Ultrasonic enhancement of the acidity, surface area and free fatty acids esterification catalytic activity of sulphated ZrO₂–TiO₂ systems

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A B S T R A C T

Different samples of sulphated zirconia and mixed zirconia/titania (SO_4^{2-}/ZrO_2 and $SO_4^{2-}/80\%ZrO_2$ $-20\%TiO_2$) were prepared with traditional- and ultrasound (US)-assisted sol–gel synthesis and tested in the free fatty acids esterification. The catalysts were characterized through acid sites quantification by ion exchange, specific surface area and porosity measurements (N_2 adsorption at 77 K), XRD, XPS and FT-IR spectroscopy. SEM–EDX and TEM analyses were also used to investigate the morphology of the samples. The results of this study demonstrate the possibility of increasing the acidity and the surface area of sulphated zirconia through the addition of TiO_2 and tune the same properties with the continuous or pulsed US. It is also demonstrated that it is necessary to combine specific values of both acidity and surface area and which type of active sites are essential to obtain better catalytic performances in the free fatty acids esterification.

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1. Introduction

Biodiesel is becoming increasingly important as an alternative fuel for diesel engines as a consequence of the diminishment of petroleum reserves and as part of the effort to save the global environment.

Biodiesel is the biofuel obtained from the biomass derived from lipid feedstock. The most common process used to convert lipids, that is, triglycerides, into biodiesel is the transesterification reaction [1,2]. Transesterification is a process where triglycerides contained in vegetable oils or animal fats react with an alcohol, usually methanol, yielding fatty acid methyl esters (FAMEs) and glycerol in presence of an alkaline catalyst [3]. The main problem posed by the use of alkaline catalysts is represented by the obligation of using feedstock with very low acidity (<0.5 wt.%). In fact, free fatty acids (FFAs) contained in raw oils give saponification problems as a consequence of their reaction with the alkaline catalyst (RCOOH + NaOH → RCOONa + H₂O). The presence of soaps during the transesterification hinders the contact between reagents and makes difficult the separation of the products. Refined, low acidity

oilseeds may be easily converted into biodiesel, but their employment not only significantly raises the production costs but also increases food and water demands [1]. It is so highly desirable to produce biodiesel from specifically selected non-edible cultures or from low-cost feedstock such as used cooking oils and animal fats [2,4,5]. The main issue posed by such raw materials is the need of standardization, especially with regard to the decrease in the acidity, so to avoid saponification reactions. In fact, crude oils and not refined greases in general are characterized by very high acidities, ranging from 3 to 40 wt.% [6].

In recent years, a great deal of attention has been focused on the study of the pre-esterification as a method to lower the acidity of the raw oils to be used for biodiesel production [5,7–10]. The esterification reaction of FFA also allows to improve the final yield in biodiesel as the obtained products are FAME, that is, biodiesel, as represented in the Scheme 1. The esterification reaction can be performed using both homogeneous [11,12] and heterogeneous catalysis [13,14]. For liquid-phase reactions, the latter approach is preferred as it brings benefits such as the easier separation of the catalyst from the products, thus facilitating catalyst recovery and reuse. Much attention has been focused on the use of ion exchange acid resins as catalysts for the FFA esterification reaction [5,7–10]. A significant outcome of these studies lies in the correlation between the catalytic activity of the tested catalysts with the acidity

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$$C_nH_mCOOH + CH_3OH \xrightleftharpoons{\text{acid catalysis}} C_nH_mCOOCH_3 + H_2O$$
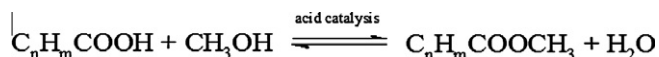
Scheme 1. Esterification reaction of a carboxylic acid with methanol.

present on the catalyst outer surface regardless of the nature of adopted catalysts [10].

As an alternative to the ion exchange resins, inorganic acid catalysts, such as zirconium sulphate and sulphated zirconia, can be used. These materials are active because of the presence at the surface of both Brønsted acidic centres and Lewis acid sites (i.e., coordinatively unsaturated (*cus*) Zr^{4+} cations), as evidenced by Morterra et al. [15]. Zirconium sulphate has been widely studied for the FFA esterification reaction [10,16] due to its high activity. Sulphated zirconia is widely studied for other different kinds of reactions, such as isomerizations, alkylations and esterification of other carboxylic acids [18], but its use for FFA esterification directly performed in the oil is reported in few studies [17].

In the present work, mixed zirconium and titanium sulphated oxides ($SO_4^{2-}/80\%ZrO_2-20\%TiO_2$) are reported as potential catalysts for the FFA esterification reaction to be performed directly in the crude oil to be used for biodiesel production. The results of this study demonstrate the possibility of increasing the surface acidity of the catalysts with the addition of TiO_2 to the ZrO_2 and the use of US during the catalysts synthesis. The effect of different power intensities and the use of pulsed US are also investigated. The beneficial effects of acoustic cavitation on catalysts properties are already clearly reported in some recent papers [19–21]. It has also been shown in the current study that how it is possible to modulate catalysts features, such as the acidity and the surface area, employing different experimental conditions during the US-assisted synthesis.

2. Experimental

2.1. Catalysts preparation

All the catalysts were synthesized using the sol–gel method. SO_4^{2-}/ZrO_2 (hereafter referred to as SZ) was synthesized using traditional sol–gel method, while $SO_4^{2-}/80\%ZrO_2-20\%TiO_2$ (hereafter referred to as SZT) was synthesized using both traditional and US-assisted sol–gel techniques. Zirconium tetra-n-propoxide (ZTNP) and titanium tetra-iso-propoxide (TTIP) were used as precursors in all the cases. i-PrOH was used as a solvent in all the synthesis with a molar ratio to the precursors (ZTNP+TTIP) equal to 15 [18,19]. Molar ratio between water and the alkoxides (ZTNP+TTIP) was kept constant at 30 as already reported elsewhere [18] in the traditional syntheses and varied in the ones with US. $(NH_4)_2SO_4$

was used as sulphating agent, keeping the molar ratio SO_4/Zr or $SO_4/Zr+Ti$ constant at 0.15 in all the cases [18].

Nitric acid was used to promote the hydrolysis of the precursors, as already reported in other works from the authors [18,19]. The molar ratio HNO_3/Zr or $HNO_3/Zr+Ti$ was kept constant at 0.21 [18].

A list of all the samples along with different synthesis parameters is provided in Table 1. Samples termed USZT refer to US-obtained sulphated $80\%ZrO_2-20\%TiO_2$. The name is followed by the US power, by the length of US pulses and by the molar ratio of water over precursors, as reported in Table 1. For example, USZT_40_0.1_30 indicates a sample $SO_4^{2-}/80\%ZrO_2-20\%TiO_2$ obtained with US, using the 40% of the maximum power, with US on for 0.1 s (pulse length) and off for 0.9 s, using a water/ZTNP+TTIP molar ratio equal to 30.

ZTNP 70% in 1-PrOH, TTIP 98%, i-PrOH, HNO_3 69.5 wt.% and $(NH_4)_2SO_4$ were used and are all Fluka products.

In the case of traditional sol–gel method, the starting solution was prepared by mixing 1.23 ml of TTIP and 5.52 ml of ZTNP with 25 ml of the solvent (i-PrOH) for 30 min in a bath thermostated at 298 K, stirring at 300 rpm through a mechanical stirrer. The aqueous solution containing the sulphating agent and HNO_3 was then added to the mixture at the rate of 0.25 ml/min. After finishing the addition, the gel was left ageing for additional 90 min under stirring.

In the case of US synthesis, a 20 kHz horn sonicator was used. The tip of the horn was placed inside the sol–gel mixture in a 100-ml water-jacketed reactor. The power was varied at 20% and 40% of amplitude of the maximum power (450 W). Also, US pulses were adopted for some syntheses.

For what concerns the US syntheses, as in the case of the traditional synthesis, the starting solutions were prepared by mixing the precursors with the solvent and stirring them for 30 min. After the mixing, the solutions were thermostated at 298 K and the aqueous solution containing the sulphating agent and HNO_3 was added at the rate of 0.25 ml/min. After finishing the addition of the aqueous solution, the gel was left ageing for additional 10 min under US irradiation.

The total synthesis time reported in Table 1 indicates the time required to perform the whole sol–gel process, while the sonication time indicates the fraction of the total synthesis time while US were functioning. As an example, consider entry 4 in Table 1. The total synthesis time is 43′0″, which is the sum of the time required for the addition of the aqueous solution to one of the precursors at a rate of 0.25 ml/min and 10 min for the ageing. Since the US was powered in pulse mode with on/off ratio 9:1, the actual sonication time is given by $(1/10) \cdot 43''0'$, that is, 4′18″.

The temperature was monitored during the course of the ultrasonic synthetic experiments. The temperature increased up to

Table 1
List of all samples and of employed synthesis parameters (max. power = 450 W).

Entry	Sample	Composition	US power (% max power)	Pulses (on/off)	H$_2$O: prec. mol ratio	Synthesis time	Sonication time
1	SZ	SO_4^{2-}/ZrO_2	–	–	30	123′0″	0″
2	SZT	$SO_4^{2-}/80\%ZrO_2 - 20\%TiO_2$	–	–		123′0″	0″
2a	SZT_773_6h		–	–		123′0″	0″
3	USZT_20_1_30		20	1		43′0″	43′0″
4	USZT_40_0.1_30		40	0.1/0.9		43′0″	4′18″
5	USZT_40_0.3_30			0.3/0.7		43′0″	12′54″
6	USZT_40_0.5_7.5			0.5/0.5	7.5	17′30″	8′45″
7	USZT_40_0.5_15				15	26′0″	13′0″
8	USZT_40_0.5_30				30	43′0″	21′30″
9	USZT_40_0.5_60				60	77′0″	38′30″
10	USZT_40_0.7_30			0.7/0.3	30	43′0″	30′6″
11	USZT_40_1_15			1	15	26′0″	26′0″
12	USZT_40_1_30				30	43′0″	43′0″