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ACIDIC AND BASIC PROPERTIES OF P_2O_5-CaO MIXED OXIDES

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P_2O_5-CaO was prepared and its acidic and basic properties were studied. It was found that P_2O_5-CaO ($0.1 \leqq P_2O_5/CaO \leqq 0.6$) had both acidic and basic properties. The maximum strength Ho of acid site and that of base site for P_2O_5-CaO (mole ratio : 0.2) were 1.5 and 17.2 respectively.

Mixed oxides which exhibit acidic properties have been reported by many workers.$^{1)}$ However, little work has been done for those which have acidic and basic properties. CaO-SiO_2, SrO-$SiO_2$$^{2)}$, and MgO-$Al_2O_3$$^{3)}$ are known to have both acidic and basic properties, each of which contains either SiO_2 or Al_2O_3. These facts suggest that the mixed oxide comprised of a basic oxide and an acidic oxide may generally exhibit acid-base bifunctional catalysis. From this point of view, we have initiated a systematic study on mixed oxides which contain P_2O_5 as an acidic oxide. The present letter reports the acidic and basic properties of P_2O_5-CaO mixed oxides(abbreviated as P_2O_5-CaO) with various compositions.

The P_2O_5-CaO was prepared from calcium hydroxide (a guaranteed reagent of Kanto Kagaku Co.) and 85% orthophosphoric acid (a guaranteed reagent of Wako Junyaku Co.) by mixing the reactants and keeping the mixture for 1-3 days at 100 °C. The obtained solid was crushed and successively calcined for 3 hr in air at 200-700°C. The acid and basic strengths of P_2O_5-CaO were determined by the conventional indicator method. The acid and basic amounts were measured by titrating the solid in anhydrous benzene with n-butylamine and benzoic acid respectively. The indicators used were 4-chloro-2-nitroaniline (pKa : 17.2), 2,4-dinitroaniline (pKa : 15.0), phenolphtalein (pKa : 9.3), bromothymol blue (pKa : 7.2), p-dimethylaminoazobenzene (pKa : 3.3), benzeneazodiphenylamine (pKa : 1.5), dicinnamalacetone (pKa : -3.0) and benzalacetophenone (pKa : -5.6).

The effect of P_2O_5/CaO molar ratio on the acidic and basic properties of P_2O_5-CaO calcined at 400°C are given in Table 1. Sample 1 has only basic character and sample 7 only acid one, but the samples from 2 to 6 have both basic and acidic properties. In the range of P_2O_5/CaO from 0.1 to 0.6, the strength of acid site becomes higher and that of base site becomes lower with the ratio of P_2O_5/CaO.

Table 1 Acidic and basic properties of P_2O_5-CaO calcined at 400°C

No. of sample (P_2O_5/CaO mole ratio)		Maximum acid strength(Ho)	Acid amount (mmol/g)[a]	Maximum basic strength(Ho)	Base amount (mmol/g)[b]
1	(0)	-	0	17.2	0.924
2	(0.1)	3.3	0	17.2	0.717
3	(0.2)	1.5	0.021	17.2	0.458
4	(0.3)	1.5	0.032	17.2	0.226
5	(0.4)	1.5	0.040	9.3	0
6	(0.6)	-3.0	0.042	7.1	0
7	(0.7)	-3.0	0.021	-	0

a) Measured using benzeneazodiphenylamine (pKa : 1.5)
b) Measured using 4-chloro-2-nitroaniline (pKa : 17.2)

The acidic and basic properties of sample 3 calcined at various temperatures are listed in Table 2. The acid and basic amounts increase sharply, in the range of 200 to 400°C, with the calcination temperature and then decrease. Comparing P_2O_5-CaO with other acid-base bifunctional catalysts we see that the former has fairly strong acid sites. Sample 3 has the maximum acid strength Ho of 1.5 as compared with 6.8 for Li_2NaPO_4, $LiNa_2PO_4$, and LiK_2PO_4, 4.8 for $Ca_3(PO_4)_2$[4] and MgO-Al_2O_3[3], and 3.3 for SiO_2-CaO [2].

Table 2 Acidic and basic properties of P_2O_5-CaO (P_2O_5/CaO : 0.2) calcined at various temperatures

Calcination temp. (°C)	Acid amount (mmol/g)			Base amount (mmol/g)		
	Ho ≦ 3.3	Ho ≦ 1.5	Ho ≦ -3.0	Ho ≧ 9.3	Ho ≧ 15.0	Ho ≧ 17.2
200	0.005	0	0	0.063	0	0
300	0.011	0.005	0	0.038	0.063	0
400	0.022	0.021	0	0.285	0.498	0.458
500	0.015	0.010	0	0.272	0.362	0.312
600	0.005	0	0	0.068	0.127	0.114
700	0	0	0	0.069	0.044	0.016

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