Table 1 summarizes data for the indium content of the crystal along profile lines I, II and III depicted in Fig. 1. It can be seen that the indium has penetrated homogeneously deep into the crystal. Recalculated atomic contents per zeolite unit cell (sum Si + Al = 96) varied from 1.06 to 1.48 for aluminium and from 1.10 to 1.59 for indium whereas an In:Al ratio very close to unity was always obtained.

It is well known that the introduction of M^{III} cations into ZSM-5 zeolites cannot be effectively accomplished *via* the

common aqueous ion exchange owing to the large size of the hydrated M^{III} ions. The introduction of gallium with reasonable rates *via* solid-state exchange in H_2 could be achieved at a temperature as high as 800 K only when high dispersity and a close contact between Ga_2O_3 and HZSM-5 were attained by prolonged ball milling prior to the reduction.^{5,6} No transfer of Ga into the zeolite was observed by EDAX even when small (0.2–0.5 μm) crystals of HZSM-5 were loosely mixed with Ga_2O_3 and then subjected to H_2 reduction at 850 K for 3 h. In contrast, a zeolite homogeneously modified with indium is produced by reduction of loosely mixed In_2O_3 and ZSM-5, even though indium is larger than gallium and despite of the fact that a zeolite crystal which is several hundred times larger and a temperature which is 177 K lower than in the gallium case are utilized. We suggest that the reductive solid-state ion exchange^{7,9} proceeds with both gallium and indium according eqns. (1) and (2) ($\text{M} = \text{Ga}, \text{In}$; $\text{Z} = \text{zeolite anionic site}$).



Thermodynamic calculations showed that the reaction (1) is much more feasible in the case of indium. The equilibrium partial pressure of the volatile product In_2O is about 4 orders of magnitude higher than the value for the Ga_2O formation in the same temperature range of 600–1000 K. Thus, if the reducibility of the metal oxide is the most important factor, the introduction of indium would occur much more easily. In addition, the relation between basicity of the metal suboxide

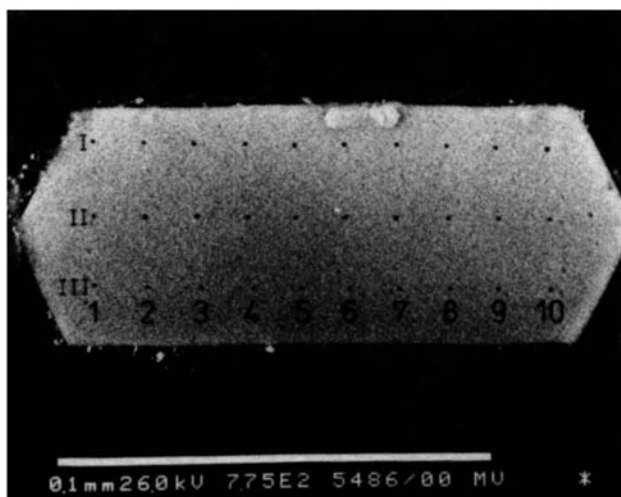


Fig. 1 SEM Micrograph of a HZSM-5 crystal modified with indium

Table 1 Distribution of indium throughout a HZSM-5 crystal

| Profile line/ <i>n</i> | Content of indium oxide wt% | | | | | | | | | |
|------------------------|-----------------------------|------|------|------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| I | 3.15 | 3.06 | 3.31 | 3.22 | 3.26 | 3.28 | 3.50 | 3.05 | 2.88 | 3.13 |
| II | 2.60 | 3.29 | 3.56 | 3.40 | 3.31 | 3.66 | 3.22 | 3.04 | 2.94 | 3.13 |
| III | 3.28 | 3.10 | 3.56 | 3.33 | 3.13 | 3.41 | 3.19 | 3.15 | 3.19 | 3.19 |

and acidity of the zeolite may be significant for the rate of the transfer process.

Finally, the method described for creating new materials with high content of finely dispersed heavy elements may be of potential for other metals and supports.

We thank the National Bulgarian Scientific Foundation for the financial support.

Received, 25th October 1993; Com. 3/06370D

References

- 1 J. R. Mowry, R. F. Anderson and J. A. Johnson, *Oil Gas J.*, 1985, 128.
- 2 H. Kitagawa, Y. Sendoda and Y. Ono, *J. Catal.*, 1986, **101**, 12.
- 3 D. Seddon, *Catal. Today*, 1990, **6**, 3.
- 4 C. R. Bayense, A. J. H. P. van der Pol and J. H. C. van Hooff, *Appl. Catal.*, 1991, **72**, 81.
- 5 V. Kanazirev, G. L. Price and K. M. Dooley, *J. Chem. Soc., Chem. Commun.*, 1990, 712.
- 6 G. L. Price and V. Kanazirev, *J. Catal.*, 1990, **126**, 267.
- 7 V. Kanazirev, G. L. Price and K. M. Dooley, in *Zeolite Chemistry and Catalysis*, ed. P. A. Jacobs, N. I. Jaeger, L. Kubelkova and B. Wichterlova, Elsevier, Amsterdam, 1991, 277.
- 8 V. Kanazirev, R. Dimitrova, G. L. Price, A. Yu. Khodakov, L. M. Kustov and V. B. Kazansky, *J. Mol. Catal.*, 1991, **70**, 111.
- 9 V. Kanazirev, Y. Neinska, T. Tsoncheva and L. Kosova, in *Proceedings of the 9th International Zeolite Conference, Montreal, 1992*, ed. R. von Ballmoos, J. B. Higgins and M. M. J. Treacy, Butterworth, 1993, **1**, 461.