Journal of Catalysis 320 (2014) 1-8

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# Immobilizing heteropolyacids on zirconia-modified silica as catalysts for oleochemistry transesterification and esterification reactions



JOURNAL OF CATALYSIS

Maryna Kuzminska<sup>a,c</sup>, Tetyana V. Kovalchuk<sup>b</sup>, Rénal Backov<sup>c</sup>, Eric M. Gaigneaux<sup>a,\*</sup>

<sup>a</sup> Université Catholique de Louvain, Institute of Condensed Matter and Nanosciences – IMCN, Croix du Sud 2, Box L7.05.17, B-1348 Louvain-la-Neuve, Belgium <sup>b</sup> National T. Shevchenko University. Vladimirskava 64. 01601 Kiev. Ukraine

National 1. Snevchenko Oniversity, vlauminskaya 04, 01001 Kiev, Okume

<sup>c</sup> Université de Bordeaux, Centre de Recherche Paul Pascal, CRPP-UPR CNRS 8641, 115 av. du Dr. A. Schweitzer, F-33600 Pessac, France

# ARTICLE INFO

Article history: Received 10 May 2014 Revised 29 August 2014 Accepted 18 September 2014

Keywords: Keggin HPA Immobilization Transesterification Esterification Biofuel Biolubricant Oleic acid Butyl stearate

# 1. Introduction

Considering the field of oleochemistry, acid catalysts are of big interest for the biofuel-dedicated transesterification and esterification reactions as well as biolubricant productions. Contrary to the alkaline synthetic paths, acidic catalysts can catalyze simultaneously both above-mentioned reactions while avoiding soap formation when low oil quality is employed [1]. Different studies showed that heteropolyacids (HPAs) are active acidic catalysts for both esterification and transesterification [2–6]. However, bulk heteropolyacids (HPAs) are soluble in polar media that make their recovery difficult. Moreover, if used in non-polar medium, the HPAs are not soluble and marginally active due to low accessibility of their active sites. In order to circumvent these penalties, different approaches were attempted to heterogenize HPA as for instances: impregnation into porous supports [7–9], entrapment in solid matrices via sol-gel [10,11], grafting on functionalized surfaces [12], and so forth. Nevertheless, the preparation of stable heterogeneous HPAs that do not leach in polar media while being well dispersed in non-polar media still remains a challenge.

# ABSTRACT

A new method of chemical immobilization of Keggin heteropolyacids (HPAs) was suggested.  $H_3PW_{12}O_{40}$ ,  $H_4SiW_{12}O_{40}$ , and  $H_3PM_{012}O_{40}$  were immobilized on the silica which was previously grafted with zirconium butoxide. The immobilization method promoted strong interaction HPA-support and yielded 25 wt% of well-dispersed HPAs, so increasing the density of acid sites. The catalysts were active in the reaction of transesterification of methyl stearate with n-butanol and esterification of oleic acid with trimethylolpropane. We demonstrate that, contrary to the immobilized  $H_3PM_{012}O_{40}$ , the  $H_3PW_{12}O_{40}$  and  $H_4SiW_{12}O_{40}$ -based catalysts are stable toward leaching in a non-polar oleic acid medium. A discussion on circumventing the leaching in non-polar versus polar media is proposed in terms of interaction strength HPA-support. The stronger interaction (i.e., better resistance for leaching) between the support and  $H_3PW_{12}O_{40}$  (or  $H_4SiW_{12}O_{40}$ ) is referred to the lower difference of electronegativity between Zr and W and the lower polarizability of the bonds Zr–O–W compared to Zr–O–Mo.

© 2014 Elsevier Inc. All rights reserved.

Particularly, some studies showed that zirconia is able to interact and stabilize dispersed HPAs [13,14]. However, due to high crystallinity of  $ZrO_2$  and often low specific surface area, the accessibility of active sites remains limited. In order to limit this drawback, the combination of  $ZrO_2$  with an amorphous support could be advantageous as the high surface area support would provide good accessibility of active species and the zirconia would chemically stabilize heteropolyacids.

In this work, we demonstrate an alternative approach to immobilize chemically HPAs on zirconia/silica support. The novelty of the suggested immobilization method relies on the use of zirconia as a linker between silica and HPA. Within the limit of our knowledge, the attempts to combine silica and zirconia with HPAs were done so far only by impregnation method or by sol-gel technique [15,16]. The difference in the HPAs immobilization may contribute positively or negatively to the catalyst texture, stability, and number of active sites. Moreover, we studied the stability of prepared materials toward leaching considering two reactions bearing industrial applications. First, we studied the stability of the prepared catalyst toward leaching in a model reaction for biofuel production, namely the methyl stearate transesterification with n-butanol. This reaction allowed us both to make screening tests and justify the efficiency of the suggested synthetic HPAs immobilization. Second, we tested the catalysts activity for the



<sup>\*</sup> Corresponding author.

*E-mail addresses:* maryna.kuzminska@uclouvain.be (M. Kuzminska), eric. gaigneaux@uclouvain.be (E.M. Gaigneaux).

clean "solvent-free" synthesis of biolubricants by oleic acid esterification with trimethylolpropane. This reaction has not been extensively studied so far, where only few reports addressed some issues to be overcome [17,18]. The reaction possesses technical and scientific difficulties among which is the intrinsic molecular hindrance of the reaction components, being furthermore very difficult to analyze analytically. Besides, the mass transfer and diffusion limitations, due to high viscosity of the reaction medium, undoubtedly minimize the reaction kinetics. In this work, we report the successful preparation of stable heterogeneous catalysts appearing as good candidates when employed for the above-mentioned complex industrial processes.

# 2. Materials and methods

# 2.1. Chemicals

Silica (Merck 60, 333 m<sup>2</sup>/g), 80% zirconium butoxide solution in n-butanol (Sigma), pentadecane (Sigma, TCI), acetonitrile, ethanol, n-butanol, toluene, hexane (all used solvents were of analytical grade or HPLC grade). Keggin HPAs ( $H_3PW_{12}O_{40}$ ,  $H_4SiW_{12}O_{40}$ ,  $H_3PMo_{12}O_{40}$ ) were used as such without any previous treatment (Sigma). Other chemicals were as follows: N,O-Bis(trimethyl-silyl)trifluoroacetamide (BSTFA) (Sigma, Alfa Aesar), oleic acid 90% (Alfa Aesar), trimethylolpropane (Alfa Aesar), methyl stearate 95% (Sigma), butyl stearate 95% (TCI).

#### 2.2. Silica grafting with zirconium n-butoxide (Step I, Fig. 4)

22 g of commercial SiO<sub>2</sub> (pre-dried in vacuum at around 200 mbar, 150 °C and for 2 h) was dispersed in 180 ml of toluene. 10 ml of zirconium n-butoxide (ca. 1 mmol/g of SiO<sub>2</sub>) was then added to the silica suspension under inert atmosphere and vigorous stirring. The mixture was stirred overnight (16 h in total) at 105 °C under reflux. Then, the reaction mixture was cooled down to room temperature, and the final product was washed four times with toluene. The obtained material – denoted  $ZrO_2/SiO_2$  – was stored under a layer of toluene.

# 2.3. Immobilization of HPA on the ZrO<sub>2</sub>/SiO<sub>2</sub> (Step II, Fig. 4)

2.5 g of corresponding Keggin HPA was dissolved in 100 ml of acetonitrile. Then, 5 g of  $ZrO_2/SiO_2$  (pre-dried in vacuum at 40 °C for 1 h) was added to the HPA solution. The mixture was stirred at 80 °C for 15 h. Finally, the materials were filtered and washed with acetonitrile in a Soxhlet apparatus to remove unreacted HPA. The so-obtained catalysts were dried in air at 110 °C overnight. Depending on the corresponding HPA used for the synthesis, the materials were denoted PW–ZrO<sub>2</sub>/SiO<sub>2</sub>, SiW–ZrO<sub>2</sub>/SiO<sub>2</sub>, and PMo–ZrO<sub>2</sub>/SiO<sub>2</sub>.

# 2.4. Characterization

#### 2.4.1. Elemental analysis

The content of Zr, P, W, and Mo was measured by inductively coupled plasma-atomic emission spectroscopy (ICP AES) on an Iris Advantage apparatus from Jarrell Ash Corporation. The amount (wt.%) of immobilized HPA was calculated by using the formula  $H_{n-}$  XM<sub>12</sub>O<sub>40</sub> (for X = P, *n* = 3 and for X = Si, *n* = 4; M = W or W).

# 2.4.2. Acidity measurements

The acidity of prepared materials was measured by potentiometric titration with n-butylamine as described elsewhere [19].

#### 2.4.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded in transmission mode using an IFS55 Equinox spectrometer (Bruker) equipped with a DTGS detector. The spectra were recorded with 100 scans between 400 and 4400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The samples were analyzed after dilution in KBr (Janssens Chimica 99%) by a weight factor of 50.

# 2.4.4. NMR spectroscopy

<sup>31</sup>P magic angle spinning (MAS) NMR measurements were performed at 202.47 MHz with a Bruker ASX 500 NMR spectrometer operating in a static field of 11.7 Teslas. The chemical shift was referenced with respect to external 85% H<sub>3</sub>PO<sub>4</sub>.

#### 2.4.5. X-ray diffraction (XRD)

XRD was used to check the crystallinity and dispersion of the active phase in the synthesized catalysts. Measurements were performed with a Siemens D5000 diffractometer equipped with a 1.6 kW source and using the K $\alpha$  radiation of Cu ( $\lambda$  = 1.5418 Å). The 2 $\theta$  range was scanned between 5° and 75° at a rate of 0.02°/s. As a control sample, SiO<sub>2</sub> was mechanically mixed with the corresponding HPA (18–25 wt.%) and the XRD profile was recorded as described above.

### 2.4.6. N<sub>2</sub> physisorption

Specific surface area and pore size were obtained through nitrogen adsorption–desorption experiments in the Micromeritics Tristar 3000. Before analysis, the samples were degassed overnight under vacuum (0.67 Pa) at 150 °C. The measurements were performed at -196 °C and with relative pressures in the range of 0.01-1.00 (*P*/*P*<sub>0</sub>). The specific surface area was calculated from the adsorption isotherm in the *P*/*P*<sub>0</sub> range of 0.05–0.30 using BET method, and denoted afterward *S*<sub>BET</sub>.

# 2.5. Catalytic studies

Before each catalytic study, the catalysts were pre-dried at 80  $^{\circ}$ C in vacuum for 2 h to keep them in the same conditions before the catalytic tests. All catalytic studies were repeated at least twice to ascertain the reproducibility of the results.

# 2.5.1. Transesterification reaction of methyl stearate (MS) with nbutanol (BuOH)

Previously, pre-dried catalyst (0.1 g) was weighed into the reactor. Then, n-butanol (3 ml) and methyl stearate (0.5 g) were added. The start of the reaction was considered after all components were mixed and the reactor placed into an oil bath at 100 °C. The reaction was performed under magnetic agitation (400 rpm) in a batch closed reactor connected to a reflux. Pentadecane was used as internal standard for the GC analysis. For sampling, 20  $\mu$ l of the reaction mixture was taken at certain time intervals and extracted with 2 ml of hexane and 2 ml of water. The organic phase was analyzed by GC. The standard deviation of the detection of butyl stearate was in the range of 0.2–0.9 (%), as calculated from three parallel tests for each GC injection of kinetic measurements.

#### 2.5.2. Control tests

All catalytic studies were compared to a "blank" test where the reaction was carried out at the same conditions as described above but without any catalyst and to the reactions catalyzed by the supports  $(0.1 \text{ g}) - \text{SiO}_2$  and  $\text{ZrO}_2/\text{SiO}_2$ .

## 2.5.3. Leaching tests

The leaching tests were performed similar as described elsewhere [20] with some modifications. The catalysts were treated with hot butanol ( $100 \degree$ C, 2 h, reflux). The ratio catalyst/butanol was the same as in the catalytic tests. The hot filtrated butanol was then used for the transesterification reaction as a reactant under the conditions described above but without any catalyst.

2.5.4. Esterification of oleic acid (OA) with trimethylolpropane (TMP)

2.70 g of oleic acid and 0.43 g of TMP (molar ratio between OA and TMP = 3:1) were weighted into the batch reactor. The mixture was heated for about 1 min to melt TMP, after which the catalyst (0.10 g) was added. The start of the reaction was considered after all components were mixed, and the reactor was placed in an oil bath at 120 °C. The reaction was performed under magnetic agitation at 400 rpm and in an open reactor. For sampling, 10  $\mu$ l of the reaction mixture was taken at certain time intervals and derivatized as described below (see Section 2.6) followed by gas chromatography (GC). Standard deviations of the GC measurements were in the range of 0.04–0.20 (mol/l) for the detection of the start.

# 2.5.5. Control tests

The "blank" test was performed in identical conditions as described above for the esterification catalytic tests but without the catalyst.

# 2.6. Analytics

# 2.6.1. Gas chromatography

For both reactions, the separation on the GC system was performed as described elsewhere [21]. The reaction of transesterification was followed by the evolution of butyl stearate, and the concentration was calculated based on the calibration curve for the analytical standard of butyl stearate. For the esterification reaction, the evolution of mono-, di-, and triesters was followed.

# 2.6.2. Derivatization of esterification products

To improve the GC detection and separation of low volatile compounds (fatty acid, mono- and di-esters), the sample was derivatized with BSTFA following the protocol [21] with some modifications. Thus, 10  $\mu$ l of the reaction mixture was first solubilized with 2 ml of acetonitrile. Then, 500  $\mu$ l of BSTFA was added and the final mixture was heated at 60 °C for 30 min with vigorous magnetic agitation. After the derivatization was finished, the final products were extracted with 2 ml of hexane followed by GC injection.

#### 2.6.3. Identification of the reaction components

Since no standards for the products of esterification of OA with TMP are available commercially to determine their retention times, the solution was synthesized from pure methyl oleate (using protocol [21], with some modifications). This ester reacted with TMP under sodium methoxide as catalyst. The methyl ester-to-TMP molar ratio and catalyst (w/w percentage) were fixed at 3:1 and 0.8%, respectively, to ensure optimal conversion. The reaction was carried out at 110 °C in the open flask for 10 h. The reaction products were neutralized to remove the catalyst and then distilled under vacuum to remove traces of water. The derivatized transesterification products were then injected to the GC to identify their retention times. Retention times for oleic acid and trimethylolpropane were identified from their commercial standards.

# 2.6.4. Response factor prediction for mono-, di-, and triesters

For the prediction of response factors of the products, standard solutions of 2-ethylhexyl butyrate (EHB), ethyl stearate (ES), n-butyl stearate (BS), and glycerol trioleate (GTO) were used. For each compound, at least three different concentrations have been injected to the GC. At each standard solution, a known amount of internal standard was added. The response factor  $K_n$  for each

injection was calculated by using the formula  $K_n = C_i/S$  (where  $C_i$  is a concentration of the solution and *S* is a ratio of peak areas between the *i* compound and the internal standard). The response factor ( $K_i$ ) of each standard was taken as an average value from all injections of the corresponding standard. Obtained response factors for known compounds were extrapolated on the basis of the number of C atoms to calculate the theoretical response factors for products of the catalytic reaction (mono-, di-, and tri-esters of OA and TMP). See calibration curve in the Supplemental information (Fig. S3).

# 3. Results and discussion

# 3.1. Efficiency of the HPA immobilization: FTIR and <sup>31</sup>P NMR spectroscopy

We studied the efficiency of the HPA immobilization through the FTIR and <sup>31</sup>P NMR spectroscopy. Table 1 depicts a summary of the main observed bands and their bond signatures. FTIR spectra in the range of 1200–600 cm<sup>-1</sup> (Fig. 1) indicate the most crucial vibrational mode changes when grafting occurs. The spectra of supported HPAs are shown after the subtraction of the spectrum of ZrO<sub>2</sub>/SiO<sub>2</sub>.

The stretching band of  $v_{Si-OH}$  at 967 cm<sup>-1</sup> almost disappeared after silica treatment with zirconium butoxide (Fig. 1a and b) as well as the band for free terminal silanols at  $3746 \text{ cm}^{-1}$  (Table 1) indicating the chemical interaction of surface silanols with Zr(OC<sub>4-</sub> H<sub>9</sub>)<sub>4</sub>. After further HPA immobilization (Fig. 1c, d, e, and Table 1), the characteristic  $v_{M-Ob-M}$  and  $v_{M-Od}$  stretching modes of the Keggin structure appear (where M is W or Mo). Other vibrations of Keggin units, such as asymmetric  $v_{asP-O}$  (or  $v_{asSi-O}$ ) and  $v_{asM-Oc-M}$ (corner-sharing oxygen connecting M<sub>3</sub>O<sub>13</sub> units), cannot be observed from the initial IR spectra as they overlap with strong stretching modes of silica Si–O–Si ( $\sim$ 1090 cm<sup>-1</sup> and  $\sim$ 800 cm<sup>-1</sup>). For this reason, the subtraction of the spectrum of the support from the ones of immobilized HPA was performed (Fig. 1c-e). From the subtracted spectra of PW- and PMo-catalysts, the P-O bands appeared broadened which indicates a slight change of symmetry of initial Keggin anions due to the interaction with the support [14].

It should be indicated also that the symmetric and asymmetric stretching  $v_{(C-H)}$  vibrations at 3000 cm<sup>-1</sup> disappeared (Table 1) after the reaction between HPA and ZrO<sub>2</sub>/SiO<sub>2</sub> that indicates the complete hydrolysis of surface C<sub>4</sub>H<sub>9</sub>O-groups after the HPA immobilization on ZrO<sub>2</sub>/SiO<sub>2</sub>.

Additional information on the structure of immobilized HPA was obtained by <sup>31</sup>P NMR. In Fig. 2, the NMR spectra of studied catalysts are compared to the ones of pure HPA. From Fig. 2, the peak at -13.7 ppm of PW–ZrO<sub>2</sub>–SiO<sub>2</sub> indicates that the Keggin structure is distorted due to the strong interactions with the support but the fundamental Keggin structure is preserved [24]. Additionally, the chemical shift indicates that there is one proton directly attached to the heteropolyanion (i.e., this proton is acidic) [25]. Similarly, the <sup>31</sup>P NMR signal of PMo–ZrO<sub>2</sub>–SiO<sub>2</sub> shows a strong interaction between support-HPA.

To sum up, FTIR and <sup>31</sup>P NMR data confirm efficient immobilization of HPA onto porous support with preserving the initial structure of Keggin units which is crucial for their stability and catalytic performance.

#### 3.2. Acidic properties

The acidity of prepared materials was performed by means of potentiometric titration with n-butylamine. This method allows measuring the total number and the strength of acid sites. In such Table 1

hands were assigned based on the literature [22.22]

Summary of the Fin	Valus observed for prepared materials. Characteristic absorption bands were assigned based on the interature [22,25].
Material	Bands, $v$ (cm <sup>-1</sup> )
SiO <sub>2</sub>	460 (Si-O out of plane deformation), 800 (Si-O bending), 967 (free silanols Si-OH stretching), intensive broad band at 1100-1225 (stretching of siloxanes Si-O-Si), broad ~3500 (hydrogen bonded OH), 3746 (free terminal silanol groups Si-OH)
$ZrO_2/SiO_2$	~3000 (C-H symmetric and asymmetric stretching modes of butoxy groups), broad ~3500 (hydrogen bonded OH), diminished (almost disappeared) at 967 (stretching of Si-O-Si or/and Si-O-Zr)
PW-ZrO <sub>2</sub> /SiO <sub>2</sub>	1078 ( $v_{asP-O}$ , from the subtracted spectrum), 983 (W-O <sub>d</sub> asymmetric ligand vibration, terminal O bonded to W atom), 893 (interligand W-O <sub>b</sub> -W, edge-sharing O connected to W), broad ~3500 (hydrogen bonded OH); the band for C-H stretching (~3000) disappeared indicating the complete hydrolysis of the butoxy groups
SiW-ZrO <sub>2</sub> /SiO <sub>2</sub>	977 (as. ligand W–O <sub>d</sub> ), 923 (interligand W–O <sub>b</sub> –W), broad $\sim$ 3500 (hydrogen bonded OH); the band for C–H stretching ( $\sim$ 3000) disappeared
$PMO = ZrO_2/SiO_2$	$-1088$ ( $v_{av}$ $\circ$ from the subtracted spectrum) 953 (as ligand Mo-O <sub>4</sub> ) 885 (interligand Mo-O <sub>8</sub> -Mo) broad $\sim$ 3500 (hydrogen bonded OH); the band



for C-H stretching (~3000) disappeared

**Fig. 1.** FTIR spectra in the range 1200–600 cm<sup>-1</sup> of: (a) SiO<sub>2</sub>, (b) ZrO<sub>2</sub>/SiO<sub>2</sub>, (c) PW–ZrO<sub>2</sub>/SiO<sub>2</sub>, (d) SiW–ZrO<sub>2</sub>/SiO<sub>2</sub>, (e) PMo–ZrO<sub>2</sub>/SiO<sub>2</sub>, (f) H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, (g) H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, (h) H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>. For shown (c)–(e) spectra, the spectrum of ZrO<sub>2</sub>/SiO<sub>2</sub> was subtracted.

method, the initial electrode potential  $(E_i)$  indicates the maximum acid strength of the surface sites and the range where the plateau is reached (meg/g solid) shows the total number of acid sites. The

strength can be defined according to the following ranges: very strong site,  $E_i > 100 \text{ mV}$ ; strong site,  $0 < E_i < 100 \text{ mV}$ ; weak site,  $-100 < E_i < 0 \text{ mV}$ ; and very weak site,  $E_i < -100 \text{ mV}$  [26].

The titration curves of the supported HPA (Fig. 3) indicate that all prepared catalysts have strong acid sites ( $E_i > 100 \text{ mV}$ ) and present similar behavior in the potentiometric titration. The acidity trend of the prepared materials decreases in the order SiW–ZrO<sub>2</sub>/SiO<sub>2</sub> ( $E_i$  370 mV) ~ PW–ZrO<sub>2</sub>/SiO<sub>2</sub> ( $E_i$  348 mV) > PMo–ZrO<sub>2</sub>/SiO<sub>2</sub> (206 mV).

In the case of SiO<sub>2</sub>, the  $E_i$  is 41 mV and it is -39 mV for ZrO<sub>2</sub>/SiO<sub>2</sub>. This last value suggests an interaction of surface silanol groups of silica and formation of butoxy groups on the surface.

#### 3.3. Content and suggested immobilization scheme

Table 2 shows the content of Zr, P, and W (Mo) of the catalysts obtained by ICP analysis.

From elemental analysis, the data demonstrate that the synthetic procedure yields up to 0.6 mmol/g of Zr (ca. 5 wt.%) and 0.1 mmol/g of HPA (18–25 wt.%). The molar ratio HPA/Zr allows to propose the manner on which the Zr species and the HPA are anchored together. Thus, the maximal theoretical HPA/Zr ratio would be 0.75 (assuming that zirconium butoxide reacted with the silanols by only one butoxy group and that the three remaining  $C_4H_9O$ -groups further reacted with HPA through the hydrolysis step). Although lower than 0.75, the HPA/Zr value (ca. 0.2, see Table 2) suggests different outcomes that may take place during the synthesis.

Taking into account experimental HPA/Zr molar ratio and steric hindrance of  $Zr(OBu)_4$  and HPAs, we would like to suggest the scheme of the HPA immobilization (Fig. 4). Thus, for the step I



Fig. 2. <sup>31</sup>P NMR of PW-ZrO<sub>2</sub>/SiO<sub>2</sub> and PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> compared to of pure HPA.



Fig. 3. Potentiometric titration curves of studied materials.

(Fig. 4), the  $Zr(OBu)_4$  is a very reactive molecule due to the presence of the highly electronegative C<sub>4</sub>H<sub>9</sub>O-group and has high affinity toward surface silanols [27]. The electrophilic Zr center would attack surface silanol and thereby would form the Si-O-Zr bond. The FTIR spectra confirmed this step (see Table 1), as the bands 3746 and 967  $cm^{-1}$  (for silanol groups) disappeared after the synthesis. Moreover, the TGA analysis of ZrO<sub>2</sub>/SiO<sub>2</sub> showed 6% of the mass loss after 300 °C which indicates the presence of residual chemically bonded butoxy groups (data are shown in the Supplemental information, Fig. S2). The further reaction between the adjacent silanol and the second leaving butoxy group (formation of bipedal Zr species) would be also possible since the conformational structure of zirconium butoxide allows it (tetrahedral arrangement of butoxy groups around Zr atom). For the same reason, the reaction between the third butoxy group and the adjacent silanol (formation of tri-pedal Zr species) would be sterically hindered. For the step II (Fig. 4), due to the well-matched electronegativity of Zr<sup>4+</sup> and W<sup>6+</sup> (1.33 and 1.7 correspondingly [28]), further reaction between Keggin units and the surface Zr oxide species will go through the formation of Zr-O-W covalent bonds at the interface of the two components [16]. Similarly, for the  $H_3PMo_{12}O_{40}$ acid, the Zr-O-Mo bonds will form. However, in this case, the difference in electronegativity between Zr<sup>4+</sup> and Mo<sup>6+</sup> is much higher (1.33 and 2.16 correspondingly) which will lead to a higher ionic character of Zr-O-Mo bond compared to the Zr-O-W. The higher

Elemental analysis (ICP AES data)

Table 2

polarizability of Zr–O–Mo bonds is not favoring the stability, especially in polar environment. And finally, the interaction between Zr center and more than one heteropolyanion is unlikely due to the large size of HPA (ca. 1 nm versus 0.072 nm for  $Zr^{4+}$  [29]).

To sum up, the surface Zr species are bipedal and the two remaining butoxy groups would be replaced by one heteropolyanion. For materials based on triprotic HPAs  $(H_3PW_{12}O_{40})$  and  $H_3$ -PMo<sub>12</sub>O<sub>40</sub>), one proton per polyanion would thus remain on the surface (as shown in Fig. 4, the HPA having to release two protons to gain two-negative charges as needed to neutralize the two time positively charged Zr center) whereas for the tetraprotic H<sub>4</sub>SiW<sub>12</sub>-O<sub>40</sub> – two protons would remain. Moreover, the suggested scheme of the synthesis leads to 0.25 maximal theoretical HPA/Zr ratio which is comparable to the experimental value 0.2.

# 3.4. Textural characteristics

The specific surface area ( $S_{BET}$ ), mean pore diameter, and pore volume are shown in Table 3. The results show that after silica modification with zirconium butoxide and further immobilization of HPAs, the surface area and pore volume of the materials decreased to the same extend. The changes of the texture of the materials suggest successful support modification with Zr(OBu)<sub>4</sub> and further HPA immobilization.

# 3.5. X-ray diffraction

X-ray diffraction profiles of immobilized HPAs (example is shown for  $PW-ZrO_2/SiO_2$ , Fig. 5a) are compared to those of the supports and to the control sample (Fig. 5a–d). We did not observe the crystalline phases for the immobilized HPA samples which suggest that HPAs are homogeneously distributed onto the support in a non-crystalline form or that crystallites are very small. The later specificity is of importance for the catalytic properties of the synthesized materials as accessibility of the active species and active surface would be enhanced.

# 3.6. Catalytic studies

#### 3.6.1. Transesterification of methyl stearate with n-butanol

The control catalytic tests (Fig. 6A) showed that the supports  $SiO_2$  and  $ZrO_2/SiO_2$  do not catalyze the reaction.

The lower activity of the  $SiO_2$  (compared to the blank test) likely comes from internal diffusion limitations. This phenomenon can be referred to the bulky reagents which retain decreased mobility

Material	Zr, mmol/g	P, µmol/g	W (Mo), mmol/g	HPA, mmol/g (calculated)	HPA/Zr (calculated)	HPA, wt.% (calculated)
SiO <sub>2</sub>	-	-	-	-	-	-
ZrO <sub>2</sub> /SiO <sub>2</sub>	0.58	-	-	-	_	_
PW-ZrO <sub>2</sub> /SiO <sub>2</sub>	0.54	0.10	1.03	0.09	0.17	25
SiW-ZrO <sub>2</sub> /SiO <sub>2</sub>	0.54	-	0.97	0.08	0.15	23
PMo-ZrO <sub>2</sub> /SiO <sub>2</sub>	0.57	0.10	1.16	0.10	0.18	18



Fig. 4. Hypothetical model of the reaction between silica and zirconium butoxide and further HPA interaction with the modified support. The number of Zr atoms per Si–OH group as well as per HPA unit was taken arbitrarily.

Table 3Textural properties of prepared materials (N2 physisorption data).

Material	$S_{\rm BET}$ , m <sup>2</sup> /g	Ø <sub>BJH</sub> , Å	Vp <sub>(BJH)</sub> , cm <sup>3</sup> /g
SiO <sub>2</sub>	443	50	0.76
ZrO <sub>2</sub> /SiO <sub>2</sub>	332	50	0.60
PW-ZrO <sub>2</sub> /SiO <sub>2</sub>	230	56	0.41
SiW-ZrO <sub>2</sub> /SiO <sub>2</sub>	216	55	0.38
PMo-ZrO <sub>2</sub> /SiO <sub>2</sub>	256	58	0.46



Fig. 5. XRD patterns for  $PW-ZrO_2/SiO_2$  (a),  $SiO_2$  (b),  $ZrO_2/SiO_2$  (c), control sample –  $SiO_2$  mixed with 25% w/w  $H_3PW_{12}O_{40}$  (d).

inside the small pores of the support. The latter is not observed with ZrO<sub>2</sub>/SiO<sub>2</sub> likely due to reduced size of the pores by zirconia-precursor which prevents the reagents from entering the pores. The catalytic data of the immobilized HPAs showed that they are catalytically active for transesterification reaction (Fig. 6B). After 24 h of the reaction, the yield of butyl stearate reached 22%, 30%, and 85% for PW-ZrO<sub>2</sub>/SiO<sub>2</sub>, SiW-ZrO<sub>2</sub>/SiO<sub>2</sub>, and PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> correspondingly. The activity of the immobilized HPAs is reversed to the known acidity of bulk HPAs as it was also observed for the homogeneous HPAs in the transesterification [2]. Thus, it is known that the acidity decreases in the order  $H_{3}PW_{12}O_{40} > H_{4}SiW_{12}O_{40} > H_{3}PMo_{12}O_{40}$ . In our case, the reversed activity trend of heterogenized HPAs (compared to the acidity order) could be referred (a) to a partly homogeneous character of the catalytic process; (b) to a higher accessibility of the active species in the heterogeneous catalysts. To validate the leaching scenario into the homogeneous phase, we treated the catalysts with hot butanol and used that butanol farther as a reagent in the transesterification reaction without any additional catalyst. Fig. 6C demonstrates the results of leaching tests. The kinetic curves for the tests with BuOH used for the treatment of PW-ZrO<sub>2</sub>/SiO<sub>2</sub> and SiW–ZrO<sub>2</sub>/SiO<sub>2</sub> (curves a and b) are superimposing with the blank test (curve d) within the error range, whereas the curve for the reaction with BuOH after PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> (c curve) is above the curve d. These observations suggest that PMo-ZrO<sub>2</sub>/ SiO<sub>2</sub> showed strong leaching of corresponding HPA into the reaction medium. Additional information on the leaching was obtained by ICP analysis of the materials before and after catalytic tests. In Table 4, the concentration of tungsten (molvbdenum) within the catalysts is compared before and after the catalytic tests. It can be seen that, after the transesterification, the amount of W (Mo) decreased by 10-17 mol% of the initial amount. The obtained results indicate that all the materials partly leached into the liquid medium. The leaching is likely caused by dissolution of the corresponding HPA into polar butanol used in excess as reagent and solvent.



**Fig. 6.** (A) Control catalytic tests of the transesterification of MS with BuOH: (a) SiO<sub>2</sub> as a catalyst; (b) blank test; (c) test with  $ZrO_2/SiO_2$ . (B) Kinetic curves of the transesterification of MS catalyzed by: (a) PW– $ZrO_2/SiO_2$ ; (b) SiW– $ZrO_2/SiO_2$ ; (c) PMo– $ZrO_2/SiO_2$ . (C) Leaching tests: transesterification of MS performed with BuOH used for the catalyst treatment. (a) Test after SiW– $ZrO_2/SiO_2$  treatment; (b) test after PW– $ZrO_2/SiO_2$  treatment; (c) test after PMo– $ZrO_2/SiO_2$  treatment; (d) blank test. On each graph (e) dot curves show the maximal product yield determined from the catalytic test with homogeneous HPA (see Supplemental information for details).

#### 3.6.2. Esterification of oleic acid with trimethylolpropane

The catalysts were also tested in the reaction which has industrial interest – namely the esterification of oleic acid with trimethylolpropane for the production of biolubricant. Fig. 7 shows the evolution of esters in the esterification of OA.

Comparison of the catalytic performances with the control test (dash curves in Fig. 7) demonstrates that the materials are catalyt-

#### Table 4

Concentration of tungsten (molybdenum) within the catalysts before and after catalytic tests (ICP AES data).

Material	W (Mo), mmol/g				
	Before catalytic test	After transesterification	After esterification		
PW-ZrO <sub>2</sub> /SiO <sub>2</sub>	1.03	0.85	1.03		
SiW-ZrO <sub>2</sub> /SiO <sub>2</sub>	0.97	0.87	0.98		
PMo-ZrO <sub>2</sub> /SiO <sub>2</sub>	1.16	1.00	0.97		



**Fig. 7.** Evolution of mono-, di-, and triesters concentration in the esterification of oleic acid with trimethylolpropane. (a) ( $\bigcirc$ ) Test with PW–ZrO<sub>2</sub>/SiO<sub>2</sub>; ( $\blacksquare$ ) test with SiW–ZrO<sub>2</sub>/SiO<sub>2</sub>; ( $\blacktriangle$ ) test with PMo–ZrO<sub>2</sub>/SiO<sub>2</sub>. Dash curves show the evolution of the product in the blank test. Lower figure is the same as the upper one but focused in the lower reaction time and product concentrations.

ically active, notwithstanding that the activity is moderate and does not differ significantly between the three studied catalysts. Only PMo–ZrO<sub>2</sub>/SiO<sub>2</sub> appears slightly more active in the beginning of the reaction (see Fig. 7, zoomed image). The kinetic curves for the evolution of esters show that the catalysts accelerate significantly the formation of mono- and diesters.

The reaction rate for triester formation in the beginning of the test remains similar to the blank test and can be explained by steric hindrance of the diester – the bulky molecule bears the last hydroxyl-group which is less accessible for the acid to attack. It is also possible that the pores of the catalyst support are too small and the formation of triester inside the pores is not favorable. The latter hypothesis suggests that the use of a support with more suitable texture (i.e., bigger pores) would facilitate the formation of bulky triester. The heterogeneous catalytic performance is close to the homogeneous HPAs (the data for the homogeneous HPA are addressed in the Supporting information). In the current case, the size of the reactants and products is too high and internal diffusion limitations take place, which explains moderate activity of the supported HPAs. The later suggests again that the support with larger pores would help to avoid this penalty.

Additional studies on the leaching during the esterification were performed by elemental analyses. The content of tungsten (molybdenum) within the materials after esterification showed that PW-ZrO<sub>2</sub>/SiO<sub>2</sub> and SiW-ZrO<sub>2</sub>/SiO<sub>2</sub> retain the same amount of tungsten as before the catalytic test (Table 4). Contrary, the PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> decreased the amount of molybdenum after the esterification. The results indicate that in the hydrophobic medium of oleic acid, PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> leached into the liquid which contrary to PW-ZrO<sub>2</sub>/SiO<sub>2</sub> and SiW-ZrO<sub>2</sub>/SiO<sub>2</sub>. The latter can be explained by the different stability of the corresponding HPAs on the surface. The hypothesis is that reaction between the support and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (or H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>) yields strong interactions support-HPA whereas the interaction support- $H_3PMo_{12}O_{40}$  is much weaker. The latter is likely due to the higher polarizability of the Zr–O–Mo bonds as a direct consequence of the difference in electronegativity between Zr and Mo (see Section 3.3).

Interesting to mention that even after the materials were used in the catalytic reactions, their FTIR spectra still contain the characteristic HPA vibrations (data are shown in Supplemental information on Fig. S4; for the FTIR measurements, the used materials were washed first with hexane and acetone after catalytic tests and dried at room temperature). The latter suggests that immobilized HPAs retain their Keggin structure even after being treated at the conditions of catalytic measurements.

To conclude, the catalytic and elemental analysis results indicate that PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> is less stable toward leaching in the non-polar medium compared to PW-ZrO<sub>2</sub>/SiO<sub>2</sub> and SiW-ZrO<sub>2</sub>/ SiO<sub>2</sub>. All three materials showed leaching in the model reaction of transesterification induced by polar butanol. However, in the industrial reaction of biolubricant production, the PW-ZrO<sub>2</sub>/SiO<sub>2</sub> and SiW-ZrO<sub>2</sub>/SiO<sub>2</sub> do not leach, showing thereby their potential toward industrial applications. We can conclude that the applied synthetic procedure is efficient for immobilization of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> for applications in non-polar media. It allows obtaining stable-toward-leaching catalysts that catalyze complex step-by-step reactions in the field of oleochemistry. The benefit of heterogenized heteropolyacids compared to the homogeneous ones lies in the higher dispersion of the active species and in the practical and economical aspects where separation and recyclability of immobilized HPAs become much easier from the liquid medium.

# 4. Conclusion

In this study, we proposed a new method for chemical immobilization of Keggin HPAs at silica through the link of zirconia. The method yields up to 25 wt.% of immobilized HPA and increased density of acid sites compared with the silica-based initial supports. The reaction between silica and zirconium butoxide likely leads to bipedal zirconium species on the surface and 0.2 M ratio of HPA/Zr. The catalytic tests demonstrate that the synthesized materials are active for both transesterification and esterification reactions of bulky molecules. On the one hand, three catalysts address partly a homogeneous catalytic behavior in the transesterification reaction due to the leaching of active species into the liquid phase. On the another hand, in the oleic acid esterification, immobilized H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> exhibit clear resistance to leaching contrary to PMo-ZrO<sub>2</sub>/SiO<sub>2</sub> that leaches even in nonpolar medium. The latter is explained by difference in interaction strength between the HPAs and the zirconia-modified silica support. The stronger interaction between the support and  $H_3PW_{12}O_{40}$  (or  $H_4SiW_{12}O_{40}$ ) is explained with the lower difference

of electronegativity between Zr and W that minimizes polarizability of the bonds Zr–O–W when compared with the Zr–O–Mo ones. For future work, we believe that by increasing the pore diameters of the catalysts as well as by changing catalytic conditions, it could be possible to increase the performance of the explored catalysts.

# Acknowledgments

The authors acknowledge the financial support from the "DGTRE, Région Wallonne" for the project "CATHESTOL" (Convention number 1117464) and the company "Mosselman s.a." for constructive interaction and the support. The authors also would like to thank Christel Gervais (Professor of UPMC, Paris) for the solid <sup>31</sup>P NMR analysis. The work was performed in the framework of IDS-FunMat doctoral program supported by the Erasmus Mundus, Program of EU-FP7.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.09.016.

#### References

- E. Santacesaria, G.M. Vicente, M. Di Serio, R. Tesser, Catal. Today 195 (2012) 2– 13.
- [2] P. Morin, B. Hamad, G. Sapaly, M.G. Carneiro Rocha, P.G. Pries de Oliveira, W.A. Gonzalez, E. Andrade Sales, N. Essayem, Appl. Catal., A 330 (2007) 69–76.
- [3] M.N. Timofeeva, Appl. Catal., A 256 (2003) 19–35.
- [4] O.d.S. Lacerda, R.M. Cavalcanti, T.M.d. Matos, R.S. Angélica, G.N. da Rocha Filho, I.d.C.L. Barros, Fuel 108 (2013) 604–611.
- [5] A.I. Tropecêlo, M.H. Casimiro, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, Appl. Catal., A 390 (2010) 183–189.

- [6] A. Zieba, L. Matachowski, J. Gurgul, E. Bielańska, A. Drelinkiewicz, J. Mol. Catal. A: Chem. 316 (2010) 30–44.
- [7] B.B. Bardin, R.J. Davis, Appl. Catal., A 200 (2000) 219-231.
- [8] S. Benadji, P. Eloy, A. Léonard, B.L. Su, K. Bachari, C. Rabia, E.M. Gaigneaux, Microporous Mesoporous Mater. 130 (2010) 103–114.
- [9] E. Grinenval, X. Rozanska, A. Baudouin, E. Berrier, F.o. Delbecq, P. Sautet, J.-M. Basset, F.d.r. Lefebvre, J. Phys. Chem. C 114 (2010) 19024–19034.
- [10] Á. Molnár, C. Keresszegi, B. Török, Appl. Catal., A 189 (1999) 217–224.
- [11] I. Dosuna-Rodriguez, E.M. Gaigneaux, in: Proceedings Book of the 1st International Congress on Catalysis for Biorefineries, 2nd-5th Oct 2011, pp. 458-463.
- [12] Y. Hanada, M. Kamada, K. Umemoto, H. Kominami, Y. Kera, Catal. Lett. 37 (1996) 229–233.
- [13] T. Rajkumar, G. Ranga Rao, J. Mol. Catal. A: Chem. 295 (2008) 1-9.
- [14] E. López-Salinas, J.G. Hernández-Cortéz, I. Schifter, E. Torres-Garcia, J. Navarrete, A. Gutiérrez-Carrillo, T. López, P.P. Lottici, D. Bersani, Appl. Catal., A 193 (2000) 215–225.
- [15] L.M. Gomez Sainero, S. Damyanova, J.L.G. Fierro, Appl. Catal., A 208 (2001) 63– 75.
- [16] F. Su, L. Ma, Y. Guo, W. Li, Catal. Sci. Technol. 2 (2012) 2367-2374.
- [17] C.O. Åkerman, Y. Gaber, N.A. Ghani, M. Lämsä, R. Hatti-Kaul, J. Mol. Catal. B: Enzym. 72 (2011) 263–269.
- [18] C.O. Åkerman, A.E.V. Hagström, M.A. Mollaahmad, S. Karlsson, R. Hatti-Kaul, Process Biochem. 46 (2011) 2225–2231.
- [19] M. del Rosario Torviso, E.N. Alesso, G.Y. Moltrasio, P.G. Vázquez, L.R. Pizzio, C.V. Cáceres, M.N. Blanco, Appl. Catal., A 301 (2006) 25–31.
- [20] M. Di Serio, R. Tesser, L. Casale, A. D'Angelo, M. Trifuoggi, E. Santacesaria, Top. Catal. 53 (2010) 811–819.
- [21] R. Yunus, O.T. Lye, A. Fakhru'l-Razi, S. Basri, JAOCS 79 (2002) 1075-1080.
- [22] R. Thouvenot, M. Fournier, R. Franck, C. Rocchiccioli-Deltcheff, Inorg. Chem. 23 (1984) 598–605.
- [23] P.L. Launer, Silicon Compounds: Register and Review, in: B. Arkles (Ed.), Petrarch Systems, 1987.
- [24] L.F. Chen, J.A. Wang, L.E. Noreña, J. Aguilar, J. Navarrete, P. Salas, J.A. Montoya, P. Del Ángel, J. Solid State Chem. 180 (2007) 2958–2972.
- [25] A. Micek-Ilnicka, J. Mol. Catal. A: Chem. 308 (2009) 1-14.
- [26] R. Cid, G. Pecchi, Appl. Catal. 14 (1985) 15-21.
- [27] C.J. Brinker, G.W. Scherer, The Physics and Chemistry of Sol–Gel Processing, Academic Press, New York, USA, 1990.
- [28] http://bilbo.chm.uri.edu/PeriodicTable/.
- [29] I.K. Song, M.S. Kaba, M.A. Barteau, Langmuir: ACS J. Surf. Colloids 18 (2002) 2358–2362.