In Situ X-ray Diffraction Study of the Phase Transitions in C4 Olefin Catalysts
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Temperatures-programmed X-ray diffraction technology is employed to study phase transitions of modified ZSM-5 catalysts for C4-olefin cracking reactions to produce propylene. The crystal phase transitions of the fresh, used and regenerated catalysts are investigated respectively with temperature increasing and decreasing under vacuum and air conditions.

The samples were prepared with following steps. HZSM-5 zeolite and Al2O3 (as binder) were fully mixed, kneaded and then molded by extruder. Elements of alkaline-earth metals and phosphorus were introduced by impregnation. After drying and calcination, the fresh ZSM-5-based catalyst was obtained. The catalyst for C4 cracking was evaluated in a fixed-bed reactor. The deactivated catalyst was regenerated through combustion with the mixture of air and nitrogen on line.

The crystal structures of the samples were recorded by X-ray powder diffraction analysis on Bruker AXS D8 Advance SSS X-ray diffractometer equipped with a graphite monochromator and scintillation counter, and using CuKα radiation (40KV and 300mA). Anton Parr XRK 900 reaction chamber was equipped, which was used to heat samples from room temperature to 900°C and provide certain experimental conditions.

The research results show the crystal phases of all these catalyst are nothing with phase transitions of these catalysts.

Keywords: rare-earth molybdate, semiconductor, electronic transport

Neutron diffraction studies of the ferroelectric phase of CdTiO3, Qingdi Zhou,2 Brendan J. Kennedy,3 Maxim Avdeev,1 School of Chemistry, The University of Sydney, Sydney, NSW 2006 (Australia).3 Bragg Institute, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai NSW 2234 (Australia). E-mail: zhou_q@chem.usyd.edu.au

Cadmium titanate (CdTiO3) is relatively poorly studied due to the toxicity of cadmium and difficulties in obtaining pure CdTiO3 since it has only a moderate stability with respect to the oxides. CdTiO3 can be synthesised with either an ilmenite or perovskite type structure. The ilmenite-like phase of CdTiO3 is unstable at high temperatures and undergoes an irreversible reconstructive phase transition to the perovskite phase near 900°C. The perovskite phase decomposes, through the loss of Cd, if heated above 1000°C. In recent years, there has been growing interest developing thin films of cadmium for a variety of uses including as a photocatalyst.

The precise structure of the perovskite phase of CdTiO3 is uncertain. This is a consequence of the combination of its ferroelectric properties and the subtleties in the various octahedral tilting schemes observed for perovskites. A ferroelectric structure for CdTiO3 at room temperature in Pn̅2̅1n, and a non-polar in Phnn have been reported. Studies showed that CdTiO3 undergoes a displacive ferroelectric phase transition at about 80 K, with X-ray analysis suggesting the low temperature phase is in Pn̅2̅1a or Pn̅2̅ma while the room temperature paraelectric phase is in Phnn.

In the present work we have used high resolution neutron diffraction methods to refine the structure of the three phases of CdTiO3, namely the paraelectric ilmenite and perovskite phases and the ferroelectric perovskite phase. It is expected that neutron diffraction will provide a more accurate and precise description of these structures compared with X-ray diffraction methods due to the presence of the heavy Cd cations. To circumvent the high neutron absorption cross section of naturally occurring Cd we used samples enriched in 114Cd. Cooling perovskite-type CdTiO3 to 4 K induces a ferroelectric phase transition, with the neutron data suggesting the low temperature structure is in Pn̅2̅1a or Pn̅2̅ma while the room temperature paraelectric phase is in Phnn.

To refine the structure of CdTiO3, we have measured high resolution neutron diffraction patterns on the BOSS diffractometer at the Research Reactions Facility at ANSTO. The patterns were refined using the full-profile Rietveld refinement method, and compared with theoretical calculations. The structure of CdTiO3 in the paraelectric ilmenite structure was refined using the space group Pn̅2̅1n. The structure of CdTiO3 in the ferroelectric perovskite structure was refined using the space group Pbma. The structure of CdTiO3 in the paraelectric ilmenite structure was refined using the space group Pn̅2̅1a. The structure of CdTiO3 in the paraelectric ilmenite structure was refined using the space group Pn̅2̅1a.

Keywords: neutron, Cd-114, ferroelectric

Figure 1. A ferroelectric structure in Pn̅2̅1a at 4 K.