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Oxidative dehydrogenation of propane on calcium hydroxyapatites partially substituted with vanadate

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Solid solutions of phosphate and vanadate calcium hydroxyapatites were synthesized and the catalytic activities for the oxidative dehydrogenation of propane to propylene on those catalysts were examined. Although the conversion of propane and the selectivity to propylene were 7.6 and 3.5% on calcium hydroxyapatite (CaHAp), the incorporation of vanadate to CaHAp by $V/P=0.05$ (atomic ratio) resulted in the enhancement of the conversion and the selectivity to 17.2 and 52.4%, respectively, corresponding to those on $Mg_2V_2O_7$ under the same reaction conditions (14.0 and 50.9%, respectively).

KEY WORDS: oxidative dehydrogenation; propane; calcium hydroxyapatite; vanadate.

1. Introduction

The oxidative dehydrogenation of propane to propylene over various hydroxyapatites [$M_{10}(PO_4)_6(OH)_2$; M = divalent cation] and magnesium vanadates has been extensively studied in our laboratory. It has been found that hydroxyapatites with M=Ca, Sr and Ba afford rather low activities for the oxidative dehydrogenation [1,2]. However the introduction of Co^{2+} into strontium hydroxyapatite (M=Sr; SrHAp) resulted in the enhancement of the conversion of C_3H_8 and the selectivity to C_3H_6 [3]. Based on the results from SrHAp doped and un-doped with Co^{2+}, it has been suggested that oxygen species, similar to lattice oxygen in oxide catalysts, as formed from hydrogen desorption of OH groups in the hydroxyapatite, may contribute to the activation of propane [3]. Furthermore the catalytic activities of magnesium vanadates (MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$) doped and un-doped with Ca^{2+} and Cu^{2+} for the oxidative dehydrogenation of propane have shown that the activities for the process may be related to the ease of removal of lattice oxygen from vanadate groups [4–6]. Those results reveal that the combination of OH and VO_4 groups, both of which are catalytic active sites on the hydroxyapatites and magnesium vanadates, respectively, may afford additional active catalysts for the oxidative dehydrogenation of propane. Recently vanadate calcium hydroxyapatites have been prepared and it has been reported that the structure of the apatites can be identified as $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ [7,8]. It should be noted that those vanadate calcium hydroxyapatites possess pairs of catalytic active sites such as OH and VO_4 groups suggested above.

In the present paper, calcium hydroxyapatites incorporated with VO_4^{3-} were prepared by the procedure reported by Boechat *et al.* [7,8], and employed as a catalyst for the oxidative dehydrogenation of propane.

2. Experimental

Calcium hydroxyapatites incorporated with VO_4^{3-}, $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ where $V/P=0$, 0.025, 0.05 and 0.10 (atomic ratio), were prepared from double precipitation of phosphate and vanadate anions through stoichiometric addition of ammoniac solutions of phosphate and vanadate to calcium nitrate under reflux conditions [7,8]. The precipitate was dried at 353 K overnight and calcined at 773 K for 3 h. It should be noted that the employment of higher calcination temperature resulted in the formation of $Ca_3(PO_4)_2$. The catalysts were characterized by XRD. Specific surface areas were measured by N_2 adsorption at 77 K by application of the BET theory. Particles of 0.85–1.70 mm were employed as a catalyst in a fixed-bed continuous flow reactor operated at atmospheric pressure. In all experiments, the catalyst (0.5 g) was heated to the reaction temperature (723 K) while maintaining a continuous flow of helium and was held at this temperature under a 25 mL/min flow of oxygen for 1 h. The reaction conditions were as follows unless otherwise stated: $P(C_3H_8)=14.4$ kPa, $P(O_2)=4.1$ or 0 kPa and $F=30$ mL/min. No homogeneous oxidation of propane was observed under the present conditions. The reaction was monitored with an on-stream Shimadzu GC-8APT gas-chromatograph with a TC detector. The conversion

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of propane was calculated from products and from the propane introduced into the feed-stream. The selectivities were calculated from the conversion of propane to each product on a carbon basis. The carbon mass balances were 100 ± 5%. The reaction rates per unit of surface area were estimated as the rate ($r = FC_0X_A/F$, in which F, C_0, X_A and W were flow rate, initial concentration of C_3H_8, conversion of C_3H_8 and catalyst weight) per catalyst surface area [9].

3. Results and discussion

XRD patterns of four catalysts are shown in figure 1. XRD patterns of calcium hydroxyapatite in the absence of VO_4 groups (figure 1a) matched the reference data for $Ca_{10}(PO_4)_6(OH)_2$ (JCPDS 9-0423). With increasing content of vanadate from V/P = 0.025 to 0.10, XRD patterns with poor crystallinity were observed (figure 1b–d). Lattice constants estimated with the results shown in figure 1, based on hexagonal structure, are described in table 1, together with the specific surface area, the apparent density and catalytic activities. The specific surface area and the apparent density were not sensitive to the V/P ratios. The lattice constants of a and c increased and decreased, respectively, with increasing V/P ratio in the catalysts, indicating that vanadates are incorporated into CaHAp as solid solution type but not a separate phase. The formation of solid solution may be further supported by the total exchange of phosphate with vanadate in calcium fluor- and chlorapatite [10].

As expected, lower activities for the oxidative dehydrogenation of propane were observed on CaHAp (V/P = 0 in table 1). Upon incorporation of vanadate into CaHAp, the conversion of C_3H_8 and the selectivity to C_3H_6 were evidently improved. Maximum conversion of C_3H_8 and selectivity to C_3H_6 reached 17.2 and 52.4%, respectively, on the catalyst with V/P = 0.05. Those vanadate-incorporated catalysts showed rather stable activities up to 6 h on-stream. Furthermore XRD patterns of the catalysts after the oxidation were matched with those before the oxidation. It should be noted that a conversion of 14.0% and a selectivity to 50.9% were observed on $Mg_2V_2O_7$ [6], one of the most active catalysts for the oxidative dehydrogenation of propane. Since the surface areas of the vanadate-incorporated catalysts were approximately 10-times greater that those of magnesium vanadates [6], the reaction rates per unit of surface area on the vanadate-incorporated catalysts were smaller than those on magnesium vanadates.

In order to examine the contribution of oxygen species in those catalysts, we observed the catalysts, the conversion of propane was studied, in the absence of oxygen on the vanadate-incorporated CaHAp (figure 2). The conversion of C_3H_8 was essentially negligible on CaHAp, indicating that oxygen species in PO_4 groups cannot be abstracted with the alkane itself. However a

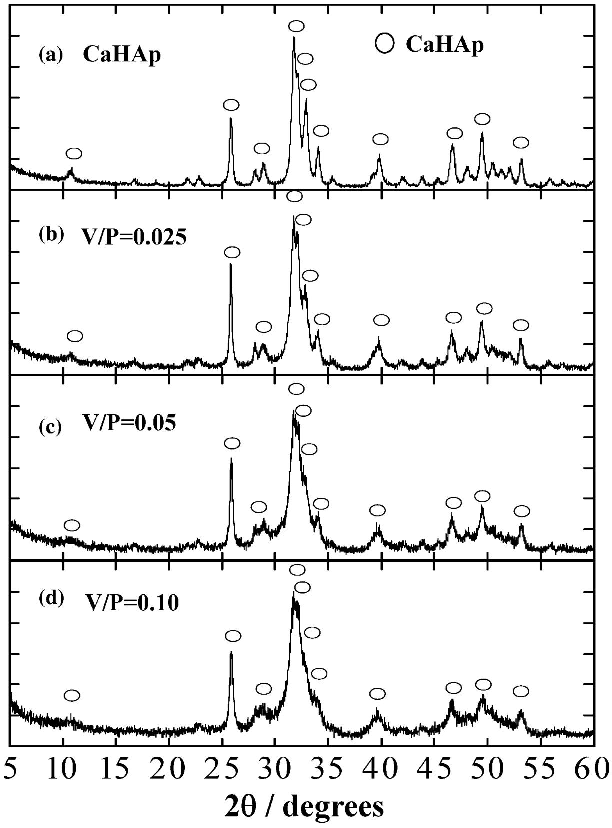

Figure 1. XRD patterns of CaHAp incorporated with VO_4^{3-}.

Table 1
Lattice constants, surface area (S.A.), apparent density (A.D.) and activities on various catalysts at 3 h on-stream

V/P	Lattice const. (Å)		S.A. m^2/g	A.D. g/mL	Conv. (%)		Select. (%)			Rate mol min^{-1} m^{-2}
	a	c			C_3H_8	O_2	C_3H_6	CO_2	CO	
0	9.426	6.881	46	0.54	7.6	70	3.5	49.8	46.6	5.91×10^{-7}
0.025	9.429	6.867	44	0.59	12.9	73	59.3	16.3	24.4	10.50×10^{-7}
0.05	9.456	6.865	44	0.64	17.2	89	52.4	20.2	27.5	14.00×10^{-7}
0.10	9.457	6.831	55	0.63	12.5	92	58.5	20.2	21.3	8.14×10^{-7}

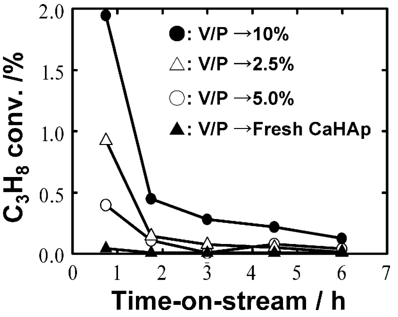

Figure 2. Propane conversion without O_2 on CaHAp incorporated with VO_4^{3-}.

measurable conversion of C_3H_8 was observed on the catalysts incorporated with vanadates but decreased during 0.45–1.75 h on-stream, indicating that the oxygen species in vanadates are abstracted by propane. Similar observations have been made with magnesium vanadate catalysts, in which the reduction of V^{5+} to V^{4+} proceeded together with the abstraction of lattice oxygen [4–6]. Although magnesium vanadates were completely converted to unidentified phases after the conversion of propane in the absence of gaseous oxygen in the feed-stream [4–6], XRD patterns to the catalysts incorporated with vanadates after propane conversion were essentially identical to those before the conversion (not shown). Although redox properties of vanadium species could not be detected due to the limiting contents of the vanadate in the catalyst, the redox nature of vanadate species directly contributes to the activities on the vanadate-incorporated CaHAp catalysts. It is worthwhile to mention that such a contribution of lattice oxygen to the catalytic reactions has been pointed out in some oxidations on oxide catalysts such as VO_x/ZrO_2 [11] and manganase oxide doped with proton and/or potassium [12], in which isotope-labeling study with ^{16}O and ^{18}O was employed.

As described above, the catalytic activities on the vanadate-incorporated catalysts are stable by 6 h on-stream. However it is important to reveal information on deactivation and regenaration on those catalysts. In order to obtain information on catalytic deactivation and regeneration, which can be expected from the results in figure 2, the catalyst with V/P = 0.10 previously employed for obtaining the results shown in figure 2 was again treated with gaseous oxygen (25 mL/min) for 1 h at 773 K and then supplied to the oxidative dehydrogenation of propane in the presence of gaseous oxygen. The activities (C_3H_8 conversion = 12.3% and C_3H_6 selectivity = 57.9%) on the retreated catalyst were comparable to those shown in table 1. Therefore oxygen-treatment will be possible to regenerate the used catalysts after the deactivation.

4. Conclusion

The incorporation of vanadate in calcium hydroxyapatite resulted in the enhancement of the catalytic activities for the oxidative dehydrogenation of propane. It is evident that the direct contribution of the lattice oxygen in the vanadate plays an important role in the enhancement. The activities observed on vanadium-incorporated catalysts essentially corresponded to those on magnesium pyro-vanadate, which is one of the most active catalysts for the oxidative dehydrogenation. The present results reveal that the modified hydroxyapatite may be another candidate as a catalyst for the oxidative dehydrogenation process although the oxide catalysts have been generally examined for the oxidative dehydrogenation process.

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