Studies on structural, textural and acid-base properties of Ca and Sr hydroxyapatites modified with alkali metal/CO$_3^{2-}$ species

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Hydroxyapatites

- Naturally occurring mineral form of Calcium apatite with the general formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and have Ca/P ratio 1.67.

- Contains both acid & basic sites in single crystal lattice and so applied as an active catalyst in many industrial potential reactions.

- Ca can be substituted by Sr, Ba, Pb, Na, K, Cu, Co, Pd etc. or vacancies and OH/PO$_4$ by HPO$_4$, AsO$_4$, VO$_4$, SiO$_4$ or CO$_3$. 

Structure of hydroxyapatite
Precipitation synthesis of apatite solids

Deficient Apatites (M/P = 0.9)

\[ \text{M}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \]

HapD & SrApD

Stoichiometric Apatites (M/P = 1.67)

\[ \text{M}_{10}(\text{PO}_4)_6(\text{OH})_2 \]

Hap & SrAp

Carbonate containing Apatites (Ca/P = 2 & 5.5)

\[ \text{Ca}_{10-x}[(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x][\text{OH}]_{2-2y}(\text{CO}_3)_y] \]

Hap-CO\textsubscript{3} & HapE-CO\textsubscript{3}

Sodium & Carbonate containing Apatites ((Ca+Na)/P = 2.2 & 5.7)

\[ \text{Ca}_{10-x-z-y/2}\text{Na}_y(\text{HPO}_4)_x(\text{PO}_4)_{6-x-z}(\text{CO}_3)_z(\text{OH})_{2-x-z} \]

HapNa-CO\textsubscript{3} & HapE-Na-CO\textsubscript{3}
Structural & textural characterizations

**BET surface area**
- Sr apatites have lower surface areas than Ca apatites due to the increase in crystallite size.
- Surface areas of carbonate rich Ca apatites are lower than other Ca apatites which is also due to the increase in crystallite size.

**SEM**
- Morphology of apatite particles varies with Ca/P ratio & carbonate content.

**XRD**
- XRD patterns have shown variation in the intensity of peaks due to changes in cell parameters.

**FTIR spectroscopy**
- Confirms A-type substitution of OH⁻ by CO₃²⁻ especially in carbonate rich apatites.
- The B-type substitution of PO₄³⁻ by CO₃²⁻ groups was also determined.
Determination of nature of acid sites

**NH₃-TPD**
- Total acid sites determined by NH₃-TPD decreases linearly with increase in Ca/P ratio & carbonate content.

**2-phenylethylamine (PEA)-XPS**
- Basic probe PEA can be retained on Bronsted sites by the formation of an ammonium cation and on Lewis sites by complex formation.
- In apatites HPO₄²⁻ groups behave as Bronsted acid sites and Ca²⁺ as Lewis acid sites.
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