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CATALYTIC ACTIVITY OF CALCIUM-DEFICIENT HYDROXYL- APATITES

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Calcium-deficient hydroxylapatites (CDHA) of the composition $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$, where $0 \leq x \leq 2$ are widely used as catalysts in processes like alcohol dehydration, decomposition of acetals, etc.

CDHA catalytic activity is attributed to the presence of HPO_4^{-2} group. However, after being used for 2 hrs in the reaction of acetal decomposition, all the HPO_4^{-2} groups in CDHA were condensed forming polyphosphate ions of the composition $\text{P}_n\text{O}_{3n+1}$. The catalyst characteristics remained unchanged during further operation. Thus, the HPO_4^{-2} groups are not the origin of the CDHA catalytic activity.

CDHA catalytic activity is suggested to be due to the presence of phosphoric acid being formed during interaction of polyphosphate ions with water vapor at elevated temperatures. CDHA catalytic activity in the mentioned reactions increases with Ca-deficiency of the sample and hence with the portion of polyphosphate. High and long-term catalytic activity of CDHA seems to be dependent on even formation of phosphoric acid in the course of operation. Other Ca-phosphates produce major part of the acid at the beginning of the operation which leads to sharp decrease in the catalyst activity. It has been shown that the main cause of catalyst aging is the destruction of the apatite structure with condensed neutral phosphate formation.

CDHA thermal stability was found to grow with increasing calcium deficiency. The principles of choice and operation of hydroxylapatite catalysts in various processes are discussed.