

Synthesis and comparison of the activities of a catalyst supported on two silicate materials



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HIGHLIGHTS

- Immobilization of $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ complex onto mesoporous supports.
- Synthesis and characterization of new mesoporous catalysts.
- The new catalysts exhibit great catalytic activity in the epoxidation of 1-octene.
- Recyclable catalysts with excellent reusability and stability.

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ABSTRACT

The focus of this work is inspecting the synthesis and comparison of the activities of a catalyst supported on two silicate materials in the epoxidation of 1-octene. The two new catalyst materials were characterized by infrared spectroscopy, elemental analysis, solid-state ^{29}Si and ^{13}C nuclear magnetic resonance, scanning electronic microscope (SEM) and analysis of nitrogen. Lastly, the two new catalysts, Silsesq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ and Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ were tested as catalysts in reactions of epoxidation of 1-octene and compared with their analogue not supported $[\text{W}(\text{CO})_3\text{I}_2(\text{thiocarbamide})]$. After an extensive literature search, we verified that our work is the first that has reported the immobilization process of $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ on silsesquioxane and silica gel functionalized with propyl-thiocarbamide groups and their applications as catalysts of reactions of catalytic epoxidation of 1-octene.

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1. Introduction

For the last few years, the demand for active heterogeneous catalysts and easy recycling has been desired by many industrial processes for many different applications. Among the various processes, the oxidation of olefins has been industrially important, because the epoxides obtained are used as intermediates in polymer synthesis reactions, production of pharmaceuticals and fine

chemicals [1]. Homogeneous catalysts are more efficient in most industrial processes and in olefin epoxidation it is no different, however, it shows significant drawbacks, such as leaching, difficulty in separation and reuse that leads to their loss [2]. Moreover, supported catalysts have some advantages such as high applicability, high sensitivity to poisoning, high possibility of modification, excellent thermal stability, long life, easy separation and recovery of the catalyst [3,4]. Recently, organometallic complexes have received special attention, because the advancement of synthetic routes have contributed to the grafting of organometallic complexes in the structure of several materials. Organometallic complexes can coordinate easily in various types of supports, resulting in robust and efficient catalysts in many industrial catalytic processes. The homogeneous catalysts based on organometallic complexes can be used as heterogeneous catalysts from the

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immobilization on a solid support. In the field of catalysis, recent studies have used various supports in the search for catalysts with high selectivity and efficient in the epoxidation of olefins, i.e. carbon nanotubes [5] organic polymers [6] and amorphous aluminum phosphate [7]. Silicon-based compounds are promising supports for grafting of organometallic complexes, due to the possibility of surface modification by a variety of organic compounds [8,9]. Thus, polyhedral oligomeric silsesquioxane are considered an important class of solid supports. Silsesquioxanes have a rigid inorganic core of Si-O-Si with nanometric size of 1,5-3 nm, high asymmetry, high thermal stability, as well as radicals that can be covalently linked to organic substituents aryl, vinyl, allyl, and aromatic ring substituted [10,11]. Thus, polyhedral oligomeric silsesquioxane and silica gel chemically modified have high surface areas and groups that can be easily modified by various organic functional groups by nucleophilic substitution [12–14].

The aim of this study was to explore the use of mesoporous supports based on silsesquioxane and silica gel modified with thiocarbamide as well as the reaction of these mesoporous materials with the complex $[W(CO)_3I_2(NCCH_3)_2]$ to optimize the synthesis of the two new catalysts. The two new Silsesq-TCA- $[W(CO)_3I_2]_3$ and Silica-TCA- $[W(CO)_3I_2]$ catalysts were tested in olefin epoxidation reactions and compared with the homogeneous catalyst $[W(CO)_3I_2(\text{thiocarbamide})]$.

2. Investigational procedures

2.1. Additional information

The chemicals were purchased from Sigma-Aldrich.

All solvents used in this study were previously purified, unless otherwise indicated.

The complex $[W(CO)_2X(NCCH_3)_2]$ ($X = I$, $X = Cl$ or $X = Br$) was prepared according to literature methods, but with modifications [15,16].

The infrared analyzes were obtained using a Nicolet 5DXB Instruments spectrometer.

The analysis of nuclear magnetic resonance of carbon and silicon were performed on a Bruker Avance 400 spectrometer in the chemical institute of Araraquara/SP.

The electronic scanning microscopy images were taken in an EVO LS15 - Carl Zeiss and coated with gold.

A Mass spectrometry with inductively coupled plasma (ICP-MS-Series X 2 - Thermo Scientific) was used in this paper.

2.2. Preparatives

2.2.1. Synthesis of organometallic complex $[W(CO)_3I_2(NCCH_3)_2]$

The complex $[W(CO)_3I_2(NCCH_3)_2]$ was prepared according to literature [15,16] with modifications.

In a flask containing dry acetonitrile (160 mL) was added about 6.54 g (18.6 mmol) of $[W(CO)_6]$ under reflux and nitrogen atmosphere for 96 h. The resulting solution was refrigerated to $-20^\circ C$, and about 4.72 g (18.6 mmol) of iodine was added. A brown-red solution was formed immediately after the addition of iodine. Finally, the solvent was removed in vacuo yielding a dark brown complex (yield 5.90 g, 90,21%).

2.2.2. Synthesis of homogeneous catalyst - $[W(CO)_3I_2(TCA)]$

A solution of $[W(CO)_3I_2(NCCH_3)_2]$ (1.00 mmol) in CH_2Cl_2 (10 mL) was added in a solution of the thiocarbamide ligand (TCA) (1.00 mmol) in CH_2Cl_2 (10 mL). The reaction was maintained at 298 K and shaken for 6 h, then the solvent was evaporated giving a yellow solid which was purified by washing with hexane and dried in vacuo (96% yield).

2.2.3. Synthesis of heterogeneous catalyst - Silsesq-TCA- $[W(CO)_3I_2]_3$

The Silsesq-TCA- $[W(CO)_3I_2]_3$ was prepared based on the study of the $[W(CO)_3I_2(NCCH_3)_2]$ immobilization on Silsesq-TCA, using the following procedure:

In a flask containing 4 L of CH_3OH was added 225 mL of 3-chloropropyltriethoxysilane (CPTES) and 135 mL of HCl under nitrogen atmosphere. The solution was vigorously stirred and after 6 weeks the white solid formed was filtered, washed and dried. The resulting material, named Octakis(3-chloropropyl)octasilsesquioxane (Silsesq-PrCl) gave a yield of 39%.

About 5.82 g of thiocarbamide was added during a period of 60 min to a suspension of 1.83 g of NaH in 100 mL of DMF under nitrogen. The reaction system was shaken at a temperature of $0^\circ C$ for three hours. Next, 10 g of Silsesq-PrCl in DMF was added to the reaction system and the temperature was raised to $80^\circ C$ for 24 h forming a yellow solution. To precipitate the nanomaterial, ethanol was added to reaction; the precipitated material was filtered to give the modified silsesquioxane Silsesq-TCA in 70% yield.

The Silsesq-TCA- $[W(CO)_3I_2]$ was prepared based on the study of the $[W(CO)_3I_2(NCCH_3)_2]$ immobilization on Silsesq-TCA, using the following procedure: A mixture of Silsesq-TCA (2.0 g), and $[W(CO)_3I_2(NCCH_3)_2]$ (4.46 g) in ethanol (50 mL) under nitrogen was shaken at room temperature over 12 h. Afterwards, the solvent was eliminated by filtration in nitrogen atmosphere and the new catalyst was washed four times with dichloromethane and ethanol and thus, dried, giving 1.7 g of Silsesq-TCA- $[W(CO)_3I_2]_3$ (85% yield), as illustrated in Scheme 1.

2.2.4. Synthesis of heterogeneous catalyst - Silica-TCA- $[W(CO)_3I_2]$

The Silica-TCA- $[W(CO)_3I_2]$ was also prepared based on the study of the $[W(CO)_3I_2(NCCH_3)_2]$ immobilization on Silica-TCA, using the following procedure:

About 37.12 mL of 3-chloropropyltrimethoxysilane were added in a flask containing in 350 mL of dry toluene and 12 g silica, the reaction was shaken during 48 h and under nitrogen atmosphere at $140^\circ C$. After 48 h, the precursor material was filtered and washed repeatedly with ethanol. The precursor material was called 3-chloropropyl silica gel (Silica-PrCl).

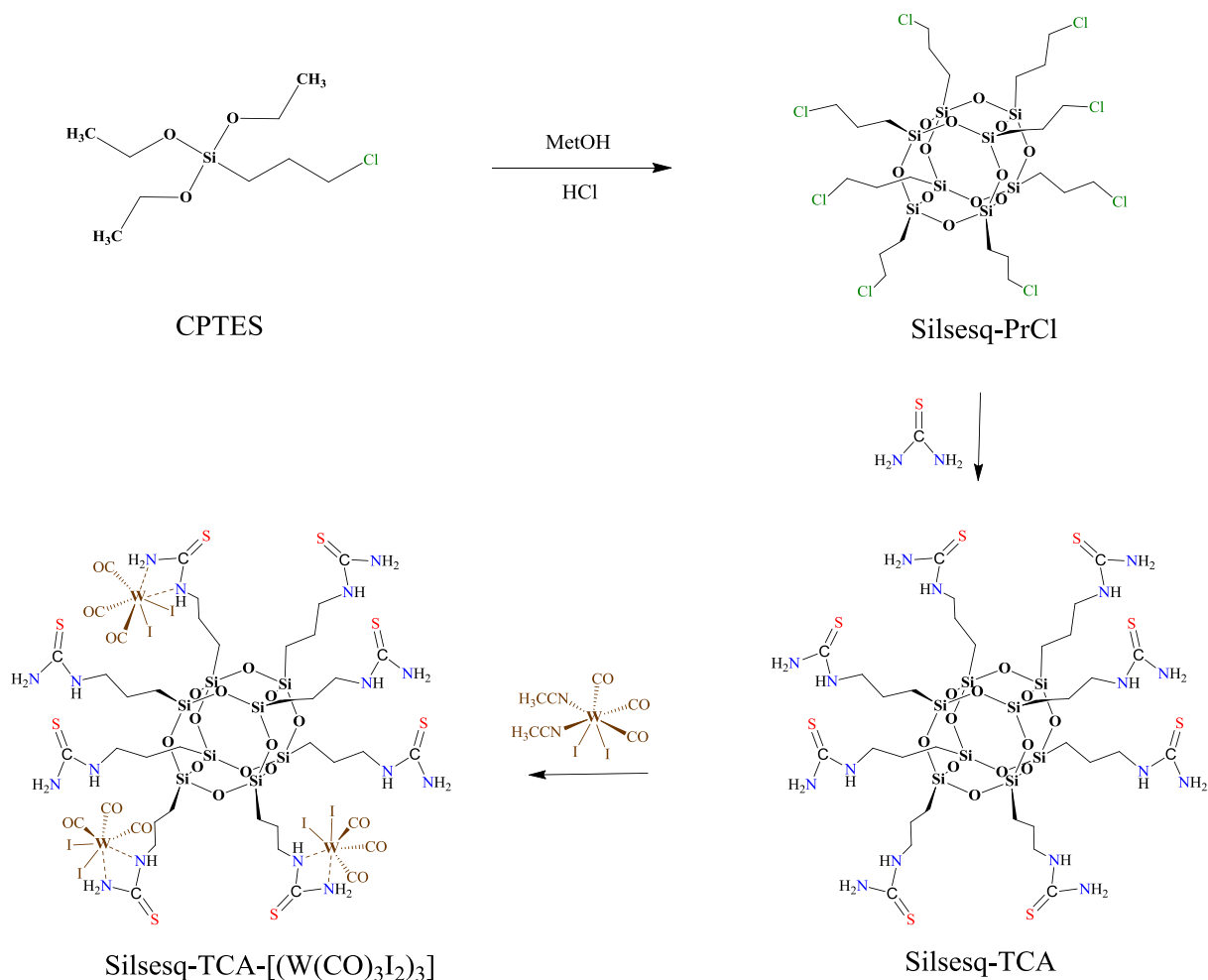
About 10 g of Silica-PrCl was added in a solution of 2.0 g of thiocarbamide dispersed in 0.70 g of NaH and in 300 mL of DMF. The suspension was shaken at $0^\circ C$ for three hours, then the temperature was increased to $80^\circ C$ and was shaken for another 48 h. The intermediate product 3-(thiocarbamide-propyl) silica gel (Silica-TCA), was filtered, washed and heated under vacuum for 10 h.

3-(thiocarbamide-propyl) silica gel (Silica-TCA) (2.0 g), was added to a solution of $[W(CO)_3I_2(NCCH_3)_2]$ (2.61 g) in pure ethanol (50 mL) under nitrogen, and the system was shaken at $25^\circ C$ over 12 h. Next, the solvent was eliminated by filtration in nitrogen atmosphere and the new catalyst was washed four times with dichloromethane and ethanol and thus, dried, giving 1.8 g of Silica-TCA- $[W(CO)_3I_2]$ (90% yield), as illustrated in Scheme 2.

2.3. Study of immobilization of $[W(CO)_3I_2(NCCH_3)_2]$ on silicon-based materials

2.3.1. Equilibrium time

The equilibrium times were studied using 120 mg of each material at temperature 298 K and under nitrogen atmosphere. The initial concentration of the complex $[W(CO)_3I_2(NCCH_3)_2]$ was 5.0×10^{-3} M in ethanol and solution volume was 50 mL for both materials. The time intervals were between 5 and 40 min for both materials, then, the materials were filtrated and the concentrations of tungsten in solution was determined.



Scheme 1. Synthesis of the Silsesq-TCA-[(W(CO)₃I₂)₃] catalyst.

2.3.2. Isotherms of immobilization

The maximum capacities of the Silsesq-TCA and Silica-TCA from ethanolic solutions were investigated at 25 °C by batch immobilization process under nitrogen atmosphere. Nearly 120 mg of each adsorbent material was added in 50 mL of solution with different concentrations of complex $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ of concentrations between 0.5×10^{-3} to 5.0×10^{-3} mol/L for Silsesq-TCA and Silica-TCA.

The previous tests showed that the equilibrium was achieved rapidly, about 20 min for Silsesq-TCA and about 30 min for Silica-TCA. The mixture was shaken for 25 min for Silsesq-Pr-TCA and 40 min for Silica-TCA, and then the solids were filtered and the amount of tungsten was analyzed by ICP-MS. The amount of adsorbed complex, N_f , in each flask was determined by the equation $N_f = (N_a - N_s)/m$. The sorption capacities of the tungsten complex for both materials were presented as sorption isotherms (N_f vs N_c).

2.3.3. Thermodynamic parameters

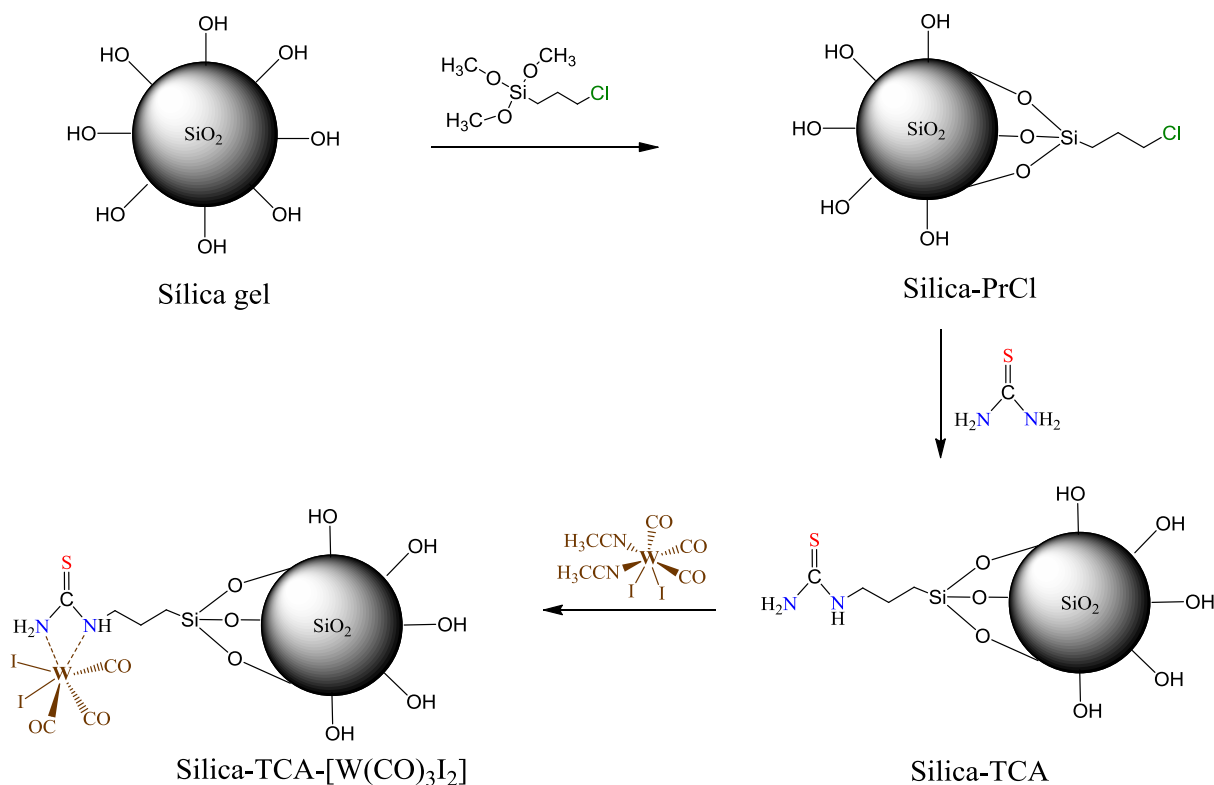
Thermodynamic studies were conducted at temperatures of 25–65 °C under nitrogen atmosphere, maintaining constant the level of the complex, the amount of adsorbent and the time in 50 mL, 120 mg and 25 min for Silsesq-TCA and 50 mL, 120 mg and 40 min for Silica-TCA, respectively [17].

2.4. Chromatographic parameters

The analyses were obtained through of a gas chromatograph coupled in a mass selective detector (Thermo Scientific) using fused silica capillary column. The carrier gas used was the helium with constant pressure mode of 70 KPa. The heating ramp of the oven was programmed varying the temperature from 60 to 200 °C (held for 2 min) at a rate of 50 °C/min. Samples of 1.5 μL were injected in a preheated inlet (250 °C) working in the splitless mode. The mass spectrometer was operated in the full scan mode in the range 30–300. To analyze of the conversion percentages, the proportion between dibutyl ether and the olefins were calculated.

2.4.1. Catalytic studies

Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂] were tested in the epoxidation of 1-octene, using tertbutyl hydroperoxide (TBHP) as oxidant at 55 °C under air atmosphere. The reactions were performed in a container with magnetic stirring and to prevent evaporation of the dichloromethane a condenser was used [17,18]. The container was loaded with 10 mmol of 1-octene, internal standard (Dibutyl ether), 0.1 mmol of homogeneous and heterogeneous catalysts, 20 mmol of oxidant and dichloromethane [17,18]. The reactions were initiated with the addition of the oxidant agent (TBHP). The samples were collected every 20 min during the first hour, then every two hours until eight hours and



Scheme 2. Synthesis of Silica-TCA-[W(CO)₃I₂] catalyst.

the last in 24 h of reaction [17,18]. To disable the oxidant agent manganese dioxide was added in each sample collected. The resulting viscous material was separated by filtration and a micro aliquot of the supernatant was injected into the GC-MS. The conversion of each substrate was evaluated by the formation of their respective epoxides in a GC-MS using the previously developed methods. Epoxidation tests without a metal catalyst were investigated and no catalytic activity was observed [17,18].

3. Results and discussion

3.1. [W(CO)₃I₂(NCCH₃)₂], [W(CO)₃I₂(TCA)], Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂]

The organometallic complex of tungsten [W(CO)₃I₂(NCCH₃)₂] is one of the most known precursors, because it possesses the advantage of replacement of nitriles with other ligands, due to the high lability of the complex [19]. Thiocarbamide is a chemically interesting compound, because it has coordinating functional groups as a nitrogen ligand that could coordinate to [W(CO)₃I₂(NCCH₃)₂], affording the stable complex [W(CO)₃I₂(TCA)].

Elemental analysis was performed for both organometallic complexes.

[W(CO)₃I₂(NCCH₃)₂]: O₃C₇H₆N₂I₂W (603.84 g/mol): calculated C 13.91%, H 1.00%, N 4.63%; found C 13.66%, H 0.91%, N 4.52%.

[W(CO)₃I₂(TCA)]: O₃C₄H₄N₂Si₂W (597.64 g/mol): calculated C 8.03%, H 0.67%, N 4.68%; found C 7.97%, H 0.59%, N 4.56%. This means that there are 1.67 mmol of thiocarbamide groups per gram of complex [W(CO)₃I₂(TCA)]₂.

Silsesq-TCA-[(W(CO)₃I₂)₃]: Si₈O₂₁C₄₁H₇₂N₁₆S₈I₆W₃ (2917.52 g/mol): calculated C 16.86%, N 7.67%, H 2.46%, W 18.90%; found C 16.56%, N 7.55%, H 2.16%, W 18.78%. The resulting product Silsesq-TCA-[(W(CO)₃I₂)₃] contained 18.78% of tungsten. This value

indicates that three tungsten units are bound to the Silsesq-TCA-[(W(CO)₃I₂)₃]. The procedure is shown in Scheme 1.

The W loading on Silica-TCA-[W(CO)₃I₂] was of 8.52% (Scheme 2). The capacity of anchoring of the complex was determined by ICP-MS and it was found a value of 0.46 mmol of tungsten groups per gram of material Silica-TCA-[W(CO)₃I₂].

The FTIR spectrum of [W(CO)₃I₂(NCCH₃)₂] shows the main absorption bands of the complex, asymmetric ν_{C≡N} bands at 2276 and 2315 cm⁻¹ and an intense stretching ν_{C=O} at 2095, 1945 and 1880 cm⁻¹.

The FTIR analysis of homogeneous catalyst ([W(CO)₃I₂(TCA)]) shows three signals in the region of 2032, 1950 and 1925 cm⁻¹. The C≡N band has disappeared after reaction with TCA ligand.

On the other hand, the FTIR spectrum of the new catalyst Silsesq-TCA-[(W(CO)₃I₂)₃] (Fig. 1A) is observed the appearance of new bands in the region of 3446, 2853, 1622, 1415, 1111 and 722 cm⁻¹ corresponding to the groups NH₂, CH₂, NH, SiCH₂, Si-O-Si, and C=S respectively. The bands SiCH₂, and CH₂ are derived of the silylating agent 3-chloropropyltriethoxysilane (CPTES), the bands of NH₂, NH and C=S from the molecule of TCA and the deformation band of Si-O-Si is characteristic and derived from silsesquioxane. The stretching ν_{C=O} bands at 2000, 1930 and 1845 cm⁻¹, confirm the immobilization of [W(CO)₃] on the POSS.

In the spectrum of Silica-TCA-[W(CO)₃I₂] (Fig. 1B) the absorption bands of ν_{C=O} is detected at 2010, 1950 and 1879 cm⁻¹, attesting the coordination of the [W(CO)₃] on silica gel. These values are also the same as in the homogeneous complex [W(CO)₃I₂(TCA)] [20].

In the ¹³C NMR spectrum of Silsesq-TCA-[(W(CO)₃I₂)₃] (Fig. 2A) three peaks are observed in 9.10 (CH₂-Si) (1), 20.85 (CH₂-CH₂Si) (2), and 39.16 ppm (CH₂-N) (3), confirming the anchoring of 3-chloropropyltrimethoxysilane. These three peaks were expected since even after a series of reactions the integrity of the organic chain was conserved. The peak at 171.85 ppm (4) region appears

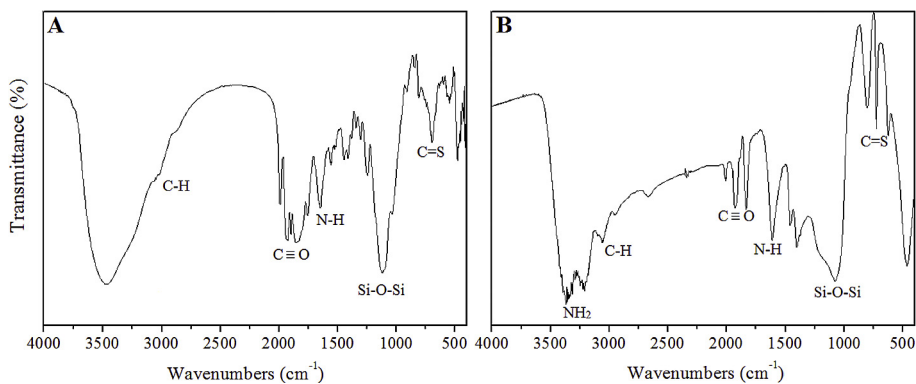


Fig. 1. FTIR spectra of Silsesq-TCA-[(W(CO)₃I₂)₃] (A) and Silica-TCA-[W(CO)₃I₂] (B).

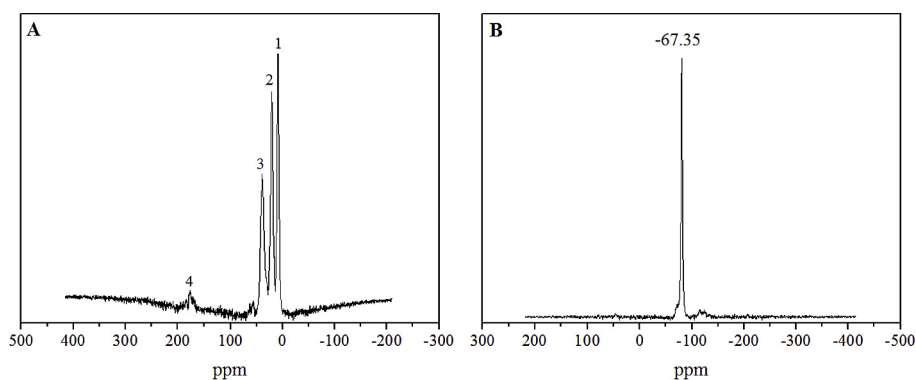


Fig. 2. ¹³C NMR spectrum of Silsesq-TCA-[(W(CO)₃I₂)₃] (A) and ²⁹Si NMR spectrum of Silsesq-TCA-[(W(CO)₃I₂)₃].

due to the incorporation of the molecule of thiocarbamide, this signal is characteristic of the carbon bonded to the sulfur present in the structure of thiocarbamide. After reaction with [W(CO)₃I₂(NCCH₃)₂] complex the resonances of the carbon atoms of the carbonyl groups of the complex are not apparent [21].

The ²⁹Si NMR solid-state spectrum of Silsesq-TCA-[(W(CO)₃I₂)₃] (Fig. 2B) shows a signal at δ -67.35 ppm, which comes in the range observed for the same compound by other authors (-66.2 to -68.0), and is typical of a T₃ species [T^m = RSi(OSi)_m(OR')_{3-m}] [22,23].

In the ¹³C NMR spectrum of Silica-TCA-[W(CO)₃I₂] (Fig. 3A) three peaks are observed in 8.03 (CH₂-Si) (1), 19.78 (CH₂-CH₂Si) (2), and 38.86 ppm (CH₂-N) (3), which are allocated to the carbon of the chain propyl of the silylating agent. The peak at 169.35 ppm (6)

region appears due to the incorporation of the molecule of thiocarbamide. After reaction with the [W(CO)₃I₂(NCCH₃)₂] the resonances peak of the carbon atoms of the carbonyl groups of the complex are not apparent, due to the absence of proton [21]. The peaks in the region of 56.87 (4) and 61.45 ppm (5) refer to the hydroxyl groups of the silica gel that unreacted during all steps of preparation of catalyst.

The ²⁹Si NMR solid-state spectrum of Silica-TCA-[W(CO)₃I₂] (Fig. 3B) shows four peaks, the two peaks in -114.42 (1) and -105.77 ppm (2) are assigned to pure surface signals and are assigned, respectively, to Si(O-Si)₃OH, corresponding to the Q³ signal; and Si(OSi)₄, corresponding to the Q⁴ signal [24]. The peak at -71.14 ppm (3) is predicted to RSi(OSi)₃ and corresponds to T³ signal. Already the peak at -61.25 ppm (4) can be assigned to the

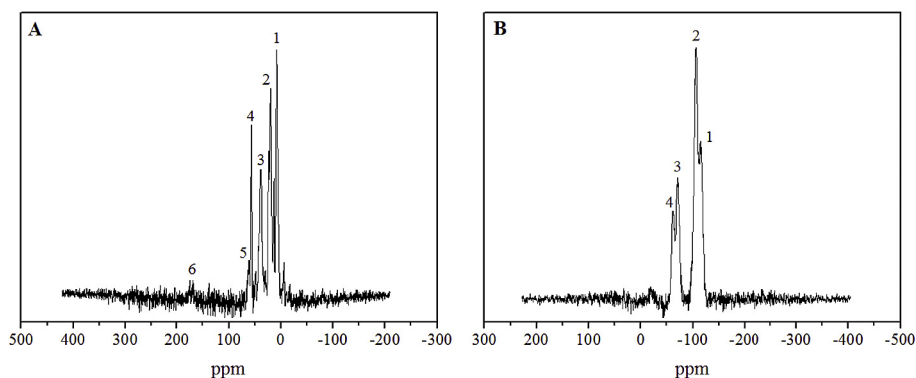


Fig. 3. ¹³C NMR spectrum of Silica-TCA-[W(CO)₃I₂] (A) and ²⁹Si NMR spectrum of Silica-TCA-[W(CO)₃I₂].

silicon atom of the silylating agent linked to a hydroxyl group, forming the structure $\text{RSi}(\text{OSi})(\text{OH})_2$. This signal is commonly referred to as T_2 signal [24,25].

Scanning electron micrographs (SEM) was performed in the heterogeneous catalyst in order to detect differences in their surfaces. The SEM images of Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ and Silica-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ are shown in Fig. 4A and B. The spheres appearance and size were similar to precursor materials, demonstrating that the surface of silsesquioxane and Silica gel have good mechanical stability and they were not destroyed during the whole reaction [26]. The surface of Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ and Silica-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ have more clusters than their starting materials. Apparently, the surface of precursor materials was smooth and became rough after the modification reactions.

The exact superficial areas of the Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ and Silica-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ were estimated by BET method (Table 1).

The relatively small value of the S_{BET} for the Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ is not estimated, since that the cubic silica core has a diameter of 0.53 nm and a spherical radius of 1–3 nm containing peripheral organic units [27]. The slow value of the S_{BET} of the Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ could have been affected by the propensity of the particles to form clusters [27]. The Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ has type IV isotherm shape with H1 hysteresis [27], typical of solids made by clusters of spherical particles of uniform size and shape. This feature is fairly typical of mesoporous solids with pore diameters in the range 2–50 nm. The absence of any micropores, the calculated average pore diameter and the relatively small S_{BET} value are in agreement with these observations.

The Silica-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ has type IV isotherm shape with a hysteresis loop style H3 [27], demonstrating that the pore dimension and shape are not well clear. This feature is frequently found for mesoporous solids containing clusters of spherical particles of fairly constant size and array, which give rise to piping pores presenting minor disparities of the cross-section along the longitudinal way.

3.2. Immobilization study of $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ on silicon-based materials

3.2.1. Immobilization isotherms of organometallic complexes

Initially, some solvents were tested in immobilization processes, such as, methanol, ethanol, water, hexane and dichloromethane. The ethanol showed the best behavior. Then, it was adopted as the medium to be used in immobilization experiments. Preliminary tests showed that the systems achieve the equilibrium condition with a quantity of adsorbent of 120 mg for both adsorbents.

Fig. 5A shows the effects of contact time for immobilization of $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ on Silsesq-TCA and Silica-TCA at 25 °C in ethanol solution. The systems achieved the equilibrium condition with a contact time of approximately 20 and 30 min for Silsesq-TCA and Silica-TCA, respectively. The immobilization rate of the Silsesq-TCA was faster than the Silica-TCA due to the immobilization sites

are much more exposed on the surface of this kind of material. The eight (thiocarbamide)propyl groups are anchored in the eight vertices of the outer surface of the silsesquioxane cube. Additionally, the silica gel has the great majority of (thiocarbamide)propyl groups anchored on the inner surface of the pores [28,29].

To investigate the immobilization capacity, a range of concentrations of the $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ in ethanol solution was shaken for 25 min for Silsesq-TCA and 40 min for Silica-TCA, using 120 mg of adsorbent at 25 °C. The maximum immobilization capacity values for $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ in ethanol solution, using Silsesq-TCA and Silica-TCA, were 1.04 and 0.45 mmol g^{-1} , respectively.

The immobilization isotherms of the organometallic complex for each material are presented in Fig. 5B. The highest values of immobilization of organometallic complex provided by Silsesq-TCA in relation to the Silica-TCA, could not be explained only by the porous structures of both materials. The greater immobilization of Silsesq-TCA could be better explained due to its larger degree of organofunctionalization. The densities of organofunctionalization of Silsesq-TCA and Silica-TCA were 5.86 and 2.14 mmol of (thiocarbamide)propyl groups per gram, respectively.

To estimate the effect of temperature, the immobilization tests were executed at five different temperatures (25, 35, 45, 55 and 65 °C). In Fig. 5C, the adsorption processes were favoured with increasing temperature, which demonstrates that the adsorption of the complex is an endothermic process.

3.2.2. Applications of isotherm models

From Fig. 5B it is possible to apply the isothermal models such as Langmuir [30], Freundlich [31,32], Temkin [33] and Dubinin-Radushchevich (D-R) [34]. The theoretical data for each model are listed in Table 2.

The Langmuir model emphasizes that the immobilization of the tungsten complex was in monolayers (homogeneous) and the anchoring the complex occurred due to the lability of acetonitrile with the atoms of nitrogen spread around the surface of the materials. It was verified also that the values of R_L (Table 2) were smaller than 1 demonstrating that the immobilization of the complex was favorable.

The parameters of the Freundlich model are shown in Table 2. The parameter n greater than 1 reflects an immobilization in multi-layered (heterogeneous) of the organometallic complex [31,32,35].

The E values obtained from the D-R model [29] (Table 2) for immobilization of the $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ on Silsesq-TCA and Silica-TCA were superior than 8 kJ/mol^{-1} , where it can be said that the immobilization of the complex was achieved by chemisorption for both materials.

Taking into account the values of the determination factors (R^2) it is notable that the order that best fits the experimental data were Langmuir > Temkin > Freundlich > D-R for Silsesq-TCA and Langmuir > D-R > Temkin > Freundlich for Silica-TCA.

The values of pseudo-first-order, pseudo-second-order and Elovich [36,37] are given in Table 3. Elovich model was the most appropriate to define the kinetic data. The determination factor of Elovich was ≥ 0.998 for both materials.

Thermodynamic parameters [38] were listed in Table 4. The negative values of ΔG indicated the spontaneous natures of immobilization of complex on the surface of Silsesq-TCA and Silica-TCA. The positive values of enthalpy change (ΔH) showed the sorptions are endothermic. The positive values of ΔS resulted from the increased randomness due to the sorption of organometallic complex.

3.3. Activity catalytic

The activity of the W-derivatized silsesquioxane and silica gel

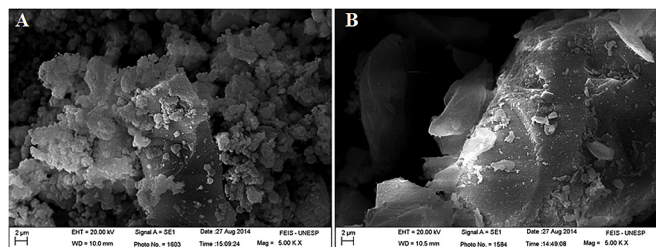


Fig. 4. SEM images for Silsesq-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ (A) and Silica-TCA- $[(\text{W}(\text{CO})_3\text{I}_2)_3]$ (B).

Table 1
Physical parameters of Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂].

Parameters	Silsesq-TCA-[(W(CO) ₃ I ₂) ₃]	Silica-TCA-[W(CO) ₃ I ₂]
BET surface area, S _{BET} (m ² g ⁻¹)	96	675
Total pore volume, V _p (cm ³ g ⁻¹)	0.61	0.35
Average pore diameter, D (nm)	410	52

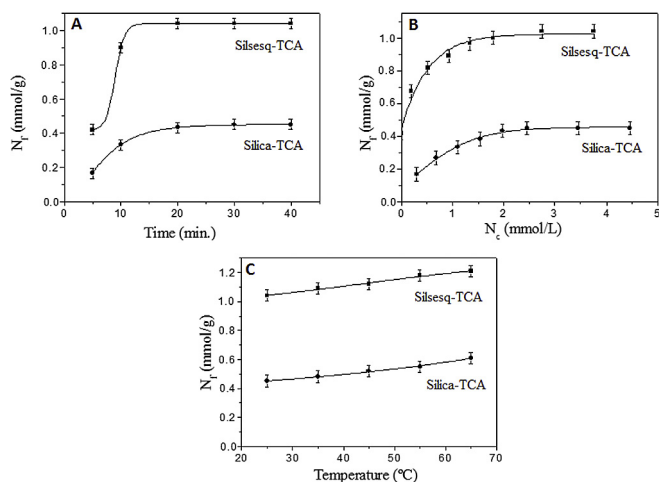


Fig. 5. Isotherms A - Effect of equilibration time, Isotherms B - Effect of concentration isotherm, and Isotherms C - Effect of temperature on the adsorption of the [W(CO)₃I₂(NCCH₃)₂].

Table 2
Isotherm parameters for sorption of organometallic complex in ethanol at 25 °C.

Adsorbent	Models	Parameters	[W(CO) ₃ I ₂ (NCCH ₃) ₂]
Silsesq-TCA	Langmuir	N _F (mmol/g)	1.07
		b (L/mmol)	8.94
		R _L	0.02
		R ²	0.998
	Freundlich	n (mol/L)	0.15
		K _F (mmol/g)	1.12
		R ²	0.967
	Temkin	A (L/mmol)	10.11
		B	0.13
		R ²	0.978
	D-R	N _F ^{max} (mmol/g)	1.01
		B ₁	0.06
E (Kj/mol)		11.78	
R ²		0.922	
Silica-TCA	Langmuir	N _F (mmol/g)	0.52
		b (L/mmol)	1.75
		R _L	0.10
		R ²	0.993
	Freundlich	n (mol/L)	0.10
		K _F (mmol/g)	1.39
		R ²	0.860
	Temkin	A (L/mmol)	8.67
		B	0.28
		R ²	0.879
	D-R	N _F ^{max} (mmol/g)	2.11
		B ₁	0.08
E (Kj/mol)		8.83	
R ²		0.974	

(Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂], respectively) as a catalyst precursor for the epoxidation of olefin were investigated for 1-octene. The same study was performed using the catalyst [W(CO)₃I₂(TCA)]. The results given in Table 5 show that both mesoporous catalysts Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂] achieve similar catalytic conversions in the

oxidation of 1-octene (72 and 68%, respectively); however, the conversion of 1-octene for homogeneous catalyst [W(CO)₃I₂(TCA)] is a little bigger. This is due to the fact that homogeneous catalysts have advantages over the heterogeneous, in particular greater selectivity and yield [18]. However, the facility with which in the heterogeneous processes products are separated and recycled, render these preferred by industry [18].

Therefore, the results presented in Table 5 shows that the heterogeneous catalysts studied in this paper combine the advantages of both types of catalysts. The same behavior was observed in the TOF values, according to the following order: [W(CO)₃I₂(TCA)] (96 mol of W⁻¹ h⁻¹), Silsesq-TCA-[(W(CO)₃I₂)₃] (86 mol of W⁻¹ h⁻¹) and Silica-TCA-[W(CO)₃I₂] (79 mol of W⁻¹ h⁻¹). In the epoxidation of 1-octene are identified two products referred to as 1-octanal and 1,2-epoxyoctane. Silsesq-TCA-[(W(CO)₃I₂)₃] has a satisfactory selectivity for formation of 1,2-epoxyoctane, 88% versus 12% for the formation of 1-octanal, whereas the Silica-TCA-[W(CO)₃I₂] has a good selectivity, 91% for 1,2-epoxyoctane and 9% for 1-octanal. On the other hand, the selectivity of the homogeneous catalyst [W(CO)₃I₂(TCA)] increases for 92% in epoxy against 8% for 1-octanal.

Table 6 shows the comparison of the catalysts prepared in this work with other types of catalysts related in the literature for the epoxidation of 1-octene. As can be seen Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂] have similar conversion capacity that their analogue not supported [W(CO)₃I₂(TCA)], and show higher conversion values than other types of catalysts in the epoxidation of 1-octene.

The advantage of newly synthesized catalytic materials is not only limited in the percentage conversion. The superiority of these catalysts based on silicon over those previously reported in the literature consists also in isolation of products of high purity with excellent yields, good reaction times, simple product separation procedure and reusability of the catalyst.

3.3.1. Study of leaching and stability

The recovery and reusability of the supported Silsesq-TCA-[(W(CO)₃I₂)₃] and Silica-TCA-[W(CO)₃I₂] catalysts were investigated in the successive epoxidation of 1-octene with TBHP as oxidant. After the first cycle the solid was separated by simple filtration, washed with dichloromethane and dried at 60 °C for reuse. The filtrates were utilized for measurement the catalysts leaching. The results displayed that only minor amounts of W catalysts were leached after the first cycle and no trace of tungsten was detected in the other cycles. As can be seen in Table 7, there was a reduction in the catalytic activity of the first to the second cycle, however, the other cycles tend to remain constant for the both catalysts and no W was detected after second cycle in the reaction mixture. This may be due to the release of the surface adsorbed W species. Also, the catalytic behavior of the separated liquid was tested by addition of fresh olefin to the filtrates after each cycle. The oxidation reaction under the same reaction conditions as when the catalyst was utilized showed that the found results are the equivalent as blank experiments.

The FTIR spectra of recycled heterogeneous catalysts showed no major change in comparison with the fresh catalysts. The

Table 3
Kinetic sorption parameters obtained using pseudo-first-order, pseudo-second-order, and Elovich models for $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$.

Sorbent	N^{EXP} (mmol/g)	Pseudo-first-order			Pseudo-second-order			Elovich		
		N^{max} (mmol/g)	K_1 (min^{-1})	R^2	N^{max} (mmol/g)	K_2 (min^{-1})	r^2	α (mmol/gmin)	B (g/mmol)	R^2
Silseq-TCA	1.04	0.54	2.24×10^{-3}	0.897	0.62	3.357	0.942	4.428	1.574	0.999
Silica-TCA	0.45	0.22	1.55×10^{-3}	0.901	0.56	1.421	0.953	3.875	1.187	0.998

Table 4
Thermodynamic parameters for $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ in ethanol.

Sorbent	t^* (°C)	ΔG° (KJ/mol)	ΔS° (J/mol K^{-1})	ΔH° (KJ/mol)
Silseq-TCA	25	-37.349	125.497	48.395
	35	-38.604		
	45	-39.859		
	55	-41.114		
	65	-42.369		
Silica-TCA	25	-28.171	94.652	34.985
	35	-29.117		
	45	-30.064		
	55	-31.010		
	65	-31.957		

* = Temperature.

absorption bands of $\nu_{\text{C}=\text{O}}$ are detected at 2020, 1950 and 1878 cm^{-1} for Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ and at 2095, 1988 and 1892 cm^{-1} for Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ confirming the strong coordination of $[\text{W}(\text{CO})_3]$ complex on the silicate materials.

The W loading on the Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ and Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ were 18.55 and 8.35% respectively. The capacity of anchoring of the complex was determined by ICP-MS and it was found a value of 1.01 mmol corresponding to about 98.8% of the starting value for the Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$, whereas for Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$, the tungsten loading was 98% corresponding to 0.454 mmol after five cycles.

4. Conclusions

The $[\text{W}(\text{CO})_3\text{I}_2(\text{NCCH}_3)_2]$ complex was immobilized on two

Table 5
Conversions and Turnover Frequencies (TOF) for epoxidation of 1-Octene promoted by Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$, Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ and $[\text{W}(\text{CO})_3\text{I}_2(\text{TCA})]$ in the presence of TBHP.

Catalytic precursor	Substrate	Conversion ^a (%)	TOF ^b
Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$	1-Octene	72	86
Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$		68	79
$[\text{W}(\text{CO})_3\text{I}_2(\text{TCA})]$		76	96

^a Conversion at 24 h.

^b In units of mol (mol of W)⁻¹ h⁻¹.

Table 6
Comparison of the conversion capacity of Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ and Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ with different catalysts in the epoxidation of 1-octene.

Catalysts	Oxidant	Conv. ^a	Ref.
Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$	TBHP	72	This work
Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$	TBHP	68	This work
$[\text{W}(\text{CO})_3\text{I}_2(\text{TCA})]$	TBHP	76	This work
MCM- $[\text{WBr}_2(\text{CO})_3(\text{C}_2\text{H}_3\text{N}_3\text{S})_2]$	TBHP	10.4	[21]
$\text{Mo}^{(\text{VI})}\text{Cl}_2\text{O}_2\text{Bipy}$	Molecular O_2	55	[39]
POSS-SB-Mo	TBHP	35	[40]
POSS-DIM3-CIM5-PW	H_2O_2	56	[41]
V-AFBNPs	TBHP	58	[42]
$[\text{MoO}_2\text{L}(\text{EtOH})]$	TBHP	64	[43]

^a Conversion (%).

Table 7
Recycling studies performed over Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ and Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ catalysts.

Catalyst	1-octene		
	Conversion (%)	Selectivity to epoxide (%)	
Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$	1° cycle	72	88 ^a
	2° cycle	67	87 ^a
	3° cycle	66	87 ^a
	4° cycle	65	86 ^a
	5° cycle	65	87 ^a
Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$	1° cycle	68	91 ^a
	2° cycle	65	91 ^a
	3° cycle	65	91 ^a
	4° cycle	64	90 ^a
	5° cycle	64	91 ^a

^a 1,2-Epoxyoctane.

silicate materials, modified with thiocarbamide, resulting in two heterogenized catalysts that were employed as highly efficient catalysts for epoxidation of 1-octene using TBHP as oxidant.

The sorption properties of the Silseq-TCA and Silica-TCA showed to be dependent of the contact time, concentration and temperature.

The Langmuir and Elovich models were the most suitable to describe the experimental data, emphasizing that the immobilization of the organometallic complex on the catalytic materials were in monolayer and by chemisorption respectively.

Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ and Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ show a high selectivity for epoxide when 1-octene olefin is used.

Silseq-TCA- $[\text{W}(\text{CO})_3\text{I}_2]_3$ showed a better conversion and TOF when compared with Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$, however, the selectivity to epoxide using Silica-TCA- $[\text{W}(\text{CO})_3\text{I}_2]$ was slightly higher.

The similar catalytic activities between heterogeneous catalysts and homogeneous species indicate that the advantages of the homogeneous systems, such as high conversion and selectivity, associated with ease of separation and recycling of the catalysts were achieved.

The reusability of these catalysts was also investigated. The obtained catalysts can be reused for at least five cycles with a slight decrease in their catalytic activity.

Conflict of interest statement

The authors declare no competing financial interest.

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