**Local structure around non-crystallized Cu-species incorporated in copper-strontium hydroxyapatite catalysts for the oxidative dehydrogenation of propane**

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**Introduction**

Although it is generally accepted that the catalytic activities on strontium hydroxyapatites (SrHAp) for the oxidative dehydrogenation of propane decrease upon addition of CCl₄ into the feedstream, greater and stable activities have been found with copper-strontium hydroxyapatites (Cu-SrHAp) in the presence of CCl₄. However the role of Cu-species in Cu-SrHAp on the enhancement of the activities in the presence of CCl₄ could not be explained since XRD of Cu-SrHAp was essentially identical to that of SrHAp. In the present report, XAFS has been employed for the analysis of Cu-SrHAp to reveal the structure of Cu-SrHAp and the role of Cu-species in those catalysts on the catalytic activities for the oxidation of propane in the presence of CCl₄.

**Experiments**

Strontium hydroxyapatite (SrHAp) was prepared from Sr(NO₃)₂ and (NH₄)₂HPO₄. The binary catalysts, Cu-SrHAp, were prepared with the incorporation of Cu²⁺ into SrHAp by stirring the hydroxyapatite in aqueous solution of Cu(NO₃)₂·3H₂O at 293 K. The resultant solid was calcined at 773 K for 3 h after drying in air overnight. The catalysts thus obtained are referred to as the “fresh catalysts”. The incorporated catalysts are denoted as CuxxSrHAp, with xx equal to 100 Cu/Sr (atomic ratio) and XRD patterns of those Cu-SrHAp were identical to that of SrHAp regardless of the atomic ratio. The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure (T=723 K, W=0.5 g, F=30 ml/min, P(C₃H₈)=14.5 kPa, P(O₂)=4.1 kPa, and P(CCl₄)=0 or 0.17 kPa). Therefore the suppression of the reduction of Cu-species by the introduction of CCl₄ appears to result in the oxidative dehydrogenation of propane in the absence and presence of CCl₄, the yield of propylene was approximately 0.35 and 3.2%, respectively and the advantageous effect of the introduction of CCl₄ was evident. XRD of Cu₁₄.₆SrHAp previously used for the oxidation in the absence and presence of CCl₄ showed that Cu-species in the catalysts converted into metallic Cu and CuCl, respectively. Therefore the extensive reduction of Cu²⁺ to Cu⁺ observed in the catalyst used in the absence of CCl₄ was suppressed by the addition of CCl₄. Since XRD only affords information on crystalline compounds but not non-crystalline amorphous species, XAFS analysis was employed. In order to obtain information on Cu²⁺, Cu⁺ and Cu₀ from XAFS, Cu K-edges of Cu foil, Cu₂O and CuO were analysed, respectively. XANES showed that the increasing order of the adsorption position from Cu K-edge was Cu²⁺ (8966 eV) < Cu₀ (8970 eV) < Cu₂O (8976 eV) < CuO (8970 eV). The shape of XANES of the catalysts used in the presence and absence of CCl₄ were evidently different from that of metallic Cu and copper oxides. A small extent reduction of Cu-species was observed from XANES of the catalysts after the oxidation in the presence of CCl₄ although the absorption edge was observed at 8971 eV from both catalysts. Therefore the suppression of the reduction of Cu-species by the introduction of CCl₄ appears to result in the enhancement of the catalytic activities.

**References**


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