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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 ($Sr_{10}(PO_4)_6(OH)_2$; SrHAp) for the oxidative dehydrogenation of propane decrease upon addition of CCl_4 into the feedstream, greater and stable activities have been found with copper-strontium hydroxyapatites (Cu-SrHAp) in the presence of CCl_4. However the role of Cu-species in Cu-SrHAp on the enhancement of the activities in the presence of CCl_4 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 CCl_4.

Experimentals

Strontium hydroxyapatite (SrHAp) was prepared from $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$. The binary catalysts, Cu-SrHAp, were prepared with the incorporation of Cu^{2+} into SrHAp by stirring the hydroxyapatite in aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ 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 SrHgAp 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, $P(C_3H_8)$ = 14.5 kPa, $P(O_2)$=4.1 kPa, and $P(CCl_4)$=0 or 0.17 kPa). X-ray absorption spectroscopy (XAFS) was measured (3 GeV) with a storage ring current of 67 mA at the High Energy Research Organization. The X-rays were monochromatized with channel-cut Si(311) crystals at the BL-10B station for the measurement of X-ray absorption fine structure (XAFS) near the Sr-K while those were monochromatized with Si(111) double monochromator and the higher order harmonics were eliminated by a focusing double mirror system at BL-9A station for the measurement of XAFS near Cu-K edges. The photon energy was scanned in the range 8.6-10.0 and 15.8-17.1 keV for Cu-K and Sr-K edges, respectively [1].

Results and Discussion

As described above, XRD patterns of fresh SrHAp, Cu6.6SrHAp, Cu8.2SrHAp and Cu14.6SrHAp were essentially identical to the reference pattern for the stoichiometric SrHAp (JCPDS 33-1348). However since X-ray absorption due to Cu species in those Cu-SrHAp was evidently observed, the presence of Cu-species in those catalysts was confirmed by XAFS analyses. The nearest neighbour distance around Cu cores in those Cu-SrHAp was approximately 0.194 nm, which was essentially identical to Cu^{2+}-O (0.195 nm) but not to Cu^{+}-O (0.185 nm) in Cu_2O and Cu^0-Cu^0 (0.255 nm) in metallic Cu, indicating that Cu-species was incorporated in Cu-SrHAp as Cu^{2+}. The present structural information on Cu-SrHAp reveals that Sr^{2+} in SrHAp is replaced by Cu^{2+}. Since the nearest neighbour distance around Sr cores in those Cu-SrHAp was approximately 0.254 nm, it is reasonable that XRD patterns of those catalysts are essentially identical to that of SrHAp. In employing Cu14.6SrHAp for the oxidative dehydrogenation of propane in the absence and presence of CCl_4, the yield of propylene was approximately 0.35 and 3.2%, respectively and the advantageous effect of the introduction of CCl_4 was evident. XRD of Cu14.6SrHAp previously used for the oxidation in the absence and presence of CCl_4 showed that Cu-species in the catalysts converted into metallic Cu and CuCl, respectively. Therefore the extensive reduction of Cu^{2+} to Co^0 observed in the catalyst used in the absence of CCl_4 was suppressed by the addition of CCl_4. Since XRD only affords information on crystalline compounds but not non-crystalline amorphous species, XAFS analysis was employed. In order to obtain information on Cu^0, Cu^+ and Cu^{2+} from XAFS, Cu K-edges of Cu foil, Cu_2O and CuO were analysed, respectively. XANES showed that the increasing order of the adsorption position from Cu K-edge was Cu (8966 eV) <Cu_2O (8967 eV) <CuO (8970 eV). The shape of XANES of the catalysts used in the presence and absence of CCl_4 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 CCl_4 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 CCl_4 appears to result in the enhancement of the catalytic activities.

References

[1] S. Sugiyama et al., J. Chem. Eng. Jpn., **36**, 210 (2003).

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