
A Comparative Investigation of Co^{2+} and Mn^{2+} Incorporation into Aluminophosphates Molecular Sieves

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Aluminophosphate molecular sieve ($\text{AlPO}_4\text{-5}$) owns a uni-directional cylindrical channel of 12-membered rings with uniform cross-sections of 0.73 nm along the c axis. Such a channel opening, comparable to the molecule size of aromatics, suggests a potential application in catalysis. However, the neutral framework and lack of proper acidic/basic properties prohibit it from further applications. The isomorphous substitution of metal ions, such as Co^{2+} , Mn^{2+} , Fe^{3+} , Cr^{3+} and Ti^{4+} , into the framework of $\text{AlPO}_4\text{-5}$ may generate highly isolated active sites and unique regio- and shape-selectivity and exhibit potential catalytic applications in the selective oxidation of alkanes and conversion of methanol to olefins.

Metal-substituted aluminophosphate-based microporous materials (MeAPOs) are generally hydrothermally synthesized from precursors containing metal ions and organic template molecules. To obtain MeAPOs with desired location of active sites and well defined atomic environment, it is crucial to get insights into the transition process of metal ion from the precursor gel into the framework.

In the present work, *in situ* experimental and Density Functional Theory (DFT) computations were performed on the Co^{2+} and Mn^{2+} intermediates formed in the synthesis process to investigate the hydrothermal crystallization process of Co^{2+} and Mn^{2+} -substituted $\text{AlPO}_4\text{-5}$. The detailed transformation processes of these two metal ions from the amorphous precursor gel to the crystal were described.

The results indicated that the syntheses of MnAPO-5 and CoAPO-5 were different in the incorporation mechanism of metal ions. For the synthesis of CoAPO-5 , Co^{2+} transferred from octahedral into tetrahedral structure with the crystal formation; while for MnAPO-5 , Mn^{2+} transition to the tetrahedral structure was much more difficult and it occurred after the appearance of long-range ordered microporous structure.