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A Pronounced Catalytic Activity of an Acidic Cesium Salt of 12-Tungstophosphoric Acid for Ester Decomposition in Solid-liquid System

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The acidic Cs salt of 12-tungstophosphoric acid (Cs/polyanion = 2.5) was much more active for liquid phase decomposition of cyclohexyl acetate than Nafion, HY-zeolite, H-ZSM-5, Al^{3+}-exchanged montmorillonite, and SO_4^{2-}/ZrO_2.

12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$) catalyzes a wide variety of reactions in both homogeneous and heterogeneous systems.1) Only a few examples, in which solid heteropoly compounds were applied to the liquid phase reactions, have been reported.2,3) Here, we wish to report that the acidic Cs salt, $H_{0.5}Cs_{2.5}PW_{12}O_{40}$, efficiently catalyzed the liquid phase decomposition of cyclohexyl acetate, while other well-known solid acids were much less active.

The decomposition of cyclohexyl acetate to cyclohexene and acetic acid was carried out in a batch reactor at 373 K under an atmosphere of N_2 with 2 ml (13.6 mmol) of reactant dissolved in 18 ml of m-xylene. Prior to the reaction, the catalysts (60 - 600 mg) were pretreated in a flow of He at elevated temperatures. The products were analyzed by a gas chromatograph using a Unisole F-200 column. The Cs salt was prepared by the same method as in the previous report.4)

Catalytic activities as well as the surface areas and the acid amounts are summarized in Table 1. $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ showed the activity higher than the parent $H_3PW_{12}O_{40}$ (about 2.5 times) and was much more active than the other solid acids given in Table 1. Adams et al.5) claimed that Al^{3+}-montmorillonite was highly active for this reaction. Table 1 reveals that $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ was much better than Al^{3+}-montmorillonite. Furthermore, it was found that the activity of the Cs salt was about 40 times as high as that of Nafion. As shown in Table 1, $SO_4^{2-}/ZrO_2$6) was comparable with Nafion and was less active than the Cs salt. Both HY-zeolite and ZSM-5 gave low activities in spite of their large amounts of acid sites. While Izumi et al.2) observed that $H_3PW_{12}O_{40}$/Activated carbon catalyzed

Table 1. Catalytic Activity for Decomposition of Cyclohexyl Acetate at 373 K

Catalyst	Pretreat. temp[a] /K	Surface area/m^2·g^{-1}	Acid amount[b] /μmol·g^{-1}	Activity[c] /mmol·g^{-1}·h^{-1}
$H_{0.5}Cs_{2.5}PW_{12}O_{40}$	573	136	30	130 (45)
$H_3PW_{12}O_{40}$	573	6	8[d]	50 (0.1)
18wt%$H_3PW_{12}O_{40}$/AC[e]	573	585	-	6 (0)
Al^{3+}-montmorillonite[f]	373	10	-	3 (-)
Nafion[g]	373	0.02	>800[h]	3 (-)
HY-zeolite[i]	723	660	867	3 (3)
SO_4^{2-}/ZrO_2[j]	643	85	-	3 (-)
H-ZSM-5[k]	808	332	416	1 (1)
SiO_2-Al_2O_3[l]	723	546	150	0.6 (0.2)

a) Pretreatment temperature in a flow of He. b) The amount of pyridine held after evacuation at 423 K; the errors are about ± 10%. c) Figures in parentheses are the activities just after the catalysts were dried at room temperature. d) Amount of proton on the surface calculated from the surface area. e) AC; Wako Pure Chemical Ind. Ltd. f) Prepared from an aqueous solution of $Al(NO_3)_3$ and montmorillonite (Kunipia-F). g) NR-50; supplied from Mitsui Toatsu Fine Chemicals Inc. h) Ion exchange capacity. i) JRC-Z-HY-4.8. j) Prepared by the same method as in Ref. 6. k) 25H; supplied from Mobil Catalysts Co. of Japan. l) SA-1, Al_2O_3; 13wt%.

etheration in the liquid phase, its activity was about 1/20 that of $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ for this reaction. When $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ was filtered after the reaction and was used again for the reaction, the activity almost remained unchanged for at least three repeated runs, indicative of very small deactivation of the catalyst. Furthermore, it is worth noting that untreated $H_{0.5}Cs_{2.5}PW_{12}O_{40}$, which contains about 0.5 H_2O per polyanion just after it was dried at room temperature, also exhibited a high activity (Table 1), while the reaction was very slow over the untreated $H_3PW_{12}O_{40}$·$25H_2O$, for which water probably reduced the acid strength. The high activities of the heteropoly compounds for this reaction are probably due to their strong acidities and high affinities for the reactant ester.

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