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| | Experiment title: CRYSTAL STRUCTURE OF ZEOLITE FERRIERITE IN Co-EXCHANGED FORMS | Experiment number: CH-515 |
| Beamline: BM01 | Date of experiment: from: 28-Aug-98 to: 01-Sep-98 | Date of report: 27-Aug-99 |
| Shifts: 9 | Local contact(s): Hermann EMERICH | <i>Received at ESRF:</i> |
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Report:

INTRODUCTION

The catalytic reduction of nitrogen oxides (NO_x) in the presence of excess oxygen is now one of the most important subjects from the viewpoint of environmental protection. Li and Armor¹ recently showed that Co²⁺-exchanged ferrierite is a particularly active catalyst for the reduction of NO_x with methane in the presence of excess oxygen. Ferrierite is known to be a natural as well as synthetic medium pore zeolite. The framework contains two systems of mutually perpendicular one-dimensional channels of 10- and 8-membered rings. This study is devoted to clarifying the structural modifications undergone by ferrierite when loaded with increasing amounts of Co cations.

EXPERIMENTAL

The as-synthesised ferrierite K_{2.7}Na_{1.1}Si_{32.2}Al_{3.8}O₇₂ · 12H₂O (Engelhard-ferrierite EZTM-500) was ion-exchanged to ammonium form (AFER) by exhaustive exchange with aqueous solutions of ammonium nitrate. Co-ferrierite samples were prepared by exchanging AFER with Co(CH₃COO)₂ aqueous solutions. By varying the exchange time different Co contents were obtained: Co-Fer.1S with Co=2.5 wt%, Co-Fer.3S with Co=4.3 wt% and Co-Fer.7S with Co=13.7 wt%. After calcination at 550°C per 2h, the three samples were rehydrated at

room conditions. Room temperature synchrotron X-ray diffraction data were collected from 2 to 42.80° 2 θ . Rietveld structure refinements were performed by the GSAS package².

RESULTS AND DISCUSSION

Assuming the framework composition of the as-synthesised zeolite (Engelhard), we found that the Co²⁺, Na⁺ and K⁺ cations in the Co-Fer.1S sample were not enough to counterbalance the framework charge. The remainder of the charge is probably compensated by the presence of Brønsted acid sites produced during thermal decomposition of the residual NH₄⁺ cations³. In the case of the Co-Fer.3S sample the ion-exchange appear to be complete. The overloaded Co-Fer.7S was completely ion-exchanged, and the excess of cobalt is probably located in an unidentified second phase outside the framework. The structure refinements of the three samples were performed using the space group *Immm*; there was no evidence for a lowering of symmetry to *P2₁/n*. The restoration of the apparent topological symmetry *Immm* was attributed to the presence of the Co(H₂O)₆²⁺ octahedron in the large ferrierite cage. In all three samples Co²⁺ was seen to be coordinated to six water molecules in a regular octahedral configuration at the centre of the ferrierite cage. The Co(H₂O)₆²⁺ octahedron has two possible configurations, differing by a rotation around the z axis. In the three samples the Co²⁺ localised from the refinements in the ferrierite cage is less than the content of cobalt measured by chemical analysis. Other Co²⁺ cation sites undoubtedly exist, but their localisation is rather difficult.

REFERENCES

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