

# Monoestolides Synthesis From Ricinoleic-Oleic Acids Using Silicotungstic Acid Sol-Gel Catalyst

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## Abstract

Sol-gel silica-supported hydrated silicotungstic acid (STA sol-gel), prepared by incorporating hydrated silicotungstic acid (STA) into silica via sol-gel technique, was used as an efficient heterogeneous catalyst for condensation reaction of a mixture ricinoleic acid (RA) and oleic acid (OA). The activity and selectivity of STA sol-gel for the condensation reaction of a mixture RA and OA have been investigated and compared with unsupported STA and homogeneous perchloric acid. STA sol-gel and bulk STA catalysts surface were characterized using X-ray Photoelectron Spectroscopy (XPS) analysis. The reactions were carried out under vacuum (2 mBar) for 10 hours at 70 °C under solvent-less conditions. The Liquid Chromatography-Mass Spectrometry (LC-MS) of reaction products results showed chromatographic peaks for the presence of three new monoestolides at retention times (t<sub>R</sub>) 9.2 min (*m/z* 577.48, as [M-H]<sup>-</sup>), 11.2 min (*m/z* 559.46, [M-H]<sup>-</sup>) and 12.6 min (*m/z* 561.48, [M-H]<sup>-</sup>). STA sol-gel catalyst is new promising heterogenous catalyst that can be used for producing estolide compounds from a mixture of RA and OA. STA sol-gel gave 100 % conversion with 60.62 % selectivity to ricinoleic-ricinoleic monoestolide acid (*m/z* 577.48, [M-H]<sup>-</sup>), 25.69 % selectivity to ricinoleic-linoleic monoestolide acid (*m/z* 559.47, [M-H]<sup>-</sup>) and 13.65 % selectivity to ricinoleic-oleic monoestolide (*m/z* 561.48, [M-H]<sup>-</sup>).

Keywords: Monoestolide synthesis; oleic acid; ricinoleic acid; STA sol-gel

## 1 INTRODUCTION

Various homogeneous catalysts and mineral acids and solid Lewis acids have been used as catalysts for the synthesis of estolide, e.g  $H_2SO_4$ ,  $HClO_4$ , *p*-toluenesulfonic acid and solid monmorillonite K-10 [1]. However, some of the procedures suffer from corrosively of strong acids, tedious work up, low yield, lengthy and involve high catalyst/substrate ratios and side reactions. Also, estolides synthesis method using a homogeneous catalyst at high temperature produces estolides which are dark in color and smell unpleasantly. As a result, the estolides produced this way are not suitable to be used in the food and bio-lubricant oil industries. There is a still need for new, mild, convenient and universally applicable method for the synthesis of estolides. In view of environmental aspects, heterogeneous catalysts are preferable for their green environmental character. Based on previous studies on estolides from oleic acid, it was found that sulphuric acid ( $H_2SO_4$ ) produced 65 % estolides, while perchloric acid ( $HClO_4$ ) produced 76 % estolides [2-3]. Very few studies have been reported on the production of estolides through heterogeneous catalyst. Surface active agent treated clay catalyst is reported to produce estolides but the estolides yield quite low ranging from 20 % to 26 % [4]. A monoestolide is formed when carboxylic acid from some fatty acids is linked to the unsaturated carbon of some other fatty acids through the ester bond as shown in Figure 1.

At present, studies on estolide synthesis using STA sol-gel have not been reported elsewhere. Intention of the present work is to study the use of an efficient catalyst based on STA sol-gel. In addition the activity and selectivity of STA sol-gel was also compared with pure STA and homogeneous  $HClO_4$  as control catalysts.

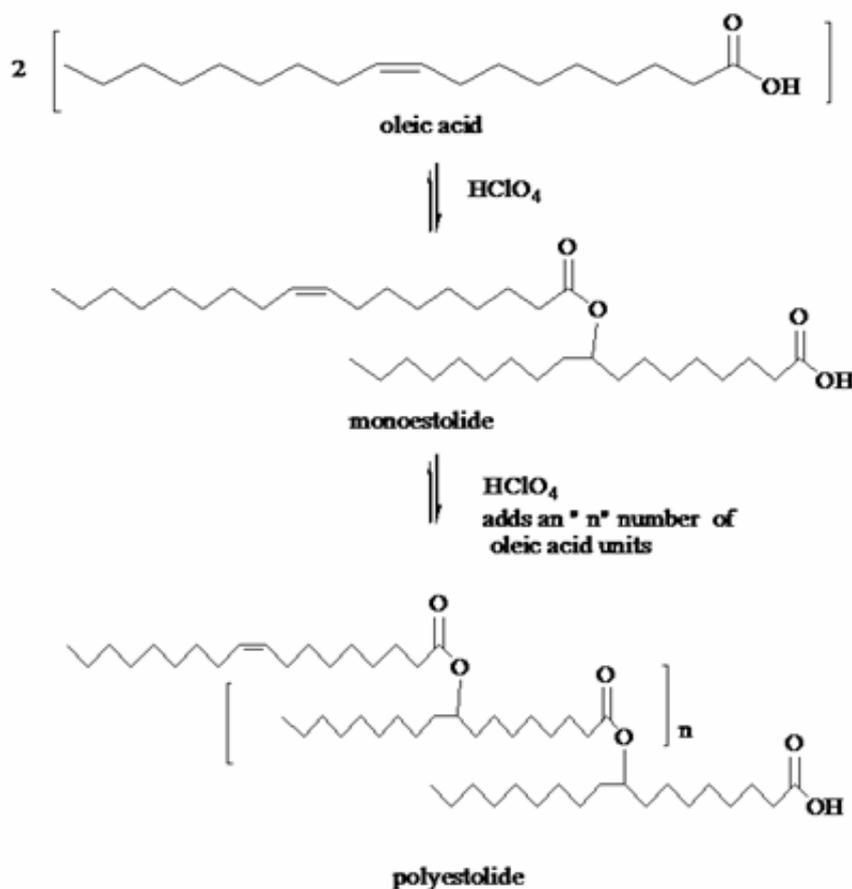


Figure 1 : Formation of estolide [5]

## 2 EXPERIMENTAL

### 2.1 Catalysts preparation

The STA sol-gel was prepared on the basis of the sol-gel method reported by Y. Izumi et al [6]. Tetraethoxy silane (TEOS, 0.2 mol, 41.60 g) was dissolved in a mixture of water (2 mol, 36.00 g), 1-butanol (0.2 mol, 14.82 g) and 12-silicotungstic acid hydrate ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , denoted STA,  $5.0 \times 10^{-4}$  mol, 1.440 g) and stirred at 80 °C during 3 h. The stirring rate and temperature were maintained at 200 rpm, 80 °C for 3 h, long enough to reach a clear, transparent and solid gel state. The hydrogel obtained was dehydrated slowly at 80 °C in reflux apparatus with methanol for 72 h, and dried at 100 °C, overnight. TEOS was a commercial product

supplied by Merck-Schuchardt, Hohenbrunn, Germany.  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  was supplied by Fluka Sigma-Aldrich Chemie GmbH, Japan.

## 2.2 Characterization of the catalyst

The X-ray Photoelectron spectroscopy (XPS) analysis of the STA and STA sol-gel catalysts were performed using XPS Axis Ultra from Kratos equipped with monochromatic Al  $K\alpha$  radiation (BE = 1486.6 eV). The samples were analyzed inside at analysis chamber pressure about  $1 \times 10^{-10}$  Pa. To correct possible deviations caused by electric charged of the samples, the C 1s peak of carbon at 284.5 eV was taken as internal standard or reference.

## 2.3 Estolide synthesis

The acid-catalyzed condensation reaction used was a slight modification of Cermak et al. [7]. The reaction was carried out in low vacuum (2 mBar) using a two-necked round bottom flask equipped with a magnetic stirrer, fitted with Dean Stark and a condenser for reflux. It was performed using the reactor namely Carousel 6 Place Reaction Station from Radleys Discovery Technologies, United Kingdom. The reactions were carried out at 70 °C using STA and STA sol-gel and perchloric acid catalysts. Reaction time was set for 10 hours. The reaction mixture consisted of 3.040 g of ra and 1.466 g of oa at a molar ratio of 2:1. The catalysts used are 10 wt% of reactant, while for perchloric acid 3 % wt of the catalyst was used. The reaction mixture filtered to remove catalysts using a filter funnel and a Whatman Grade #1 filter paper. Potassium hydroxide in ethanol was added to the product so that the pH was adjusted to 6-7. Subsequently, the fatty acid sediment produced was filtered using a filter funnel and filter paper, Whatman Grade #1. The organic layer was dried over dry sodium sulphate and filtered through a Buchner funnel with a whatman grade #1 filter paper.

## 2.4 Analysis and characterization of the estolide product

LC-MS (ToF) analyses were performed on a Waters 2795 separation module filter with an auto injector (20- $\mu\text{L}$  injection loop), coupled to an Altech ELSD 500 evaporative light scattering detector, and a Bruker MicrotofQ mass spectrometer. A  $\text{C}_{18}$ -reversed phase column chromatography was carried out with a column (250 mm x 2.00 mm, 5 $\mu\text{m}$  C-18, 300 $^{\circ}\text{A}$ ) supplied by Phenomenex Jupiter. Parameters for separation method were mobile phase flow rate of 0.2 mL/ min: 0 to 4 min 80% acetonitrile, 20 % acetone; 6 to

10 min 100 %; acetone; 11 to 30 min 80 % acetonitrile, 20 % acetone. The ELSD drift tube was set at 55 oC with nebulizer set at 20 psi (138 kpa) N<sub>2</sub> flow rate of 2.0 standard liters per minute.

### 3 RESULTS AND DISCUSSION

#### 3.1 Analysis of estolide products

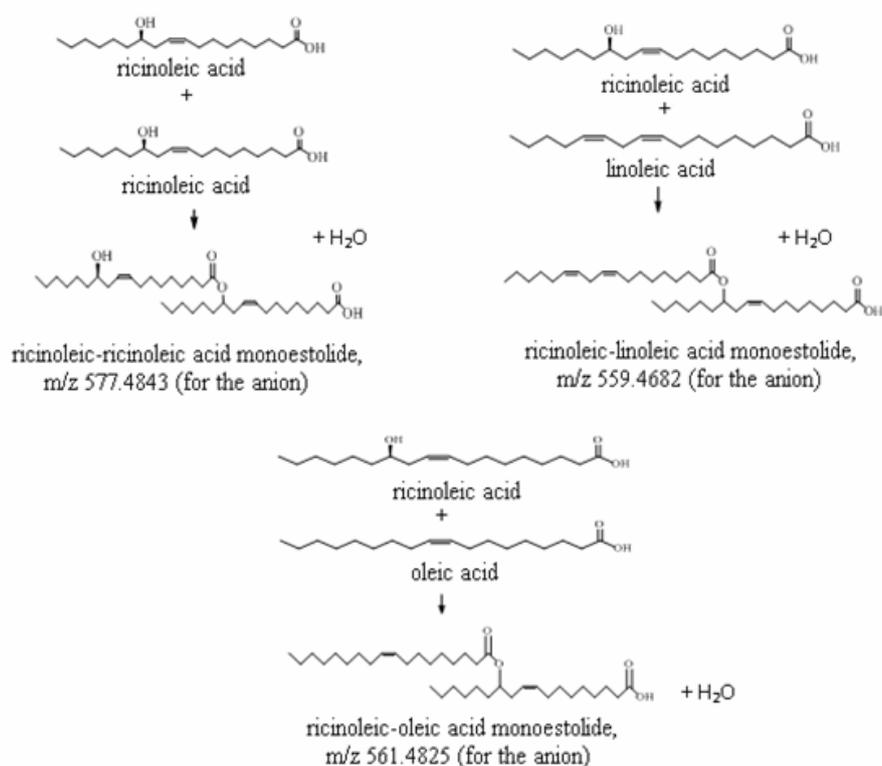
LC/MS analytical data obtained from condensation reaction of a mixture RA and OA (no catalyst or control reaction, sample no. **0**), homogeneous perchloric acid (sample no. **1**), STA (sample no. **2**) and STA sol-gel (sample no. **3**) are summarized in Table 1.

**Table 1** : LC-MS data obtained from samples nos. 0, 1, 2 and 3

Sample nos.	Peak no./ tR (min.)/ m/z / peak areas (arbitrary units)							
0	1/ 4.4 / 297.2370/ 4023608	-	-	2/ 5.1 / 281.2448/ 1890348	3/ 5.7 / 283.2611/ 2339780	-	-	-
1	2/ 4.4 / 297.2395/ 2766346	3/ 4.8 / 297.2394/ 800088	4/ 4.9 / 279.2274/ 697216	5/ 5.1 / 281.2470/ 1778755	6/ 5.9 / 283.2633/ 1948165	7/ 9.2 / 577.4843/ 972568	8/ 11.2 / 559.4682/ 1213129	9/ 12.6 / 561.4825/ 212165
2	1/ 4.4 / 297.2428/ 3194826	-	2/ 4.9 / 279.2308/ 1826813	3/ 5.1 / 281.2505/ 4995138	4/ 5.7 / 283.2667/ 3419890	5/ 8.9 / 577.4846/ 986370	6/ 10.2 / 559.4688/ 923852	7/ 11.9 / 561.4831/ 922066
3	1/ 4.6 / 297.2403/ 272273	2/ 5.2 / 297.2402/ 25287	3/ 5.4 / 279.2326/ 768826	4/ 5.9 / 281.2423/ 667613	5/ 7.1 / 283.2593/ 298036	6/ 9.5 / 577.4770/ 115755	7/ 10.4 / 559.4699/ 272063	8/ 11.7 / 561.4850/ 74272

Typical ion chromatograms (TIC) of reactants and the products were taken under negative-ion mode. Analysis of the reaction mixtures by negative-mode ESI LC-MS (ToF), showed that the starting material (sample no. **0**) consisted of ricinoleic acid, oleic acid and stearic acid, whereas samples nos. 1, 2 and 3 contained three new compounds which were identified by their *m/z* values. The *m/z*

values of the (M - H)<sup>-</sup> ions corresponding to compounds represented by chromatographic peaks 7, 8 and 9 or 5, 6 and 7 or 6, 7 and 8 in Table 1 such as for sample no. 1 were 577.4770 (mass error 22.51 ppm, 577.4900 calculated for C<sub>36</sub>H<sub>65</sub>O<sub>5</sub>), 559.4699 (mass error 0.18 ppm, 559.4700 calculated for C<sub>36</sub>H<sub>63</sub>O<sub>4</sub>) and 561.4850 (mass error 8.90 ppm, 561.4800 calculated for C<sub>36</sub>H<sub>65</sub>O<sub>4</sub>), respectively illustrated in Figure 2 are in agreement with those reported previously [5].



**Figure 2** : Proposed chemical reactions and structures for monoestolide products.

The calculated percentage yield of monoestolide compounds *m/z* 577.4770, 559.4699, and 561.4850, (all *m/z* as anion). Their reaction conversion and selectivity with different catalysts have been shown in Table 2. From Table 2, it was found that the conversion and selectivity to monoestolide products become higher when STA sol-gel was used as catalyst. The catalytic activity for STA sol-gel increases due to the wide dispersion of STA on the surface of SiO<sub>2</sub>

catalysts exhibit higher activity than bulk STA. STA sol-gel gave 100 % conversion with 60.62 % selectivity to ricinoleic-ricinoleic monoestolide acid ( $m/z$  577.48, [M-H]<sup>-</sup>), 25.69 % selectivity to ricinoleic-linoleic monoestolide acid ( $m/z$  559.47, [M-H]<sup>-</sup>) and 13.65 % ricinoleic-oleic monoestolide ( $m/z$  561.48, [M-H]<sup>-</sup>).

**Table 2 :** Catalytic data for synthesis of monoestolide from a mixture RA and OA.<sup>a</sup>

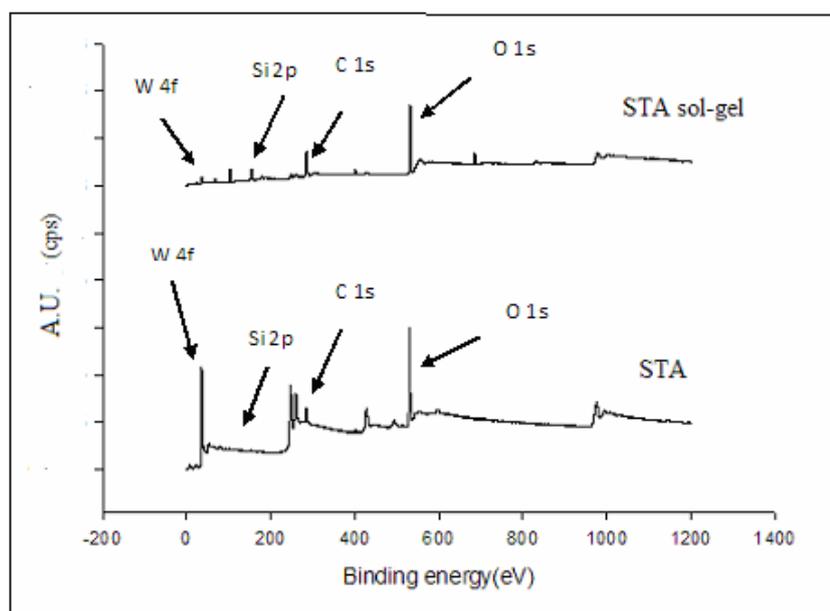
Catalyst	<sup>b</sup> Conversion (%)	<sup>b</sup> Selectivity (%)			<sup>b</sup> Total monoestolides
		$m/z$ 577	$m/z$ 559	$m/z$ 561	
Perchloric acid	80.06	88.25	10.86	0.88	79.95
Bulk STA	74.44	41.20	55.23	3.56	74.43
STA sol-gel	100.00	60.62	25.69	13.65	100.00

<sup>a</sup>Reaction conditions: 10 wt. % catalyst from RA, the reaction mixture consisted of 3.040 g of RA and 1.466 g of OA at a molar ratio of 2:1, reaction temperature 70 °C, and reaction time 10 h.

<sup>b</sup>conversion, <sup>b</sup>selectivity, <sup>b</sup>total monoestolides = these parameters were calculated using methyl oleate as internal standard by HPLC technique.

### 3.2 Surface Analysis Using XPS analysis

Surface composition and variations of BEs of the C1s, O1s, Si2p and W4f peaks of STA and STA sol-gel were obtained by XPS analysis. Figure 3 shows XPS wide scan spectra of STA and STA sol-gel.



**Figure 3** : XPS wide scan spectra curve of STA and STA sol-gel

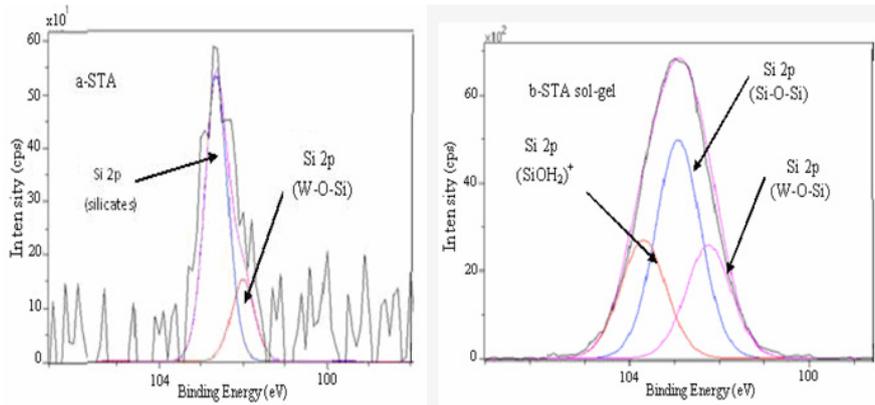
The photoelectron peaks in the XPS spectra for bulk STA and STA sol-gel show the present C1s, O1s, Si2p and W4f as expected. The binding energies of C1s, O1s, Si2p and W4f determined by XPS are summarized in Table 3.

**Table 3** : Binding energies (eV) for the surface main components of (a) STA and (b) STA sol-gel obtained by XPS (Reference C 1s = 284.5 eV)

Sample	Corrected binding energy (eV)			
	Si2p	O1s	W4f7/2	W4f5/2
a	102.5	531.5	36.8	39.0
	103.3	532.8		
b	103.0	532.1	36.5	38,7
	103.7	532.9	35.5	37.7
	104.3	533.7		

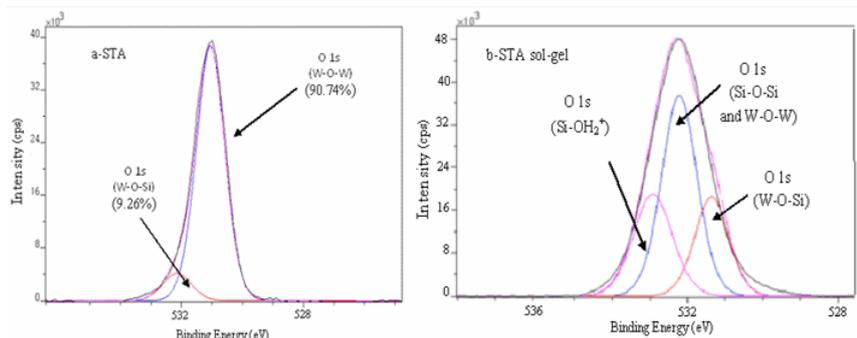
It is found that from Figure. 4a, the bulk STA has Si2p binding energy of 102.5 and 103.3 eV, respectively. The value of Si2p binding energy of STA sol-gel are 103.0, 103.7 and 104.5 eV (Figure 4b),

indicating the formation of W-O-Si, Si-O-Si and  $\text{SiOH}_2^+$ . The value of 103.7 eV is attributed to  $\text{SiO}_2$ , which is well agreed with the literature [8-11].



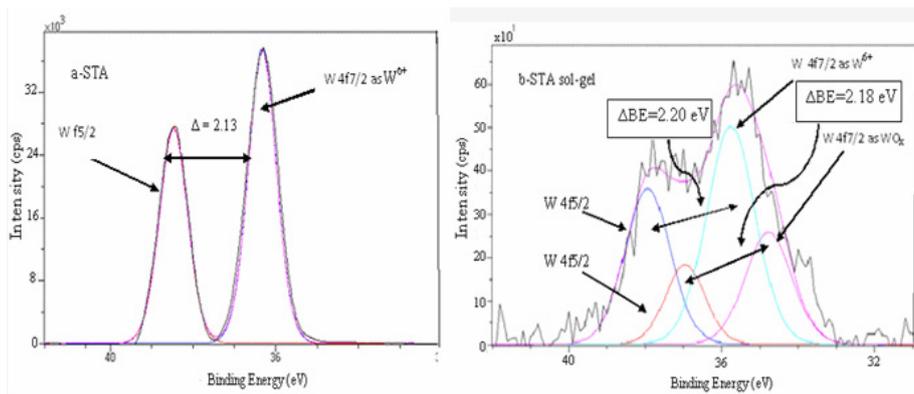
**Figure 4 :** XPS spectra of Si2p observed and calculated by curve fitting of (a) STA and (b) STA sol-gel

The O1s narrow scan spectrum recorded from bulk STA is shown in Figure 5a and contains two distinct chemical states of O 1s. It shows that the main (90.74 %, 531.5 eV) and intermediate (9.26 %, 532.8 eV) contributions to the presence of W-O-W and W-O-Si bond respectively [12]. The O1s narrow scan spectra recorded from sample STA sol-gel is very different from the bulk STA (Figure 5b). The spectra consisted of the main signal at the 532.9 eV can be associated with Si-O-Si bond and a much weaker signals at the 532.1 and 533.7 eV, which might be from W-O-W and adsorbed water to form as  $\text{SiOH}_2^+$ .



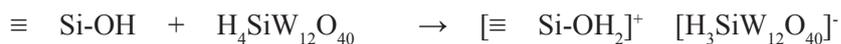
**Figure 5 :** XPS spectra of O1s observed and calculated by curve fitting of (a) STA and (b) STA sol-gel

The W4f narrow scan spectra recorded from bulk STA (Figure 6a) composed of a doublet photoelectron with binding energies of 36.8 and 39.0 eV respectively with  $\Delta BE = 2.13$ . The W4f XPS spectra recorded from bulk STA (Fig. 6a) composed of spin-orbit doublet with binding energies for the W4f7/2 and W4f5/2 of 36.8 and 39.0 eV respectively. The values are typical of the presence of W (VI) [12]. The W4f spectra recorded from STA sol-gel is less well resolved than that of bulk STA (Fig.6b). The W4f also fitted on the basis of two different W contributions; the major component photoelectron region which has a spin orbit doublet at 35.5 eV (W4f7/2) and a second doublet, the minor component photoelectron region at 37.7 eV (W4f5/2). The spin orbit doublet, W4f7/2 has a binding energy which is the same value as the bulk STA, appearing at lower binding energy may represent the partial reduction of STA on the silica surface and the formation of an oxide of the type  $WO_x$  as  $WO_2$  in which W has an oxidation state lower than VI.



**Figure 6 :** XPS spectra of W4f7/2 and 4f5/2 observed and calculated by curve fitting of (a) STA and (b) STA sol-gel

Based from other researchers' works [9,12], we suggest that there are some interactions between  $(H_3SiW_{12}O_{40})^-$  with the silanol groups at silica surface to give ion pairs in the form  $(\equiv SiOH_2^+)(H_3SiW_{12}O_{40}^-)$  from the reaction as below:



#### 4 CONCLUSION

This study shows that the synthesis of estolides, STA catalyst and STA sol-gel catalyst illustrates better catalytic activity and selectivity than the homogeneous catalyst perchloric acid. Therefore, an environmental friendly approach for the estolide synthesis using STA sol-gel catalysts are provided. STA sol-gel gave 100 % conversion with 60.62 % selectivity to ricinoleic-ricinoleic monoestolide acid ( $m/z$  577.48, [M-H]<sup>-</sup>), 25.69 % selectivity to ricinoleic-linoleic monoestolide acid ( $m/z$  559.47, [M-H]<sup>-</sup>) and 13.65 % selectivity to ricinoleic-oleic monoestolide ( $m/z$  561.48, [M-H]<sup>-</sup>). STA sol-gel is new promising heterogeneous catalysts that can be used for producing estolide compounds from ricinoleic acid and oleic acid. The analysis of STA and STA sol-gel catalysts by XPS showed that the O1s narrow scan spectra recorded from sample STA sol-gel is very different from the bulk STA. The O1s peak shows the appearance of a new oxygen species at higher binding energy (533.7 eV), suggesting the presence of SiOH<sub>2</sub><sup>+</sup>. Furthermore, another significant peak for Si2p binding energy of STA sol-gel at 104.5 eV, indicating the formation of SiOH<sub>2</sub><sup>+</sup>. This suggests that there are some interactions between (H<sub>3</sub>SiW<sub>12</sub>O<sub>40</sub>)<sup>-</sup> with the silanol groups at silica surface to give ion pairs in the form (≡ SiOH<sub>2</sub><sup>+</sup>)(H<sub>3</sub>SiW<sub>12</sub>O<sub>40</sub>)<sup>-</sup>.

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