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Transesterification of rapeseed oil with ethanol
I. Catalysis with homogeneous Keggin heteropolyacids

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Abstract

Heteropolyacids (HPA) with Keggin structure were evaluated as homogeneous Br∅nsted acid catalysts in the reaction of rapeseed oil transesterification with methanol and ethanol at 358 K and atmospheric pressure. Rapeseed oil transesterification with ethanol over anhydrous Keggin HPAs leads to higher conversion level than H_2SO_4 compared at equivalent H^+ concentration and H_2O/H^+ molar ratio. By contrast, Phosphoric acid, a quite weaker mineral acid, structurally close to $H_3PW_{12}O40$, is not operative under similar conditions. This demonstrates the advantages of strong Br∅nsted acids in vegetable oil transesterification with ethanol in mild conditions. It is worth noticing that differences in acid strength between anhydrous Keggin heteropolyacids, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, measured by calorimetry, did not correlate simply the catalytic activity. Indeed, the proton solvation with water molecule was shown to be a crucial parameter. Then, Mo samples exhibited higher activities due to their ability to lose crystallization water at lower temperatures compared to W samples. Finally, it was shown that higher transesterification rates were obtained with ethanol than methanol in presence of HPA.

Keywords: Biodiesel; Transesterification; Rapeseed oil; Vegetable oil; Heteropolyacids

1. Introduction

The use of vegetable oils, a renewable raw source, to produce a diesel base is strongly encouraged since it will contribute to reduce our dependence upon fossil fuel. In the European union, a minimal proportion of 2% biofuels is imposed since 2005 and the objectives announced by the European union, 5.7% are targeted in 2010 [1].

Vegetable oil cannot be used directly in the present engine due to its too high viscosity, nearly 10 times that of diesel fuel. That is why transesterification of triglycerides to produce fatty alkyl esters, termed as biodiesel, is widely used since biodiesel have a reduced viscosity and can be mixed with any conventional fuel, without engine modification [2]. The preferred commercial catalysts are still alcohol soluble sodium and potassium hydroxide catalysts. The reaction proceeds in liquid phase, in batch conditions, at moderate temperatures (<373 K) and atmospheric pressure. The homogeneous basic catalysis is generally preferred due to its relative efficiency and low cost: high conversion levels of the triglyceride may be obtained in short reaction time. However, the homogeneous basic catalysis suffers from many drawbacks as its sensitivities to moisture and to free fatty acid [3]:

- Moisture traces are responsible of triglycerides hydrolysis and consequently of soap formations caused by the reaction between the free acids and alkaline cations. The soap formation reduces the catalyst efficiency and renders uneasy the recovery of biodiesel and glycerol phases [4].
- For the same reason, vegetable oil with high free acids content cannot be transesterified directly via a basic catalysis. Accordingly the use of low cost raw materials is excluded

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because of their high free acid content as some crude vegetable oils or fats of animal origin.

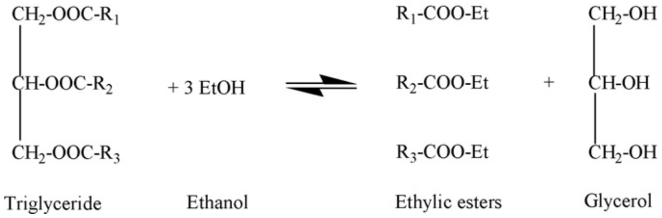
The replacement of soluble bases by liquid acid catalysts such as H_2SO_4, HCl or H_3PO_4 could have been an attractive alternative since it is expected that acidic catalysts are less sensitive towards the presence of water and free acids [5,6]. Though acid catalysts have these notable advantages, they are not preferred in transesterification reaction due to their known lower activity than the conventional transesterification alkaline catalysts. Higher temperatures and longer reaction times are generally required [7–9]. For acid-catalyzed transesterification by H_2SO_4 for instance, reaction temperatures from 353 to 393 K were reported while the basic homogeneous catalysis may be operative at ambient temperature. Moreover, higher alcohol/triglyceride molar ratios are required [10]. It is noteworthy to recall the pioneering work of Freedman et al. [7] who reported that sodium alkoxide led to a complete conversion of soybean oil at 333 K in 1 h while 1%H_2SO_4 requires 20 h at 350 K or 3 h at 390 K to obtain a complete conversion.

Heteropolyacids present a potential interest since they are known to be very strong Br∅nsted acids [11]. It is expected that performing the triglyceride transesterification with acids of higher strength than conventional liquid acids would increase the reaction rates and make the reaction fast enough in mild conditions.

Heteropolyacids can be employed as heterogeneous or homogeneous catalysts depending of their composition and of the reaction media. The Keggin heteropolyacid as $H_3PW_{12}O_{40}$ for instance, is soluble in methanol and ethanol while the ammonium salt is insoluble in alcohol. Recently, esterification of palmitic acid with methanol was studied in presence of the ammonium salt of 12-tungstophosphoric acid [12]. The reaction was carried out at atmospheric pressure, under reflux conditions, with 5 wt% of solid catalyst. Not to our surprise, the partially exchanged catalyst was found to be more active than the fully exchanged ammonium salt $(NH_4)_3PW_{12}O_{40}$.

More recently, the use of Keggin heteropolyacids for triglyceride (TG) transesterification has been reported [13]. TG transesterification was performed together with fatty acid esterification showing the potential of the acid catalysis in this field. Note that supported $H_3PW_{12}O_{40}$ catalysts were evaluated in this study and the temperatures investigated were higher than 150 °C. The authors concluded that hydrous zirconia supported PW was a promising catalyst and that the active sites would be a combination of Lewis acid sites and hydroxyl groups provided by the support.

It appeared interesting to us to undertake a deeper study of the potentialities of Keggin type heteropolyacids for the transesterification of vegetable oil with light alcohols. Our goal was to try to elucidate whether the strong Br∅nsted acid sites of HPA, often considered as super acid, could catalyze the transesterification reaction in mild conditions. The expected issue of the present work is to evaluate the performances of homogeneous Keggin HPA with respect to usual soluble bases and acids on the base of Turn Over Number determination in order to get a overview of the potential advantages or drawbacks of this type of catalysts in the transesterification of vegetable oils with alcohol (see Scheme 1).



Scheme 1. Reaction of transesterification of vegetable oil with ethanol.

2. Experimental procedures

2.1. Materials

Commercial $H_3PW_{12}O_{40}\cdot nH_2O$, $H_3PMo_{12}O_{40}\cdot nH_2O$, $H_4SiW_{12}O_{40}\cdot nH_2O$ were purchased from Aldrich and re-crystallized from deionized water solutions before use. $H_4SiMo_{12}O_{40}\cdot nH_2O$ was prepared according to the method described in ref. [14] and purified through ether extraction and re-crystallization. The Keggin structures were checked by solid NMR, IR spectroscopy and TGA-DTA. The hydration levels of the re-crystallized HPA were determined by TGA using a Setaram 92-12 apparatus.

2.2. Microcalorimetry studies of NH_3 adsorption

The acidic properties were measured by NH_3 adsorption at 80 °C, using a TianCalvet calorimeter coupled with a volumetric equipment. The heteropolyacids' samples (0.1 g) were first evacuated at 200 °C for 1 h under secondary vacuum, then placed into the calorimeter up to the stabilization of the temperature (one night), then contacted with small doses of gas up to equilibrium and the differential enthalpy of adsorption was recorded together with the amount of adsorbed ammonia.

2.3. Catalytic testing

The transesterification reaction was carried out in a 100 cm^3 glass reactor, which was equipped with a reflux condenser and a magnetic stirrer, at atmospheric pressure. Reaction temperatures and the molar ratio alcohol/ester functions (3xTG) were varied between 60 and 85 °C and 1.2 and 6, respectively. The catalyst amount was adjusted in order to introduce between 1 and 7 mol% of active sites (H^+ or OH^-) based on the quantity of ester functions (mol TG × 3). Ethanol, methanol and rapeseed oil were purchased from Aldrich and stored in presence of molecular sieves 5A°. The oil acidity is lower than 1 mg KOH/g. The reaction was carried out as follows: the solid heteropolyacid was first weighed and placed in an oven at 120 or 200 °C for 15 h. Then, the catalyst was rapidly added and dissolved into the dry alcohol quantity in the glass batch reactor. Finally, the oil amount was introduced when the heteropolyacid was completely dissolved. Then the reactor was rapidly heated up to the reaction temperature when placed in the oil bath warmed at the reaction

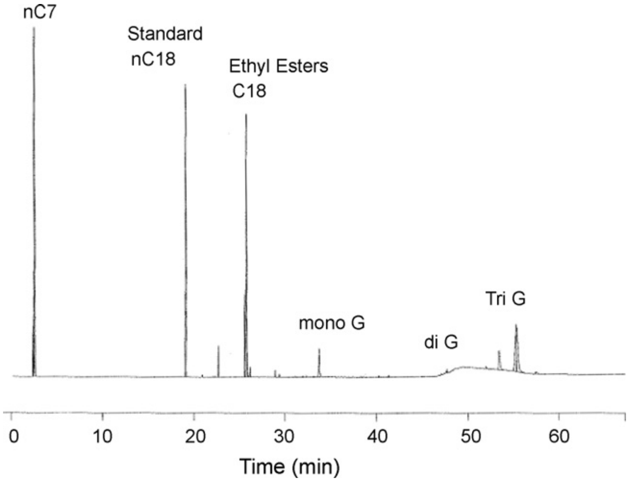


Fig. 1. GC analysis of the reaction mixture produced by transesterification of rapeseed oil with ethanol catalyzed by dehydrated $H_3PW_{12}O_{40}$.

temperature. The reaction was conducted for 3 or 5 h. The reaction was stopped by removing the bath oil and quenching the reaction medium by mean of a water/ice mixture. Because of the heterogeneity of the reaction medium, samples were not collected all along the course of the reaction. Chromatographic analysis of the reaction medium was realized after the complete reaction progress, that is to say after 3 or 5 h. For that, known amounts of heptane and water were then added to the reactor in order to obtain a clear separation of the products into two phases. The ‘‘organic one’’ which contains the biodiesel, alcohol and the unreacted oil was weighed and an aliquot of the internal standard, octadecane, was added to perform the GC analysis. The GC analysis was carried out by means of a capillary column purchased from Varian; CP 9048 (length: 30 m, diameter: 0.32 mm, thickness of the stationary phase: 0.1 μm). This column allows the separation of triglycerides, diglycerides, monoglycerides and fatty methyl and ethyl esters. Helium was used as carrier gas. The injector and detector temperatures were, respectively, 280 and 340 °C. The split ratio was fixed at 100. The oven temperature program was as follows: start at 80 °C (1 min), ramp at 5 °C min^{-1} to 300 °C, then ramp at 25 °C min^{-1} to 380 °C. The samples were prepared for the analysis in order to get 10 wt% of fatty products in *n*-heptane. 0.5 μl of sample was injected into the column. Typical chromatograms are provided in Fig. 1.

The TG conversion was calculated as follows:

$$\text{Conversion TG}\,(\%\,\text{mol}) = 100 \times \frac{[\text{TG}_\text{i}(\text{mol}) - \text{TG}_\text{f}\,(\text{mol})]}{\text{TG}_\text{i}(\text{mol})}$$

where TG_i and TG_f are, respectively, the initial and final mole numbers of TG.

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments were conducted with conventional mineral base or acid, KOH and H_3PO_4 in mild conditions, 1 atm and 60 °C, and compared to the 12-tungstophosphoric acid, $H_3PW_{12}O_{40}\cdot 24H_2O$. To conduct comparable experiments, the acid or base quantity was determined in order to introduce equivalent quantities of active species (H^+ or OH^- mol%) in the reaction medium based on the amount of ester function (the amount of ester functions is three times that of triglycerides). Due to the high solubility of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) in alcohols, this set of experiments allows the comparison of alcohol soluble catalysts (acidic or basic) under close enough conditions, without the occurrence of additional diffusion limitations associated to the use of a heterogeneous catalyst. Table 1 provides the results of rapeseed oil transesterification with methanol in presence of the three homogeneous catalysts. As indicated in Table 1, a complete conversion of the rapeseed oil was reached within 2 h in presence of KOH while the soluble acids, H_3PO_4 and $H_3PW_{12}O_{40}$, were inefficient. In a first analysis, these data are in good agreement with the earlier studies of Freedman et al. [15] who reported the higher efficiency of the basic catalysis compared to the acidic in the transesterification of vegetable oil with alcohols. Obviously, the direct comparison of basic and acid catalysis is not straightforward, first of all due to the well-known negative impact of trace amounts of water on the activity of acid catalysts in general. In the above preliminary set of experiments if the quantity of active sites H^+ or OH^- were equivalent from one experiment to another, the water content was quite different. Effectively, if anhydrous sodium hydroxide pellets were used as basic material, hydrated solid 12-tungstophosphoric acid ($H_3PW_{12}O_{40}\cdot 24H_2O$) and 85% cc H_3PO_4 were used as Brønsted acids. Clearly, the water amounts in the reactant media were quite different, which renders the catalytic performances’ comparison un-reliable. Therefore, 12-tungstophosphoric acid was also evaluated after a thermal treatment at 240 °C for 2 h prior to use. Under these conditions, the dehydrated heteropolyacid exhibited a measurable conversion. In view of the evident impact of water traces on the reaction, in the following experiments, solid heteropolyacids were systematically dehydrated in static conditions in an oven and immediately dissolved to the required amount of dry alcohol for the reaction.

Table 1
Reaction of rapeseed oil transesterification with methanol in presence of methanol soluble catalysts KOH, H_3PO_4, $H_3PW_{12}O_{40}$

Catalyst	H^+ (OH^-)/–COOR (mol%)	Conversion (%)
KOH	5.6	93
KOH	5.9	94
H_3PO_4	7.1	<5
$H_3PW_{12}O_{40}\cdot 24H_2O$	6.0	<5

Conditions: MeOH/–COOR = 1.2, T oil bath = 60 °C, stirring rate = 500 rpm, reaction duration = 2 h.

3.2. Search of favorable reaction conditions

Table 2 presents a summary of several experiments realized with dehydrated 12-tungstophosphoric acid, in order to find the most convenient experimental conditions to conduct the

Table 2
Activity of dehydrated 12-tungstophosphoric acid for rapeseed oil transesterification with ethanol

EtOH/–COOR	H^+/–COOR (mol%)	Reaction duration	TG conversion (%)
1.8	1.5	5 h	12
6.4	1.6	5 h	48
6	1.7	3 h	27

Dependence with the ethanol/ester ratio and with the reaction duration. *Conditions*: T oil bath = 85 °C, stirring rate = 500 rpm. *Catalyst pretreatment*: dehydration of the required quantity of HPA at 120 °C for 15 h.

transesterification reaction in presence of heteropolyacids as catalysts. The temperature, reaction duration, alcohol/ester function ratio (= alcohol/3 × TG ratio) were the main variables tested. The quantity of Br∅nsted sites, with respect to the quantity of ester functions, was reduced to ~1.5 mol% instead of ~6 mol% in the preliminary experiments. Thus, some facts must be highlighted: (i) the use of ethanol in excess of 6:1 favored significantly the oil conversion, as observed before [5,16,17]. This positive effect is generally ascribed to the chemical equilibrium shift. Note that the improved oil solubility in an excess of alcohol as reported by Madras et al. [16] could also favor the reaction. (ii) The oil conversion, measured after 3 h of reaction, was 27% while it reached 48% after 5 h. In that way, over dehydrated HPW, almost 50% of oil was converted at 85 °C using ethanol in excess of 6:1 with respect to the ester function. Thus, in the following, the reaction was stopped after 3 h in order to draw more reliable correlations between the catalyst features and its performances; a reduced impact of the reaction products being expected under shorter reaction duration.

3.3. Comparison of the Keggin type heteropolyacids

Table 3 shows the results of ethanolysis of rapeseed oil using Keggin heteropolyacids as catalysts, $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$. The experimental conditions were those determined in the previous section; $T = 85$ °C, a 6:1 ethanol to ester functions molar ratio, products analysis after 3 h of reaction.

It is interesting to observe that under these conditions all the tested heteropolyacids exhibited a significant activity together with sulfuric acid while phosphoric acid was revealed almost inactive under the used conditions. This result appears to be consistent with the respective acidity of HPA solutions and mineral acids. Indeed, as reported by Kozhevnikov et al. [18], the acidity of diluted HPA solutions is greater than equimolar solutions of strong mineral acids (i.e. H_2SO_4) by near one H_0 unit only (*Hammett indicator*). In other respects, H_3PO_4 is a weaker acid than H_2SO_4; its constant dissociation is lower by five orders of magnitude. Thus, the significant weaker acidity of phosphoric acid compared to the other Br∅nsted acids is most likely responsible for its lack of activity.

Concerning the respective activity of the four Keggin heteropolyacids, the changing of the peripheral atom from W to Mo increased significantly the conversion level and the use of Si instead of P as central atom further reduced the HPA activity. The observed results were not the expected ones with respect to the known acidity order of the tested heteropolyacids. Indeed, it was reported that the strength of diluted equimolar HPA solutions would vary following the order: $PW_{12} > SiW_{12} >$ P-$PMo_{12} > SiMo_{12}$, based on Hammett indicator measurements which well agree the dissociation constants of the heteropolyacids [18]. Note that this order is consistent with the acidity strength of solid HPA too [19,20] even if discrepancies still remain in the literature.

In order to better understand the significantly higher activity of Mo based HPA, additional characterizations of these solids were accomplished, regarding their intrinsic acid strength but also their hydration state, this former parameter might have a real impact on the catalytic performance of solid heteropolyacids according to previous investigations in this field [21,22].

3.4. Microcalorimetric investigation of acidity strength of Keggin heteropolyacids

Among the acidic features of HPA, number, nature and strength of the sites, the latest one, the strength of sites, is most likely the least available data. Calorimetric measurements are generally considered as reliable techniques to measure the acidic strength of solid acids. In the present work, the acid strength of the four Keggin heteropolyacids was examined by means of microcalorimetry applied to the sorption of ammonia. The solid heteropolyacids were evacuated for 1 h at 200 °C to the residual pressure of 10^{-4} torr. According to our previous investigation of HPW, this activation procedure would insure

Table 3
Reaction of rapeseed oil transesterification with ethanol in presence of Keggin heteropolyacids PW, PMo and SiMo

Catalysts	H^+/–COOR (mol%)	TG conversion (%)	Selectivity (mol%)		
			Ethylic ester	Monoglyceride	Diglyceride
$H_3PW_{12}O_{40}\cdot 24H_2O$	1.7	27	95	4	0
$H_3PMo_{12}O_{40}\cdot 28H_2O$	1.6	55	51	36	12
$H_4SiW_{12}O_{40}\cdot 24H_2O$	2.0	20	44	17	35
$H_4SiMo_{12}O_{40}\cdot 13H_2O$	2.0	45	63	31	6
H_2SO_4 (>95%)	1.3	27	62	25	10
H_3PO_4 (85%)	1.0	<5%	–	–	–

Comparison with H_3PO_4. *Conditions*: T oil bath = 85 °C, stirring rate = 500 rpm, mol ratio EtOH/–COOR = 6, reaction duration = 3 h. *Catalyst pretreatment*: dehydration of the required amount of HPA at 120 °C in for 15 h.

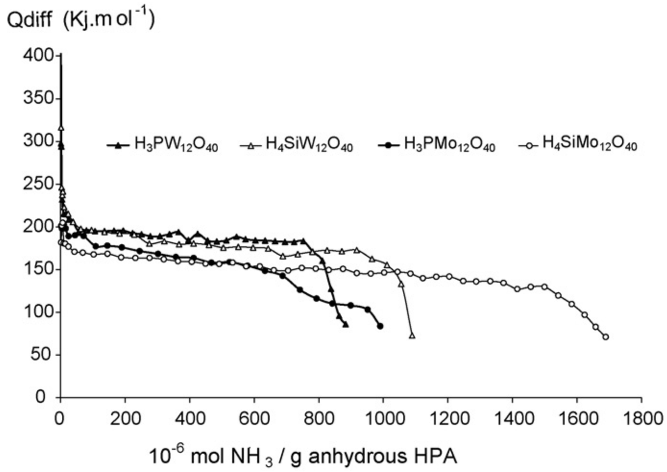


Fig. 2. Differential heat of adsorption as a function of the amount of adsorbed ammonia.

the formation of anhydrous phosphotungstic acid without affecting the number of protons per Keggin Unit, [21]. Note that there are several earlier calorimetric studies of the acidity of HPW who have faced the problem of the choice of the convenient pretreatment procedure [19,23,24]. Not to our surprise, a significant effect of the activation procedure on the differential heat of ammonia adsorption is generally observed. It was reported that both the heat of ammonia adsorption and the amount of neutralized sites were affected by the pretreatment. In view of the published reports, it appears that there is a general agreement on the fact that a pretreatment at higher temperatures lead to a reduced heat of ammonia adsorption. However, discrepancies exist on the advised temperature values probably accounting for distinct experimental conditions as duration of evacuation, temperature of NH_3 sorption among others. Note that, if the question of acidity strength of phosphotungstic acid, $H_3PW_{12}O_{40}$, was addressed by calorimetric studies by several teams [19,23–25] solely the earlier work of Moffat et al. compared the acid strength of Keggin heteropolyacids: PW, SiW, PMo and SiMo [19]. This justifies the present investigation.

Fig. 2 shows the differential heat of ammonia adsorption as a function of the amount of adsorbed ammonia over $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$.

As a general comment, we can observe that the four calorimetric curves are characterized by the presence of a significant plateau. This is in agreement with some reported calorimetric curves obtained over W based HPA [19,26]. In our knowledge, as mentioned above, the unique reported study of the strength of Mo based HPA is that of Moffat and co-workers in 1993 [19]. The curves obtained over PMo and SiMo showed a continuous decrease of the differential heat of ammonia adsorption. Most likely, the differences may result from the solids evacuation conditions. The differential heat profiles obtained in the present work are characterized by the presence of an extended plateau which characterizes the homogeneity of the acid strength of the HPA catalysts. A priori, these results are consistent with the molecular structure of solid hydrated HPA clusters where all protons have equivalent and unlocalised positions surrounding the Keggin anions. However, dehydration of the HPA is known to induce crystallographic structure changes and the acidic protons were described to be directly linked to external oxygen atoms [27,21]. Since the external oxygen atoms of the Keggin anions are not equivalent, Brønsted sites with distinct strengths might be produced accordingly. The present results evidenced that anhydrous HPA have Brønsted sites of quite homogeneous strengths. This is particularly true for the W based HPA which exhibit only a slight progressive decrease of the heat of ammonia adsorption with the NH_3 loading. The plateau levels, pointed at half NH_3 coverage or at lower NH_3 loadings (<200 molNH_3 g^{-1}) are reported in the Table 4 together with the number of titrated protons. The values deduced at half NH_3 loading confirm the expected strength order: $PW_{12} > SiW_{12} > PMo_{12} > SiMo_{12}$. Nevertheless, note that the differential heat of adsorption recorded at low NH_3 coverage evidences the close acidity strength between SiW and PW. Moreover, we can notice that the total number of titrated H^+ is in relative good agreement with the number of H^+ deduced from the HPA composition for PW, SiW, SiMo. Discrepancies are observed for the PMo sample.

The present study has confirmed the order of acidity strength of the Keggin HPA: PW > SiW > PMo > SiMo. Then, as a matter of fact, as already suggested above, it is clear that the catalytic results presented above did not correlate the strength of anhydrous solid HPA.

3.5. Thermogravimetric study

The presence of water in the reactant media may influence the activity of heteropolyacid as already evidenced in other acidic reaction [28]. The water control was undertaken by performing thermogravimetric analysis immediately after the pretreatment applied to the HPA samples before the catalytic tests. The TGA curves are presented in Fig. 3 and the HPA water contents deduced from the different weight losses are given in Table 5. The thermogravimetric results revealed that for the Mo

Table 4
Total number of protons titrated by ammonia per 1 g of anhydrous HPA

	$H_3PW_{12}O_{40}$	$H_4SiW_{12}O_{40}$	$H_3PMo_{12}O_{40}$	$H_4SiMo_{12}O_{40}$
H^+_{tit}/gHPA$_{anhy}$	900	1100	1000	1700
H^+_{th}/gHPA$_{anhy}$	1030	1387	1643	1940
Q_{diff} (kJ mol^{-1}) Low NH_3 coverage	195	195	180	170
Q_{diff} (kJ mol^{-1}) Half coverage	185	175	160	150

(H^+_{tit}/gHPA$_{anhy}$), theoretical number of protons (H^+_{th}/gHPA$_{anhy}$). Differential heat (Q_{diff}) of ammonia adsorption at low NH_3 coverage (<200 molNH_3 g^{-1}) and half coverage.

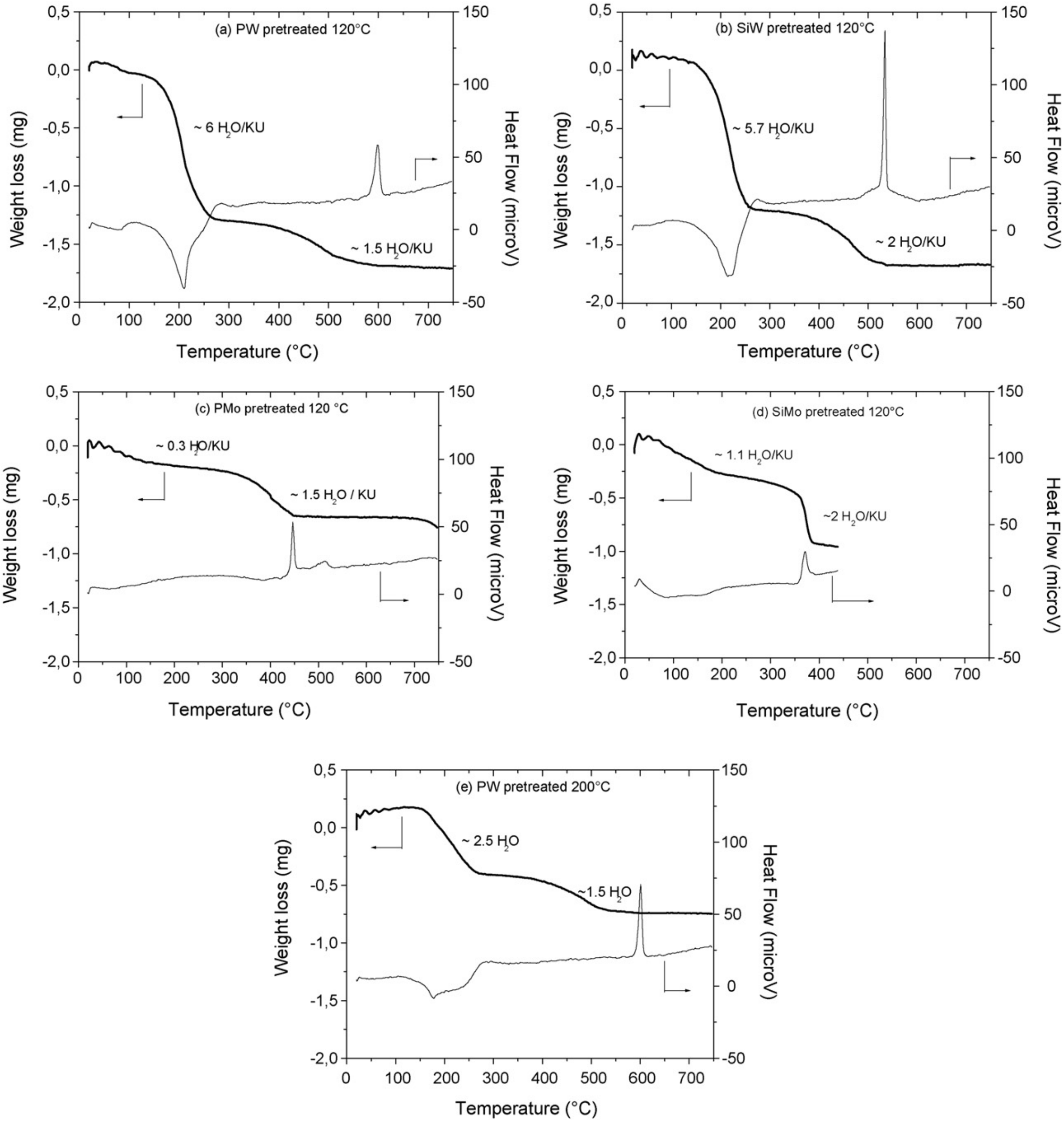


Fig. 3. Thermogravimetric curves of Keggin heteropolyacids treated overnight at 120 or 200 °C (a) PW treated at 120 °C (b) SiW treated at 120 °C (c) PMo treated at 120 °C. (d) SiMo treated at 120 °C (e) PW treated at 200 °C.

containing HPA, the loss of crystallization water is almost complete upon the thermal treatment at 120 °C (Fig. 3c and d) by contrast with the W based HPA which retains ~6 H_2O/KU which corresponds to the stable hexahydrate (Fig. 3a and b). After activation at 200 °C, PW still retains some crystallization water molecules ~2.5 H_2O/KU (Fig. 3e). Note that after such thermal treatment, all the HPA retain their entire proton content, as deduced from the constitution water loss recorded in the range of 200–450 °C and 300–550 °C for Mo and W samples, respectively. For the P based HPA, the constitution water loss equals 1.5 mol/KU which corresponds to the expected three protons per KU and for the Si based HPA, the constitution water loss is higher, 2 mol/KU, which represents exactly four protons per KU.

3.6. *Influence of the Brønsted sites solvation by water*

Therefore, it is evident that the catalytic experiments described above were not carried out at equivalent H_2O/H^+ molar ratio. Thus, the apparent lack of correlation between the activity and the acid strength is readily rationalized taken into account the H^+ solvation state. It appears evident that the higher activity measured over PMo and SiMo samples may result from the lower H_2O/H^+ molar ratios which characterize the reactant

Table 5
Amount of residual crystallization water measured by thermogravimetric analysis after overnight thermal treatment in an oven over the Keggin heteropolyacids PW, SiW, PMo, SiMo

HPA	*T* activation (°C)	Water losses (mol/KU)		H_2O/H^+
		Crystallization	Constitution	
$H_3PW_{12}O_{40}\cdot 24H_2O$	120	6	1.5	2
$H_3PMo_{12}O_{40}\cdot 28H_2O$	120	0.3	1.5	0.1
$H_4SiW_{12}O_{40}\cdot 24H_2O$	120	5.7	2	1.4
$H_4SiMo_{12}O_{40}\cdot 13H_2O$	120	1.1	2	0.3
$H_3PW_{12}O_{40}\cdot 24H_2O$	200	2.5	1.5	0.8
H_2SO_4 (>95%)	–	–	–	<0.15
H_3PO_4 (85%)	–	–	–	0.3

Table 6
Activity of dehydrated 12-tungstophosphoric acid for Rapeseed oil transesterification with ethanol

Catalyst pretreatment	H^+/–COOR (mol%)	H_2O/H^+ (mol/mol)	TG conversion (%)	Carbon balance (%)
120 °C for 15 h	1.7	2	27	102
200 °C for 15 h	1.6	0.8	40	93

Influence of the catalyst dehydration level. *Conditions*: T oil bath = 85 °C, stirring rate = 500 rpm, ROH/–COOR = 6; reaction duration = 3 h. *Catalyst pretreatment*: dehydration of the required quantities of HPA at 120 or 200 °C for 15 h.

medium. This interpretation was readily confirmed upon subjecting the PW to a thermal treatment at a higher temperature, 200 °C instead of 120 °C which reduced the residual hydration water to a H_2O/H^+ molar ratio of 0.8 instead of 2. As expected, the TG conversion level was significantly increased (Table 6), but the conversion does not reach the level obtained with PMo and SiMo. In an attempt to rationalize the influence of the Brønsted acid strength and its solvation by water molecules, we examined the variation of the Turnover numbers as a function of the H_2O/H^+ molar ratio for the HPA series as well as for H_2SO_4 and H_3PO_4 (Fig. 4). This figure evidenced the generally higher activity of HPA samples over sulfuric or phosphoric acids accounting, most likely, for their higher acid strength. It is noteworthy that this holds true even when their Brønsted sites are more hydrated, at least up to one order of magnitude in the case of PW.

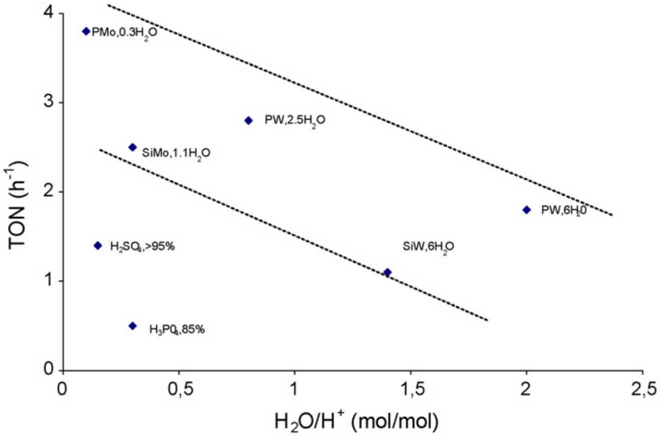


Fig. 4. Transesterification of rapeseed oil with ethanol over homogeneous Brønsted acids HPA, H_2SO_4 and H_3PO_4. Dependence of TON with H_2O/H^+ ratios. *Conditions*: T oil bath: 85 °C, stirring rate: 500 rpm, ROH/–COOR = 6; reaction duration = 3 h. H^+/–COOR: from 1 to 2.

These results have shown that TG transesterification over Brønsted acids is sensitive to trace amounts of water in the reactant media. However, Brønsted acid of high strength, as in the case of HPA, appears to be more water resistant than usual mineral acids. Finally, the present results appear to be at variance with the general view which describes the acid-catalyzed triglyceride transesterification as a water tolerant reaction by contrast to the base-catalyzed biodiesel production. It would be more sensible to consider that the acid-catalyzed transesterification is certainly more but not totally water tolerant in a sense that soap formation may be avoided. As demonstrated above, this appears to depend on the catalyst acid strength in case of homogeneous catalysis.

Table 7
Comparative activity of dehydrated 12-tungstophosphoric acid for rapeseed oil transesterification with ethanol or methanol

Alcohol	H^+/–COOR (mol%)	ROH/–COOR	T oil bath (°C)	TG conversion (%)
Methanol	3	8.9	80	11
Ethanol	3	6	80	60

Conditions: stirring rate = 500 rpm, reaction duration = 5 h. *Catalyst pretreatment*: dehydration of the required quantities of HPA at 200 °C.

3.7. TG transesterification with ethanol or methanol

Most of the previous results were undertaken with ethanol since ethanol is the ideal alcohol due to its renewable origin which would make the biodiesel totally biogenerated. However it is widely known that base-catalyzed transesterification occurs more rapidly with methanol than with ethanol [9] and that the contrary may hold true over acid catalysts [7]. To check that important aspect, tests were carried out over PW catalysts in presence of methanol or ethanol. The results were reported in Table 7. It is clear that the rapeseed oil transesterification occurs faster with ethanol than with methanol in complete opposition to what is established in presence of a basic catalyst. This is consistent with the earlier studies of Freedman et al. [7]. If the use of higher alcohol would favor an enhanced contact between the alcohol and the fatty reactant and products, the reverse order observed in presence of a basic catalyst may result for the distinct mechanism.

4. Conclusion

Biodiesel production by transesterification of rapeseed oil with ethanol has been investigated over ethanol soluble Brønsted acids as Keggin heteropolyacids, sulfuric acid and phosphoric acids. The work addressed the crucial question of the role of acid strength on the catalytic performance. This was achieved by performing experiment with equivalent amount of protonic sites and by the control of their solvation state in the reactant media. The acid site strength and the water content were measured by calorimetric and thermogravimetric techniques. In agreement with earlier calorimetric investigations, the following strength order was measured: PW > SiW > P-PMo > SiMo, and the respective differential heats of ammonia adsorption as follows: 185, 175, 160, 150 kJ mol^{-1}. It was shown that HPA-catalyzed transesterification achieves higher reaction rates than conventional mineral acids accounting for their higher acid strength. Thus, HPA have the capacity the produce biodiesel in mild conditions. The apparent higher activity of Mo based HPA with respect to the W based polyoxometallates of higher strength, was explained by the ability of Mo sample to loss hydration water at lower pretreatment temperatures.

TG transesterification with ethanol over HPA is sensitive to traces amount of water, however this effect appears to be less detrimental than over sulfuric or phosphoric acids which is ascribed to their higher acid strength.

Finally, homogeneous catalysts, although effective as HPA in mild conditions, would lead to serious contamination problems as used acids neutralization and equipments corrosion. Accordingly, the design of solid acid catalysts is strongly desired and the use of solid HPA for TG transesterification will be addressed in a forthcoming paper.

References

[1] www.prolea.com.
[2] A.W. Schwab, M.O. Bagby, B. Freedman, Fuel 66 (1987) 1372–1378.
[3] US 20050204612 (A).
[4] US 2 838 433.
[5] H. Fukuda, A. Konda, H. Noda, J. Biosci. Bioeng. 92 (5) (2001) 405–416.
[6] M. Al-Widyan, A. Al-Shyoukh, Bioresour. Technol. 85 (2002) 253–256.
[7] B. Freedman, E.H. Pryde, T.L. Mounts, J.A.O.C.S. 61 (10) (1984) 1638–1643.
[8] D.E. Lopez, J.G. Goodwin Jr., D.A. Brucea, E. Lotero, Appl. Catal. A: Gen. 295 (2005) 97–105.
[9] E. Lotero, Y. Lin, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwin Jr., Ind. Eng. Chem. Res. 44 (2005) 5353–5363.
[10] B. Freedman, E.H. Pryde, T.L. Mounts, J.A.O.C.S. 61 (10) (1984) 1638.
[11] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[12] B.Y. Giri, K. Narasimha Rao, B.L.A. Prabhavathi Devi, N. Linguiab, I. Suryanarayana, R.B.N. Prasad, P.S. Sai Prasad, Catal. Commun. 6 (2005) 788.
[13] Mangesh, G. Kulkarni, R. Gopinath, L. Charan Meher, A.K. Dalai, Green Chem. 8 (2006) 1056.
[14] M.T. Pope, Inorganic Chemistry Concepts, vol. 8, Springer, Berlin, 1983.
[15] B. Freedman, R.O. Butterfield, E.H. Pryde, J.A.O.C.S. 63 (10) (1986) 1375.
[16] G. Madras, C. Kolum, R. Kunan, Fuel 83 (2004) 2029.
[17] US 2 838 433 – 2003 - IFP.
[18] I.V. Kozhevnikov, S.Ts. Khankhasaeva, S.M. Kulikov, Kinet. Catal. 29 (1988) 76.
[19] L.C. Jozefowicz, H.G. Karge, E. Vasilyeva, J.B. Moffat, Microporous Mater. 1 (1993) 313.
[20] N. Essayem, C. Lorentz, A. Tuel, Y.B. Taarit, Catal. Commun. 6 (2005) 539.
[21] N. Essayem, A. Holmqvist, P.Y. Gayraud, J.C. Vedrine, Y. Ben Taarit, J. Catal. 197 (2) (2001) 273.
[22] N. Essayem, Y.Y. Tong, H. Jobic, J.C. Vedrine, Appl. Catal. A: Gen. 194–195 (2000) 109.
[23] F. Lefebvre, F.X. Liu-Cai, A. Auroux, J. Mater. Chem. 4 (1) (1994) 125.
[24] B.B. Bardin, R.J. Davis, Appl. Catal. A: Gen. 200 (2000) 219.
[25] E.F. Kozhevnikova, I. Kozhevnikov, J. Catal. 204 (2004) 164.
[26] F.X. Liu-Cai, B. Sahut, E. Faydi, A. Auroux, G. Hervé, Appl. Catal. A: Gen. 185 (1999) 75.
[27] I.V. Kozhevnikov, A. Sinnema, R.J.J. Jansen, H. Van Bekkum, Catal. Lett. 27 (1994) 187.
[28] N. Essayem, G. Coudurier, J.C. Vedrine, D. Habermarcher, J. Sommer, J. Catal. 183 (1999) 292.