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Keywords: rare-earth molybdate, semiconductor, electronic transport

MS05.P21

Acta Cryst. (2011) A67, C246

In Situ X-ray Diffraction Study of the Phase Transitions in C4 Olefin Catalysts

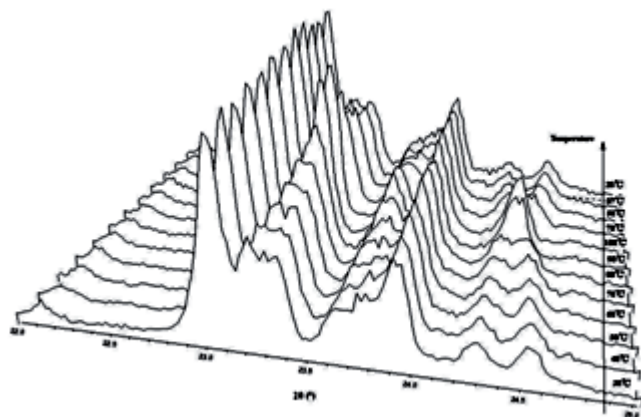
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Temperature-programmed X-ray diffraction technology is employed to study phase transitions of modified ZSM-5 catalysts for C4-olefin cracking reactions to produce propylene. The crystal phase transitions of the fresh, used and regenerated catalysts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

The samples were prepared with following steps. HZSM-5 zeolite and Al_2O_3 (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 $\text{CuK}\alpha$ 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 changed into orthorhombic structure when the temperature is increased to a certain degree no matter what kind of their initial crystal structure (monoclinic or orthorhombic)(shown in fig.1). The experimental conditions whether under vacuum or air prove further the water has nothing with phase transitions of these catalysts.



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Keywords: XRD, phase transition, ZSM-5

MS05.P22

Acta Cryst. (2011) A67, C246

Neutron diffraction studies of the ferroelectric phase of CdTiO_3
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Cadmium titanate (CdTiO_3) is relatively poorly studied due to the toxicity of cadmium and difficulties in obtaining pure CdTiO_3 since it has only a moderate stability with respect to the oxides. CdTiO_3 can be synthesised with either an ilmenite or perovskite type structure. The ilmenite-like phase of CdTiO_3 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 CdTiO_3 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 CdTiO_3 at room temperature in $Pc2_1n$, and a non-polar in $Pbnm$ have been reported. Studies showed that CdTiO_3 undergoes a displacive ferroelectric phase transition at about 80 K, with X-ray analysis suggesting the low temperature phase is in $Pn2_1a$ or $P2_1ma$ while the room temperature paraelectric phase is in $Pbnm$.

In the present work we have used high resolution neutron diffraction methods to refine the structure of the three phases of CdTiO_3 , 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 ^{114}Cd . Cooling perovskite-type CdTiO_3 to 4 K induces a ferroelectric phase transition, with the neutron data suggesting the low temperature structure is in $Pna2_1$ (Figure 1). Solid solutions of the type $\text{Cd}_{1-x}\text{Ca}_x\text{TiO}_3$ could be prepared. Invariably this required the use of relatively high temperatures resulting in the formation of perovskite-type oxides and we did not find any evidence to suggest appreciable amounts of Ca could be incorporated into the ilmenite type CdTiO_3 structure. Interestingly we could not prepare solid solutions of the type $\text{Cd}_{1-x}\text{Sr}_x\text{TiO}_3$ using conventional methods. There are only 5% of Sr and 5% of Ca can be doped in CdTiO_3 in the solid solution of $\text{Ca}_x\text{Sr}_x\text{Cd}_{1-x}\text{TiO}_3$. This is somewhat remarkable given the relative ease with which oxides of the type $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ can be prepared and suggests the A-O bonding is playing a significant, but poorly understood role in stabilising the oxides. There is ample evidence that altering the A-cation significantly alters the hybridisation between the B-site metal t_{2g} d states and the O p π orbitals.

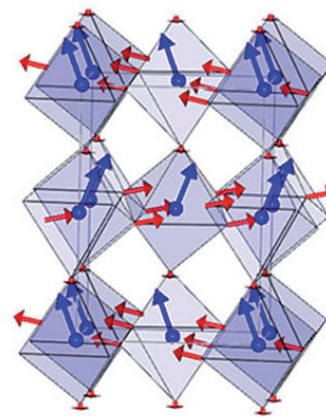


Figure 1. A ferroelectric structure in $Pna2_1$ at 4 K.

Keywords: neutron, Cd-114, ferroelectric