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Catalytic Performance of Carbon Nanotubes Supported 12-Tungstosilicic Acid in the Electrooxidation of Cyclohexane to Cyclohexanone and Cyclohexanol

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Abstract

Carbon nanotubes-supported 12-tungsto-silicic materials (referred as CNT- SiW_{12}-x, where x is the loading of $H_4SiW_{12}O_{40}$, abbreviated as SiW_{12} were prepared and characterized by means of FTIR, XRD, and polarography. The prepared catalysts and attached onto glassy carbon (GC) electrodes by using polyvinylidene difluoride (PVDF) as binder. The resulting carbon supported SiW_{12} modified electrodes were investigated by cyclic voltammetry (CV) and tested for the electrooxidation of cyclohexane to cyclohexanone (K) and cyclohexanol (A). It has been found that the cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide (CyOOH) are formed as major products of the reaction. Exchanged electronic charge and reaction time had an obvious influence on the catalytic performance of the catalyst. Short reaction time and low exchanged electronic charge favor the formation of cyclohexanol. High exchanged electronic charge and long reaction time favor the electrooxidation of cyclohexanol to cyclohexanone. The optimum condition for the formation of the cyclohexanone, which is needed for the production of the ε-caprolactam, is high exchanged electronic charges.

Keywords: Heteropolyanions; Carbon nanotubes; Cyclohexane electrooxidation; Modified carbon electrode

Introduction

The partial oxidation of low-cost raw hydrocarbons to more valuable oxygenated products is an economically interesting process [1]. However the chemical inertness of the hydrocarbons makes the activation of its C-H bonds very difficult, usually requiring drastic reaction conditions, such as high temperature and pressure [2]. Most hydrocarbon oxidations are unselective, whether conducted in the gas or liquid phase [3,4]. Among hydrocarbon oxidation reactions, the oxidation of cyclohexane to cyclohexanone and cyclohexanol is a very attractive reaction. In fact, Cyclohexanone (K) and cyclohexanol (A) (known as K/A oil mixture) are important chemicals used in the manufacture of nylon-6 and nylon-66, respectively [5,6]. The industrial production of the K/A oil mixture is achieved in a homogeneous catalysis process using soluble transition metal salts (such as cobalt naphthenate) at high temperature and pressure. However due to the fact that the cyclohexanol and cyclohexanone products are more reactive than the cyclohexane reactant, high selectivities (>80%) of the K/A oil mixture only could be observed at low cyclohexane conversion (<5%) [7]. Moreover, this homogeneous industrial process produces more amount of cyclohexanol, and additional steps are needed to improve the K/A mole ratio in the final products [8]. The major challenge in this field is to find an alternative heterogenous process that can improve both, the selectivity of K/A oil and the conversion of cyclohexane. An interesting approach is to use electrochemical process. Recently great attention has been paid to the research in the field of organic electrosynthesis owing to the advent of nuclear power, which will make electricity cheaper compared to chemical oxidants and reductants. Furthermore, in electrochemical processes less hazardous chemicals are used, and high product purity and selectivity of products can be obtained in mild reaction conditions. This research work deal with the electrosynthesis of K/A oil mixture by cyclohexane electrooxidation. To do this, a series of modified carbon nanotubes supported heteropolyanions electrodes have been fabricated and tested.

Materials and Experimental Methods

Preparation of the catalysts

The 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) was prepared according to a now well-known method [9]. In order to bind SiW_{12} on the carbon nanotubes (CNTs), oxygenated groups must be created on the carbon support (functionalization). The process of carbon functionalization was performed by using concentrated nitric acid according to the following steps: 0.1 g sample of Carbon was suspended in 100 ml nitric acid (65%), and heated for 5 hours at 80°C, then cooled at room temperature. The treated carbon was then washed with deionised water to pH 7, and dried at 100°C overnight. The resulting functionalized CNTs were then added to the desired amount of the prepared SiW_{12} already dissolved in acetone under stirring for 30 min. After removing the excess acetone by heating at 60°C, the prepared catalyst was dried in an oven at 80°C. A series of SiW_{12} catalysts supported on CNTs having various compositions have been prepared. They are denoted CNT-SiW_{12}-x where x is the weight in mg of SiW_{12} per 100 mg of CNTs:

CNT-SiW_{12}-50; CNT-SiW_{12}-100; CNT-SiW_{12}-150; CNT-SiW_{12}-200; CNT-SiW_{12}-300.

Preparation of working electrode

Prior to modification, Glassy Carbon electrode was cleaned by polishing with (0.5-0.05 μm) Al_2O_3 powder. Then after a suspension of

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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 µl was pipetted onto the surface of the glassy carbon electrode and the solvent was allowed to evaporate at 80°C for 12 hours in the oven. After preparation the modified electrodes were examined by cyclic voltammetry and tested for the cyclohexane electrooxidation reaction.

Characterization of the catalysts

The Characterization of the CNTs supported SiW_{12} catalysts have been performed by means of infrared (IR) spectroscopy, XRD, 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. Polarography measurements were performed by means of METROHEM 797 VA COPMUTRACE (Version 1.2) 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 to -0.800 V].

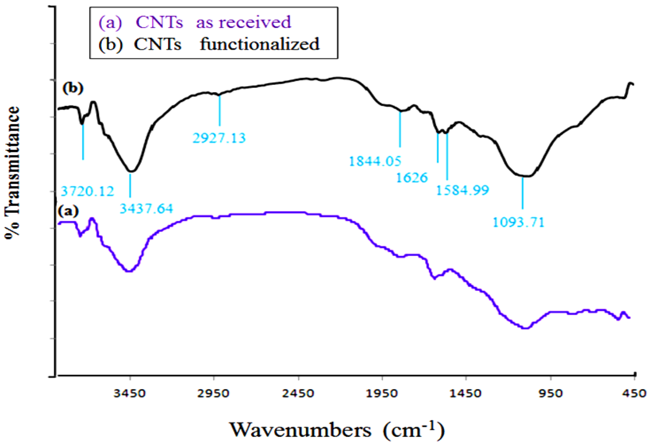


Figure 1: FT-IR spectrum of CNTs: (a) before oxidation; (b) after oxidation. Range temperature 25-800°C; heating rate 20 min/°C.

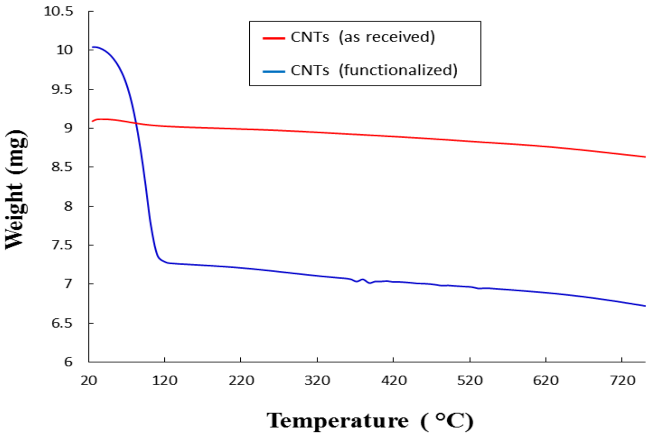


Figure 2: TGA of CNT (a) before oxidation; (b) after oxidation. Range temperature 25-800°C; heating rate 20 min/°C.

Electrochemical experiments

Cyclic voltammetry: The cyclic voltammetry was performed in a conventional three-electrode single-compartment Pyrex glass cell using a computerized potentiostat/galvanostat (Autolab, PGSTAT30) with NOVA 1.8 software. The reference and the auxiliary electrodes were SC and pure Pt-foil, respectively. The cell was filled with 0.5 M H_2SO_4 until the lower ends of the electrodes were immersed.

Electrooxidation of cyclohexane: 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: 5 ml of cyclohexane, 10 ml of hydrogen peroxide (30% in aqueous solution) and 5 ml of *tert*-butanol were charged in the cell and were heated at 50°C under stirring. After 2 hours 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).

Results and Discussion

Characterization of the carbon support

FTIR: FTIR spectra of CNTs before and after oxidation are shown in Figure 1. The peaks which are identified at 1386, 1720 and 3448 cm^{-1} characterize C-O, C=O and O-H bonds of the oxidized carbon [10]. Peaks at 1720 and 3448 cm^{-1} can be attributed to acidic groups like carboxyl and phenol. Peak at 1580 cm^{-1} assigns C=C bond in CNTs which appeared after disappearing of bond symmetry because of connection of oxygenated functional groups [11-13]. FTIR results showed that the oxidation treatments produce oxygenated groups such as carboxylic and hydroxyl, in the carbon surface. These groups are responsible for changing both the acid-basic character of the carbon black [14].

Thermogravimetric analysis (TGA): The thermograms of the CNTs before and after oxidation are shown in Figure 2. It can be seen from the figures that, for both CNTs the loss of weight for the oxidized carbon is more important than that for no oxidized carbon. This is due to elimination of oxygen groups in the form of water and oxygenated compounds.

Characterization of the series of catalysts

FTIR: The FT-IR spectra of the samples are shown in Figure 3. Figure 3(a) showed the characteristic features of functional groups created in the functionalized CNTs support. The peaks at 1700 cm^{-1}, 2848 cm^{-1}, and 2920 cm^{-1} indicate the existence of the carboxylic acid groups, aldehyde group, and methylene group respectively. Peaks around 1450-1320 cm^{-1} are an indication of the presence of aromatic groups [10,14]. Aldehyde and derivatives of benzene are detected by peaks at 875 and 761 cm^{-1}. The infrared spectrum of $H_4SiW_{12}O_{40}\cdot 13H_2O$ is shown in Figure 3(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 [9,15] for this heteropoly acid.

The typical pattern of $H_4SiW_{12}O_{40}$ is partly obscured by the carbon bands. In particular the band at 1018 cm^{-1}, assigned to γ_{as}Si-O, is

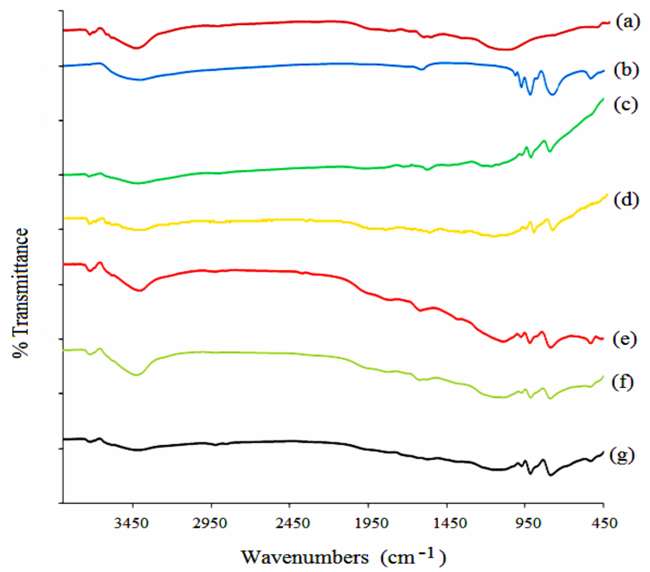


Figure 3: IR spectra of (a) Functionalized CNTs; (b) $H_4SiW_{12}O_{40}$; (c) CNT-SiW_{12}-50; (d) CNT-SiW_{12}-100; (e) CNT-SiW_{12}-150; (f) CNT-SiW_{12}-200; (g) CNT-SiW_{12}-300.

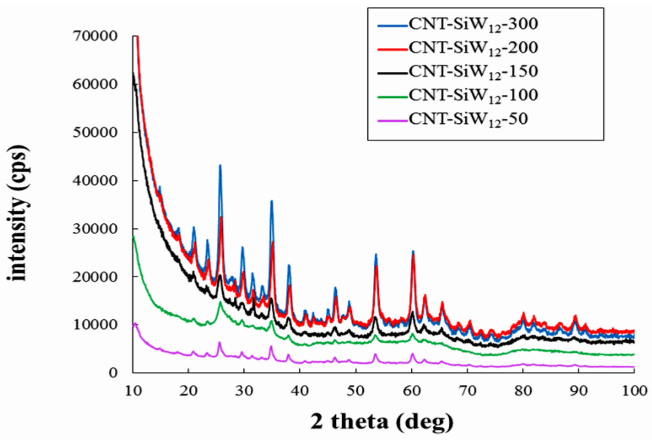


Figure 4: XRD spectra of the prepared CNT-SiW_{12}-x series of catalysts.

Catalyst	Nominal mass (mg)	Experimental mass (mg)
CNT-SiW_{12}-50	50	25.0
CNT-SiW_{12}-100	100	90.3
CNT-SiW_{12}-150	150	110.1
CNT-SiW_{12}-200	200	141.5
CNT-SiW_{12}-300	300	251.5

Table 1: Determination of the amount of SiW_{12} loaded on the CNTs support by polarography.

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.

X-Ray diffraction

The XRD patterns of the CNT- SiW_{12}-x- series are shown in Figure 4. In each one of the ranges of 2θ, 16-23°, 25-30°, and 31-38°, the compounds showed the characteristic peak of the Keggin structure [16-19]. This result which indicated that the Keggin structure of the heteropolyanions in the synthesized catalysts was not altered is in agreement with that obtained by FTIR.

Polarography

The loading of SiW_{12} on CNTs support was measured by polarography. The results reported in Table 1, showed that the nominal loadings are slightly different of the experimental ones.

Cyclic voltammetry of the prepared materials

Before testing the prepared series of electrocatalysts for the electrocatalytic oxidation of cyclohexane, cyclic voltammetry measurements were performed to test the electrochemical properties of the CNTs support and the series of the CNTs supported catalysts. Cyclic voltammetry was carried out in 0.5 M H_2SO_4 at 25°C at a sweep rate of 50 mV s^{-1} under high-purity nitrogen.

Cyclic voltammetry of the carbon support: The obtained cyclic voltammograms of the functionalized and fresh CNTs support are shown in Figures 5 and 6. It can be seen that the capacitance of the functionalized CNTs was higher than that of the as received CNTs. This fact is due to the created functional groups on the surface of the CNTs [20].

Cyclic voltammetry of the CNT-SiW_{12}-x series: Figure 7 shows cyclic voltammograms of the series of CNT-SiW_{12}-x. It can be seen from this figure that the series exhibit three redox couples with the formal potentials (*Ef*) of -615.6 mV, -229.9 mV, and, -452.3 mV respectively, similar to those of SiW_{12} dissolved in aqueous solution. The three redox couples correspond to two one-electron processes and one two-electron process, respectively [21-23]. The first one-electron process has no proton participation, the second one-electron process is accompanied by one proton participation, and the third two-electron process is accompanied by two protons participation. The uptake of proton during the SiW_{12} reduction is to avoid charge concentration of SiW, which is commonly found for heteropolyanion compounds [24,25]. According to the above results, the three-redox processes of the series of CNT-SiW_{12}-x can be described as follows:

$$SiW_{12}O_{40}^{4-} + e^- \leftrightarrow SiW_{12}O_{40}^{5-}$$

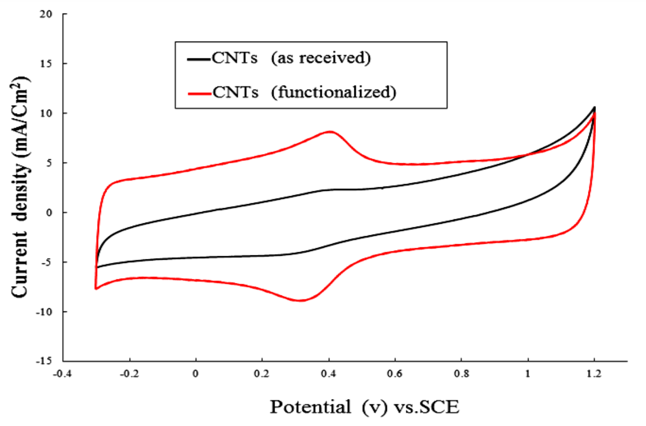


Figure 5: Cyclic voltammograms of CNTs before and after functionalization. Cyclic voltammetry was performed in a 0.5 M H_2SO_4 solution a scan rate of 50 mV s^{-1}.

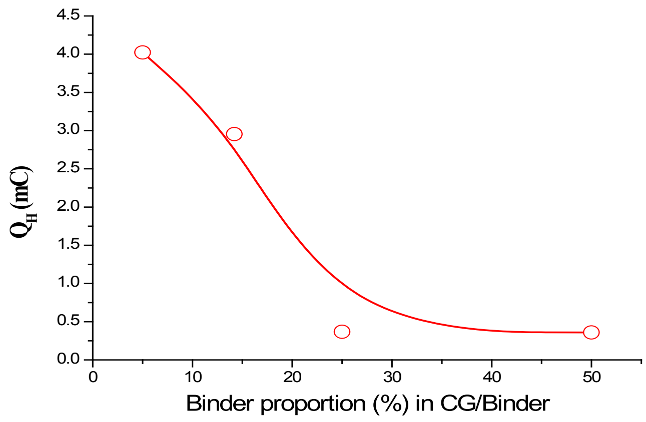


Figure 6: The electronic charges exchanged in the CNT-SiW_{12}-300 catalysts with various PVDF proportions.

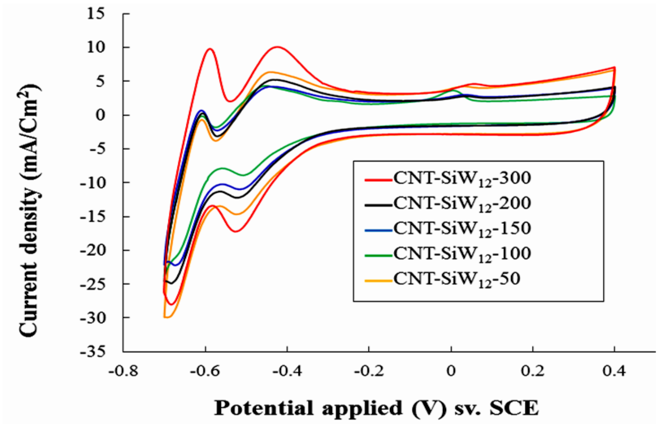


Figure 7: Cyclic voltammograms of CNT-SiW_{12}-x series of catalysts in 0.5 M H_2SO_4 solution with an average scan of 50 mVs^{-1}.

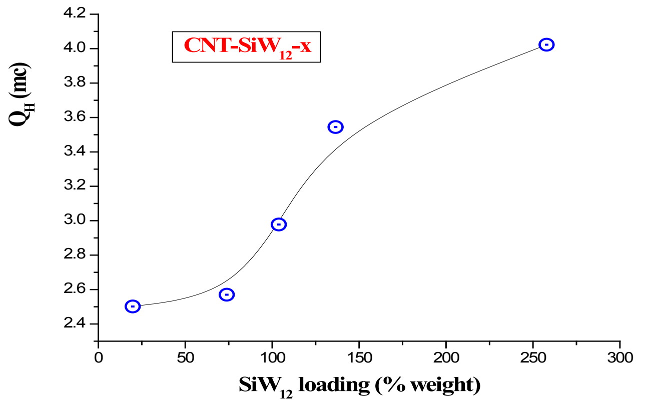


Figure 8: Effect of SiW_{12} loading on the CNTs supported CNT-SiW_{12}-x catalysts on the exchanged electronic charges.

$$SiW_{12}O_{40}^{5-}+e^-+H^+ \Leftrightarrow H\,SiW_{12}O_{40}^{5-}$$

$$HSiW_{12}O_{40}^{5-}+2e^-+2H^+ \Leftrightarrow H_3SiW_{12}O_{40}^{5-}$$

The overall-redox processes of the CNT-SiW_{12}-x can be described as follows:

$$SiW_{12}^{VI}O_{40}^{4-}+ne^-+nH^+ \Leftrightarrow H_nSiW_n^{V}W_{12-n}^{VI}O_{40}^{4-} \text{ (n is equal to 1or 2)}$$

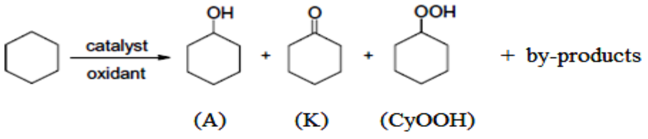
Figure 8 shows the dependence of SiW_{12} loading on the CNTs support of the series CNT-SiW_{12}-x on the exchanged electronic charges. It can be seen that at lower loadings the exchanged electronic charge increased rapidly whereas at higher ones the charge increased slightly.

Electro catalytic oxidation of cyclohexane

The electro catalytic activity of the CNT-SiW_{12}-x series of catalysts was investigated in the electrooxidation of cyclohexane. The reactions were carried out using H_2O_2 as oxidant at 50°C and the product cyclohexanone (K), cyclohexanol (A) and cyclohydroperoxide (CyOOH) were formed (Scheme 1).

The results of the effect of exchanged electronic charge of the CNT-SiW_{12}-x series of catalysts on the conversion of cyclohexane are shown in the Figure 9. It can be seen that the selectivity of the products as well as the conversion of cyclohexane depends strongly on the exchanged electronic charge. The increase of the exchanged electronic charge increased the conversion and the selectivity of cyclohexanone. As for the cyclohexyl hydroperoxide and the cyclohexanol, the results showed that they increased when the exchanged electronic charges increased from 2.5% to 3.0% mC then after they decreased when the charge was increased up to 4.0 mC. These results suggest that both cyclohexanol and cyclohexyl hydroperoxide were further oxidized to cyclohexanone. So, optimum conditions to obtain high selectivity of cyclohexanone, suitable for the production of the ε-caprolactam is operating at high exchanged electronic charges.

Figure 10 depicts the effect of the SiW_{12} loading on the conversion and selectivity. It can be seen that the conversion and the selectivity of cyclohexanone increased significantly with the SiW_{12} loading. The conversion and the selectivity of cyclohexanone were 33.4% and 17.5% respectively when CNT-SiW_{12}-25 was used, and they reached a value



Scheme 1: Cyclohexane oxidation products.

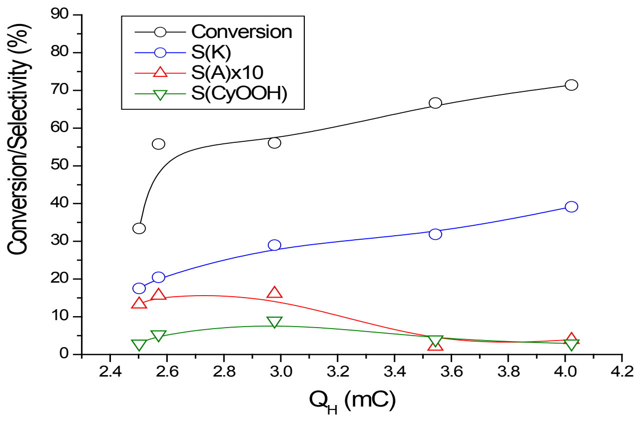


Figure 9: Effect of the exchanged electronic charge of the series of catalysts on the conversion and the selectivity of the products.

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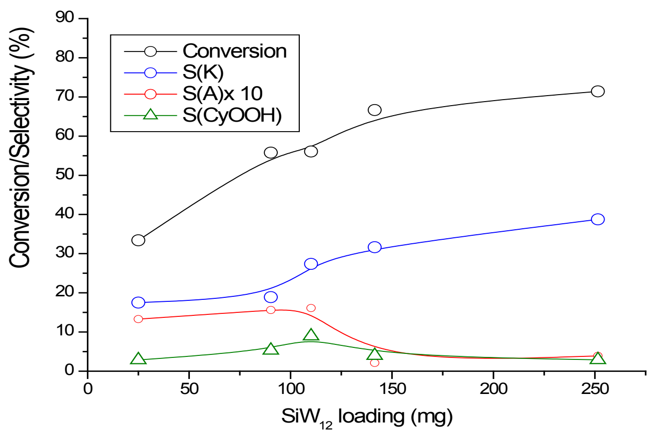

Figure 10: Effect of SiW_{12} loading on the CNTs support of the series of catalysts on the conversion and the selectivity of the products.

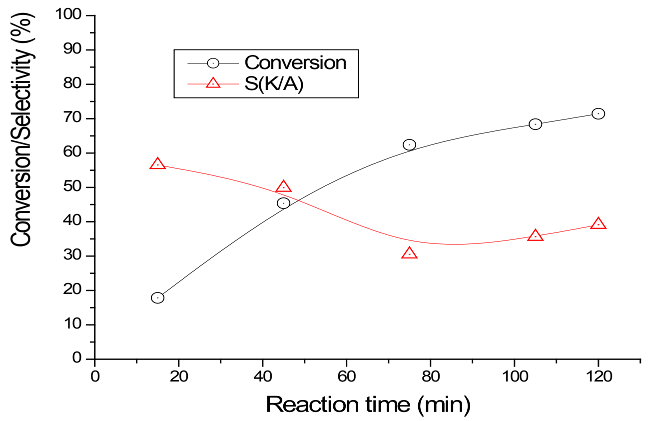

Figure 11: Effect of reaction time on the conversion and K/A selectivities for the electrooxidation reaction over CNT-SiW_{12}-300 catalyst at 40°C.

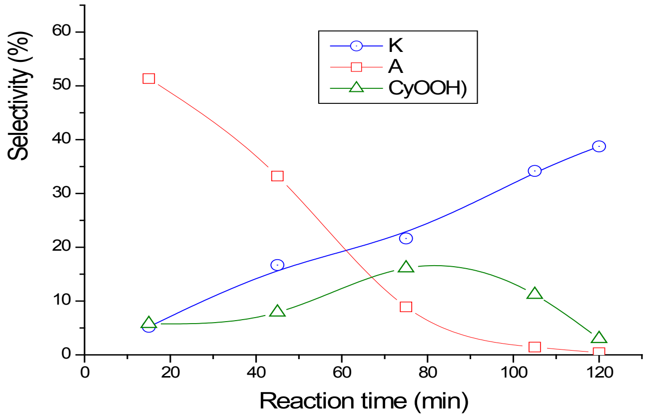

Figure 12: Effect of reaction time on the selectivities of the products for the electrooxidation reaction over CNT-SiW_{12}-300 catalyst at 40°C.

of 71.4% and 38.75% with CNT-SiW12-300. As for the cyclohexyl hydroperoxide and cyclohexanol, it has been found that their selectivity decreased at high loadings. This result seems to indicate that both cyclohexanol and cyclohexyl hydroperoxide have undergone further oxidation leading to cyclohexanone.

The results of the effect of reaction time on the cyclohexane electrooxidation over CNT-SiW_{12}-300 catalyst at 313 K are shown in Figures 11 and 12. Figure 11 illustrates the changes of the conversion and selectivity of the K/A oil mixture with reaction time. It can be seen that the conversion increased with reaction time, it increased from 17.8% to 71.4% when the reaction time was extended from 15 min to 120 min. Contrary to the conversion, the K/A oil mixture decreased with the reaction time. It decreased from 56.6% to 39.1% within the same range of time. The observed decrease of the K/A oil mixture while the increase of the conversion indicated that the K/A oil are further oxidized (to adipic acid and hexanoic acid…). So, the suitable conditions for the production of K/A oil mixture is short reaction time. Compared to the conversion (3.9%) and the K/A oil selectivity (78%) obtained at the industrial process [7], the conversion (17.8%) and the K/A oil selectivity (56.6%) obtained over CNT-SiW_{12}-300 catalyst can be considered as a positive completion.

The effect of the reaction time on the product distribution is shown in the Figure 12. The results showed that the selectivity of cyclohexanol decreased with time in favor of that of cyclohexanone. This result clearly indicates that the cyclohexanol was further oxidized to cyclohexanone. As for CyOOH, The selectivity of CyOOH increased to reach a culmination and then declined gradually. This may indicates that CyOOH was further oxidized to cyclohexanone or to both cyclohexanol and cyclohexanone. This result confirm that CyOOH is an intermediate product in the electrooxidation of cyclohexane; the cyclohexane electrooxidation process is composed of the process of converting cyclohexane to cyclohexanol to cyclohexanone and that of cyclohexyl hydro peroxide to cyclohexanol to cyclohexanone. These results are in agreement with those reported in the literature [26,27]. 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). Taking into account that cyclohexanol is more active than cyclohexane and can be converted to cyclohexanone easily, two possible pathways were proposed for the products formation [27]:

(1) CHHP → cyclohexanol → cyclohexanone

(2) Cyclohexanone ← CHHP → cyclohexanol (then cyclohexanol → cyclohexanone)

Conclusion

A series of CG-SiW_{12}-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_{12}-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. Electrocatalytic tests showed that the electrooxidation of cyclohexane led to cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide as major products for all the series of catalysts. The obtained conversion is relatively high whereas the selectivity is relatively low compared to those obtained in the industrial process.

Exchanged electronic charge and reaction time had an obvious influence on the catalytic performance of the catalyst. Short reaction time and low exchanged electronic charge favor the formation of cyclohexanol. High exchanged electronic charge and long reaction time favor the electrooxidation of cyclohexanol to cyclohexanone. Thus, the optimum condition for the formation of the cyclohexanone, which is needed for the production of the ε-caprolactam, is high, exchanged electronic charges.

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