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Catalytic Behavior of Calcium Phosphates for Decompositions of 2-Propanol and Ethanol

The present work was carried out to present catalytic characteristics of calcium phosphates selected on the basis of the following viewpoints: (i) structural and compositional resemblances, (ii) same composition but different structures, (iii) same structure but slightly different compositions, and (iv) variation of Ca/P ratio. Decompositions of 2-propanol and ethanol were adopted as catalytic test reactions over calcium phosphates.

Table 1 lists calcium phosphates used here with their abbreviations and preparation methods. Octacalcium phosphate (OCP) was prepared by the hydrolysis of α-$Ca_3(PO_4)_2$ (α-TCP) at 343 K and pH 4.8 for 3 h (*1*). Calcium deficient hydroxyapatite (DAp), $Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z} \cdot nH_2O$; Ca/P = 1.51, $z = 0.94$, $n = 3.4$, was prepared by the hydrolysis of $CaHPO_4 \cdot 2H_2O$ (DCPD) at 313 K and pH 8.5 for 3 h (*2*). 2-Propanol and ethanol were reagent grades and used without further purification. The acidity and acid strength were measured by titration of 0.01 *N* benzene solution of *n*-butylamine in the presence of Hammett indicators. The catalytic decompositions of 2-propanol and ethanol were conducted by passing the alcohol vapors with a N_2 carrier gas of 20 ml min^{-1} through

TABLE 1

Preparation of Calcium Phosphates

Classification	Abbreviation	Compound	Ca/P (molar ratio)	Preparation	BET area (m^2 g^{-1})
A[a]	OCP	$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	1.35	See text	24
	DAp	See text	1.51	See text	66
	DCPD	$CaHPO_4 \cdot 2H_2O$	1.00	Commercial reagent	1.2
B	γ-C_2P	γ-$Ca_2P_2O_7$	1.00	DCPD heated at 773 K for 18 days	~1
	β-C_2P	β-$Ca_2P_2O_7$	1.00	DCPD heated at 1133 K for 3 h	~1
	α-C_2P	α-$Ca_2P_2O_7$	1.00	DCPD heated at 1573 K for 24 h	~1
C	α-TCP	α-$Ca_3(PO_4)_2$	1.50	β-TCP heated at 1573 K for 2 h	~1
	β-TCP	β-$Ca_3(PO_4)_2$	1.50	γ-C_2P + $CaCO_3$ heated at 1273 K for 5 days	~1
	Al-TCP	Al-containing β-TCP	1.44[b]	α-TCP + 0.25 $AlPO_4$ heated at 1623 K for 7 h	~1
D	HAp	$Ca_{10}(PO_4)_6(OH)_2$	1.67	β-C_2P + excess $CaCO_3$, at 1473 K for 3 h in H_2O vapor and washed with NH_4Cl solution	~1
	FAp	$Ca_{10}(PO_4)_6F_2$	1.67	3β-TCP + CaF_2, 1373 K for 2.5 h in N_2	~1
	CAp	$Ca_{10}(PO_4)_6Cl_2$	1.67	β-C_2P + $CaCO_3$ + excess $CaCl_2$, at 1473 K for 3 h in N_2 and washed with NH_4Cl solution	~1

[a] Thermal dehydration change: OCP—150°C $\sim\rightarrow$ 0.5 HAp + 3 $CaHPO_4$—200°C → 0.5 HAP + 1.5 C_2P—600°C $\sim\rightarrow$ 2β-TCP + 2β-C_2P (1); DAp—~700°C → $Ca_{9.06}(P_2O_7)_{0.94}(PO_4)_{4.12}(OH)_2$—700 ~ 800°C → HAp + β-TCP (6); DCPD—150 ~ 160°C → $CaHPO_4$—400°C $\sim\rightarrow$ γ-C_2P.

[b] (Ca + Al)/P ratio.

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a 0.5 g bed of catalyst packed in a Pyrex V-tube reactor with an inner diameter of 6 mm. The reactor packed with the catalysts was heated and kept to desired temperatures in a stream of N_2 gas for 1 h prior to introduction of 2-propanol or ethanol vapor. Partial pressures of the alcohols in the carrier gas were 5.9 kPa both. Outlet gasses from the reactor were analyzed by gas chromatography.

Considering literature data on acidic and basic surface properties of calcium phosphates, it was speculated that the catalysts of A and B groups were acidic and the catalysts of C and D groups were amphoteric between $+3.3 \leq H_0 \leq +9.3$. The strongest acid strength of, for example, OCP and DAp was observed to be $+1.5 < H_0 \leq +3.3$ at calcination temperatures of 573–773 K, and at lower and higher temperatures to be $+3.3 < H_0 \leq +4.8$. No basic sites of $H_0 \geq +7.1$ were detected in both catalysts heated at various temperatures up to 1173 K. Cumulative acidities were measured for only OCP as shown in Fig. 1. The increase and decrease in acid strength and acidity with calcination temperature would be due to liberation of adsorbed H_2O molecules which weakened acidic character originated from HPO_4^{2-}, OH^- vacancies and lattice H_2O (*3–5*), and also due to thermal changes such as additional formation of HPO_4^{2-} by the reaction of PO_4^{3-} with lattice H_2O (*1*, *6*) and decrease of HPO_4^{2-} amount by its condensation–dehydration.

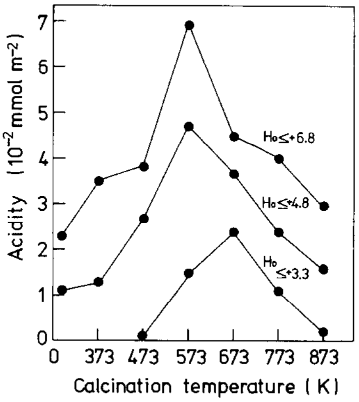

FIG. 1. Variation of cumulative acidity of OCP as a function of calcination temperature: Acidity of $H_0 < +1.5$ was zero.

Dehydration and dehydrogenation degrees of the alcohols over the catalysts were measured at various temperatures and plotted against the temperatures (all the figures are omitted). Catalytic characteristics of the calcium phosphates for the decomposition of the alcohols are summarized in Table 2. Main reactions were simply intramolecular dehydration and/or dehydrogenation. Intermolecular reactions such as hexadiene formation (*7*) from 2-propanol was not observed. The temperature at 50% conversion was used as an approximate index for expressing the degree of catalytic activity. Although it was difficult to elucidate what parameters, e.g., Ca/P or Ca/O ratio, Ca–O bond length, acidity, etc., related quantitatively to the catalytic activity and selectivity, some apparent tendencies could be pointed out. A- and B-catalysts having acidic surface property were also acidic in catalytic behavior, while C- and D-catalysts were amphoteric. A-catalysts containing acid phosphate groups and water molecules exhibited strong dehydration character. In B-, C-, and D-catalysts without acid phosphate groups and water molecules, the degree of dehydrogenation tended to go up with an increase in Ca/P ratio. The difference in dehydration/dehydrogenation selectivity between the two alcohol decompositions might suggest that dehydrogenation of 1-ols were easier than that of 2-ols. By-products as shown in the footnotes of Table 2 were detected mainly over catalysts having dehydrogenation character. The differences in catalytic activity and the selectivity in each of the B-, C-, and D-catalysts reflect structural and compositional effects on the catalytic behavior. For example, γ-C_2P is regarded as a metastable phase and contains a trace H_2O and not so strong P–O–P bond compared with the other C_2Ps, so that γ-C_2P seemed to cause a comparatively high activity and selectivity. A similar idea held

TABLE 2

Catalytic Decomposition of Alcohols over Calcium Phosphates

Classification	Catalyst	Ca/P (molar ratio)	2-Propanol				Ethanol			
			Temperature at 50% conversion (K)	Decomposition[a]			Temperature at 50% conversion (K)	Decomposition[a]		
				$-H_2O$	$-H_2$	Others		$-H_2O$	$-H_2$	Others
A	OCP	1.35	528	◎	X	X	623	◎	X	tr.[d]
	DAP	1.51	528	◎	X	X	633	◎	X	tr.[d]
	DCPD	1.00	568	◎	X	X	—	—	—	—
B	γ-C_2P	1.00	628	◎	X	X	743	◎	tr.	X
	β-C_2P	1.00	703	◎	X	X	773	◎	△	X
	α-C_2P	1.00	703	◎	X	X	798	◎	△	X
C	α-TCP	1.50	718	◎	tr.	tr.[c]	873	○	○	△[e]
	β-TCP	1.50	753	△	○	tr.[c]	823	△	○	△[e]
	Al-TCP	1.44[b]	793	△	○	tr.[c]	858	tr.	◎	△[e]
D	HAp	1.67	683	tr.	◎	tr.[c]	793	X	◎	○[f]
	FAp	1.67	733	tr.	◎	tr.[c]	818	tr.	◎	○[f]
	CAp	1.67	753	△	○	tr.[c]	833	tr.	◎	○[f]

[a] $-H_2O$ and $-H_2$ mean intramolecular simple dehydration and dehydrogenation, respectively. Others are reactions other than the $-H_2O$ and $-H_2$. Symbols represent decreasing degrees of reaction: ◎, much; ○, middle; △, slight; tr., trace; X, no.

[b] See footnote *b* of Table 1.

[c] Slight coking and trace acetaldehyde were recognized above ca. 693 K.

[d] Trace acetone appeared at 573–663 K and disappeared above 673 K.

[e] Strong coking and trace propylene were recognized above ca. 823 K.

[f] Strong coking, trace propylene, trace acetone, and considerable CO_2 were recognized above ca. 773 K.

roughly for α-TCP which also has a metastable phase below 1453 K and has a "looser" structure than the β-form (*9*). The Al-TCP having a more contracted β-structure than β-TCP was the most inactive among the C-catalysts. The substitutions of F^- and Cl^- for OH^- in HAp tended to soften the selectivity slightly. A similar effect of substitution was already known in the case of the substitution of Cu^{2+} or Ni^{2+} for Ca^{2+} in HAp, i.e., the substitution caused a large increase in activity for dehydrogenation of alcohols with little effect on the dehydration function of HAp (*10*).

Zero-order kinetics (*4*) were confirmed for the dehydration over some of the catalysts (figures are omitted). Activation energies obtained were 160 kJ mol^{-1} for 2-propanol and 130 kJ mol^{-1} for ethanol over OCP and DAp, and 125 ± 20 kJ mol^{-1} for 2-propanol over B-catalysts, α-TCP and β-TCP. The zero-order kinetics suggests that desorption of products from the catalyst surface is rate-controlling (*4*). According to such an explanation, the dehydration of 2-propanol over the calcium phosphates was considered to be rate-controlled by desorption of, at least, H_2O from the catalyst surface since the enthalpy of immersion of hydroxyapatite in water was higher than that in 2-propanol (*11*).

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