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Preparation and Characterization of Carbon Nanotubes-Supported Pt–$SiW_{12}O_{40}$ Catalyst for Electrooxidation of Cyclohexane to Cyclohexanone/Cyclohexanol

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$H_4SiW_{12}O_{40}$ (abbreviated as SiW) and Pt supported on carbon nanotubes (CNTs) with different Pt/SiW ratios were prepared and characterized by FTIR, XRD, ICP-OES, polarography, and TEM. The prepared catalysts were then after attached onto glassy carbon (GC) electrodes by using polyvinylidene difluoride (PVDF) as binder. The resulting electrodes were characterized by cyclic voltammetry (CV) and tested for the electrooxidation of cyclohexane. The TEM results showed that addition of SiW to the catalyst increased the dispersion of the Pt particles. The results of CV showed that increasing the SiW loading, increased the exchanged electronic charge Qh (mC). As for the electrocatalytic tests, it has been found that the cyclohexanone (K), cyclohexanol (A) and cyclohexyl hydroperoxide (CyOOH) are formed as major products of the reaction. Higher loadings promoted cyclohexanone production whereas lower ones favored cyclohexyl hydroperoxide. The conversion and selectivity enhancement was attributed to the high dispersion of the active phase in the catalyst.

Keywords: Carbon nanotubes; Heteropolyanions; cyclohexane; modified carbon electrode; cyclohexanone; cyclohexanol; electrocatalysis

1. INTRODUCTION

Cyclohexanone (K) and cyclohexanol (A) mixture (known as K-A oil mixture) are the main industrial precursors of, respectively, □-caprolactam and adipic acid, intermediates in the production of polyamide fibers and plastics, such as Nylon-6 and Nylon-6, 6 [1, 2]. Currently, K-A oil mixture is produced on an industrial scale by homogeneous catalysis using a soluble cobalt carboxylate catalyst at 423–473 K and 8–15 bar of air pressure. The conversion is kept at about 4% to prevent the formation of excessive amounts of by-products by over-oxidation, giving ~80% selectivity for K-A oil mixture

[3]. Besides the low conversion, this process has many drawbacks such as, easy deactivation and environmental problems (difficulty in removing the catalyst from the products). However, due to the rising demand for the K-A oil mixture and the large-scale of its production which exceeds106 ton/year [4], this process continues to be a challenging problem [5]. Although scientists have intensified research trying to improve the conversion of cyclohexane and the selectivity to desired products over the past few decades [6-9], the oxidation of cyclohexane remains the least efficient of all major industrial processes [10]. An alternative way is using electrocatalysis. Electrocatalytic process can be used to achieve a clean and complete conversion of a starting material to product under mild experimental conditions. The most commonly used electrocatalysts are noble metals supported on carbon which are expensive [11–13]. Therefore it is of crucial importance to find alternatives to the noble metals or to reduce their content for carbon electrodes modified. Heteropolyanions are the suitable materials for the carbon electrodes modifications. The focus on these kinds of compounds for the fabrication of chemically modified electrodes is due to their excellent electrochemical and electrocatalytic properties [14-16]. Carbon is frequently used as the catalyst support because of its relative high stability in both acid and basic media, good electronic conductivity and high specific surface area. However, functionalization of the carbon support surface is required to anchor the electrocatalyst particles [17-19]. This research work deals with the electro-oxidation of cyclohexane to the K-A oil mixture using a 12-tungsto-silicic acid modified carbon electrode. To our knowledge, the present study is the first to evaluate CNTs supported heteropolyanions/Pt catalysts for cyclohexane oxidation.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

2.1.1 Materials

Carbon nanotubes (CNTs) (>95%) and hexachloroplatinic acid ($H_2PtC_{l6}.(H_2O)_6$) ≥ 37.50% Pt basis were purchased from ALDRICH. Na_2SiO_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 [20]. In order to bind SiW on the carbon nano tubes (CNTs), oxygenated groups have been created on the carbon support (functionalization). The process of carbon functionalization was performed by using concentrated nitric acid according to the following steps: 0.1g sample of Carbon was suspended in 100 ml nitric acid (65%), and heated for 5 hours at 80^{o}C, then cooled at room temperature. The treated carbon was then washed with deionised water to pH 7, and dried at 100^{o}C overnight. The resulting functionalized CNTs was then added to the desired amount of the prepared SiW already dissolved in acetone under stirring for 30 min. After removing the excess of acetone by heating at 60°C, the prepared catalyst was dried in an oven at 80°C. A series of SiW catalysts supported on CNTs having various compositions have been prepared. They are denoted CNT- SiW-Pt-x, where x is the mass fraction of SiW [x=SiW/(SiW + Pt)] in the carbon support:

CNT-SiW-Pt-0; CNT-SiW-Pt-25; CNT-SiW-Pt-50; CNT-SiW-Pt–75; CNT- CNT-SiW-Pt-1.

2.1.3 Preparation of working electrode

Prior to modification, Glassy Carbon electrode was cleaned by polishing with (0.5 μm - 0.05μm) Al_2O_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 10μl 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, SEM, and TEM. IR spectra were recorded with an infrared spectrometer SHIMADZU FT- IR NICOLET- 6700 (4000-400 cm−1) as KBr pellets. The XRD powder patterns were recorded on an Ultima IV, X-ray diffractometer: Rigaku) using Cu-Kα 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 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 $SiW_{12}O_{40}^{4-}$ 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-μ3 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 H_2SO_4 solution purged with N_2 gases using a scan rate of 0.02 V 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^{o}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 μM).

3. RESULTS AND DISCUSSION

3.1. Characterization of the catalysts

3.1.1. FTIR

FTIR spectra of as-received and functionalized CNTs are shown in figure 1(a). The peaks which are observed at 1386, 1720 and 3448 cm-1 characterize C-O, C=O and O-H bonds of the oxidized carbon [21]. Peak at 1585 cm-1 assigns C=C bond in CNTs [22-23]. The presence of a broad and intense band at 3720 cm-1 suggests attachment of –COOH groups (not H-bonded) on the sidewall [24]. Typical –C–H stretching frequencies present on benzene rings of nanotubes is observed at 2927 cm-1. The peak observed at 1626 cm-1 corresponds to a stretching frequency of carbonyl (CO) groups. Thus, FTIR results showed that the oxidation treatments produce oxygenated groups such as carboxylic and hydroxyl, in the carbon surface. The infrared spectrum of $H_4SiW_{12}O_{40}\cdot 13H_2O$ is shown in figure 1(b). The main characteristic features of the Keggin structure are observed at 917 cm^{-1} (gas Si-Oa), at is 970 cm^{-1} (gas Mo-Od), at 850 cm^{-1} (gas Mo-Ob-Mo) and at 767 cm^{-1} (gas Mo-Oc-Mo). This result is in agreement with those reported in the literature [25, 26] for this heteropoly acid. The typical pattern of $H_4SiW_{12}O_{40}$ is partly obscured by the carbon bands figure 1 (c) to (g). In particular the band at 1018 cm^{-1}, assigned to γ_{as}Si-O, is completely masked into the strong 1100 cm^{-1} band of the carbon: In the 1000-300 cm^{-1} range, subtraction of the carbon absorption is possible for the samples, showing that the Keggin structure is preserved on the support.

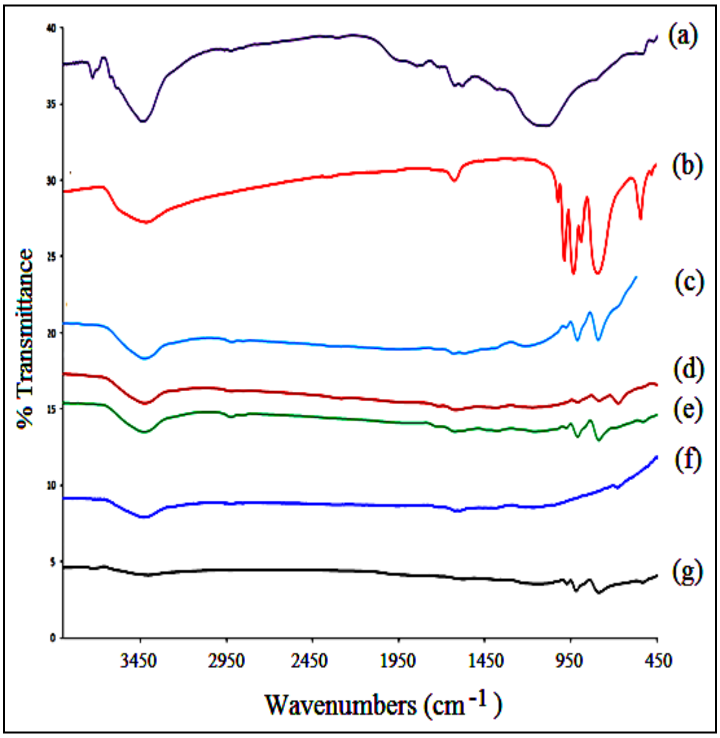


Figure 1. FT-IR spectra of (a) functionalized CNTs, (b) SiW, (c) CNT-SiW-Pt-1; (d) CNT-SiW-Pt-0.25; (e) CNT-SiW-Pt-050; (f) CNT-SiW-Pt-0.75; (g) CNT-SiW-Pt–1;

3.1.2 X-Ray Diffraction

The XRD patterns of CNTs and the CNT-SiW-Pt-x- series are shown in figure 2. In each one of the ranges of 2θ, 16^{o} –23^{o}, 25^{o}–30^{o}, and 31^{o}–38^{o}, the CNT-SiW-Pt-1 (catalyst composed only of SiW on CNTs) showed the characteristic peak of the Keggin structure [27, 28]. The spectrum of the CNT-SiW-Pt-0 catalyst showed the characteristic peak of the Pt. It can be seen from the figure that Pt supported on CNTs support forms a face centered cubic (fcc) structure and has major peaks at around 2□ = 39.9° (111), 46.6° (200), 67.5° (220), 81.9° (311), and 85.6° (222) . As for the CNT-SiW-Pt-0.25 and CNT-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 the peaks at 31^{o}–38^{o} ‘are completely masked into the strong 39.9° and 46.6° peaks’ of the Pt: even for the highest SiW content, it is impossible to perform a correct subtraction of the contribution of SiW because of the nature of the very strong 39.9° and 46.6° peaks,’ and of the too high contrast between the intensities of the respective signals of Pt and SiW. In the 25^{o}–30^{o} the characteristic lines of the Keggin structure at 25.6^{o} and 29.7^{o} can be observed for the samples with high SiW content, showing that the Keggin structure is 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 mean size of Pt particles calculated from the diffraction of the Pt (220) peak according to Scherrer’s formula [29, 30], are 3.6nm for CNT-SiW-Pt-0, 3.1 nm for CNT-SiW-Pt-0.25, and 2.5 nm for CNT-SiW-Pt-0.50

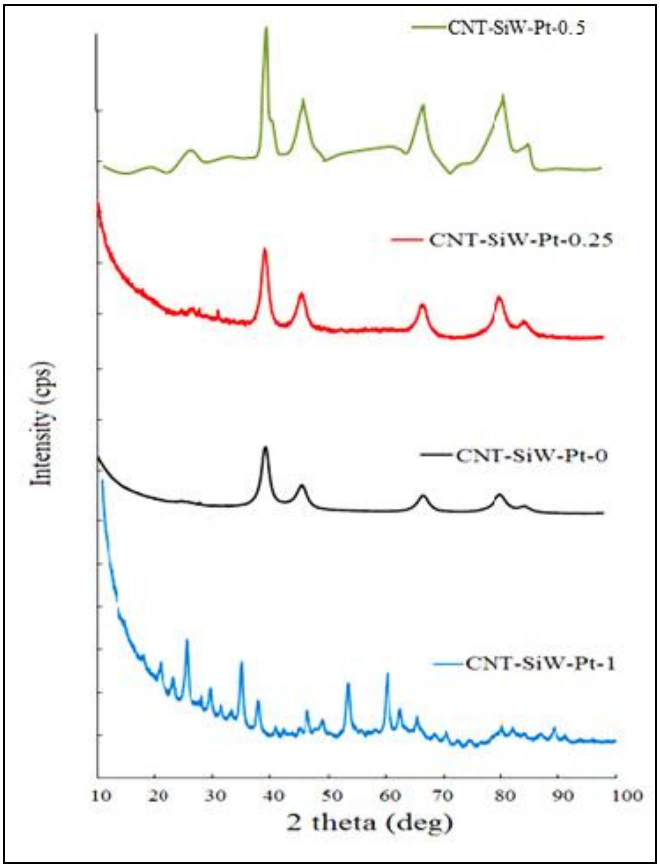


Figure 2. XRD patterns of the prepared CNT –SiW-Pt-x series of catalysts. CNT-SiW-Pt-0; CNT-SiW-Pt-0.25; CNT-SiW-Pt–1.

3.1.3 Polarography/ICP-OES

The loading of SiW and Pt on the CNTs support was measured by polarography and ICP-EOS respectively. The results reported in table 1, showed that in generally the nominal %weight is slightly different of the experimental one.

Table 1. Nominal and experimental mass fraction of SiW and Pt loaded on the CNTs support determined by polarography and ICP-OES.

	Nominal mass fraction		Experimental mass fraction	
Catalyst	SiW (%)	Pt(%)	SiW (%)	Pt(%)
CNT- SiW-Pt-0	0.00	0.10	0.00	1.00
CNT- SiW-Pt-25	0.25	0.75	0.22	0.78
CNT- SiW-Pt-50	0.50	0.50	0.52	0.48
CNT- SiW-Pt-75	0.75	0.50	0.78	0.22
CNT- SiW-Pt-100	1.00	0.00	1.00	0.00

3.1.4 Transmission Electronic Microscopy

The TEM micrographs of CNT- SiW-Pt-0 and CNT- SiW-Pt-0.25 are shown in the figure 3. The results show a more homogenous and uniform particle distribution for CNT- SiW-Pt-0.25 material compared to CNT- SiW-Pt-0 one. In the case of the catalyst constituted only of Pt material, particles are in the average range of about 2.5–4 nm, while for the catalyst containing both Pt and SiW materials, they are in the average range (0.5–3 nm). This result indicates that the use of a SiW allows the physical separation of the Pt particles and thereby hinders their agglomeration into larger crystallites. Thus, it increases the distribution of the Pt particles. These results are in good agreement with XRD results.

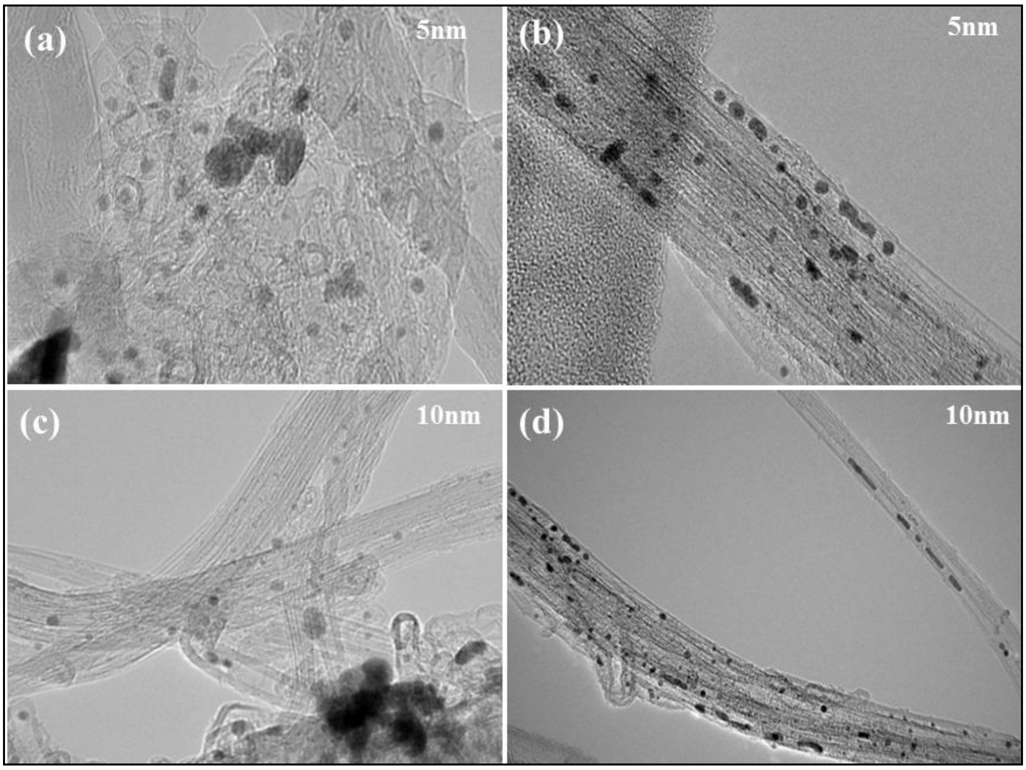


Figure 3. TEM images of: (a,b) CNT- SiW_{12}-Pt-0 and (c,d) CNT- SiW_{12}-Pt-0.25.

3.2 Cyclic voltammetry

3.2.1. Cyclic voltammetry of the carbon support

Before testing the prepared series of electrocatalysts (CNT- SiW-Pt-x) for the electrocatalytic oxidation of cyclohexane, CNTs support were characterized by cyclic voltammetry measurements in order to test the electrochemical properties of the CNTs support and the series of the CNT- SiW-Pt-x catalysts. The obtained cyclic voltammograms of the functionalized and the as received CNTs support are shown in figure 4. It can be seen that the capacitance of the functionalized CNTs was higher than that of the as received CNTs. This result is in agreement with those of some reported studies where it has been mentioned that the capacitance of the initial capacity of the CNTs was significantly increased after functionalization [31-37]. In the opinion of the authors, this improvement is due to the fact that the created functional groups increase the number of contact sites between the electrode and the electrolyte molecules, which in turn increase the overall charge transfer between them.

After functionalization, the CNTs were then after used to prepare a series of CNTs/binder with various ratios. The prepared series of CNTs/binder was studied in order to determine the optimum catalyst/binder ratio in term of electroactivity. It was found that the highest exchanged electronic charge was obtained for the catalyst having a binder proportion equal to 5%. This ratio was maintained for the fabrication of all the electrodes.

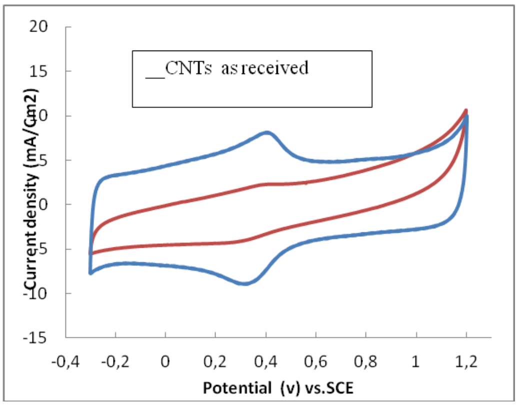


Figure 4. Cyclic voltammetry of as-received CNTs and after functionalization. Cyclic voltammetry was performed in a 0.5 M H_2SO_4 solution a scan rate of 50 mVs^{-1}.

3.2.2 Cyclic voltammetry of the CNT- SiW$_{12}$-Pt-x series

The cyclic voltammograms of the CNT-SiW-Pt-x series of catalysts (figure.5) showed five regions related to the release of the hydrogen and the reduction of oxygen.

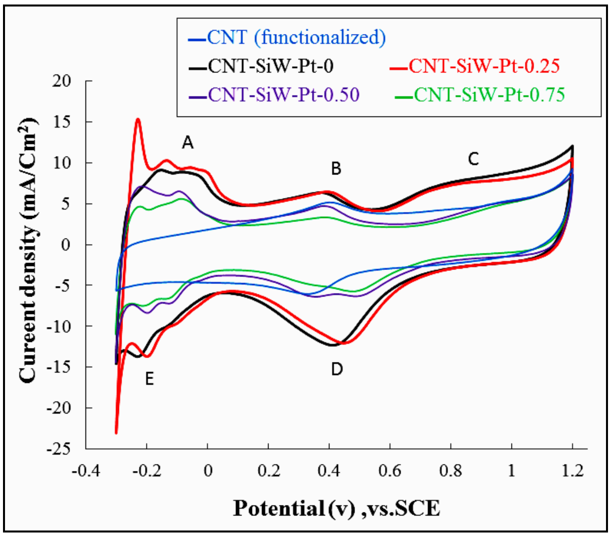


Figure 5. Cyclic voltammograms of CNT-SiW-Pt-x series of catalysts in 0.5 M H_2SO_4 solution with an average scan of 50 mV s^{-1}

Figure 6 shows the variation of the charge exchanged in function of the SiW loading for the series CNT-SiW-Pt-x. It was found that when the loadings increased up to 0.25%, the exchanged electronic charge increased sharply, then after it decreased until 77%. at higher ones the charge. When the amount was increased beyond 77%, the exchanged electronic charge remained stable. The maximum of the exchanged electronic charge observed for a 25% of SiW loading, might be due to the synergistic effect between SiW and Pt atoms. The low exchanged electronic charge observed for the catalyst, which do not contain the heteropolyanions, that is it contains only the Pt can be explained by the aggregation of Pt particles. When it occurs, agglomeration 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).

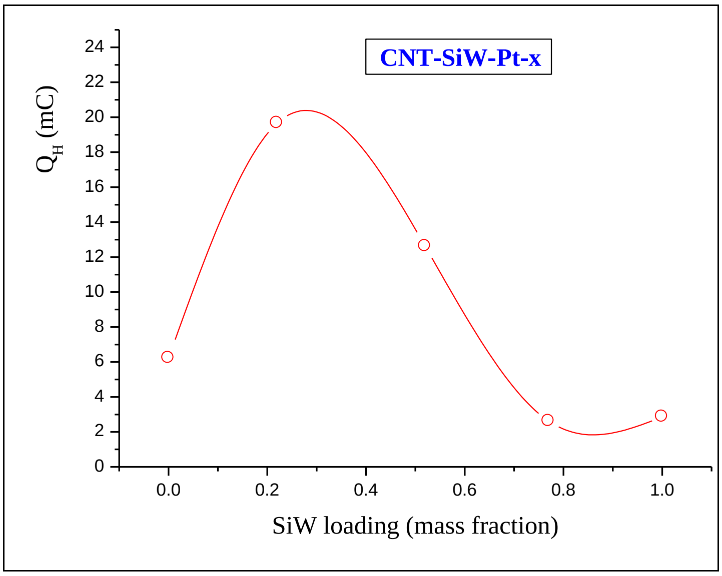
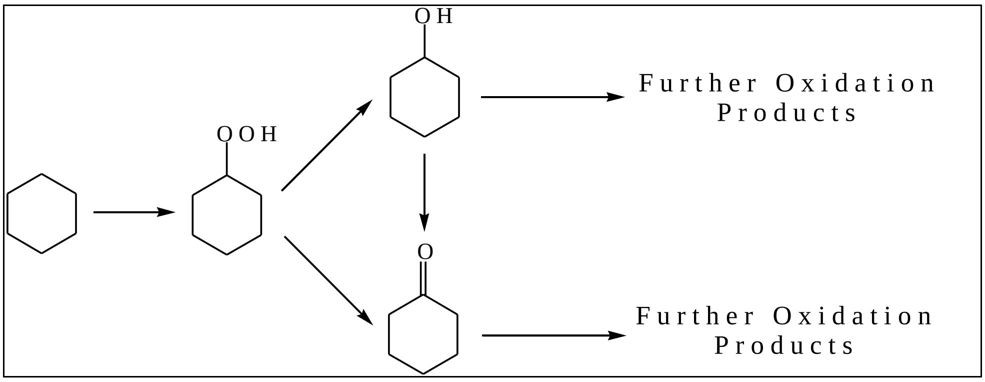


Figure 6. Effect of SiW loading on the CNTs support on the exchanged electronic charge of the CNT-SiW-Pt-x series of catalysts.

3.3. Electrocatalytic oxidation of cyclohexane

The series of the prepared catalysts CNT-SiW-Pt-x were tested for the electrocatalytic oxidation of cyclohexane. For all the catalysts tests, it has been found that the cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide were formed as major products of the electrooxidation [38, 39]. The effect of the SiW loading on the conversion and the selectivity is shown in figure 7. It can be seen that the conversion and the selectivity of K/A oil mixture decreased when the loading of SiW increased from 0% to 77%. Beyond 77%, the conversion remained almost stable. In the case of cyclohexyl hydroperoxide, it was found that a lower SiW mass fraction is more favorable for cyclohexyl hydroperoxyde formation, and a maximum in the cyclohexyl hydroperoxyde formation was observed at 0.52 mass fraction. As for the cyclohexanol formation, no significant change was observed in its selectivity in all the range of SiW mass fraction. This result suggests that both cyclohexanol and cyclohexyl hydroperoxide have undergone further oxidation leading to cyclohexanone. In a previous study [40] in which we have investigated the effect of reaction time on the electro oxidation reaction behavior, we have 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) [39]. Taking into account that cyclohexanol is more active than cyclohexane and can be converted to cyclohexanone easily, two possible pathways (Scheme 1) were proposed for the products formation.



Scheme 1. Proposed pathways for cyclohexane electrooxidation.

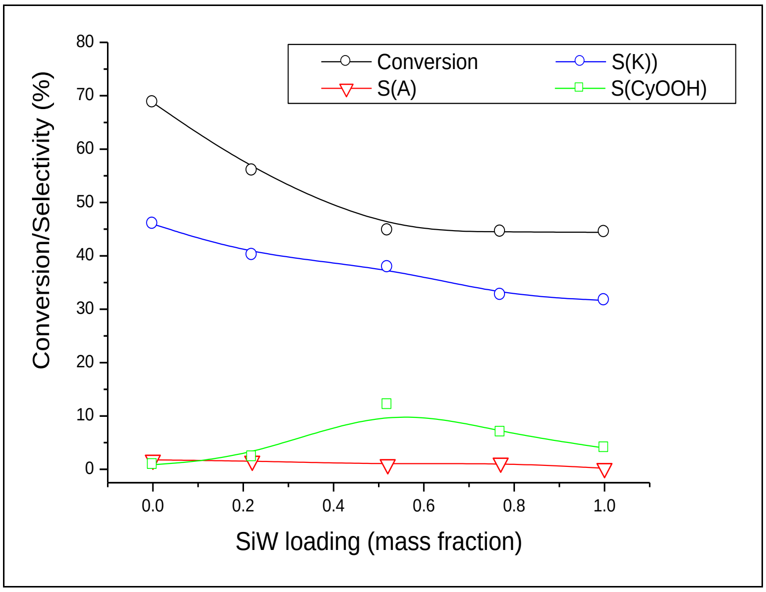


Figure 7. Effect of SiW loading on the CNTs support of the series CNT- SiW-Pt-x catalysts on the conversion and selectivity of the cyclohexanone, cyclohexanol and cyclohyl hydroperoxide.

The results of the effect of exchanged electronic charge of the series of catalysts on the conversion and the selectivity are shown in figure 8. It can be seen that at lower exchanged electronic charges, the conversion and the selectivity of cyclohexanone increased with the increase of the exchanged electronic charges, whereas at relatively higher ones they remained almost constants.

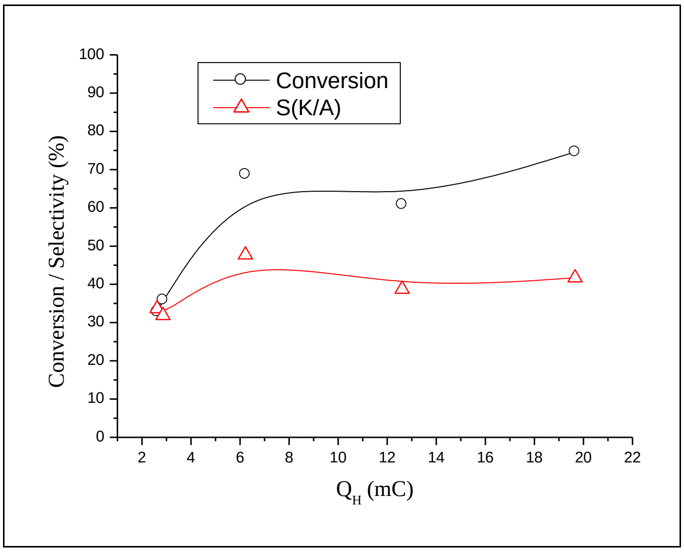


Figure 8. Effect of the exchanged electronic charge on the CNTs support of the series CNT- SiW-Pt-x catalysts on the conversion and the selectivity of the K/A oil mixture.

The higher exchanged electronic charge for electrochemical reactions would imply a faster electrode reaction, which should be an important factor in the efficient electrocatalysts. The value of charge transfer coefficient is affected by size of the catalyst particles, so it can be dependent on the catalysts dispersion. As observed in the TEM micrographs, the CNT- SiW-Pt-0.25 catalyst shows high particle dispersion, which could be related to the better electrocatalytic activity for the electrooxidation of cyclohexane. The low conversion and selectivity value obtained over CNT-SiW-Pt-0, could be related to the low dispersion as observed by TEM. Thus, optimum condition to obtain high conversion and high selectivity of K/A oil mixture is high exchanged electronic.

4. CONCLUSION

A series of CNT- SiW-Pt-x catalysts were synthesized, characterized by means of FT-IR, XRD, and polarography. The results showed that the Keggin structure of the incorporated SiW in the carbon support was not altered.

Stable SiW modified carbon electrodes in the reacting media were successfully fabricated by using polyvinylidene difluoride (PVDF) as binder.

Characterization by cyclic voltammetry (CV) and tests in the cyclohexane oxidation showed that all the series of catalysts were electroactive. The obtained conversion is relatively high whereas the selectivity is relatively low compared to those obtained in the industrial process.

The optimum condition for the formation of the cyclohexanone, which is needed for the production of the □-caprolactam is high exchanged electronic charges.

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