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Development of a 12-Tungstosilicate-Modified Carbon Electrode for Cyclohexane Electrocatalytic Oxidation

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A series of carbon graphite-supported 12-tungsto-silicic ($H_4SiW_{12}O_{40}$, abbreviated as SiW_{12}) catalysts with various loadings, were prepared and characterized by means of FTIR, XRD, and polarography. These series of catalysts were attached onto glassy carbon (GC) electrodes by using polyvinylidene difluoride (PVDF) as binder. The resulting carbon supported SiW_{12} modified electrodes were characterized by means of 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 the major products of the reaction. The results of the CV showed that increasing the SiW_{12} loading, increased the exchanged electronic charge Qh (mC). Higher loadings promoted cyclohexanone production whereas lower ones favored cyclohexyl hydroperoxide formation.

Keywords: heteropolyanions, carbon functionalization, cyclohexane electrooxidation, modified carbon electrode

1. INTRODUCTION

Partial oxidation reaction of hydrocarbons into valuable oxygenated compounds is a key process in the chemical industry. However, this reaction is not selective, whether conducted in gas or liquid phase [1–3]. Among hydrocarbon oxidations, that of cyclohexane to cyclohexanone (K) and cyclohexanol (A) mixture (known as K-A oil mixture), is considered as an important commercial reaction [1]. In fact , both cyclohexanone and cyclohexanol are the main industrial precursors of, respectively, ε-caprolactam and adipic acid, intermediates in the production of polyamide fibers and plastics, such as Nylon-6 and Nylon-6, 6 [2]. For the production of ε-caprolactam, the ketone is considered as the most valuable product and consequently a high K/A-ratio is desired. 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 less than 3.9%

conversion to prevent the formation of excessive amounts of by-products by over-oxidation of the relatively reactive oxygenates, giving ∼78% selectivity for K-A oil mixture [4, 5]. 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 (∼106 ton/year in 2006) [6], this process continues to be a challenging problem. Therefore, it is a great practical interest to develop a more efficient, easily separable, reusable, and environmental-friendly catalyst for cyclohexane oxidation process. An alternative way is using an electro-catalyst. Electrocatalytic process can be used to achieve a clean and complete conversion of a starting material to product under extremely mild experimental conditions. The most commonly used electrocatalysts are noble metals supported on carbon which are expensive [7–12]. 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 [13-18]. 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 [19–23]. 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.

2. MATERIALS AND METHODS

2.1. Preparation of the catalysts.

The 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$, abbreviated as SiW_{12}) was prepared according to a now well-known method [24]. In order to bind $HSiW_{12}$ on the carbon graphite (CG), 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: 0.1g 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 desired amount of the prepared $HSiW_{12}$ was dissolved in 2ml acetone with stirring to get a transparent solution, then a 0.1g sample of carbon was added to each round bottom flask and stirred with heating for 30min. Excess acetone was removed by heating at 60°C in an oil bath, then after the prepared catalyst was dried in an oven at 80°C. A series of $HSiW_{12}$ catalysts supported on CG having various compositions have been prepared. They are denoted CG-SiW_{12}-x where x is the weight in mg of $[SiW_{12}O_{40}]^{4-}$ per 100mg of carbon support:

CG-SiW_{12}-50; CG- SiW_{12} -100; CG- SiW_{12} -150; CG- SiW_{12} -200; CG- SiW_{12} -300;

2.2. 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.

2.3. Characterization of the catalysts

The Characterization of the CG 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 (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].

2.4. Electrochemical experiments

2.4.1. Cyclic voltammetry

The cyclic voltammetry (CV) 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.

2.4.2. 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: 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 μM).

3. RESULTS AND DISCUSSION

3.1. FTIR

The FT-IR spectra of the samples are shown in figure 1. The infrared spectrum of the CG is shown in Fig. 1(a). The peak at around 1700 cm^{-1} indicates the existence of the carboxylic acid groups. The peak around 2920 cm^{-1} is thought to be of the methylene group. The aldehyde group is also detected by a peak at 2848 cm^{-1}. Peaks around 1450–1320 cm^{-1} are an indication of the presence of aromatic groups [19, 25]. Aldehyde and derivatives of benzene are detected by peaks at 875 and 761 cm^{-1}. The peak centered at 1580 and 1174 cm^{-1} was assigned to be the C-C stretch of the GC backbones and the C-O stretch of the acid group, respectively. It has been also reported that the peak of C-O shifts to 1733 cm^{-1}, as a result of functionalization and that frequency corresponds to the carboxylate ester. 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 [24, 26] 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 γasSi-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.

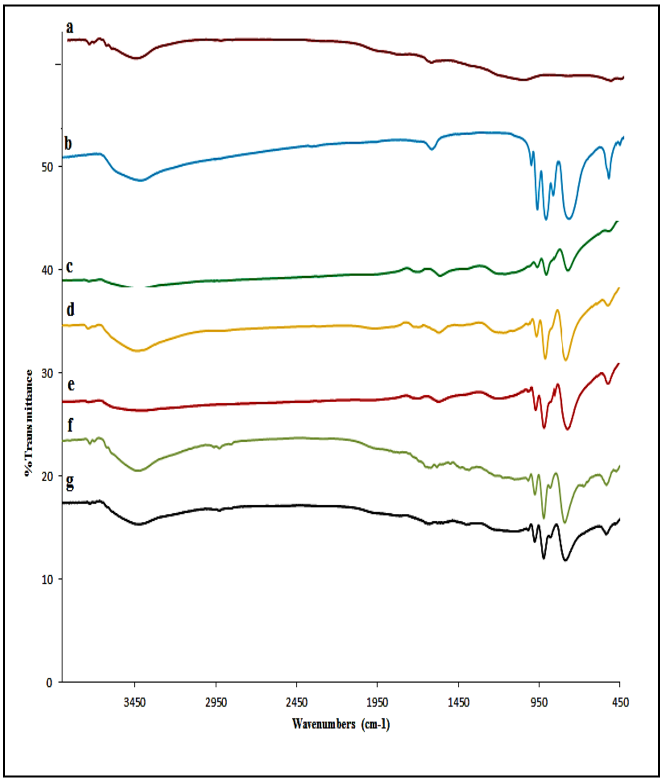

Figure 1. IR spectra of: a) CG; b**)** $H_4SiW_{12}O_{40}$ **; c)** CG-SiW_{12}-50**;** d) CG-SiW_{12}-100; e) CG-SiW_{12}-150 ; f) CG-SiW_{12}-200; g) CG-SiW_{12}-300

3.2. X-Ray Diffraction

The spectra of X-ray diffraction of the CG–SiW_{12}-x- series are shown in figure 2. 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 [27-31]. So the preservation of the Keggin structure in the synthesized catalysts was confirmed by FTIR and XRD.

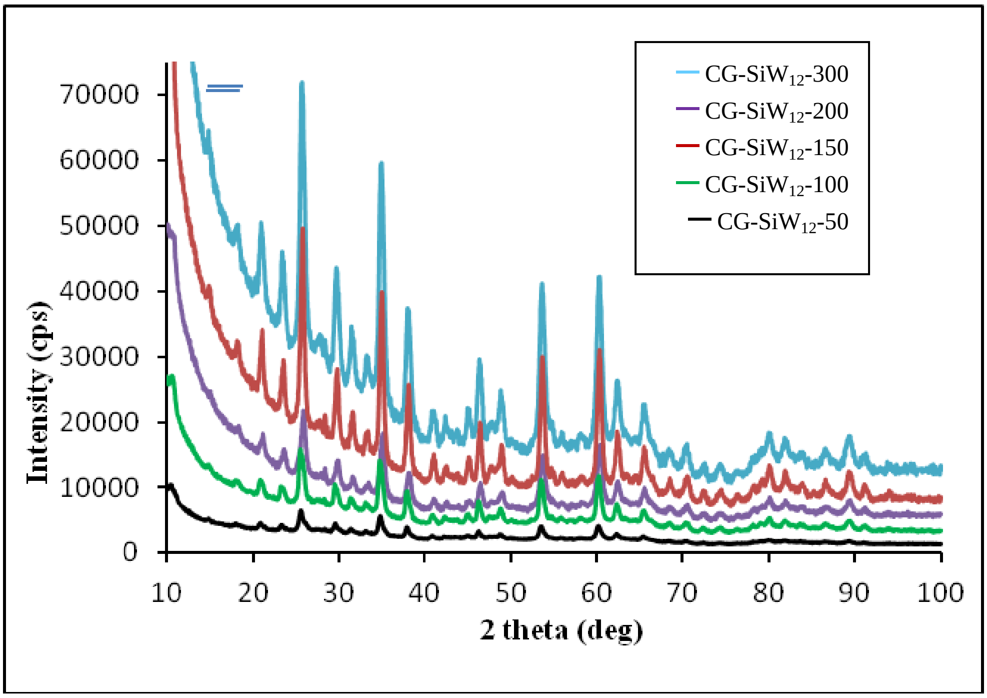

Figure 2. XRD spectra of the prepared CG–SiW_{12}-x series of catalysts.

3.3. Polarography

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

Table 1. Determination of the of SiW_{12} loaded on the CG support by polarography.

Catalyst	Nominal mass (mg)	Experimental mass (mg)
CG-SiW_{12}-50	50	33.0
CG- SiW_{12} -100	100	86.3
CG- SiW_{12} -150	150	141.3
CG- SiW_{12} -200	200	192.0
CG- SiW_{12} -300	300	235.0

3.4. 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 CG support and the series of the CG 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.

3.4.1 Cyclic voltammetry of the carbon support

The obtained cyclic voltammograms of the functionalized and fresh CG support are shown in figure 3. It can be seen that the capacitance of the functionalized CG was higher than that of the fresh CG. This fact is due to the created functional groups on the surface of the CG [32].

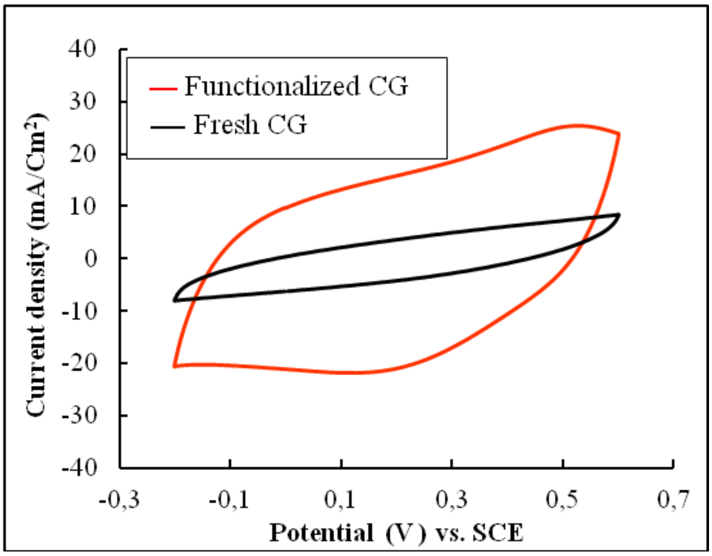

Figure 3. Cyclic voltammetry of CG before and after functionalization. Cyclic voltammetry was performed in a 0.5 M H_2SO_4 solution a scan rate of 50 mV s^{-1}.

3.4.2 Cyclic voltammetry of the CG-SiW-x series

Figure 4 shows cyclic voltammograms of the series of CG–SiW_{12}-x. It can be seen from this figure that the series exhibit three redox couples with the formal potentials (*E*f) of -615.6 mV, -229.9 mV, and, - 452.3mV 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 [33-35]. 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_{12}, which is commonly found for heteropolyanion compounds [36–38]. According to the above results, the three-redox processes of the series of CG–SiW_{12}-x can be described as follows:

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

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

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

The overall-redox processes of the CG–SiW12-x can be described as follows:

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

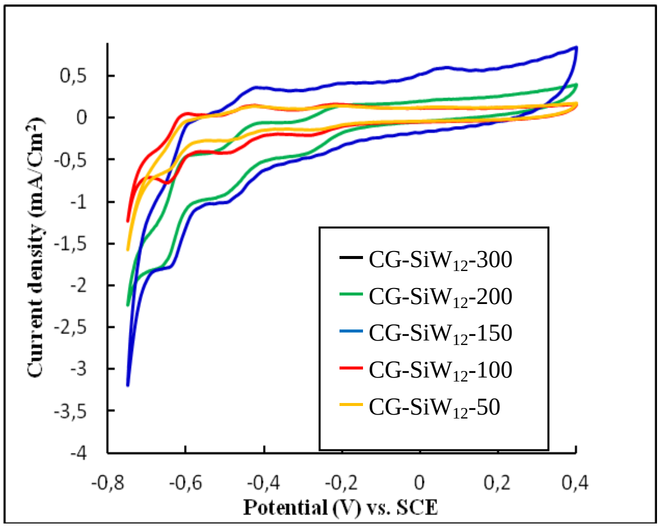

Figure 4. Cyclic voltammetry of CG-SiW_{12}-x series of catalysts in 0.5 M H_2SO_4 solution with an average scan of 50 mV s^{-1}

Figure 5 shows the dependence of SiW_{12} loading on the CG support of the series CG-SiW_{12}-x on the exchanged electronic charges. It can be seen that at lower loadings the exchanged electronic charge increased slightly whereas at higher ones the charge increased significantly.

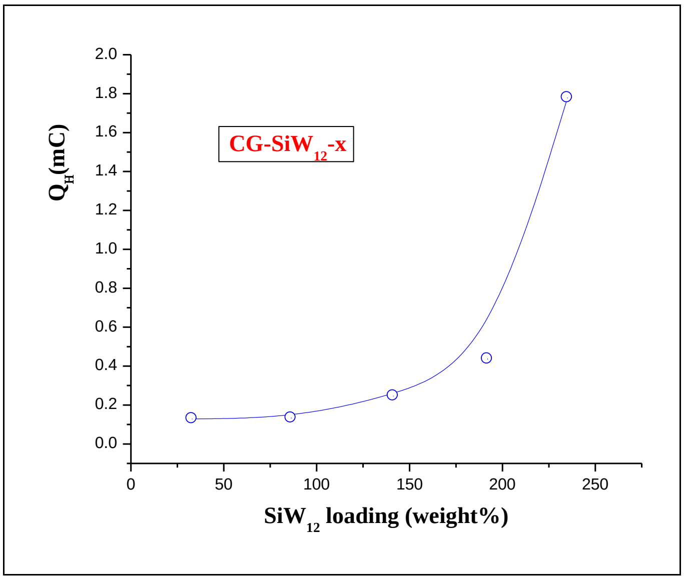

Figure 5. Effect of SiW_{12} loading on the CG support on the exchanged electronic charge of the series CG-SiW_{12}-x of catalysts.

3.5. Electrocatalytic oxidation of cyclohexane

The series of the prepared catalysts CG-SiW_{12}-x were tested for the electrocatalytic oxidation of cyclohexane. For all the catalysts tests, it has been found that the cyclohexanone, cyclohexanol and cyclohexyle hydroperoxide were formed as major products of the electrooxidation.

The results of the effect of exchanged electronic charge of the series of catalysts on the conversion and the selectivity are shown in figure 6. It can be seen that the conversion and the selectivity of both cyclohexanone and cyclohexyl hydroperoxide increased linearly at lower exchanged electronic charges, whereas at relatively higher ones the conversion and the selectivity of cyclohexanone increased but that of cyclohexyl hydroperoxide decreased. As for the selectivity of cyclohexanol, it was found that there was no significant change when the exchanged charge increased.

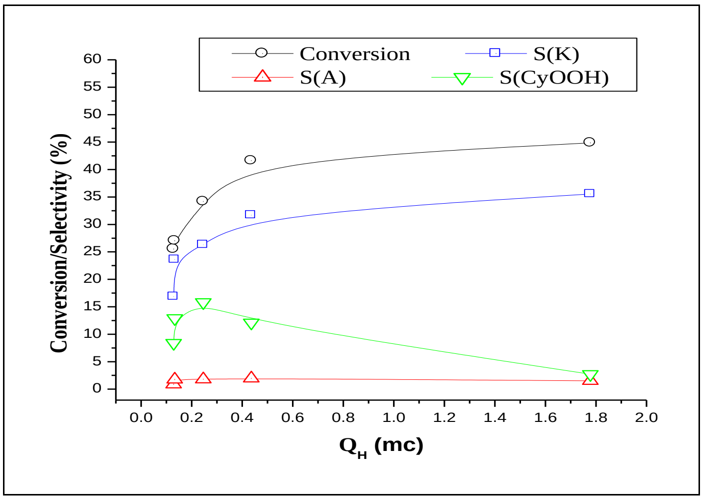

Figure 6. Effect of the exchanged electronic charge of the series of catalysts on the conversion and the selectivity.

In order to determine the optimum SiW_{12} loading on the CG supported SiW_{12} catalyst for the cyclohexane oxidation, the effect of the SiW_{12} loading on the conversion and the selectivity was investigated. It can be seen from the results in figure 7, that the conversion and the selectivity of cyclohexanone are directly proportional to the SiW_{12} loading. As for the cyclohexyl hydroperoxide, one can see that at low SiW_{12} loading the selectivity increases with SiW_{12} loading then after it decreases in favor of that of cyclohexanone. No significant change was observed in the selectivity of cyclohexanol. This result suggests that both cyclohexanol and cyclohexyl hydroperoxide have undergone further oxidation leading to cyclohexanone. Compared to the industrial homogeneous catalytic process in which cyclohexane conversion is less than 3.9% and the selectivity to cyclohexanol and cyclohexanone is 78% [7, 8], the electrocatalytic process lead to a relatively high conversion and selectivity of K-A Oil mixture. Optimum condition to obtain high selectivity of cyclohexanone, suitable for the production of the □-caprolactam is high exchanged electronic charges.

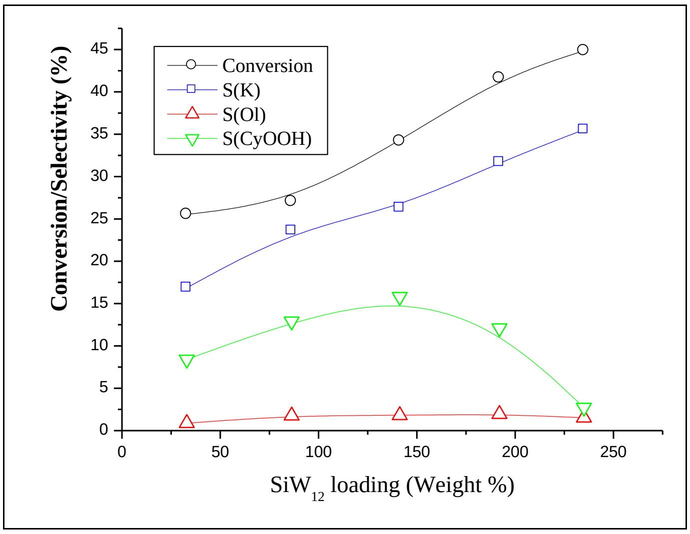

Figure 7. Effect of SiW_{12} loading on the CG support of the series of catalysts on the conversion and the selectivity.

4. 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_{12} 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. 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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