

Effects of the incorporation of calcium into magnesium pyro-vanadate on the oxidative dehydrogenation of propane and the local structure around vanadium

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Introduction

Magnesium *pyro*-vanadate ($\text{Mg}_2\text{V}_2\text{O}_7$) is one of the active catalysts for the oxidative dehydrogenation of propane to propylene. The ease of removal of the lattice oxygen from the catalyst explains the great activities for the oxidative dehydrogenation [1]. Although the contribution of the lattice oxygen to the oxidation of propane is evident, the influence of component divalent cation on the oxidation and the structure is still unclear. In the present report, Ca^{2+} -incorporated $\text{Mg}_2\text{V}_2\text{O}_7$ is employed for the oxidative dehydrogenation of propane and the effect of the incorporation of Mg^{2+} on the local structure around vanadium is analyzed by X-ray absorption fine structure (XAFS). Furthermore the XAFS results obtained from calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) partly substituted with vanadate (V-CaHAp), which showed great activities for the oxidative dehydrogenation of propane [2], are also described.

Experimental

Magnesium *pyro*-vanadate that incorporated Ca^{2+} , which are denoted as $\text{Mg}_{2-x}\text{Ca}_x\text{V}_2\text{O}_7$, was prepared from $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and NH_4VO_3 as shown in the previous report on magnesium vanadates [1]. The preparation of V-CaHAp was prepared with the preparation procedure described in our previous paper [2]. Fixed-bed continuous flow reactor operated at atmospheric pressure was employed for the catalyst activity test under the following conditions: $T=723\text{ K}$, $W=0.5\text{ g}$, $P(\text{C}_3\text{H}_8)=14.4\text{ kPa}$, $P(\text{O}_2)=4.1\text{ kPa}$ and $F=30\text{ ml/min}$. X-ray absorption fine structure (XAFS) near V K-edge was measured (2.5 GeV) with a storage ring current of 353-418 mA at the High Energy Research Organization. The X-rays were monochromatized with Si(111) at BL-7C station. The absorption spectra were observed using ionization chambers in a transmission mode.

Results and Discussion

The catalytic activities for the oxidative dehydrogenation of propane on $\text{Mg}_{1-x}\text{Ca}_x\text{V}_2\text{O}_7$ and V-CaHAp together with $\text{Mg}_2\text{V}_2\text{O}_7$ were described in Table 1. As expected, the acceptable conversion of C_3H_8 together with the great selectivity to C_3H_6 was observed on $\text{Mg}_2\text{V}_2\text{O}_7$. On $\text{Mg}_{2-x}\text{Ca}_x\text{V}_2\text{O}_7$, the decrease and the increase of the conversion of C_3H_8 and the selectivity to C_3H_6 , respectively, with increasing Ca^{2+} -content in the catalyst

were observed. On V-CaHAp, comparable activities for the formation of C_3H_6 to those on $\text{Mg}_2\text{V}_2\text{O}_7$ were observed while the activities were strongly influenced by V-content in the catalysts.

Table 1. Activities on $\text{Mg}_{1-x}\text{Ca}_x\text{V}_2\text{O}_7$ and V-CaHAp

Catalyst	Conversion (%)		Selectivity (%)		
	C_3H_8	O_2	C_3H_6	CO	CO_2
$\text{Mg}_2\text{V}_2\text{O}_7$	14.0	87	50.9	29.3	19.8
$\text{Mg}_{1.90}\text{Ca}_{0.10}\text{V}_2\text{O}_7$	7.7	36	64.4	20.4	15.2
$\text{Mg}_{1.80}\text{Ca}_{0.20}\text{V}_2\text{O}_7$	5.1	39	76.8	12.8	10.4
V-CaHAp (V/P=0)	7.6	70	3.5	46.6	49.8
V-CaHAp (V/P=0.05)	17.2	89	52.4	27.5	20.2
V-CaHAp (V/P=0.10)	12.5	92	58.5	21.3	20.2

It should be noted that the mobility of the lattice oxygen was strongly influenced by the incorporation of Ca^{2+} into $\text{Mg}_2\text{V}_2\text{O}_7$ and vanadate into CaHAp (not shown). Therefore the influence of the incorporation of Ca^{2+} to $\text{Mg}_2\text{V}_2\text{O}_7$ and that of vanadate to CaHAp on the activities and the mobility of lattice oxygen were evident. However it is not clear that Ca^{2+} and vanadate are certainly incorporated into the corresponding site: Mg^{2+} site in $\text{Mg}_2\text{V}_2\text{O}_7$ and PO_4^{3-} site in CaHAp since XRD patterns of $\text{Mg}_{2-x}\text{Ca}_x\text{V}_2\text{O}_7$ and V-CaHAp were essentially identical to $\text{Mg}_2\text{V}_2\text{O}_7$ and CaHAp. The nearest-neighbor distances around V in $\text{Mg}_2\text{V}_2\text{O}_7$ and $\text{Mg}_{1.80}\text{Ca}_{0.20}\text{V}_2\text{O}_7$, that were calculated from XAFS data, were 0.175 and 0.177 nm, respectively, indicating that the distance of V-O became longer after the incorporation of larger Ca^{2+} into $\text{Mg}_2\text{V}_2\text{O}_7$, indicating that Mg^{2+} is certainly substituted by Ca^{2+} [3]. However XAFS analysis of V-CaHAp could not be carried out since the absorption intensity was not sufficient. The employment of the fluorescence mode may be needed for the analysis of V-CaHAp.

References

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