

Hydrolysis of Palm Olein Catalyzed by Solid Heteropolyacids

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ABSTRACT: The hydrolysis activity of superacids on palm olein, including tungstophosphoric acid and molybdophosphoric acid and their partially ion-exchanged cesium (Cs) salt, were investigated and compared with macroporous cation-exchanged resin and aluminum-incorporated mesoporous molecular sieve. The activities of the superacids supported on the resin and silica were also determined. The reactions were carried out in a stirred batch reactor with continuous steam injection at temperatures from 140 to 180°C. The reaction kinetics, obtained by regression, are first order with respect to TG of the superacids and Cs salts. Of the catalysts studied, the superacids loaded onto cation-exchanged resins were the most active on a weight basis. However, in terms of the turnover number per acid site, the Cs salt of tungstophosphoric acid had 13 times the activity of the cation-exchanged resin. The original superacids had lower activities than the Cs salts in terms of their turnover number. The observations are qualitatively in line with the higher acid strengths of the catalysts, as confirmed by the low activity of the aluminum silicate mesoporous molecular sieve, which is known to have a high concentration of low- to moderate-strength acid sites. The activation energy of the reaction with the Cs salts was $\sim 49 \text{ kJ mol}^{-1}$. This is rather low as compared to that catalyzed by the cation-exchanged resin.

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KEY WORDS: Al-MCM-41, cation-exchanged resin, heteropolyacid, hydrolysis, kinetics, palm olein.

Fat splitting without catalyst is economical only above 210°C. Modern continuous fat-splitting units operate at 210–260°C and 2000–6000 kN/m² with countercurrent flow of water to oil. About 96–98% of hydrolysis takes place within 2 h (1,2). High reaction temperatures can only be used in a pressure autoclave, which requires a higher investment in energy, equipment, and maintenance. Thus, interests in ambient-temperature lipase-catalyzed fat splitting emerged around 1980 (1–4). However, it has not been widely used in commercial fat splitting, although efforts to immobilize the enzyme on solid supports and to carry out the reaction at temperatures above ambient have resulted in some success (2–4). Acid catalysts are generally effective for accelerating hydrolysis reactions. However, when a homogenous acid catalyst is used at high temperature, material corrosion occurs. The corrosion can be avoided by employing solid acid. Cation-exchanged resin-catalyzed hydrolysis of TG has been studied (5,6); however, the lower rate of hydrolysis and relatively low degree of hydrolysis make it unsuitable for industrial use. Heteropoly-

acid-based solid-acid systems have received much attention owing to their strong acidity, high thermal stability, and simple preparation (7,8). Their activities for esterification (9) and hydrolysis of simple esters (10) have been reported. The present work focused on the kinetics of TG hydrolysis catalyzed by heteropolyacid-based solid acids.

EXPERIMENTAL PROCEDURES

Tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (H_3W), and molybdophosphoric acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (H_3Mo), were purchased from BDH Chemical (Poole, United Kingdom) and used directly without purification. H_3W and H_3Mo were dried overnight at 120°C before used. Polystyrene sulfonic acid cation-exchange resin (CT165) was a gift from Purolite International Limited (Pontyclun, United Kingdom). Cesium salt, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ($\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$), was prepared according to the method of Tatematsu *et al.* (11), where an aqueous solution of H_3W (0.0025 M) was titrated with an aqueous solution of Cs_2CO_3 (0.048 M). The solution was evaporated to dryness using a vacuum oven at room temperature. It was used as the catalyst after calcination at 300°C for 4 h. H_3W - and H_3Mo -loaded CT165 were prepared by immersing CT165 in an aqueous solution of H_3W and H_3Mo . The samples with 16 and 13 wt% loading of H_3W and H_3Mo were designated as CT165- H_3W and CT165- H_3Mo , respectively. The synthesis of an aluminum-incorporated mesoporous molecular sieve (Al-MCM-41) was carried out by mixing appropriate amounts of tetraethylorthosilicate (TEOS) and aluminum *sec*-butoxide (AlsB) into a templating solution of tetradecylamine (C_{14}NH_2) in ethanol (EtOH) with vigorous stirring. The molar ratio of TEOS/AlsB/ C_{14}NH_2 /EtOH/ H_2O was 12:1:3:232:1776, where the Si/Al = 12. The resulting solutions were maintained at ambient temperature for 24 h, filtered, washed with ethanol, and finally calcined at 550°C for 6 h. H_3W - SiO_2 was synthesized by adding appropriate amounts TEOS and H_3W to a premixed aqueous solution of C_{14}NH_2 and Na_2EDTA . The molar ratio of TEOS/ H_3W / Na_2EDTA / C_{14}NH_2 /EtOH/ H_2O was 79:1:112:19:1520:11640. Refined, bleached, deodorized palm olein, which is the liquid fraction of palm oil, was obtained from a local supermarket and had the following composition in term of FA: C12:0 (0.3%), C14:0 (1.0%), C16:0 (41.0%), C18:0 (4.0%), C18:1 (43.0%), and C18:2 (10.7%). The percentages of FFA, MG, DG, and TG were as 0.4, 0.2, 6.1, and 93.3%, respectively.

Nitrogen adsorption isotherms were obtained from a Micromeritics Instruments Model ASAP 2000 V2.05 (Norcross, GA) at liquid nitrogen temperature. Less than 0.1 g of calcined

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sample was first evacuated at 150°C and a pressure of less than 10^{-5} torr for more than 3 h before adsorption. BET surface areas were calculated from adsorption data at relative pressures less than 0.3. FTIR spectra were obtained from KBr disks using a FTIR PerkinElmer 2000 spectrometer (Shelton, CT).

The concentration of acid sites on CT165 was calculated from the ion-exchange capacity using ASTM standard method D2187-77 (12), whereas the acid concentration of heteropoly acids was calculated from the chemical formula, acid concentration of $Cs_xH_{3-x}PW_{12}O_{40} = (1/\text{relative molecular mass of } Cs_xH_{3-x}PW_{12}O_{40}) \cdot (3 - x)$. The surface acidities (acid concentrations on the surface) of H_3W and $Cs_{2.5}H_{0.5}W$ were calculated from acid concentrations and surface areas according to the equation: surface acidity = (acid concentration) · (surface area) · (0.00296) (13).

The hydrolysis experiments were carried out in a 100-mL, three-necked, round-bottom flask immersed in a constant temperature bath. Typically, about 2.5 g of catalyst for 50 mL of the preheated, refined palm olein was used. Steam was continuously injected at a rate of 4.1 mL/min of liquid water. The reaction mixture was continuously stirred with a mechanical stirrer for up to 6 h.

Samples were analyzed by the following procedure. To 0.1 mL of sample, 0.5 mL pyridine and 0.5 mL chloroform were added and mixed well. Then the solution was mixed with 0.2 mL hexamethyldisilazane followed by 0.1 mL trimethylchlorosilane (5). The mixture was allowed to stand for at least 5 min before the supernatant was injected into a gas chromatograph fitted with a 50-cm glass column with an internal diameter of 3 mm packed with 1% Dexil 300 (Supelco, Bellefonte, PA).

RESULTS AND DISCUSSION

The characteristics of the catalysts used are shown in Table 1. Al-MCM-41 had the highest surface area ($1091 \text{ m}^2 \text{ g}^{-1}$), followed by $Cs_{2.5}H_{0.5}W$ ($90 \text{ m}^2 \text{ g}^{-1}$). The surface area of H_3W , H_3Mo , and CT165 were below $10 \text{ m}^2 \text{ g}^{-1}$. The pores of

TABLE 1
Characteristics of Solid Acids^a

Catalyst	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Pore diameter (Å)	Acid concentration (mmol g^{-1})	Surface acidity ($\mu\text{mol g}^{-1}$)
H_3W	5.8 ^b	77 ^b	1.0 ^c	17 ^d
H_3Mo	3.0 ^b	103 ^b	1.3 ^c	—
CT165	2.5 ^{e,f}	>1000 ^{b,f}	5.0 ^g	—
Al-MCM-41	1091 ^b	26 ^b	—	—
$Cs_{2.5}H_{0.5}W$	90 ^b	24 ^b	0.16 ^c	43 ^d

^a H_3W , $H_3PW_{12}O_{45}$ (tungstophosphoric acid); H_3Mo , $H_3PMo_{12}O_{40}$ (molybdophosphoric acid); CT165, polystyrene sulfonic acid cation-exchange resin; Al-MCM-41, aluminum-incorporated mesoporous molecular sieve; $Cs_{2.5}H_{0.5}W$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (cesium salt).

^b N_2 adsorption.

^cAcid amount calculated from the composition.

^dCalculated from the equation (Ref. 13): surface acidity = (acid concentration) · (surface area) · (0.00296).

^eHg intrusion method.

^fData from manufacturer.

^gDetermined from the ion-exchange capacity using standard method (Ref. 12).

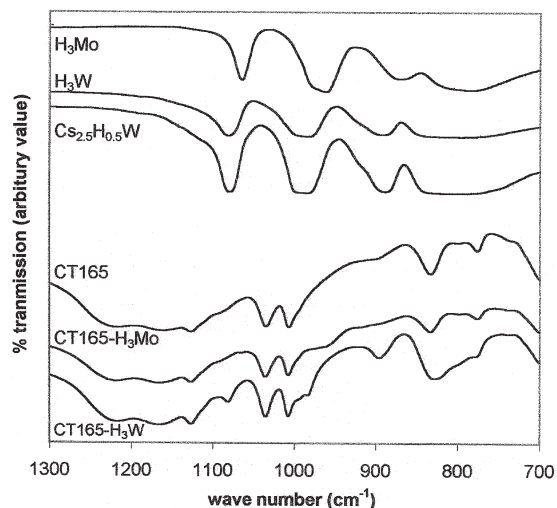


FIG. 1. Infrared spectra of catalysts.

$Cs_{2.5}H_{0.5}W$ and Al-MCM-41 were determined as mesopores. However, those of H_3W , H_3Mo and CT165 were in the macropore region. $Cs_{2.5}H_{0.5}W$ had the lowest acid concentration but showed higher surface acidity than H_3W . The primary structures of H_3W , H_3Mo , $Cs_{2.5}H_{0.5}W$, CT165- H_3W , and CT165- H_3Mo were identified by FTIR. In Figure 1, H_3W shows the characteristic IR bands at 1081 (P–O in the central tetrahedral), 983 (terminal W=O), 893, and 795 cm^{-1} (W–O–W) associated with the asymmetric vibrations in the Keggin polyanion. Whereas H_3Mo showed the characteristic IR bands at 1065 (P–O in the central tetrahedral), 962 (terminal Mo=O), 870, and 784 cm^{-1} (Mo–O–Mo) associated with the asymmetric vibrations in the Keggin polyanion, $Cs_{2.5}H_{0.5}W$ and CT165- H_3W showed all the characteristic IR bands of the Keggin structure. Mo–O–Mo IR bands of CT165- H_3Mo cannot be seen clearly in Figure 1. However, P–O and Mo=O IR bands still can be identified after the IR spectrum was magnified (Figs. 2A and 2B). This indicated that the primary Keggin structure was preserved after supporting the heteropolyacids onto CT165. Interactions between

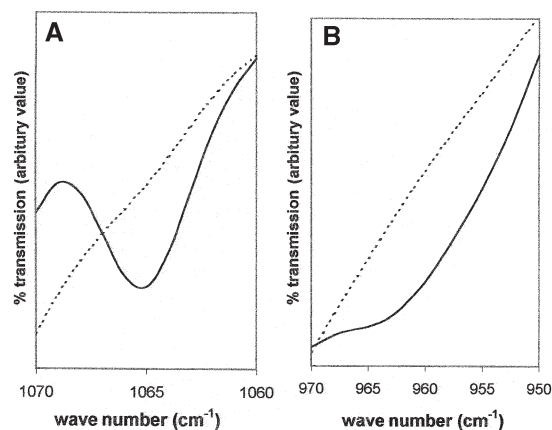


FIG. 2. Magnified infrared spectra of CT165- H_3Mo (solid line) and CT165 (broken line).

TABLE 2
TG Hydrolysis Catalyzed by Various Solid Acids at 5-h Reaction Time^a

Catalyst	Weight of catalyst (g)	Reaction temp. (°C)	Amount of TG (mL)	% TG hydrolysis at 5 h	TON ^b (min ⁻¹ mol ⁻¹)
H ₃ W	10.0	170	50	15.2	5
CT165	2.5	155	50	61.8	16
CT165-H ₃ W	2.5	155	50	71.5	22
CT165-H ₃ Mo	2.5	155	50	74.5	22
H ₃ W-SiO ₂	2.0	170	50	3.2	37
Al-MCM-41	0.5	155	25	1.2	*
Cs _{2.5} H _{0.5} W and CT165 (50 wt%)	2.5	155	50	63.2	33
Cs _{2.5} H _{0.5} W	2.5	180	50	31.5	269
Cs _{2.5} H _{0.5} W	2.5	170	50	28.0	238
Cs _{2.5} H _{0.5} W	2.5	155	50	24.6	210
Cs _{2.5} H _{0.5} W	2.5	140	50	9.3	79

^aWater consumption for the steam injection = 4.1 mL/min.

^bTON, turnover number, calculated from the percentage of TG hydrolysis in 5 h divided by total mol of H⁺ and 300 min. *Too low to be determined. For other abbreviations see Table 1.

heteropolyacids and CT165 were obvious, especially with H₃W, as indicated by the shifts to higher wave numbers of P=O (1081 to 1083 cm⁻¹), terminal W=O (983 to 987 cm⁻¹), and W-O-W (890 to 896 cm⁻¹).

The activity of the reaction catalyzed by various solid acids is tabulated at Table 2. The reaction temperatures are from 140 to 180°C. However, for those reactions involving CT165 as the catalyst, the reaction temperature was set at 155°C. This is the highest temperature at which CT165 can be used without thermal degradation (5). Thermal decomposition of H₃W and H₃Mo will only happen above 510°C. When H⁺ of H₃W is substituted by Cs⁺, it will further stabilize the catalyst (7). Thus, heteropolyacids and their salts are suitable to be used in high temperature reactions.

At 170°C, the hydrolysis for H₃W and Cs_{2.5}H_{0.5}W was 15.2 and 28.0%, respectively. Cs_{2.5}H_{0.5}W showed better catalytic function compared to H₃W despite its lower acid concentration and lower weight used in the reaction, which was due to its higher surface acidity. The surface acidities of Cs_{2.5}H_{0.5}W and H₃W were 43 and 17 μmol g⁻¹, respectively. Koyano *et al.* (13) and Na *et al.* (14) reported that the surface acidity of Cs_xH_{3-x}W initially decreased from $x = 0$ to 2, where at $x = 0$ and $x = 2$, the surface acidity was 14 and 0.4 μmol g⁻¹, respectively. When H⁺ was substituted by Cs⁺, at $x = 2.5$, the surface acidity was 60 μmol g⁻¹ before dropping to zero at $x = 3$ (13). Figure 3 shows a typical result of hydrolysis catalyzed by Cs_{2.5}H_{0.5}W at 180°C. Hydrolysis catalyzed by Al-MCM-41 with Si/Al = 12 was the lowest rate among the catalysts (Table 2). The low activity was the result of its weaker acid sites (15,16). However, CT165 at 155°C showed higher activity because of the presence of stronger acid sites and their better accessibility to reactants through larger pores (5).

It is well established that hydrolysis of TG is first order with respect to reactant concentrations. The first-order plot for TG hydrolysis catalyzed by Cs_{2.5}H_{0.5}W at 140 to 180°C is shown in Figure 4. The plots follow first-order kinetics fairly well. The

first-order rates were tabulated as follows: Cs_{2.5}H_{0.5}W: 140°C, 0.0180 k (h⁻¹); 155°C, 0.0304 k ; 170°C, 0.0488 k ; 180°C, 0.0636 k ; Cs_{2.5}H_{0.5}W and CT165 (50 wt%): 155°C, 0.2116 k ; CT165: 155°C, 0.2469 k . In Table 2, the highest turnover number (TON) at 155°C was with Cs_{2.5}H_{0.5}W, followed by the mixture of CT165 and Cs_{2.5}H_{0.5}W, heteropolyacid-loaded CT165, and original CT165. Cs_{2.5}H_{0.5}W had 13 times the activity of the cation-exchange resin in term of TON. The high TON of Cs_{2.5}H_{0.5}W was due to the superacidity of the H⁺, as its Hammett function (H_0) was about -13.2, which is stronger than H₂SO₄ ($H_0 = -11.9$) (10).

The activation energy for hydrolysis catalyzed by Cs_{2.5}H_{0.5}W, estimated from an Arrhenius plot (Fig. 5), was 49 kJ mol⁻¹. This is only one-fifth the activation energy of CT165 (5). The heteropolyacid-loaded cation-exchanged resins were most active by weight. Over 75% hydrolysis was achieved after 5 h (Fig. 6). Heteropolyacid-loaded CT165 was about 10% more active than the original CT165. This might be due to the uniform dispersion of heteropolyacids on the surface of CT165 as well as the synergistic effect of acid sites from

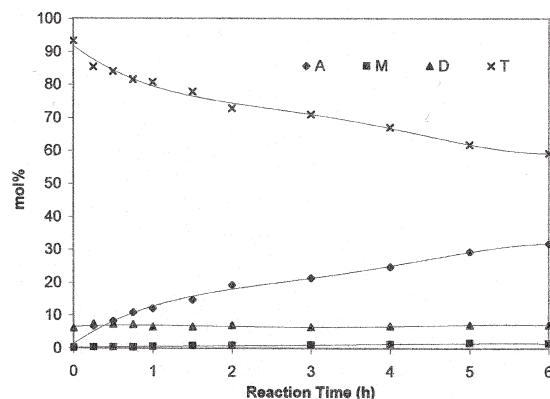


FIG. 3. Changes in concentration of TG (T), DG (D), MG (M), and FA (A), with time, of hydrolysis catalyzed by Cs_{2.5}H_{0.5}W at 180°C.

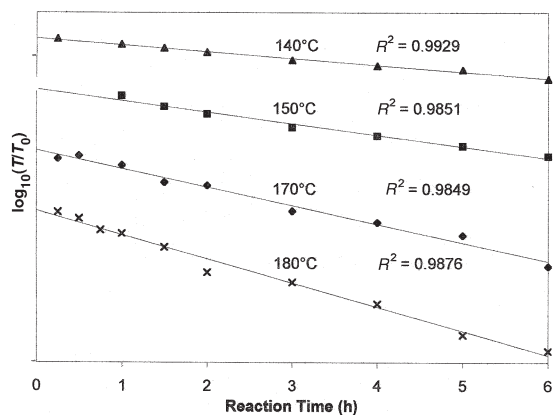


FIG. 4. First-order rate plot for hydrolysis catalyzed by $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$, where T_0 = initial concentration of TG and T = concentration at time t .

both heteropolyacids and CT165. However, heteropolyacid-loaded CT165 deviated from first-order kinetics with respect to TG (Fig. 7). They were best fitted by a curve (broken line in Fig. 7) rather than a linear line. This was presumably because the acid sites from CT165 and heteropolyacid were of different strengths and were in different environments.

The accessibility of acid sites by reactants plays a major role in determining the rate. Some of the acid sites might have been inaccessible to reactants because their molecular size was larger than the pore diameter of the heterogeneous catalyst, in which the majority of the acid sites were situated inside the pores. Acid sites hidden in the primary particles of the catalyst were also inaccessible. In such a case, surface area of the catalyst is important to ensure accessibility of the acid sites. H_3W had an average pore diameter of 77 Å, which was larger than $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$, but it was less active than $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$ because of its small surface area. This was caused by more inaccessible acid sites in H_3W than in $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$; hence, surface acidity became the constraining factor. Al-MCM-41 had high surface area and moderate pore diameter but its acid strength was much lower than heteropolyacids and CT165; thus, it showed the lowest activity. CT165 was one of the most active catalysts owing to its high acid concentration and large pore diameter. Its pore diameter was larger than 1000 Å, which definitely gave minimum diffusion restriction to reactants and reaction products. A high acid concentration with high acid strength in

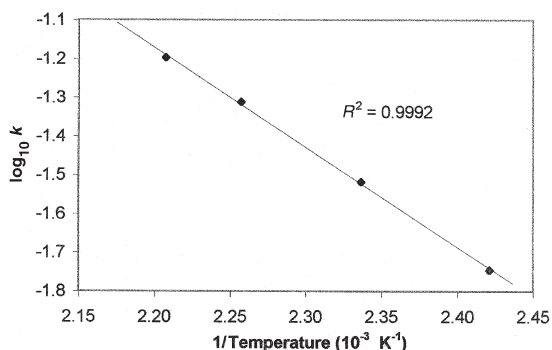


FIG. 5. Arrhenius plot for hydrolysis of TG catalyzed by $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$.

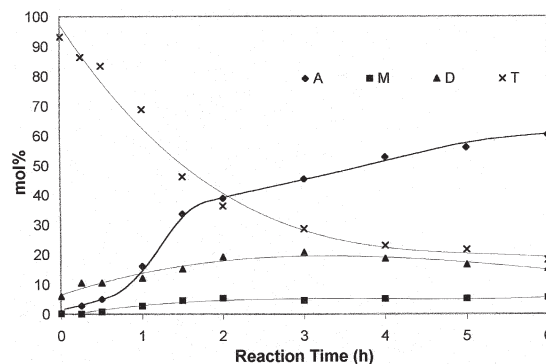


FIG. 6. Changes in concentration of TG (T), DG (D), MG (M), and FA (A), with time, of hydrolysis catalyzed by CT165- H_3W at 155°C.

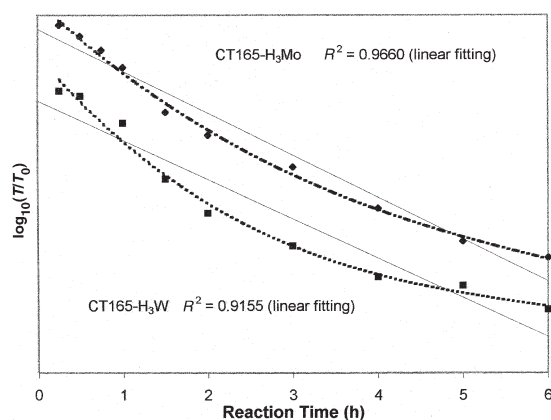


FIG. 7. First-order rate plot of CT165- H_3Mo and CT165- H_3W . R^2 is for the linearly fitted curve (solid line).

large pores is required for high activity in hydrolysis of relatively large TG molecules.

Some fat-splitting processes operate at medium pressure and at temperatures between 150 and 190°C. Heteropolyacid-loaded CT165 in such processes might be a useful alternative catalyst in medium-pressure processes with temperatures at or below 155°C. However, $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$ may not be suitable as an alternative catalyst even though it can withstand higher temperatures as more $\text{Cs}_{2.5}\text{H}_{0.5}\text{W}$ is required to achieve the same degree of splitting.

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