

## Fabrication of Carbon Graphite-supported Pt–SiW<sub>12</sub>O<sub>40</sub> Catalysts Effect of the Pt Loading on the Electrooxidation of Cyclohexane

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Received: December 27, 2013, Accepted: April 04, 2014, Available online: April 08, 2014

**Abstract:** *H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (abbreviated as SiW) and Pt supported on carbon graphite (CG) with different Pt/SiW ratios were prepared and characterized by FTIR, XRD, ICP-OES, polarography, and TEM. The prepared catalysts were then after successfully attached onto glassy carbon electrodes by using polyvinylidene difluoride (PVDF) as binder. The resulting electrocatalysts were characterized by cyclic voltammetry (CV) and tested for the electrooxidation of cyclohexane. It has been found that the addition of SiW to the catalyst increased the dispersion of the Pt particles. The results of the electrocatalytic tests showed that cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide are formed as major products of the reaction. Higher Pt loadings promoted cyclohexanone production.*

**Keywords:** *Heteropolyanions, carbon graphite, cyclohexane oxidation, modified carbon electrode*

### 1. INTRODUCTION

The oxidation of hydrocarbons into high added value oxygenated organic compounds is considered as one of the most important way for up-grading natural resources (oil and gas) [1–4]. Among the hydrocarbons oxidation reactions, that of cyclohexane to cyclohexanone (K) and cyclohexanol (A) (known as K/A oil mixture) is of great interest. In fact, cyclohexanol and cyclohexanone are important intermediates in the production of polyamide fibers and plastics, such as Nylon-6 and Nylon-6,6 [3, 7, 8]. More than 106 tonnes of K/A oil are produced worldwide per annum [9]. In addition, they have also many applications in the fine and petrochemical industry.

Currently, K/A oil mixture is produced on an industrial scale by oxidation of cyclohexane in a homogeneous process. The oxidation is carried out at 150°C and 1–2 MPa pressure, using cobalt salt as homogeneous catalyst [10]. In this process the oxidation requires high temperature for the activation of the C-H bond of cyclohexane [11]. However, high temperatures favor the oxidation of cyclohexanol and cyclohexanone in further oxidized compounds [12]. Therefore, in order to obtain the selectivity between 70 and 80% for the K/A oil mixture, the conversion must be kept low (3–

8%) [8, 13, 14]. Thus, it is obvious that this homogeneous catalyst has many drawbacks such low conversion, environmental problems, easy deactivation and difficulty in regeneration of the catalysts, and complicated procedures needed for the separation of the catalyst and products. That is why cyclohexane oxidation is considered to be among the least efficient in all major industrial chemical processes. Taking into account the great demand in cyclohexanone and cyclohexanol compared to the low production of these products, the oxidation of cyclohexane continues to be a challenge [3]. Therefore, it is a great interest to develop a more efficient, easily separable and reusable catalyst for cyclohexane oxidation process. An alternative way is using an electro-catalysis process. In fact, electrons are inherently "environmentally friendly" compared to using large quantities of redox reagents [15–18]. Furthermore, the advent of nuclear power will make electricity cheaper compared to chemical oxidants and reductants. In addition, in electrocatalysis process, the oxidation is achieved by the electronic exchange between the electrode and the reactant, thus, the temperatures can be lowered. This research work deals with the electro-oxidation of cyclohexane to cyclohexanone and cyclohexanol using a carbon supported Pt-heteropolyanions (Pt-SiW) modified electrode. Carbon graphite was functionalized to anchor the Pt and heteropolyanions particles [19–23].

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## 2. MATERIALS AND METHODS

### 2.1.1. Materials

Carbon graphite (CG) was purchased from AVONCHEM. Hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot (\text{H}_2\text{O})_6$ )  $\geq 37.50\%$  Pt basis were purchased from ALDRICH.  $\text{Na}_2\text{SiO}_3$  Sodium metasilicate Hydrogen peroxide (30% in aqueous solution) were obtained from WINLAB. Cyclohexane > 99.5%, Cyclohexanone, Cyclohexanol, tert-butanol 99%, polyvinylidene difluoride (PVDF) from BDH. All other chemicals were of analytical grade and used as received.

### 2.1.2. Preparation of the catalysts

The 12-tungstosilicic acid (SiW) was prepared according to a now well-known method [24]. To attach the Pt and SiW on the carbon graphite (CG) support, oxygenated groups have been created on its surface (functionalization). The process of carbon functionalization was performed by using concentrated nitric acid according to [25]. To 100m g of the resulting functionalized carbon graphite in 5 ml of acetone which was ultrasonicated to prevent agglomeration, a 0.3 g solution of chloroplatinic acid (in 20 ml deionized water) was added drop-by-drop to the carbon slurry. An aqueous solution of sodium borohydride as a reducing agent was then added to the carbon slurry/chloroplatinic acid mixture. The supported catalyst (platinum on functionalized carbon) was then filtered, washed with excess deionized water and allowed to dry for 12 h at 100 °C in a vacuum oven. The resulting CG-Pt catalyst was thereafter added to a solution of acetone containing a desired amount of  $\text{H}_4\text{SiW}_{12}$  under stirring at 60°C. After total removal of acetone, the prepared catalyst was dried in an oven at 80°C. A series of Pt -SiW supported on CG with different ratios have been prepared. They are denoted CG- SiW-Pt-x, where x is the mass fraction of Pt [ $x = \text{SiW}/(\text{SiW} + \text{Pt})$ ] in the carbon support:

CG-SiW-Pt-0; CG-SiW-Pt-25; CG-SiW-Pt-50;  
CG-SiW-Pt-75; CG- CG-SiW-Pt-1.

### 2.1.3. Preparation of working electrode

Prior to modification, Glassy Carbon electrode was cleaned by polishing with (0.5  $\mu\text{m}$  -0.05 $\mu\text{m}$ )  $\text{Al}_2\text{O}_3$  powder. Then after a suspension of the desired amount of the catalyst dissolved in acetone was added to a suspension of the desired amount of polyvinylidene difluoride (PVDF) as a binder dissolved in N-methylpyrrolidone (NMP). The resulting mixture was stirred until colorless. Then after it 10 $\mu\text{l}$  was pipetted onto the surface of the glassy carbon electrode and the solvent was allowed to evaporate at 80°C for 12hours in the oven. After preparation the modified electrodes were examined by cyclic voltammetry and tested for the cyclohexane electrooxidation reaction.

### 2.2. Characterization of the catalysts

The Characterizations of the CNT- SiW-Pt-x series of catalysts have been performed by infrared FTIR, XRD, ICP-OES, polarography, and TEM. IR spectra were recorded with an infrared spectrometer SHIMADZU FT- IR NICOLET- 6700 (4000-400  $\text{cm}^{-1}$ ) as KBr pellets. The XRD powder patterns were recorded on an Ultima IV, X-ray diffractometer: Rigaku) using  $\text{Cu-K}\alpha$  radiation. The loaded mass of Pt and SiW was determined by using an inductively coupled plasma optical emission spectroscopy (ICP-OES) system (Thermo Scientific model ICAP 6000 series, Cambridge,

UK). For this purpose, samples were dissolved in  $\text{HNO}_3$  acid (E-Merck) with high pressure microwave digestion in Teflon tube vessel system (MARSX; CEM) at 450 K and 170 psi. The loaded mass of SiW was determined by polarography. Measurements were performed by means of METROHEM 797 VA COPMUTRACE (Version1.2) three-electrode apparatus using a mercury dropping electrode as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. The sample was dissolved in aqueous 1 M HCl / dioxan mixture (50/50 v/v) (30 mg of sample into 50 ml solution, i.e., a concentration of around 0.05 M. Under these conditions  $\text{SiW}_{12}\text{O}_{40}^{4-}$  anion exhibits reversible waves in the range [- 0.15 - - 0.800 V].

### 2.3. Electrochemical experiments

#### 2.3.1. Cyclic voltammetry

Cyclic voltammetry (CV) studies were performed with (AUTOLAB- $\mu 3$  Aut71138) electrochemical, using conventional three-electrode system with CNT- SiW-Pt-x as the working electrode, platinum as the counter electrode and Hg/HgCl (Saturated Calomel Electrode) as reference electrode. All measurements were carried out in 0.5M  $\text{H}_2\text{SO}_4$  solution purged with  $\text{N}_2$  gases using a scan rate of 0.02 V  $\text{s}^{-1}$  for CV.

#### 2.3.2. Electrooxidation measurements

The prepared electrodes were tested for the electrooxidation of cyclohexane in an electrochemical jacketed cell fitted with a reflux condenser. The standard procedure is as follow: 5ml of cyclohexane, 10ml of hydrogen peroxide (30% in aqueous solution) and 5ml of tert-butanol were charged in the cell and were heated at 50°C under stirring. After 2hours of reaction time, the mixture was cooled and analyzed by means of a Gas Phase Chromatograph (Thermo Scientific Trace GC Ultra) equipped with a TCD and FID detectors. The products were separated with a capillary column (TR 5, ID 0.53 mm Film 1  $\mu\text{M}$ ).

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of the catalysts

#### 3.1.1. CG support

The FT-IR spectra of the as received (Figure1a) and functionalized CG (Figure1b) are shown in figure 1. The peak around 2920  $\text{cm}^{-1}$  is due to the methylene group. The aldehyde group is detected by a peak at 2848  $\text{cm}^{-1}$ . Peaks around 1450–1320  $\text{cm}^{-1}$  are an indication of the presence of aromatic groups [23, 30]. The peaks at 1580 and 1174  $\text{cm}^{-1}$  was assigned to be the C-C stretch of the GC backbones and the C-O stretch of the acid group, respectively. The peak at around 1720  $\text{cm}^{-1}$  is assigned to the C=O strength vibration in the COOH group [31], which means that the acid treatment has introduced some COOH groups. Thus, FTIR results showed that the oxidation treatments produce oxygenated groups such as carboxylic and hydroxyl, in the carbon surface.

Figure 2 depicts the FT-IR spectra of the functionalized CG (figure 2a), SiW (figure 2b), and CG supported catalysts (figure 2c-2g). The infrared spectrum of the functionalized CG is shown in Fig. 1(a). The main characteristic features of the Keggin structure are observed at 917  $\text{cm}^{-1}$  (gas Si-Oa), at is 970  $\text{cm}^{-1}$  (gas Mo-Od), at 850  $\text{cm}^{-1}$  (gas Mo-Ob-Mo) and at 767  $\text{cm}^{-1}$  (gas Mo-Oc-Mo). This result is in agreement with those reported in the literature [29, 32] for this heteropoly acid. The typical pattern of SiW is partly

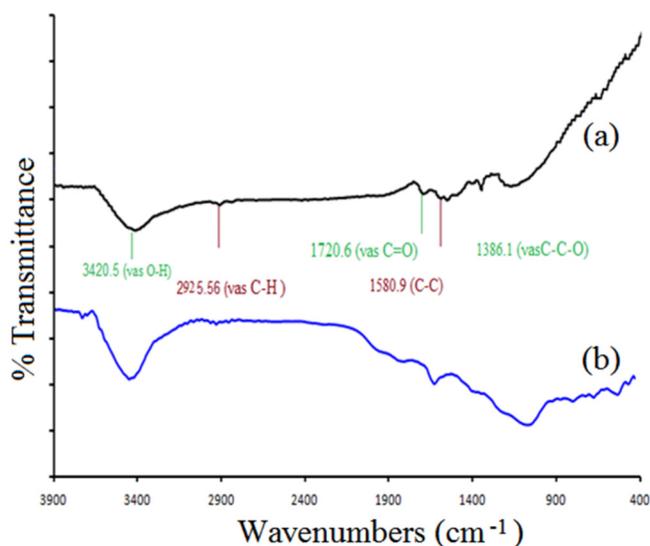


Figure 1. FT-IR spectra of (a) as-received CG; (b) functionalized CG

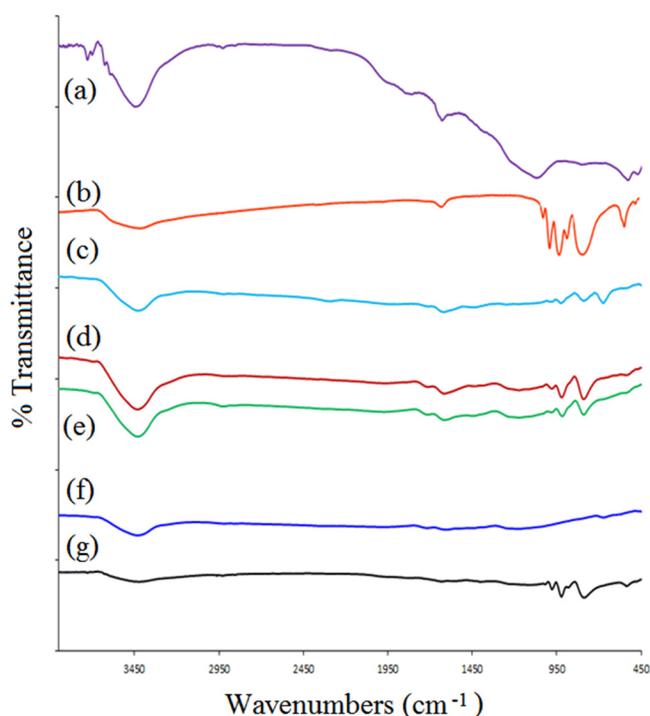


Figure 2. FT-IR spectra of : (a) functionalized CG, (b) SiW, (c) CG -SiW-Pt-0; (d) CG-SiW-Pt-0.25; (e) CG-SiW-Pt-0.50; (f) CG-SiW-Pt-0.75; (g) CG-SiW-Pt-1

obscured by the carbon bands. In particular the band at 1018 cm<sup>-1</sup>, assigned to  $\gamma$ Si-O, is completely masked into the strong 1100 cm<sup>-1</sup> band of the carbon: In the 1000-300 cm<sup>-1</sup> range, subtraction of the carbon absorption is possible for the samples, showing that the Keggin structure is preserved on the support.

In the Keggin structure : O<sub>a</sub> = oxygen atom common to the SiO<sub>4</sub>

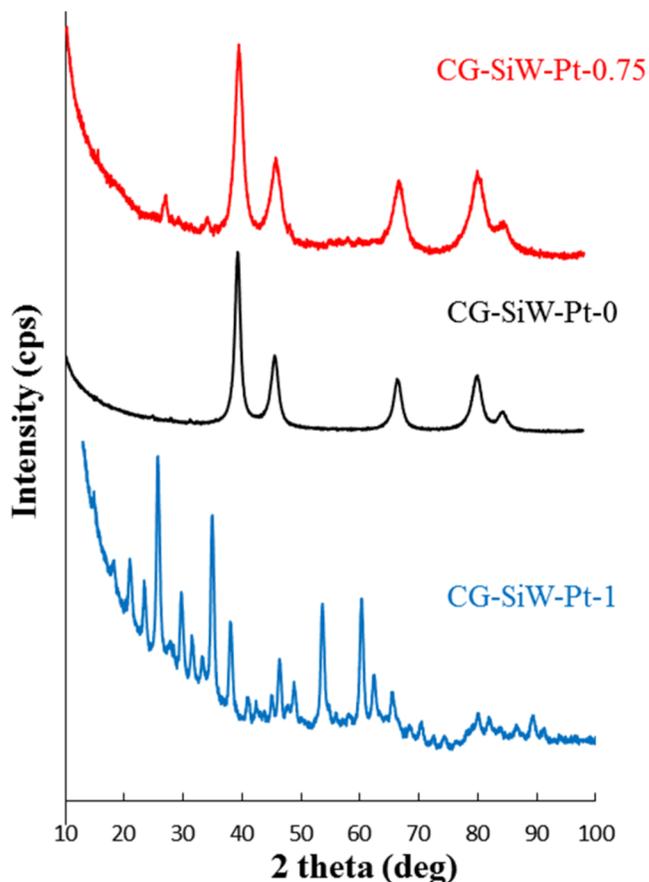


Figure 3. XRD patterns of the prepared CG -SiW-Pt-x series of catalysts. CG -SiW-Pt-0; CG -SiW-Pt-0.25; CG -SiW-Pt-1

tetrahedron and to a trimolybdc group; O<sub>b</sub> = oxygen atom connecting two trimolybdc groups; O<sub>c</sub> = oxygen atom connecting MoO<sub>6</sub>octahedra inside a trimolybdc group; and O<sub>d</sub> = terminal oxygen atom..

### 3.1.2. X-Ray Diffraction

The XRD patterns of CG-SiW-Pt-x series are shown in Figure 3. In each one of the ranges of 2 $\theta$ , 16°–23°, 25°–30°, and 31°–38°, the CG -SiW-Pt-0 (catalyst constituted only of SiW on CG) showed the characteristic peak of the Keggin structure [33, 34]. The spectrum of the CG -SiW-Pt-1 catalyst showed the characteristic peak of a face centered cubic (fcc) Pt structure and has major peaks at around 2 $\theta$  = 39.9° (111), 46.6° (200), 67.5° (220), 81.9° (311), and 85.6° (222). As for the CG -SiW-Pt-0.25 and CG-SiW-Pt-0.75 catalysts, it can be seen that the typical pattern of SiW is partly obscured by that of the Pt, in particular, by the strong 39.9° and 46.6° peaks of Pt. In the 25°–30° the characteristic lines of the Keggin structure at 25.6° and 29.7° were observed, indicating that the Keggin structure was preserved on the support. Thus, the incorporation of both the heteropolyanions and the Pt in the synthesized catalysts was confirmed by FTIR and XRD.

The thermograms of the as received and functionalized CG are shown in figures 4. It can be seen from the figures that the loss of

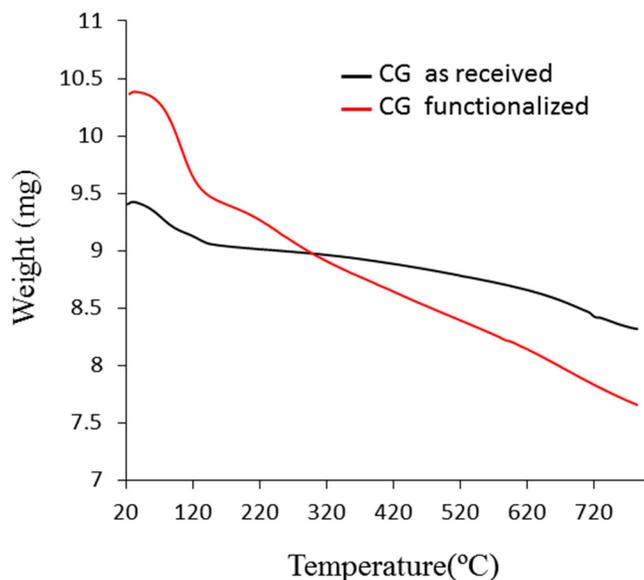


Figure 4. Thermal gravimetric analysis of the functionalized (a) and the as-received CG (b).

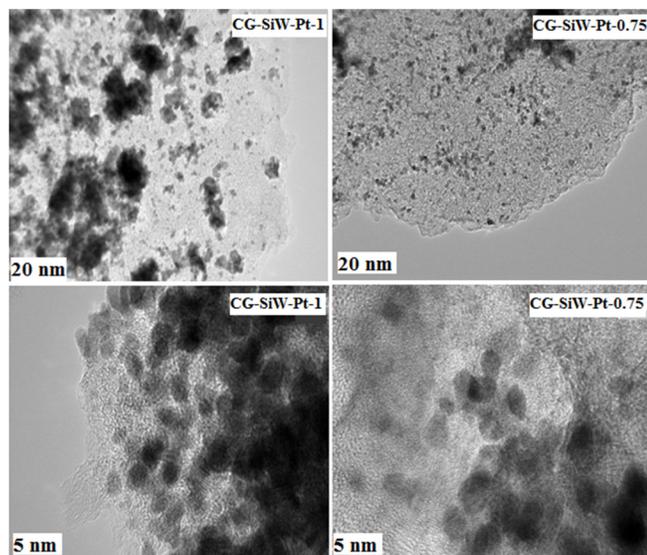


Figure 5. TEM images of CG- SiW-Pt-1(a) and CG-SiW-Pt-0.75 (b) (20 nm)

weight for the functionalized CG is more important than that for the as received. This is due to elimination of oxygen groups in the form of water and oxygenated compounds.

### 3.1.3. Polarography/ICP-OES

The loaded mass of Pt and SiW on the CG support was determined by polarography and ICP-EOS respectively. The results are reported in Table 1. In general, we note that experimental values are close to the nominal ones.

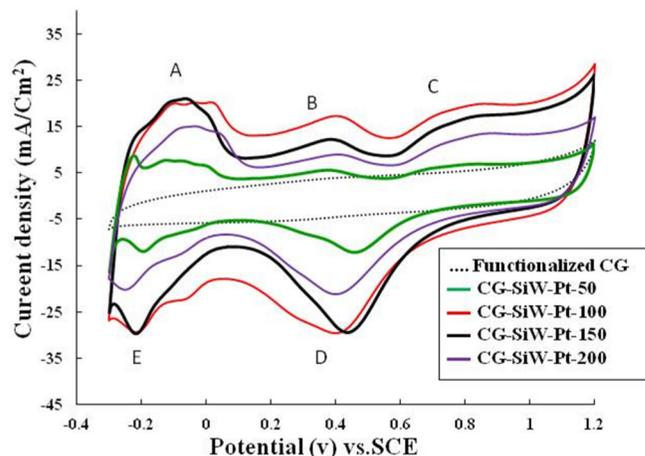


Figure 6. Cyclic voltammograms of CG-HSiW-Pt-x series of catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with an average scan of 50 mV s<sup>-1</sup>

### 3.1.4. Transmission Electronic Microscopy

The results of TEM analysis of the carbon graphite supported SiW/Pt catalysts are shown in the figure 5. It can be seen from the micrographs that the Pt particles are well dispersed when the catalyst is constituted of SiW and Pt particles. In contrast, when the catalyst is constituted only of Pt particles, large particles indicating the aggregation of Pt particles are observed. The approximate size of Pt particles in the catalyst containing only Pt particles is between 3nm and 4.8nm whereas in the case containing both Pt and SiW particles, the size of Pt particles is between 0.6nm and 3nm. This result indicates that the presence of SiW units allowed the separation of the Pt particles and thereby hindered their agglomeration into larger crystallites.

## 3.2. Electrochemical measurements

### 3.2.1. Cyclic voltammetry of the prepared materials

Figure 6 show the cyclic voltammograms of the CG-SiW-Pt-x series of catalysts. It can be seen that the CG-SiW-Pt catalyst has a high current density than CG-Pt which does not contain SiW. Five regions, related to the release of the hydrogen and the reduction of oxygen were observed. They can be described as follow:

- The region A which represent the desorption of the hydrogen from the Pt surface
- The region B corresponds to the double layer
- The region C at about 1.2 V indicated the oxygen adsorption on the Pt surface
- The region D at about 0.45 V indicated the oxygen desorption from the Pt surface
- The region E indicated the hydrogen adsorption on the Pt surface

Figure 7 shows the variation of the charge exchanged in function of the Pt loading for the series CG-SiW-Pt-x. It can be seen that exchanged electronic charge increased to reach a culmination at about 0.65 and then declined sharply. The maximum of the exchanged electronic charge observed for a 65% of loading might be due to an optimum synergistic effect between SiW and Pt particles. The low exchanged electronic charge observed for the CG-SiW-Pt-

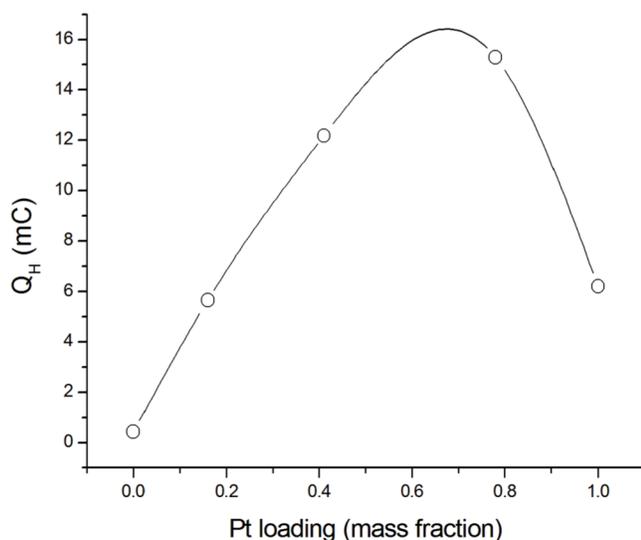


Figure 7. Effect of the Pt/(Pt+SiW) (mass fraction) in the CG-SiW-Pt-x catalysts on the exchanged electronic charges.

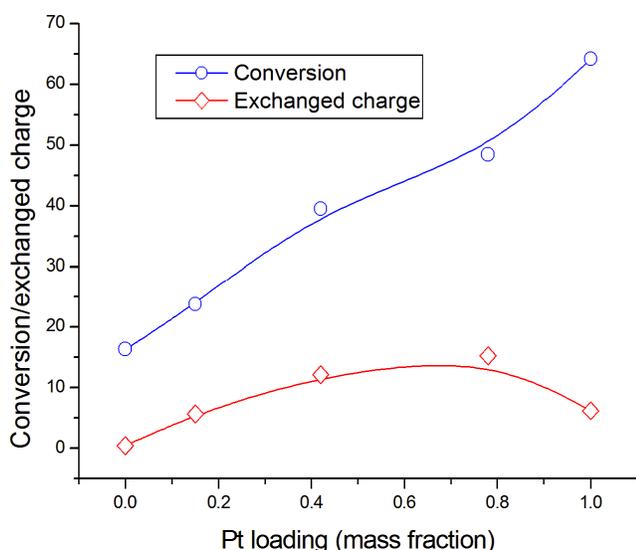


Figure 8. Effect of Pt loading in the series of CG-SiW-Pt-x catalysts on the conversion and the exchanged electronic charge.

1 catalyst (the catalyst that does not contain SiW), can be explained by the aggregation of Pt particles which causes a decrease in the number of surface metal atoms per unit mass of metal and therefore decreases the number of active sites of the catalyst (ripening).

### 3.3. Electrocatalytic oxidation of cyclohexane

The performance of the series of the prepared catalysts CG-SiW-Pt-x for the electrocatalytic oxidation of cyclohexane was investigated. It has been found that all the prepared catalysts led to the formation of cyclohexanone and cyclohexanol and cyclohexyl hydroperoxide. The effect of the Pt loading on the conversion and on the exchanged electronic charge is shown in the Figure 8. The re-

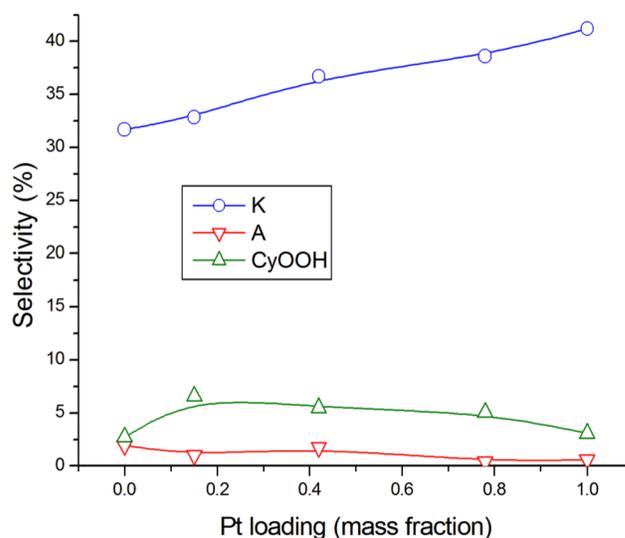


Figure 9. Effect of Pt loading on the selectivity of the electrooxidation products. Reaction carried out over CG-SiW-Pt-x catalysts at 50°C for 2 hours.

sults showed that the conversion increased linearly with the increase of Pt loading. This result was expected as the Pt material is more oxidant than SiW. As for the exchanged charge, it can be seen that it increased with the Pt loading for all the catalysts except for the CG-SiW-Pt-1 (which does not contain the heteropolyanions). This result seems to indicate that besides the exchanged electronic charge, textural or/and structural factors of the catalyst affect the electrooxidation reaction.

As for the effect of the Pt loading on the selectivity of the electrooxidation products (figure 9), it has been found that increasing the Pt loading increased the selectivity of cyclohexanone. As for the cyclohexyl hydroperoxide (CyOOH), it was found that its selectivity increased when the Pt mass fraction increased up to 0.15 then after it decreased. This result indicated that cyclohexyl hydroperoxide was further oxidized to cyclohexanone. In the case of the cyclohexanol, no significant change was observed. These results are in agreement with those reported in the literature [35, 36]. In fact, it has been reported that CyOOH is the intermediate of the cyclohexane oxidation and two mechanisms were proposed for CyOOH decomposition: heterolytic (CyOOH→cyclohexanone) and hemolytic (CyOOH →cyclohexanol). Therefore two possible pathways were proposed for the products formation [36]:

- (1) CHHP → cyclohexanol → cyclohexanone
- (2) cyclohexanone ← CyOOH → cyclohexanol  
(then cyclohexanol → cyclohexanone)

## 4. CONCLUSION

Electrooxidation of cyclohexane to cyclohexanone and cyclohexanol was studied over a series of CG-SiW-Pt-x catalysts with various Pt-SiW ratios.

Thanks to the polyvinylidene difluoride (PVDF) binder, stable electrocatalysts in the reacting medium were successfully fabricated.

Characterizations by means of thermogravimetry, FT-IR, XRD, and polarography showed that the Pt and SiW were incorporated into the carbon support. The Keggin structure of the heteropolyanions was not altered. The presence of the heteropolyanions in the catalyst allowed more homogeneous distribution of the Pt particles.

Electrocatalytic tests showed that the electrooxidation of cyclohexane led to cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide as major products.

High exchanged electronic charge favored the formation of cyclohexanone which is needed for the production of the  $\epsilon$ -caprolactam.

Compared to the industrial process, this result can be considered as a positive completion.

## 5. ACKNOWLEDGMENTS

The Investigators extend their appreciation to the National Plan for Science and Technology at King Saud University for funding the work through the research group project No 09-NAN863-02.

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