INFRARED-SPECTROSCOPIC DETECTION AND DISTINCTION OF INDIUM CATIONS OF DIFFERENT OXIDATION STATES IN ZEOLITES

R. Magdolna Mihályi a, Hermann K. Beyer a, Yanka Neinska b, Vesselina Mavrodinova b and Christo Minchev b

a Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri út, 59-67, H-1025 Budapest, Hungary
b Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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Abstract

In⁺ cations introduced by reductive solid-state ion exchange into zeolites (Y, ZSM-5, mordenite) and cationic InO⁺ species created by oxidation of the incorporated univalent cations were found to be detectable and distinguishable by IR spectroscopy using pyridine as probe molecule. Relatively weak interactions of In⁺ lattice cations with pyridine give rise, after degassing at temperatures not higher than 370 K, to typical bands at 1446 and 1599 cm⁻¹. After oxidation to InO⁺, these bands are shifted to 1452 and 1610 cm⁻¹, being significantly more resistant towards degassing. Because of restrictions in the accessibility of InO⁺ to pyridine, the respective bands are absent in the spectra of mordenite.

Keywords: Indium lattice cations, zeolites, IR spectroscopy

INTRODUCTION

Many efforts have been devoted to find catalysts for the removal of environmentally harmful nitric oxides in exhaust gas. Recently, indium-containing zeolites were found to be promising catalysts for the reduction of nitric oxides with, e.g., methane [1] and ethylene [2] as reducing agents. Among the methods for the incorporation of indium species into zeolites, a technique first reported by Kanazirev et al. [3,4] is of greatest importance. Univalent indium cations were found to be incorporated into zeolites when mechanical mixtures of crystalline In₂O₃ and Brönsted acid are heat-treated in hydrogen. This process, called
reductive solid-state ion exchange (RSSIE), was assumed to proceed via In$_2$O as intermediate according to the equation

$$\text{In}_2\text{O}_3 + 2\text{H}_2 + 2\text{H}^+Z^- \rightarrow 2\text{In}^+Z^- + 3\text{H}_2\text{O}. \quad (1)$$

Further, it could be evidenced by IR spectroscopy and TPR/TPO techniques that In$^+$ cations, once incorporated by RSSIE into zeolites, can be oxidized with O$_2$ to InO$^+$ and again restored by subsequent reduction [5-7]. These oxidation/reduction cycles proved to be fully reversible. Because of this redox behavior, indium-containing zeolites may be potential catalysts for a broader spectrum of catalytic oxidation and reduction processes.

In the present study common and structure-dependent features of indium cations incorporated by RSSIE into zeolites of different framework topology (FAU, MFI, MOR) are reported. It is shown that univalent and trivalent cationic indium species located in zeolites can be detected and clearly distinguished by IR spectroscopy using pyridine as probe molecule.

**EXPERIMENTAL**

The chemical composition of the parent zeolites used in this study are listed in Table 1. NH$_4$NaY and NH$_4$-mordenite were prepared by conventional ion exchange of commercial NaY and Na-mordenite. H-ZSM-5 was obtained by calcination (820 K, air) of the template-containing precursor prepared according to the synthesized type B in ref. 8. Extra-framework aluminium could not be detected in these samples by $^{27}$Al MAS NMR. Al and Na were determined by AAS after wet digestion with hydrofluoric acid. Ammonium was determined by the Kjeldahl method. Mixtures of the parent zeolites and crystalline In$_2$O$_3$ were prepared by grinding the components in an agate mortar in amounts corresponding to an In/Al ratio of 1.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si$^a$</th>
<th>Al (mmol/g)$^b$</th>
<th>Na</th>
<th>NH$_4$</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$-Y</td>
<td>11.9</td>
<td>4.77</td>
<td>1.33</td>
<td>2.96</td>
<td>2.5</td>
</tr>
<tr>
<td>NH$_4$-MOR</td>
<td>14.7</td>
<td>2.30</td>
<td>0.01</td>
<td>1.73</td>
<td>6.4</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>16.1</td>
<td>0.39</td>
<td>0.05</td>
<td>----</td>
<td>40.3</td>
</tr>
</tbody>
</table>

$^a$Calculated from mass balance deficit  
$^b$Fired at 1270 K