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Mendeleev Commun., 2013, **23**, 46–48

Mendeleev Communications

Supported cesium polyoxotungstates as catalysts for the esterification of palm fatty acid distillate

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DOI: 10.1016/j.mencom.2013.01.017

$H_3PW_{12}O_{40}$ and $Cs_xH_{3-x}PW_{12}O_{40}$ supported on SiO_2, MCM-41 and ZrO_2 were prepared and applied as solid acid catalysts for the esterification of palm free fatty acid with methanol. The $Cs_xH_{3-x}PW_{12}O_{40}$ supported catalysts are resistant to the leaching of Keggin units into the reaction medium.

Biodiesel is of considerable current interest as a green and alternative fuel. The biodiesel feeds containing high free fatty acid (FFA) are cheaper than oils without FFA but they require a two-step process, esterification and transesterification.[1] The polluting corrosive liquid acid catalysts are replaced by solid acid catalysts: zeolites,[2] MCM-41,[3,4] mixed metal oxides,[5] T_2O_5/ZrO_2[6] and Cs exchanged polyoxometalate (POM) ($Cs_xH_{3-x}PW_{12}O_{40}$).[7] $Cs_xH_{3-x}PW_{12}O_{40}$ is a water-insoluble strong Brönsted acid, and it possesses high thermal stability ($\geqslant 500\,°C$) and water tolerance.[8] It exhibits high esterification activity but suffers from a separation problem. POMs in their acid types showed high acid-catalytic activity.[9] However, they are unsuitable for esterification due to their high solubility in polar media. Insoluble solid acid catalysts with high thermal stability and surface area can be made by supporting them on suitable supports such as SiO_2,[10] TiO_2,[11] ZrO_2,[12] Ta_2O_5,[13] zeolite,[14] SBA-15[15] and MCM-41.[16] The POM/MCM-41 prepared by impregnation suffered from leaching.[17,18] POM/MCM-41 catalysts synthesized by a direct method possessed larger surface areas, larger pore sizes and pore volumes than the impregnated sample; they showed higher activity in esterification and less leaching.[19]

Crude palm oil contains a high amount of FFAs; the latter are removed by distillation (as called palm fatty acid distillate or PFAD). Its price is only half of refined oils. PFAD can be used as a feedstock for biodiesel production with catalysts such as H_2SO_4[20] and modified ZrO_2 (with WO_3^-, SO_4^- and TiO_2^-)[21] or without catalysts.[22]

PFAD consists of 93 wt% FFA (45.6% palmitic, 33.3% oleic, 7.7% linoleic, 3.8% stearic, 1.0% myristic, 0.6% tetracosenoic, 0.3% linolenic, 0.3% ecosanoic, 0.2% ecosenoic, and 0.2% palmitoleic acids) and the rest are triglycerides, diglycerides and monoglycerides. MCM-41 (BET surface area, 988 $m^2\,g^{-1}$; pore size, 2.9 nm) and hydrous ZrO_2 (BET surface area, 288 $m^2\,g^{-1}$; pore size, 2.9 nm) were prepared according to published procedures.[23,24] $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ was prepared by dropwise addition of a solution of Cs_2CO_3 to a solution of $H_3PW_{12}O_{40}$.[25]

The immobilized catalysts were prepared by two methods: sol-gel hydrothermal method and two-step impregnation method.[†]

The XRD patterns of the supported catalysts (20% loading) are shown in Figures 1–3.[‡] The patterns of the 10% loading are similar. No peaks related to POMs were observed in cases of SiO_2 and MCM-41 supports suggesting a high dispersion as a non-crystalline form.[27] According to the XRD pattern of CsHPW/ZrO_2 (Figure 3), both tetragonal and monoclinic phases of ZrO_2 are present, monoclinic being predominant. The characteristic diffraction peaks observed at 10.3° and 24.4° in case of a 20% loading

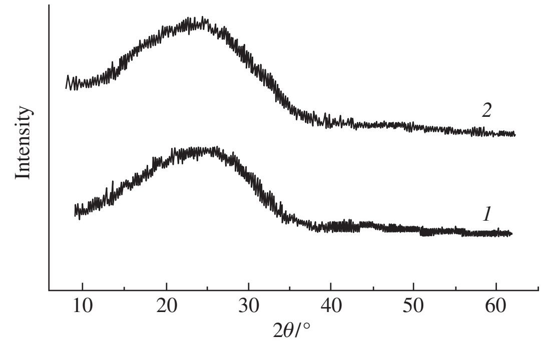

Figure 1 XRD patterns of (*1*) HPW/SiO_2 and (*2*) CsHPW/SiO_2.

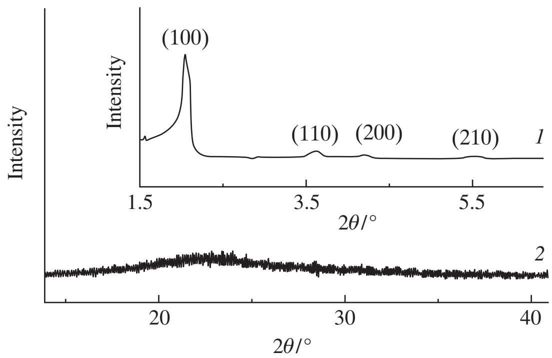

Figure 2 XRD patterns of CsHPW/MCM: (*1*) low angle and (*2*) wide angle.

† (I) *Sol-gel hydrothermal method.* Tetraethyl orthosilicate (3.26 g, 0.016 mol) was dissolved in ethanol (10 ml). $H_3PW_{12}O_{40}$ or $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ (15 or 20 wt%) was added. This mixture was added slowly to an ethanol solution (5 ml) of triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymer or P123 (2.32 g, 4.0×10^{-4} mol). The pH of the mixture was controlled at ~1 by HCl. After stirring for 3 h, the mixture was dried at 110 °C *in vacuo* and calcined at 400 °C for 5 h, resulting in HPW/SiO_2 and CsPW/SiO_2.

(II) *Two-step impregnation method.*[26] MCM-41 or hydrous ZrO_2 (2 g) was impregnated with a solution of Cs_2CO_3 (0.06 mmol, 10 ml), and the mixture was stirred for 12 h; then, it was evaporated to dryness and calcined at 500 °C for 2 h. Then $H_3PW_{12}O_{40}$ (15 or 20 wt%) was impregnated by incipient wetness impregnation, using 1-butanol as a solvent. The solid was calcined at 350 °C for 3 h.

‡ Specific surface areas were measured using the BET method on a BELSORP-mini instrument. XRD measurements were performed on a Rigaku DMAX 2002/Ultima Plus powder X-ray diffractometer. The amounts of Cs and W were determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin Elmer model PLASMA-1000).

Table 1 Chemical analysis and textural parameters of catalysts.

Catalyst	Method	POM (%)[a] loading	POM (%)[a] analyzed	S_{BET}/ $m^2 g^{-1}$	Pore volume/ $cm^3 g^{-1}$	Cs : W[b] molar ratio
HPW/SiO_2	I	15	14.8	260	0.14	0
		20	19.4	237	0.15	0
$CsHPW/SiO_2$	I	15	14.7	273	0.15	1.5:12
		20	19.5	230	0.12	1.5:12
CsHPW/MCM	II	15	14.8	745	0.68	1.7:12
		20	19.4	696	0.60	1.1:12
$CsHPW/ZrO_2$	II	15	14.7	75	0.19	1.5:12
		20	19.2	64	0.17	1.0:12

[a]Deduced from the chemical analysis of W by ICP. [b]Deduced from the chemical analysis of Cs and W by ICP.

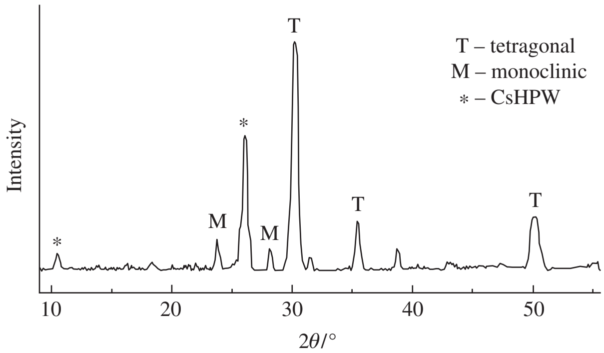

Figure 3 XRD patterns of $CsHPW/ZrO_2$.

Table 2 Catalytic esterification of PFAD with methanol.

Entry	Catalyst	Loading (%)	Amount of catalyst (wt%)	t/h	T/°C	Methanol/PFAD molar ratio	FAME (wt%)	Loss of W (%) after the 3rd run	FAME (wt%) of the 3rd run
1	HPW/SiO_2	15	10	8	75	12	80	5	71
2	HPW/SiO_2	20	10	8	75	12	85	10	72
3	$CsHPW/SiO_2$	15	10	8	75	12	76	0.3	75
4	$CsHPW/SiO_2$	20	10	8	75	12	79	1.1	76
5	CsHPW/MCM	15	10	8	75	12	80	0	79
6	CsHPW/MCM	20	10	8	75	12	88	0	87
7	CsHPW/MCM	20	10	4	85	12	87	0.2	86
8	CsHPW/MCM	20	10	4	85	15	89	0.2	89
9	CsHPW/MCM	20	12	4	85	15	92	0.1	90
10	$CsHPW/ZrO_2$	15	10	8	75	12	68	1.0	65
11	$CsHPW/ZrO_2$	20	10	8	75	12	74	1.1	71

catalyst suggests the presence of the intact Keggin ion structure of CsHPW on ZrO_2. Chemical analysis and textural parameters of catalysts are given in Table 1.[‡] The determined POM loadings are close to the actual loadings.

Catalytic activities of different catalysts in the esterification of PFAD with methanol[§] were compared, and the results are shown in Table 2.

The data obtained demonstrate that the HPW/SiO_2 catalyst exhibited higher activity than the $CsHPW/SiO_2$ due to its higher acidity, similar to $H_4SiW_{12}O_{40}$ and Cs-$H_4SiW_{12}O_{40}$ in the esterification of palmitic acid.[28] However, the HPW/SiO_2 suffers from leaching after repeated uses (entries 1, 2). After the third run, the amount of W remained on the support decreased. On the contrary, the CsHPW supported on MCM-41 shows negligible leaching; this is due to interaction between CsHPW and MCM-41, which was reported to be stronger than that with SiO_2, and their insolubility in methanol prevented the leaching of the active phase from the channels of MCM-41.[29] The activity of the catalysts increased with increasing loading. The 20% CsHPW/MCM-41 (entry 6) is more active than the 15% loading (entry 5), variation in number of acidic sites depended on the amount of Cs on the support and related to the growing number of acid sites.[23] By increasing the reaction temperature from 75 to 85 °C, a comparable yield of FAME could be obtained using a shorter reaction time (entries 6 and 7). The FAME yield can also be further increased by raising methanol content (entry 8). An excess amount of methanol was used in order to shift the equilibrium to the FAME formation, but it can be recycled. 92% FAME was obtained using 12 wt% catalyst (entry 9). Both 15 and 20% loadings of $CsPW/ZrO_2$ catalyst exhibit lower activity than the CsPW/MCM ones, this might be due to their lower surface area and also acidity. The $CsPW/ZrO_2$ (20% loading), which has a lower Cs : W ratio, shows better performance, similar to that of CsHPW/MCM-41.

The data on the reusability of the catalysts indicate that a large drop in activity in case of the HPW/SiO_2 is caused by leaching. However, for the insoluble CsHPW supported catalysts, the decreased activity might be due to the surface coverage. The main advantages of using a heterogeneous catalyst are that no washing step is required and the catalyst can be easily separated and reused.

[§] The reaction was performed in a 100 ml Parr high pressure reactor. PFAD (10 g) was firstly melted at 60 °C and mixed with methanol followed by the catalyst. Molecular sieve was added along with the reactants to dehydrate the components during the reaction in order to inhibit the hydrolysis of fatty acid methyl esters (FAMEs) back to fatty acids. The reaction mixture was heated and stirred at 500 rpm. After the reaction, the catalyst and molecular sieve were separated. The methanol was removed by evaporation. Methyl ester product was neutralized by washing repeatedly with water in a separatory funnel and the remaining water was finally removed by rotary evaporation. FAMEs were analyzed using a Shimadzu GC17A chromatograph fitted with a DB1 capillary column (film thickness, 0.25 mm; i.d., 0.32 μm; length, 30 m) and a flame ionization detector. The sample was prepared by adding 0.05 ml of FAMEs to 5 ml of n-hexane, and methyl heptadecanoate was used as an internal standard.

This work was supported by a research grant 'The 90th Anniversary of Chulalongkorn University Fund'.

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Received: 15th August 2012; Com. 12/3968