

Biodiesel production from sunflower oil by tungsten oxide supported on zirconium doped MCM-41 silica

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ABSTRACT

A series of zirconium doped MCM-41 silica supported WO_x solid acid catalysts, with WO_3 loading ranging from 5 to 25 wt%, has been prepared by impregnation with ammonium metatungstate. After activation at 700 °C, these catalysts are active in the transesterification of sunflower oil with methanol at 200 °C, with a biodiesel yield higher than 80% after 2.5 h of reaction. The maximum activity (82 wt% of FAME yield) is found for the catalyst with 15 wt% WO_3 loading, which is able to simultaneously catalyze the esterification and transesterification of simulated used oils, with an acidity degree as high as 9.1%. Moreover, this catalytic activity is maintained in the presence of 5 wt% of water and after three cycles of reutilisation, without any treatment of the catalyst.

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1. Introduction

Biodiesel is a non-petroleum based fuel consisting of fatty acid alkyl esters derived from the transesterification of vegetable oils or animal fats with alcohols of low molecular weight, which has been revealed as a promising alternative to petro-diesel, thus helping to overcome limited fossil fuel resources and environmental concerns. In recent years, the interest in biodiesel has increased due to new legislation constraints requiring a major reduction in vehicles emissions. Biodiesel is recognized as a “green fuel” as it is a safe, renewable, non-toxic, and biodegradable material [1]. Furthermore, biodiesel is an oxygenated fuel (more than 10% oxygen) which ameliorates fuel combustion, and does not contain sulphur compounds, thus leading to zero SO_x emissions, and significant reductions in hydrocarbons, CO and soot present in the exhaust gases, after combustion [2]. An additional advantage is that biodiesel may be blended with conventional diesel, and can be used in conventional diesel engines without any or minor modifications [3]. However, the cost of triglycerides, used as raw materials for biodiesel production, represents an important drawback for the economical feasibility of biodiesel as alternative fuel. This aspect could be improved by using low cost feedstocks, like used cooking oils or animal fats, but these feedstocks often contain large quanti-

ties of free fatty acids (FFAs) and water, making them unsuitable for the homogeneous alkaline catalyzed process due to the formation of soaps [4].

Liquid acid catalysts are not recommended as they need longer reaction time and require the use of corrosion-resistant materials [5]. However, carrying out the transesterification reaction under heterogeneous conditions, in the presence of solid catalysts, could greatly simplify the technological process; in this case, catalysts can be easily separated by filtration from reactants and products and offers the possibility of using a continuous reactor operation. Several reviews on the use of heterogeneous either acid or base catalysts for biodiesel production have been published [6–11]. We have recently developed new families of solid catalysts based on CaO supported on SBA-15 [12] and thermally treated calcium zincate dihydrate [13], which have shown to be very active in the transesterification of sunflower oil with methanol, although in the latter case, and in spite of its excellent kinetic behaviour, they suffer from deactivation in the presence of free fatty acids and water. This is the reason why, in many cases, the use of heterogeneous base catalysts requires a first step that consists in the neutralization of free fatty acids.

In this context the use of solid acid catalysts could help to overcome this problem since they are able to simultaneously catalyze the transesterification of vegetable oils and the esterification of free fatty acids [14]. Thus, strong solid acid catalysts, such as sulfated zirconia and Nafion resins, are able to carry out transesterification reactions with methanol [15–17], although the former suffers from

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deactivation even at low temperature (60 °C), possibly due to the sulphur leaching [15,18], and the later can be only used at temperatures below 280 °C to preserve resin stability [16]. On the other hand, tungsten oxide-based materials comprise another interesting class of acid solids, reported as strongly acidic by Hino and Arata [19] for the first time. The catalytic activity of these catalysts has been described to depend on the WO_x surface density, activation temperature and ZrO_2 area. Thus, the formation of superficial WO_x domains of intermediate size on ZrO_2 appears to be necessary to delocalize a charge imbalance of these heteropolytungstate clusters, which is compensated by Brønsted acid sites [20,21].

Furuta et al. [22,23] have reported that soybean oil can be transformed into biodiesel at 250 °C with maximum conversion, by using a tungstated zirconia–alumina activated at 800 °C. These results are in agreement with those reported by López et al. [24], who found 800 °C as the optimum activation temperature for transesterification of triacetin. However, Ramu et al. [25] have studied the activity of this family of catalysts in the esterification of palmitic acid with methanol and they found that the maximum activity was achieved after activation at 400–500 °C, where tetragonal zirconia and amorphous tungsten oxide coexist. Park et al. [26] have employed pellet-type WO_3/ZrO_2 catalysts for the esterification of oleic acid with methanol in a continuous flow process at 75–200 °C; at the steady state, conversions were close to 70% in a 140 h durability test. These authors also used this kind of catalysts for the esterification of a waste acid oil with methanol at 150 °C, obtaining 96% of conversion after 2 h reaction time [27].

As regards to the support of the active phase, ordered mesoporous silica presents significant advantages with respect to conventional porous solids, owing to its high specific surface area, large pore size and thermal stability [28–30]. Moreover, the incorporation of heteroatoms into the siliceous framework allows to render to this mesoporous solid into acid material which can then be employed as catalysts or supports of active phases for different catalytic reactions, as is the case of zirconium doped mesoporous MCM-41 silica [31–33].

In this paper, we present the results of the transesterification of sunflower oil with methanol in the presence of WO_3 supported on Zr-MCM-41 catalysts, with different WO_3 loadings and activated at 700 °C. The influence of experimental parameters, such as reaction time, percentage of catalyst, methanol/oil molar ratio, presence of free fatty acids and water and reutilisation of the catalyst, on the catalytic behaviour has been evaluated in order to optimize experimental conditions for biodiesel production.

2. Experimental

2.1. Catalyst preparation

The synthesis and characterization of a zirconium doped mesoporous silica with a Si/Zr molar ratio of 5 (Zr-MCM-41), used as support, has been previously reported [34]. Before impregnation of the active phase, the support was steamed at 190 °C during 4 h to generate surface –OH bonds, thus facilitating the anchoring of the active phase. The incorporation of tungsten species was performed by incipient wetness impregnation using aqueous solutions of ammonium metatungstate. The concentration of the precursor solution was adjusted to give rise to catalysts with WO_3 percentages ranging between 5 and 25 wt%. After impregnation, all materials were dried at 60 °C and then activated at 700 °C during 2 h. This activation temperature has been selected since it was the most effective for this family of catalysts previously employed in the esterification of oleic acid with methanol [35]. The catalysts were labelled as x - WO_3 where x is the weight percentage of WO_3 .

2.2. Characterization techniques

Textural parameters were evaluated from nitrogen adsorption–desorption isotherms at –196 °C, as determined by an automatic ASAP 2020 system from Micromeritics. Temperature-programmed desorption of ammonia (NH_3 -TPD), previously adsorbed at 100 °C, was carried out from room temperature to 550 °C, with a heating rate of 10 °C min^{-1} and maintaining the sample at 550 °C for 15 min. The evolved ammonia was analyzed by online gas chromatography (Shimadzu GC-14A) provided with a TCD. The 1-butene isomerization reaction was performed in a tubular glass flow microreactor. Samples (70 mg) were pretreated for 2 h in a helium flow (30 mL min^{-1}) at 400 °C, and experiments were carried out at this temperature ($\tau = 67.2 g_{cat} (g_{1-but})^{-1} h$ and 120 min of time on stream). The 1-butene reactant and the reaction products were analyzed by an on-line gas chromatograph (Shimadzu GC-14B) equipped with a wide-bore KCl/AlCl₃ column and provided with a FID detector.

2.3. Catalytic test

The methanolysis of edible sunflower oil was performed at 200 °C by using a Parr high pressure reactor with 100 mL capacity and a stirring rate of 600 rpm. Before reaction, catalysts were activated at 700 °C during 2 h. In a typical experiment, 15 g of oil was incorporated to the reactor together with the methanol and 1.5 g of catalyst. The methanol/oil molar ratio was 12. After 7 h of reaction, the system was cooled and then an aliquot (2 mL) was taken and treated with 1 mL of distilled water and shaking for few minutes. Later, 1 mL of dichloromethane was added, and this mixture was again agitated and set aside to develop two phases: the non-polar phase containing dichloromethane, mono-, di- and triglycerides and methyl esters of fatty acids (FAME) (and traces of methanol and glycerol) and the polar phase containing water, glycerol and methanol (and traces of esters). The dichloromethane was then removed from the organic phase by evaporation at 90 °C. 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 μm). The solvents were filtered through a 0.45 μm 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 35 min was employed. Injection volumes of 15 μL and a flow of rate of 1 mL min^{-1} were used. The column temperature was held constant at 40 °C. All samples were dissolved in 2-propanol–hexane (5:4 v/v). The weight content in FAME determined by HPLC was considered to represent the FAME yield (in wt%) of the catalytic process, assuming that, during the neutralization and the washing process of the ester phase, only traces of esters were transferred to the polar phase and that only the extraction of methanol and glycerol take place.

3. Results and discussion

3.1. Catalyst characterization

Zirconium doped MCM-41 silica, with a Si/Zr molar ratio of 5 (21.5 wt% of Zr) is a mesoporous solid, which has been previously studied by different characterization techniques [34]. Thus, it was found by EXAFS that zirconium exhibits a coordination number of 7–8, which is compatible with the preferential location of these species on the pore surfaces. In a previous paper, we have studied the catalytic properties of a new family of catalysts, based on WO_x

Table 1
Textural and acid properties of WO₃ supported on Zr-MCM-41 silica.

Catalyst	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	d (Å)	Acidity (μmol NH ₃ g ⁻¹)	Acidity/S _{BET} (μmol NH ₃ /m ²)
Zr-MCM-41	535	0.62	46.4	548	1.0
5-WO ₃	414	0.59	57.3	430	1.0
10-WO ₃	355	0.49	55.2	353	1.0
15-WO ₃	328	0.45	55.1	405	1.2
20-WO ₃	254	0.39	61.8	400	1.6
25-WO ₃	224	0.37	66.7	335	1.5

supported on this zirconium doped mesoporous MCM-41 silica, in the esterification of oleic acid with methanol [35]. The characterization of these catalysts by several techniques revealed the existence of nanoparticles of WO_x/ZrO₂ formed during the thermal activation of the catalysts at 700 °C, mainly located onto the pore walls. The (WO)_x surface density of these particles can accommodate a proton neutralizing the negative charge delocalized across an extended W–O network, resulting in an electronic structure similar to those of heteropolyacids [20,21,36]. However, the mesoporous structure of the support is preserved after the thermal treatment, as deduced from the XRD data at low diffraction angles, where the reflection at 2θ ~ 2° is still observed. This behaviour is different from that reported for a similar system formed by WO₃ supported on Zr doped SBA-15 [37], since, after calcination at high temperatures, the segregation of WO₃/ZrO₂ particles was not observed; the support is stable with well dispersed WO₃ on the pore walls, for a loading of 0.20 g of WO₃ per gram of support. This means that the structure of Zr-SBA-15 is more stable than that of Zr-MCM-41, as already was observed for catalysts based on calcium oxide supported on both MCM-41 and SBA-15 silicas [12].

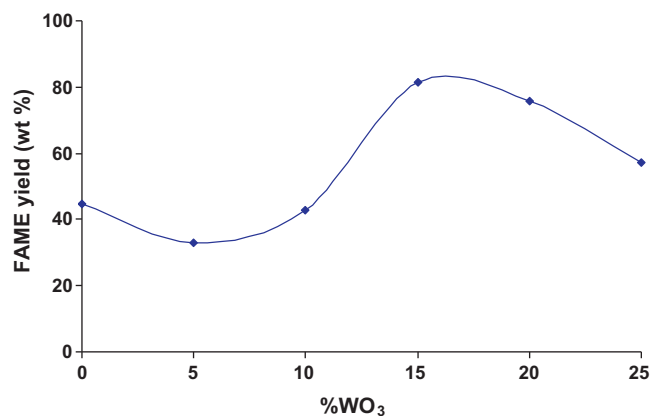
The incorporation of the WO_x species into the pores leads to a decrease in both the specific surface area and the acidity of these catalysts with respect to those of the support (535 m² g⁻¹ and 548 μmol NH₃ g⁻¹, respectively) (Table 1). However, the acidity per surface unit increases with the tungsten loading. It is worth keeping in mind that ammonia desorption allows to determine the total acidity of catalysts, i.e., Brønsted and Lewis acid centres. Although it is well established in the literature that the Lewis acid sites are the major responsible for the transesterification reaction, the contribution of Brønsted acid sites is also widely recognized to be important, so the effective acidity of catalysts has been determined by using the isomerisation reaction of 1-butene at 400 °C, since only Brønsted acid sites with medium and strong strength are active in this reaction [38,39]. Among all the catalysts, the 15-WO₃ is the most active in this reaction since it exhibits the highest conversion and the maximum yield of isobutene, being revealed as the most acid catalyst with the strongest acid sites (Table 2). At the same time, this catalyst exhibits the highest amount of ammonia desorbed.

3.2. Transesterification process

The catalytic performance in the transesterification of sunflower oil with methanol of WO₃-based catalysts has been initially evaluated under the following experimental conditions: 10 wt%

Table 2
1-butene isomerization data at 400 °C, obtained with x-WO₃ catalysts.

Catalyst	Conv. (%)	Cis-2-butene yield (%)	Trans-2-butene yield (%)	Iso-butene yield (%)
Zr-MCM-41	65.6	27.0	36.1	2.4
5-WO ₃ -700	67.4	27.4	38.1	1.5
10-WO ₃ -700	67.9	27.8	36.9	3.3
15-WO ₃ -700	77.4	31.0	40.1	6.4
20-WO ₃ -700	70.5	28.6	39.0	2.9
25-WO ₃ -700	70.1	27.9	37.8	4.4

**Fig. 1.** Evolution of the FAME yield in the transesterification of sunflower oil with methanol for catalysts with different WO₃ loading and activated at 700 °C (reaction conditions: methanol/oil molar ratio = 12, catalyst = 1.5 g, stirring rate = 600 rpm, T = 200 °C and reaction time = 7 h).

of catalyst with respect to the oil weight, methanol/oil molar ratio = 12, reaction temperature = 200 °C, stirring rate = 600 rpm and reaction time = 7 h. The evolution of the FAME yield as a function of the WO₃ loading (Fig. 1) reveals that a maximum value of 82% is attained with the 15 wt% WO₃ catalyst, which could be attributed to a more suitable dispersion of WO_x/ZrO₂ nanoparticles on the surface of the mesoporous support. The other compounds formed in the catalytic reaction were mono- and diglycerides. The decrease in the conversion observed for loadings higher than 15 wt% could be explained by taking into account that Zr-MCM-41 contains only 21.5 wt% of ZrO₂, and a 25 wt% of WO₃ loading represents an important excess and consequently tungsten may be as crystalline WO₃ particles. These WO₃ particles lack acidity because they are not interacting with zirconia [21], being inactive in the transesterification reaction. Table 3 summarizes the sunflower oil conversion and the TOF values for this series of catalysts. The maximum values correspond to the 15-WO₃ catalyst with a 97.6% of oil conversion and a TOF of 1.65 × 10⁻² molecules of FAME formed per minute and acid site. The contribution of the uncatalyzed thermal reaction has been also measured under similar experimental conditions, and, after 7 h of reaction at 200 °C, the value found for the biodiesel formation was 38 wt%.

The catalytic performance in the transesterification reaction of this series of catalysts matches well with the acidity studies, which revealed that the 15-WO₃ catalyst was the most acid solid, especially in the 1-butene isomerization reaction (Table 2). On the other hand, it must be noted that the 15-WO₃ catalyst is quite effective in the transesterification reaction specially if we consider the reaction temperature (200 °C), which is lower than that used by Furuta et al. [22,23] for the transesterification of soybean oil with methanol (250–300 °C). The 15-WO₃ catalyst is also more active than those based on WO₃/ZrO₂ previously reported by Jacobson et al. [40], which, at 200 °C, only attained 67% of conversion of a waste cooking oil containing 15 wt% of free fatty acids, after 10 h of reaction; in

Table 3
Catalytic activity of x-WO₃ catalysts in the transesterification of sunflower oil with methanol at 200 °C.

Catalyst	Oil conversion (%)	TOF (×10 ² molecules FAME min ⁻¹ acid site ⁻¹)
5-WO ₃	64.1	6.3
10-WO ₃	66.5	9.9
15-WO ₃	97.6	16.5
20-WO ₃	97.0	15.5
25-WO ₃	87.6	13.7

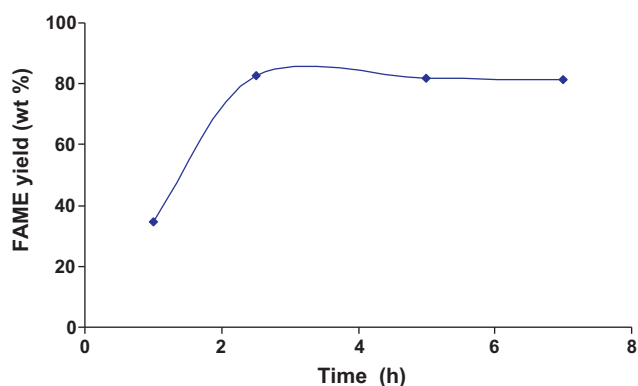


Fig. 2. Evolution of the FAME yield in the methanolysis of sunflower oil of the 15-WO₃ catalyst as a function of the reaction time (reaction conditions: methanol/oil molar ratio = 12, catalyst = 1.5 g, stirring rate = 600 rpm, T = 200 °C).

this case, the average activity value is similar ($2.1 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$), but the authors do not report any contribution of the uncatalyzed reaction. Nevertheless, our catalytic results are difficult to compare with those obtained by López et al. [24,41] in the transesterification of tricaprilyn with ethanol by using a tungstated zirconia activated at 800 °C, since they used a temperature as low as 120 °C for the transesterification reaction.

The influence of different experimental parameters on the biodiesel formation from sunflower oil has been accomplished by using the 15-WO₃ catalyst, which has demonstrated to be the most active among the series of prepared catalysts. Thus, the reutilisation of solid catalysts is a key property in the study of biodiesel production, under heterogeneous conditions, as it reduces the process cost by making unnecessary the subsequent neutralization and washing steps. To analyze this reusability, the 15-WO₃ catalyst was employed for various cycles of methanolysis of sunflower oil. For this purpose, after each catalytic run, the catalyst was eliminated by filtration and reused in a new cycle without any treatment, such as washing or calcination. The results obtained show that this catalyst can be reused for three cycles without loss of catalytic activity since the biodiesel formation decreases only 7% after the first run and then the conversion into FAME is maintained.

The stability of the 15-WO₃ catalyst has been also tested against the presence of water in the oil, by adding 5 wt% of water to the reactants. The FAME formation is maintained (82%), thus revealing that water molecules are not preferentially adsorbed on the catalyst surface, which could hinder the access of reactant molecules to the active sites. The water adsorption on the acid sites would form a layer around protons, and consequently not only the strength of acid sites is weakened but also these clusters become less hydrophobic, making it more difficult for the hydrophobic oil molecules to approach them and causing the catalyst deactivation.

On the other hand, another key point to take into account in the biodiesel production is the evaluation of the degree of leaching of the active phase. With this goal, we have determined the possible leaching of the active phase by analyzing the presence of W in the filtered solution, after the transesterification reaction at 200 °C, by ICP. The results reveal that leaching is negligible since the concentration of tungsten found is lower than 0.3 ppm.

Other interesting aspect to be studied is the reaction time, since high biodiesel yield must be reached in a short time to make heterogeneous process competitive with the industrial homogeneous one. It can be shown in Fig. 2 that a steady state with 82 wt% of biodiesel formation is achieved after 2.5 h. Therefore, the 15-WO₃

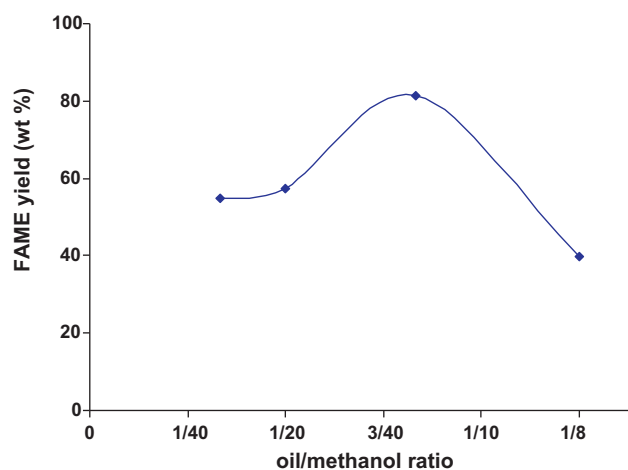


Fig. 3. Influence of the oil/methanol molar ratio on the transesterification of sunflower oil with methanol over the 15-WO₃ catalyst (reaction conditions: catalyst = 1.5 g, stirring rate = 600 rpm, T = 200 °C and reaction time = 7 h).

catalyst is not only active at 200 °C but it also requires a quite short time to give rise high FAME yields. After 2.5 h of reaction, the contribution of the uncatalyzed reaction to the FAME formation was only 16 wt%.

The influence of the methanol/sunflower oil molar ratio on the FAME yield was also evaluated (Fig. 3). The highest conversion to methyl esters was obtained for a methanol:sunflower molar ratio of 12/1, i.e., four times the stoichiometric molar ratio. Since both forward and reverse transesterification reactions could follow a second order reaction for alcohol-to-oil mole ratio lower than 30/1, these results indicate that a high concentration of methanol is necessary to increase the rate of reaction [5,42]. On the other hand, it is assumed that the ester is chemisorbed on the active acid sites where the carbonyl group would form a carbonium ion. Thus, when the concentration of methanol is in excess the approach of methanol to the carbocation enhances the conversion; however, an ulterior increment of this ratio leads to a decrease in the conversion, possibly, due to the flooding of active sites with alcohol molecules rather than ester molecules, similarly to that occurs in the esterification reaction of FFAs [43].

The study of the influence of the amount of catalyst has demonstrated that a maximum FAME yield of 92% is achieved when 13.3 wt% of catalyst with respect to the weight of oil, with a methanol/oil molar ratio of 12/1.

Finally, one of the most important aspects to be considered in biodiesel production is the ability of a solid catalyst to simultaneously give the esterification of free fatty acids and the transesterification of triglycerides, in order to allow the use of used vegetable oils as feedstock. With this purpose, a waste oil was simulated by adding several quantities of oleic acid to 10 g of sunflower oil, thus reproducing oils with acidity degrees ranging between 2.9° and 9.1° (defined as g of oleic acid per 100 g of oil). The results obtained reveal that the 15-WO₃ catalyst is able to fully accomplish both reactions with biodiesel yield close to 100%, even for an acidity degree of 9.1°. Interestingly, the maximum FAME formation was maintained even in the presence of an acidity degree of 9.1 and 5 wt% of water. Therefore, this family of catalysts could catalyze the production of biodiesel from used oils, avoiding the previous step of FFAs esterification. This step is necessary in the case of base homogeneous catalysis where the presence of FFAs can suppose a source of soaps and, under heterogeneous conditions, it would lead to a partial neutralization of the solid base catalyst and the formation of soaps.

4. Conclusions

The incorporation of WO_x species on a mesoporous zirconium-doped silica leads to the formation of WO_x/ZrO_2 nanoparticles with acid properties. The catalyst with WO_3 loading of 15 wt% is the most active, maintaining its activity after three reaction cycles and being able to simultaneously produce the esterification of FFAs and the transesterification of triglycerides present in a used oil, with an acidity degree of 9.1° , at temperatures as low as 200°C , in a short time and even in the presence of 5 wt% of water.

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