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# Zirconium doped MCM-41 supported WO<sub>3</sub> solid acid catalysts for the esterification of oleic acid with methanol

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## 1. Introduction

The abusive use of petroleum is increasing air pollution levels and accelerating global warning due to the increase in atmospheric  $CO_2$ . Recently, important efforts are being made in many countries to develop clean alternative fuels from renewable resources [1,2]. Among the potential biofuels, biodiesel derived from vegetable oil is revealing as a promising substitute for conventional diesel fuel. Furthermore, biodiesel does not contain sulphur compounds, thus leading to zero  $SO_x$  emissions after combustion. On the other hand, biodiesel is an oxygenated fuel (more than 10% oxygen), which could increase the rate of fuel combustion, reducing the production of CO and soot. However, the enhanced combustion of biodiesel increases the temperature in the engine cylinders giving rise to an increment in the  $NO_x$  emissions compared to those produced by petro–diesel.

Biodiesel consists in a mixture of alkyl esters of fatty acids formed by transesterification of vegetable oils or animal fats with methanol or ethanol [3,4]. The rate of the transesterification reaction is faster employing a base catalyst, and for this reason the industrial process uses, as catalysts, alkaline hydroxides or methoxides dissolved in methanol, under homogeneous conditions. However, this method implies some problems as the removal of the base after reaction and biodiesel purification, which generate an important volume of aqueous wastes. Heterogeneous catalysis is

# ABSTRACT

A series of zirconium doped MCM-41 silica supported WO<sub>x</sub> solid acid catalysts, with WO<sub>3</sub> loading ranging from 5 to 25 wt%, has been prepared by impregnation with ammonium metatungstate, and subsequent activation at temperatures between 450 and 800 °C. XRD, Raman and UV–vis spectroscopies have allowed us to establish that at temperatures higher than 700 °C occurs the formation of  $(WO)_x/ZrO_2$  nanoparticles on the surface of MCM-41 support, which exhibit acidic properties and are active in the esterification of oleic acid with methanol at 65 °C. WO<sub>3</sub> loadings of 15–20 wt%, after activation at 700 °C, lead to the most active catalysts, with conversion values close to 100%. The catalyst with 15 wt% WO<sub>3</sub> is stable even when the reaction is carried out at 200 °C, reusable at least during four cycles and no leaching of tungsten species in the liquid phase was found.

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preferable, since it offers an easy separation of solid catalysts from reactants and products by filtration and the possibility of using a continuous reactor operation [5–7]. Recently, we have developed new heterogeneous base catalysts, such as Mg/M (M = Al and Ca)[8], CaO stabilized in siliceous SBA-15 [9], and the system CaO/ZnO, prepared from calcium zincate dihydrate as precursor, which is very active [10].

In biodiesel production, the cost of raw materials, mainly triglycerides, represents the majority of the overall production cost. However, there are large amounts of low cost feedstock, like non-edible oils, fried waste oils and animal fats which could be converted to biodiesel, thus lowering the production costs. At the same time, the process of biodiesel production should be rendered more environmentally friendly. The problem of processing low cost feedstocks lies in their large amount of free fatty acids (FFA) that cannot be converted into biodiesel using a base catalyst [11]. Thus, neutralization of FFAs must be carried out by addition of a base excess, but this leads to the formation of soaps difficult to separate, hence requiring a high consumption of water and additional separation steps. A suitable pre-treatment for this purpose is the previous esterification of these FFAs by employing hydrochloric or sulphuric acids as catalysts, but this requires the use of corrosion-resistant materials and ulterior neutralization before the homogeneous or heterogeneous transesterification processes in the presence of a base catalyst, but this process generates large amounts of salts for subsequent environmental disposal [12].

For this reason, the use of solid acid catalysts offers many advantages; they have especially the ability to simultaneously catalyze the esterification and transesterification reactions, and many of

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them have been already reported in the literature to be active in both reactions. Thus, Nafion resins maintain high catalytic activities, although the reaction temperature must be lower than 280 °C in order to preserve resin stability [13–15]. Another solid acid catalyst very active in these reactions is sulphated zirconia, but it presents leaching of sulphur at even mild temperatures [13,16].

Tungsten oxide-based materials comprise another interesting class of acid solids, first reported as a strongly acidic system by Hino and Arata [17]. These authors found catalytic activity for isomerization of light alkanes with high cracking selectivities a lowtemperature, which depended on WO<sub>x</sub> surface density, oxidation temperature and ZrO<sub>2</sub> area [18]. The formation of superficial WO<sub>x</sub> domains on ZrO<sub>2</sub> of intermediate sizes appears to be necessary to delocalize a charge imbalance of these heteropolytungstate clusters compensated by Brönsted acid sites. The acid properties of this system are enhanced by addition of small amount of noble metal (<1 wt% Pt) due to the partial reduction of some W(VI) species, thus leading to the formation of more Brönsted acid sites in a reactant environment containing H<sub>2</sub> or hydrocarbons [19].

However, the esterification of fatty acids and the transesterification of triglycerides using acid catalysts have been scarcely studied. Furuta et al. reported that soybean oil can be converted to biodiesel at 250 °C, reaching maximum conversion when tungstated zirconia alumina activated at 800 °C is used [20]. These results are in agreement with those reported by López et al., which found 800 °C as optimum calcination temperature [21]. At higher temperatures, the formation of crystalline WO<sub>3</sub> in detrimental of heteropolytunstates clusters leads to decay in the catalytic activity. However, Ramu et al. have studied the activity of this family of catalysts in the esterification of palmitic acid with methanol and they reached the highest activities after activation at 400–500 °C, where tetragonal zirconia and amorphous tungsten oxide coexist [22].

On the other hand, the use of MCM solids as catalytic support has resulted in significant improvements for many reactions when compared to conventional and commercial catalysts. The family of mesoporous MCM-41 presents attractive properties to be used as support, such as a narrow pore size distribution, very high specific surface areas and high thermal stability [23,24]. Recently, many catalytic reactions have been successfully studied by using mesoporous pure or heteroatoms-doped silica as support of diverse active phases [25–27].

In this paper, we describe the preparation of a series of catalysts based on  $WO_x$  supported on zirconium doped mesoporous MCM-41 silica with the aim of obtaining highly dispersed  $WO_x$  on the pore walls of this support. The influence of parameters such as activation temperature and  $WO_3$  loading on the acid properties has been studied; finally, the catalytic behaviour in the esterification of oleic acid with methanol has been evaluated.

### 2. Experimental

#### 2.1. Catalysts preparation

The synthesis of a zirconium doped mesoporous silica with a Si/Zr molar ratio of 5, hereinafter Zr-MCM-41, used as support, has been previously described [28]. Before impregnation with the active phase, the support was steamed at 190 °C during 4 h to generate surface OH groups. The incorporation of tungsten species was performed by incipient wetness impregnation by using ammonium metatungstate aqueous solutions. The concentration of the precursor solution was adjusted to achieve WO<sub>3</sub> percentages in the resulting catalyst ranging between 5 and 25 wt%. After impregnation, all materials were dried at 60 °C. The influence of the activation temperature was followed by activation of the sample containing 10 wt% of WO<sub>3</sub> at several temperatures (450–800 °C) during 2 h. The

study of the different WO<sub>3</sub> loading was carried out after thermal activation at 700 °C. The catalysts were labelled as x-WO<sub>3</sub>-T, where x is the weight percentage of WO<sub>3</sub> and T the activation temperature.

#### 2.2. Characterization of catalysts

X-ray powder diffraction patterns were obtained by using an XiPert Pro MPD automated diffractometer equipped with a Ge (111) primary monochromator (strictly monochromatic Cu K<sub> $\alpha$ 1</sub> radiation) and an XiCelerator detector. UV–visible spectroscopy studies were carried out in the diffuse reflectance mode with a Shimadzu MPC3100 spectrophotometer and BaSO<sub>4</sub> as reference.

Raman spectra were recorded on a Raman Senterra (Bruker) micro-spectrometer equipped with a thermoelectrically cooled CCD detector. Excitation radiation at 532 nm was used as supplied from an Argon laser. Raman spectra were performed from powder samples without any previous treatment.

The textural parameters were evaluated from the nitrogen adsorption–desorption isotherms at -196 °C, as determined by an automatic ASAP 2020 system from Micromeritics. Prior to nitrogen adsorption, samples were evacuated at 400 °C (heating rate  $10 \,^{\circ}\text{C min}^{-1}$ ) for 1 h. Pore volume was determined with the BJH method.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was carried out to evaluate the total acidity of the catalysts. Catalysts were pre-treated at atmospheric pressure by flowing helium  $(35 \text{ mL} \text{ min}^{-1})$  from room temperature to  $550 \,^{\circ}$ C, with a heating rate of  $10 \,^{\circ}$ C min<sup>-1</sup>, and maintaining the sample at  $550 \,^{\circ}$ C for 10 min. Then, samples were cooling until  $100 \,^{\circ}$ C under a helium flow and after adsorption of ammonia at this temperature, the NH<sub>3</sub>-TPD was performed between 100 and  $550 \,^{\circ}$ C with a heating rate of  $10 \,^{\circ}$ C min<sup>-1</sup>, by using a helium flow and maintained at  $550 \,^{\circ}$ C for 15 min. The evolved ammonia was analyzed by on-line gas chromatography (Shimadzu GC-14A) provided with a TCD.

The catalytic isomerization reaction of 1-butene was performed in a tubular glass flow microreactor. Samples (70 mg) were pretreated for 2 h in a helium flow ( $30 \text{ mLmin}^{-1}$ ) at  $400 \,^{\circ}\text{C}$  and the experiments were carried out at this temperature, with a  $\tau = 67.2 \text{ g}_{\text{cat}} (\text{g}_{1-\text{but}})^{-1}$ h and time on stream of 120 min. The 1butene and the reaction products were analyzed on-line in a gas chromatograph (Shimadzu GC-14B) equipped with a wide-bore KCl/AlCl<sub>3</sub> column and provided with a FID detector.

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Al K<sub> $\alpha$ </sub> radiation (300 W, 15 kV, 1486.6 eV) with a multi-channel detector. Spectra of pelletized samples were recorded in the constant pass energy mode at 29.35 eV, using a 720  $\mu$ m diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. All recorded spectra were always fitted using Gaussian–Lorentzian curves to more accurately determine the binding energy of the different element core levels. Because the W 4f signal partially overlaps the Zr 4p signal from the support, when analysing the W 4f signal of W-containing catalysts, the contribution due to Zr 4p signal of the support was considered.

#### 2.3. Esterification of oleic acid with methanol

The esterification of oleic acid with methanol was carried out in liquid phase at atmospheric pressure. In a typical experiment, 3 mL of oleic acid was put in a 200 mL round bottom flask and then 25 mL of dry methanol was added. When the mixture of reactants was at 65 °C, 0.5 g of catalyst was added and the reaction mixture was refluxed under vigorous stirring. Aliquots (ca. 0.75 mL) were taken at different reaction times. After filtration, 0.15 mL of solution was diluted until 2 mL with 2-propanol/hexane (5:4 v/v). The resulting solution was analyzed by high performance liquid chromatography (HPLC) using a JASCO liquid chromatograph equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055), column oven (co-2065) using a PHENOMENEX LUNA C18 reversed-phase column (250 mm × 4.6 mm, 5  $\mu$ m). The solvents were filtered through a 0.45  $\mu$ m filter prior use and degassed with helium. A linear gradient from 100% methanol to 50% methanol + 50% 2-propanol/hexane (5:4 v/v) in 15 min was employed. Injection volumes of 15  $\mu$ L and a flow of rate of 1 mL min<sup>-1</sup> were used. The column temperature was held constant at 40 °C.

# 3. Results and discussion

# 3.1. Catalyst characterization

Zirconium doped MCM-41 is a mesoporous solid previously studied by different characterization techniques [28]. Thus, it was found by EXAFS that zirconium exhibits a coordination number of 7–8, compatible with a preferential location of these species at the pore surfaces. We have prepared a series of catalysts containing different WO<sub>3</sub> loading (5–25 wt%) supported on this mesoporous solid, which were also activated at different temperatures (450–800 °C).

As described in Section 2, Zr-MCM-41 was impregnated with ammonium metatungstate by using the incipient wetness method. In aqueous solutions of this ammonium salt, the following equilibrium takes place [29]:

$$W_{12}O_{41}^{10-} + 21H_2O = 12WO_4^{2-} + 14H_3O^+$$

After addition of the support to this solution, the anchoring of W(VI) oxo-species, preferentially in the monomeric form, occurs on the support surface. After calcination, the polymerization of monomeric units by formation of W–O–W bridges leads to  $(WO)_x$  clusters. When these  $(WO)_x$  clusters are supported on  $ZrO_2$  the resulting system can accommodate protons due to the existence of the negative charges delocalizated across the extended W–O network, similarly to that observed for heteropolyacids [30–32].

The X-ray diffractograms at high angle of the catalysts containing 10 wt% of WO<sub>3</sub> after activation at different temperatures (Fig. 1) point to the existence of two groups of samples; the first one formed by catalysts activated between 450 and 700 °C, whose X-ray patterns only present the typical broad band of amorphous silica walls



Fig. 1. XRD patterns of catalysts with 10 wt% of WO<sub>3</sub>, activated at different temperatures.



Fig. 2. XRD patterns of catalysts with different WO\_3 loadings, after activation at 700  $^\circ\text{C}.$ 

of the mesoporous MCM-41 solid, whereas the second group corresponds to samples activated at higher temperatures. These XRD patterns exhibit broad reflections at  $2\theta = 29.9^{\circ}$ ,  $34.4^{\circ}$ ,  $50.3^{\circ}$  and  $60.0^{\circ}$ , characteristics of tetragonal ZrO<sub>2</sub>. Since pure Zr-MCM-41 is thermally stable even after calcination at 900 °C, the presence of these reflections clearly indicates that at high temperatures exists a strong interaction between (WO)<sub>x</sub> and the support, leading to the extraction of ZrO<sub>2</sub> from the mesoporous support. However, in this series of catalysts, the diffraction peaks of WO<sub>3</sub> are not observable, revealing a good dispersion of this phase. After thermal activation of the catalysts, the mesoporous structure of the support is maintained since DRX patterns at low angles show a broad and intense peak centred at  $2\theta = 2^{\circ}$ , similar to the pristine support.

Fig. 2 exhibits the diffraction patterns of catalysts after activation at 700 °C. Among these diffractograms, only those corresponding to samples containing WO<sub>3</sub> loading above 10 wt% present peaks at 23.1°, 23.6° and 24.6°, which are associated to WO<sub>3</sub>, together with the peaks of tetragonal zirconia. These results demonstrate that the interaction between  $(WO)_x$  and superficial ZrO<sub>2</sub> on the pores of Zr-MCM-41 is very strong, especially at high activation temperatures and for high WO<sub>3</sub> loading, leading to the extraction of this superficial zirconia and the formation of  $(WO)_x/ZrO_2$  nanoparticles together with crystalline WO<sub>3</sub>. This strong interaction between  $(WO)_x$  and zirconia has been already observed by López et al. for a catalyst containing 16 wt% of WO<sub>3</sub> after calcination at temperatures above 750 °C, where the formation of crystalline WO<sub>3</sub> was found, being the interaction between  $(WO)_x$  and the support strong enough to prevent the transformation of tetragonal zirconia into the monoclinic form [21]. This behaviour is different to that found for a similar system formed by WO<sub>3</sub> supported on Zr doped SBA-15, where the catalyst is stable after calcination at high temperatures and no segregation of ZrO<sub>2</sub> particles is observed [33].

The presence of pure WO<sub>3</sub> particles on the support surface for catalysts with WO<sub>3</sub> loading higher than 10 wt% could be explained by taking into account that Zr-MCM-41 contains only 21.5 wt% of ZrO<sub>2</sub>, and, for WO<sub>3</sub> loading of 15 wt% or higher, there is an excess of active phase in comparison with conventional catalysts prepared supporting this phase on pure zirconia, where a WO<sub>3</sub> loading of 16 wt% already favours the formation of crystalline WO<sub>3</sub> at high activation temperatures [21,32].

UV-vis diffuse reflectance absorption spectra of catalysts containing different WO<sub>3</sub> loading and activated at 700 °C (Fig. 3) show a sharp absorption between 210 and 260 nm due to the ligand to metal charge transfer ( $O_{2p}$ -W<sub>5d</sub>- $O_{2p}$ ), being both tetrahedral and

![](_page_3_Figure_1.jpeg)

Fig. 3. Diffuse reflectance UV-vis absorption spectra of the catalysts with WO\_3 loadings of 5–25 wt% after activation at 700  $^\circ\text{C}.$ 

octahedral W(VI) species responsible of these absorptions [34,35]. The mesoporous support also absorbs at 210 nm. On the other hand, a broad band between 300 and 330 nm appears in all catalysts, which becomes more intense and shifts to the red with increasing the WO<sub>3</sub> loading. This band could be assigned to the formation of two-dimensional polytungstate on zirconia by W–O–W bonds between well dispersed (WO)<sub>x</sub> species. These extended domains of W–O–W leads to a narrowing of the HOMO–LUMO gap [36]. The tail of these spectra at 350 nm could correspond to the microcrystalline WO<sub>3</sub>.

The catalysts with 10 wt% of WO<sub>3</sub>, activated at different temperatures, show similar spectra, i.e., containing the same absorption at 210 and 260 nm, whereas that at 300–330 nm shifts to low energies. Therefore, an increasing of the activation temperature and the WO<sub>3</sub> loading favour the extraction of ZrO<sub>2</sub> from the pore walls and the formation of (WO)<sub>x</sub>/ZrO<sub>2</sub> nanoparticles or microcrystalline WO<sub>3</sub> on the support surface. Both effects tend to increase the (WO)<sub>x</sub> density and domain size.

Raman spectra of catalysts with different WO<sub>3</sub> loading and activated at 700 °C are shown in Fig. 4. In all cases, a Raman feature at 1019 cm<sup>-1</sup> is observed which is assigned to the symmetric stretching mode of terminal W=O bonds present in monotungstate and polytungstates (WO<sub>x</sub>) species at the surface of ZrO<sub>2</sub> [37]. WO<sub>x</sub>

![](_page_3_Figure_6.jpeg)

 $\begin{array}{l} \textbf{Fig. 4.} \\ Raman \ spectra \ of \ catalysts \ activated \ at \ 700 \ ^\circC: \ bulk \ WO_3 \ (a), 5 \ wt\% \ WO_3 \ (b), \\ 10 \ wt\% \ WO_3 \ (c), 15 \ wt\% \ WO_3 \ (d), 20 \ wt\% \ WO_3 \ (e) \ and \ 25 \ wt\% \ WO_3 \ (f). \end{array}$ 

species also exhibit Raman bands below  $680 \, \text{cm}^{-1}$ , but overlapping with those from zirconia. At the same time, bands corresponding to crystalline WO<sub>3</sub> appear at 807, 720 and 273 cm<sup>-1</sup>, assigned to W–O stretching, W–O bending and W–O–W deformation modes, respectively [38]. Raman scattering cross section for crystalline WO<sub>3</sub> are much intense than for surface polytungstate species, as a result those bands dominate the spectra, even being the polytngstate species the most abundant [39]. These results are in agreement with those found by XRD and UV–vis spectroscopy where the presence of diffraction lines of WO<sub>3</sub> and red-shifted absorptions were observed for loadings higher than 15%. However, the Raman spectra reveal that in all the catalysts the formation of crystalline WO<sub>3</sub> is detected, but their crystal sizes in catalysts with low WO<sub>3</sub> loading are below the detection limit of the X-ray diffraction technique.

In order to get information about the chemical state of tungsten in these compounds, XPS spectra of catalysts have been obtained. The binding energy values corresponding to the Zr 3d, Si 2p and O 2s appear at 182.5, 103.5 and 532.7 eV, respectively, in accordance with the values previously found by Eliche-Quesada et al. for this support [40]. All XPS spectra in the W 4f region are similar to that shown in Fig. 5. The core level spectrum displays two overlapped peaks corresponding to W 4f  $_{7/2}$  and W 4f  $_{5/2}$  with binding energies of 36.0 and 37.8 eV, respectively. From these values and the difference in energy, it can be inferred the exclusive presence of W(VI), thus precluding the existence of W(V) [41,42]. However, some authors have found this oxidation state for tungsten, owing to its partial reduction during the calcination step, possibly by oxygen losing from the framework [43,44].

On the other hand, superficial W/Zr atomic ratios of catalysts have been calculated from XPS measurements. The theoretical W/Zr bulk ratio for the catalysts with 10 wt% of WO<sub>3</sub> is 0.20; however, for the catalysts with this WO<sub>3</sub> loading and activated at different temperatures (Table 1) the surface W/Zr atomic ratios vary between 0.12 and 0.18. These results reveal a good dispersion of the active phase, and a superficial enrichment of tungsten which is favoured at high activation temperatures, due to the formation of polytungstates or WO<sub>3</sub>, as can be inferred from XRD, Raman and UV-vis absorption data. For catalysts with different WO<sub>3</sub> loadings and activated at 700 °C, only surface W/Zr atomic ratios are lower than the theoretical ones for catalysts with 5 and 10 wt% of WO<sub>3</sub>. For catalysts with higher loadings, both theoretical and surface W/Zr atomic ratios match well, indicating that, for high loadings and after activation at 700 °C, the formation of these polytungstates and WO<sub>3</sub> is more easily accomplished.

![](_page_3_Figure_11.jpeg)

Fig. 5. W 4f core level spectrum of the 15-WO<sub>3</sub>-700 catalyst.

![](_page_4_Figure_1.jpeg)

Fig. 6. NH<sub>3</sub>-TPD of catalysts with 10 wt% of WO<sub>3</sub>, activated at different temperatures (A) and catalysts with different WO<sub>3</sub> loadings, activated at 700 C (B).

Table 1W/Zr atomic ratios, obtained from XPS analysis, of catalysts.

Catalyst	W/Zr atomic ratio
5-WO <sub>3</sub> -700	0.10
10-WO <sub>3</sub> -700	0.16
15-WO <sub>3</sub> -700	0.32
20-WO <sub>3</sub> -700	0.45
25-WO <sub>3</sub> -700	0.63
10-WO <sub>3</sub> -450	0.12
10-WO <sub>3</sub> -550	0.13
10-WO <sub>3</sub> -650	0.16
10-WO <sub>3</sub> -700	0.16
10-WO <sub>3</sub> -750	0.18

The textural parameters of the support and catalysts are compiled in Table 2. The nitrogen adsorption isotherms are of Type IV in the IUPAC classification and similar to that observed in the case of the support. However, the incorporation of the active phase progressive decreases the amount of nitrogen adsorbed, and the specific surface area and pore volume were lower to those corresponding to the mesoporous support. This decrease could be

#### Table 2

Catalyst	$S_{\rm BET} (m^2g^{-1})$	$V_{\rm p}~({\rm cm^3g^{-1}})$	$d_{\rm p}({\rm \AA})$	Acidity (µmol NH3 des/m <sup>2</sup> )
Zr-MCM-41	535	0.62	46.4	1.01
10-WO <sub>3</sub> -450	442	0.56	57.3	1.05
10-WO <sub>3</sub> -550	524	0.69	52.7	1.13
10-WO <sub>3</sub> -650	403	0.54	53.6	1.00
10-WO <sub>3</sub> -700	355	0.49	55.2	0.99
10-WO <sub>3</sub> -750	330	0.56	67.9	0.93
10-WO <sub>3</sub> -800	253	0.45	71.1	1.00
5-WO <sub>3</sub> -700 10-WO <sub>3</sub> -700 15-WO <sub>3</sub> -700 20-WO <sub>3</sub> -700 25-WO <sub>3</sub> -700	414 355 328 254 224	0.59 0.49 0.45 0.39 0.37	57.3 55.2 55.1 61.8 66.7	1.04 0.99 1.24 1.58 1.49

attributed to the presence of nanoparticles of  $(WO)_x/ZrO_2$  in the pores and on external surface, which are partially blocking the access to mesopores. Therefore, the greater is the activation temperature and the WO<sub>3</sub> loading the greater the decrease in the textural parameters. Nevertheless, the average pore diameters became larger for catalysts activated at 750 and 800 °C and for those having 20–25 wt% of WO<sub>3</sub>, which could be attributed to the generation of additional porosity associated to  $(WO)_x/ZrO_2$  and WO<sub>3</sub> particles located on the external surface of support, as previously observed for other supported phases [45–47].

The acid properties of this family of catalysts were evaluated by NH<sub>3</sub>-TPD, and the results obtained for catalysts with 10 wt% of WO<sub>3</sub> and activated at different temperatures are plotted in Fig. 6A. As can been observed, the total acidity of these catalysts decreases when the activation temperature rises. The extraction of zirconia and the subsequent formation of  $(WO)_x/ZrO_2$  nanoparticles located on the external surface hinders the access of ammonia molecules to the pores. On the other hand, this decrease in the surface acidity is parallel to that of the surface area values. Table 2 also display the acidity values, expressed as µmol of NH3 desorbed per surface unit (square meter), for this series of catalysts, which are close to one for all of them. However, the acid properties of catalysts with different WO<sub>3</sub> loading show a different variation (Fig. 6B). In fact, these acidity values became higher for catalysts with greater WO<sub>3</sub> loading. That means that the  $(WO)_x/ZrO_2$  nanoparticles, which increase with the WO<sub>3</sub> content, as deduced from XRD, Raman and UV-vis spectroscopies, could contribute to the total acidity.

By considering that the esterification reaction of an organic acid with an alcohol via heterogeneous catalysis is primarily catalyzed by protons, it is interesting to study the behaviour of this family of acid catalysts in the 1-butene isomerization reaction in order to gain insights about the strength of their Brönsted acid sites [21]. The isomerization of 1-butene can occur through a first step consisting in a double bond shifting, giving *cis*- and *trans*-2-butenes, which easily reaches the thermodynamic equilibrium and needs strong acid sites with Hammett function of  $0.82 > H_0 > -4.04$  [48]. In a second step, methyl migration gives rise to *iso*-butene or *iso*-butane. Table 3

<ul> <li>Butene isomerization data obtained at 400 °C</li> </ul>	C, after 2 h of time on stream.
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Catalyst	Conversion (%)	Cis-2-butene (%)	Trans-2-butene (%)	Iso-butene (%)
5-WO <sub>3</sub> -700	67.4	40.9	56.9	2.2
10-WO <sub>3</sub> -700	67.9	40.9	54.3	4.8
15-WO <sub>3</sub> -700	77.4	40.0	51.8	8.3
20-WO <sub>3</sub> -700	70.5	40.5	55.4	4.2
25-WO <sub>3</sub> -700	70.1	39.8	53.9	6.4
10-WO <sub>3</sub> -800	67.1	42.1	54.8	3.1
10-WO <sub>3</sub> -750	68.9	40.9	51.2	7.9
10-WO <sub>3</sub> -700	67.9	40.9	54.3	4.8
10-WO <sub>3</sub> -550	69.3	40.6	54.1	5.3

This second isomerization requires stronger acid sites ( $H_0 < -6.63$ ) and the reaction takes place on Brönsted acid sites via carbenium ion intermediates in a three-step mechanism [49].

The experimental values, obtained after 2 h of time on stream at 400 °C, reveal that all catalysts are active in this reaction, being more selective toward the formation of double bond isomerization products, indicating the presence of Brönsted acid sites of mild strength (Table 3). The highest conversion and selectivity toward *iso*-butene are found for catalysts with WO<sub>3</sub> contents of 15 and 20 wt%, thus being the most acid catalysts. These catalysts are also those presenting high acidity expressed as µmol of NH<sub>3</sub> desorbed per square meter (Table 2).

#### 3.2. Esterification of oleic acid with methanol

This family of acid catalysts has been tested in the esterification of oleic acid with methanol at 65 °C. The amount of catalyst used was 18.7 wt% with respect to the weight of oleic acid and the methanol/oleic acid/molar ratio was 67. The evolution of the conversion against reaction time is shown in Fig. 7 for catalysts containing different WO<sub>3</sub> contents, activated at 700 °C. From this plot, it can be deduced that the reaction rate is low under the selected experimental conditions, since 24h are necessary to attain high conversions. Moreover, it is noteworthy that only catalysts activated at 700 and 750 °C reached high conversion, with values of 67%, after 24 h (Fig. 8). From these results, an activation temperature of 700 °C was selected to activate the other catalysts with different WO<sub>3</sub> loading. Conversions close to 100% are only reached for catalysts with WO<sub>3</sub> loading higher than 10 wt% (Fig. 9), after 24 h of reaction time. The selectivity of the reaction toward methyl ester was always 100%.

These results suggest that the catalytic behaviour depends on both the thermal activation of catalysts and the WO<sub>3</sub> loading. Concerning the activation temperature, only catalysts with 10 wt% of WO<sub>3</sub> activated at temperatures higher than 700 °C are quite active.

![](_page_5_Figure_9.jpeg)

![](_page_5_Figure_10.jpeg)

![](_page_5_Figure_11.jpeg)

**Fig. 8.** Influence of the activation temperature on the conversion for catalysts with 10 wt% of WO<sub>3</sub> (reaction conditions: methanol/oleic acid molar ratio=67, catalyst = 18.7 wt% and T = 65 °C, reaction time = 24 h).

That means that at these temperatures occurs the extraction of superficial  $ZrO_2$  with the concomitant formation of  $(WO)_x/ZrO_2$  nanoparticles, which  $(WO)_x$  surface density is suitable to generate Brönsted acid sites able to catalyze the esterification reaction. However, an activation temperature of 800 °C decreases the conversion, possibly due to the loss of OH groups in the process of formation of crystalline WO<sub>3</sub> which is inactive, according to Barton et al. [31]. These authors have demonstrated that in WO<sub>3</sub> domains a fraction of the protons are located inside the WO<sub>3</sub> crystals, thus being inaccessible to the reactant molecules.

On the other hand, the conversion depends on the WO<sub>3</sub> loading; in fact, only catalysts containing 15–25 wt% of WO<sub>3</sub> are very active. This fact points out that the formation of  $(WO)_x/ZrO_2$  nanoparticles, after thermal activation at 700 °C, is important when the WO<sub>3</sub> loading increases, as deduced from XRD patterns where diffraction peaks of ZrO<sub>2</sub> were observable together with those of crystalline

![](_page_5_Figure_15.jpeg)

**Fig. 9.** Evolution of the conversion for catalysts with different WO<sub>3</sub> loadings and activated at 700 °C (reaction conditions: methanol/oleic acid molar ratio = 67, catalyst = 18.7 wt% and T = 65 °C, reaction time = 24 h).

 $WO_3$ . The high conversion observed for these catalysts is expected by considering the high acidity deduced from  $NH_3$ -TPD and the formation of *iso*-butene in the isomerization of 1-butene, thus revealing as the most acid catalysts. However, for the catalyst with 25 wt% of WO<sub>3</sub> the conversion is lower, possibly due to the presence of crystalline WO<sub>3</sub> phase. It is necessary to consider, as previously noted, that Zr-MCM-41 contains only 21.5 wt% of ZrO<sub>2</sub>, and thus a 25 wt% of WO<sub>3</sub> loading represents an important excess and as a consequence tungsten may be as crystalline WO<sub>3</sub>, which is not active.

The catalytic behaviour of our family of catalysts could be explained by taking into account both the different catalyst preparation method and the nature of the vegetable oil used, since, for instance, Ramu et al. [22] studied the esterification of palmitic acid with methanol. These authors found the higher catalytic activity after activation of the catalysts at 400-500 °C. Thus, the different behaviour could be attributed to the different nature of the support employed. The use of the Zr-MCM-41 support requires high temperatures and high WO<sub>3</sub> loadings to generate the  $(WO)_x/ZrO_2$ nanoparticles, which are active in this esterification reaction. However, in both works, the maximum TOF attained is very similar and close to  $0.8 \text{ mmol } h^{-1} \text{ g}_{cat}^{-1}$ . Nevertheless, our esterification results are better than those reported by Kim and co-workers [50] in the esterification of palmitic acid with methanol (TOF of  $0.06 \text{ mmol } h^{-1} \text{ g}_{cat}^{-1}$ ), which can be explained by considering that these authors accomplished the esterification of oleic acid with methanol in the presence of an excess of soybean oil, and the transesterification reaction also takes place. On the other hand, in general, it is difficult to compare our results with those reported in literature, because the experimental conditions employed in each case are different, such as the reaction temperature [51]. Our catalysts exhibit similar catalytic activity than those reported by Furuta et al. [20] with similar conversion after 20 h, but working in the last case at reaction temperatures ranging between 175 and 200 °C. Rao et al. prepared a series of catalysts by a surface grafting method of  $(WO)_x$  on zirconium phosphate [52], which exhibited excellent activity and high TOF (21.9 mmol  $h^{-1}$  g<sub>cat</sub><sup>-1</sup>), presenting potential application in industrial biodiesel production, but this system is different to a tungstated zirconia, being more comparable to a supported heteropolyacid.

Finally, to improve the catalytic activity of these catalysts, especially to reduce the reaction time, the influence of the catalyst amount and the reaction temperature on the catalytic performance have been evaluated. Thus, by increasing the amount of catalyst up to 37.4 wt%, the conversion is 80% after 15 h of reaction. However, more significant is the effect of the reaction temperature, since at 200 °C, using only 18.7 wt% of catalysts, the conversion is close to 100% after 4 h of reaction.

A key aspect in the preparation of biodiesel is the evaluation of the degree of lixiviation of the active phase. With this purpose we have analyzed by ICP the filtered liquids after the reaction of esterification of oleic acid with methanol at  $200 \,^{\circ}$ C and the amount of W found in solution is lower than 0.3 ppm, pointing to that lixiviation is negligible.

On the other hand, we have studied the influence of the water on the reaction of esterification by adding 5.5 wt% of water to the reactants at 200 °C. The conversion was maintained close to 97%, pointing to that water is not adsorbed on the active centres and oleic acid molecules can approach to produce the esterification reaction.

Moreover, the catalyst reutilization is a key parameter to consider the viability of a solid catalyst for biodiesel production, since it can reduce the overall process costs. In order to evaluate the reusability of this family of catalysts, the 15-WO<sub>3</sub>-700 catalyst was repeatedly used for the esterification of oleic acid with methanol at 200 °C. After a first catalytic run, the catalyst was filtered and reused without any treatment, such as washing or calcination. This experiment was repeated four times and in all cases the conversion was maintained close to 97%, thus revealing that catalysts are very stable against lixiviation and poisoning, even under drastic experimental conditions.

Therefore, these active catalysts, based on  $(WO)_x/ZrO_2$  as active phase, are potential candidates to catalyze the transesterification reaction of vegetable oils with methanol, and, at high temperatures (200 °C), it could be thought that they could simultaneously favour both reactions, the esterification of FFAs and the transesterification of used oils with methanol in a single step, thus suggesting their potential industrial applications in biodiesel preparation from low cost feedstocks like used cooking oils.

# 4. Conclusions

The use of Zr-MCM-41 as a support for the preparation of catalysts containing WO<sub>3</sub> leads to the segregation of  $(WO)_x/ZrO_2$ nanoparticles when the catalyst precursors are activated at temperatures higher than 700 °C, and especially for high WO<sub>3</sub> loading. These nanoparticles are acid, as deduced from NH<sub>3</sub>-TPD and the isomerization reaction of 1-butene, and they are active in the esterification reaction of oleic acid with methanol at 65 °C. The catalysts with WO<sub>3</sub> loading of 15 and 20 wt%, after thermal activation at 700 °C, are the most active, giving rise to conversions close to 100%. The catalyst with 15 wt% WO<sub>3</sub> is stable even when the reaction is run at 200 °C, reusable at least during four cycles and no leaching of tungsten species in the liquid phase was found.

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