

## Nanosized and Reusable SiO<sub>2</sub>/ZrO<sub>2</sub> Catalyst for Highly Efficient Biodiesel Production by Soybean Transesterification

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O catalisador nanoestruturado SiO<sub>2</sub>/ZrO<sub>2</sub> foi preparado pelo método sol-gel e apresentou uma área superficial de 131,50 ± 14 m<sup>2</sup> g<sup>-1</sup>. As imagens de microscopia eletrônica de varredura mostraram que o catalisador apresentou partículas muito homogêneas de 250 nm de diâmetro. Este material foi aplicado na transesterificação do óleo de soja para a produção de biodiesel. A conversão do óleo em biodiesel teve um rendimento de 96,2 ± 1,4 % em 3 h de reação de transesterificação catalisada pelo material SiO<sub>2</sub>/ZrO<sub>2</sub> (SiZr). O catalisador foi recuperado e reutilizado por seis vezes, mantendo uma eficiência catalítica de 84,1%.

Nanosized SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst with high surface area (131.50 ± 14 m<sup>2</sup> g<sup>-1</sup>) was prepared by the sol-gel method. The material presented highly homogeneous particles with an average diameter of 250 nm according to SEM images. It was applied in the transesterification of soybean oil for biodiesel production. The biodiesel conversion reached a yield of 96.2 ± 1.4 % after 3 h of transesterification reaction catalysed by SiO<sub>2</sub>/ZrO<sub>2</sub> (SiZr). The catalyst was recovered and reused six times, maintaining a catalytic efficiency of about 84.1 %.

**Keywords:** transesterification, biodiesel, silica, zirconium

### Introduction

Fuels developed from renewable feedstocks (methane, ethanol, biodiesel, diesel-like, biogasoline) have presented advantages such as low emissions. Among these alternative fuels, fatty acid methyl or ethyl esters, known as biodiesel, are produced from renewable vegetable or animal fats and oils.<sup>1-6</sup> This eco-friendly fuel is oxygenated and almost free of sulfur, making it a cleaner burning fuel than petroleum diesel, with reduced emissions of SO<sub>x</sub>, CO<sub>x</sub>, unburnt hydrocarbons and particulate matter.<sup>7-8</sup> Thus, biodiesel is a green fuel that can replace fossil fuels in order to reduce greenhouse gas emissions, as plants, during photosynthesis, can make use of the CO<sub>2</sub> generated from its combustion.

Generally, sodium or potassium hydroxides are used as catalysts when producing biodiesel.<sup>9</sup> However, the application of hydroxides in the transesterification of vegetable oils produces soaps by neutralization of the free fatty acid in the oil and by triglyceride saponification.<sup>9</sup> Thus, removal of these catalysts is technically difficult

and brings extra cost to the final product purification.<sup>10,11</sup> In order to minimize these problems, heterogeneous catalytic systems have been developed to produce biodiesel by transesterification, with the advantages of not leading to triglyceride saponification and of allowing easy separation of the catalyst from the product.<sup>9,12,13</sup> In this way, the present investigation reports a synthetic route to produce nanosized SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst and its application in the transesterification of vegetable oil.

### Experimental

The catalyst was synthesized via a sol-gel method, using tetraethylorthosilicate (TEOS) (ACROS) and ZrOCl<sub>2</sub> (Aldrich) as the SiO<sub>2</sub> and ZrO<sub>2</sub> sources respectively. 66.6 g of TEOS were added to 300 mL of ethanol and received the addition of 2 mL of HNO<sub>3</sub> for pre-hydrolysis. The mixture was maintained under vigorous stirring for 30 min and then 50 mL of an aqueous solution containing 15 g of ZrOCl<sub>2</sub> were added dropwise at 50 °C to produce SiO<sub>2</sub>/ZrO<sub>2</sub> in the mol % ratio of 80/20. Stirring was continued for 120 min to promote hydrolysis and condensation. After

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condensation, the resulting gel was placed in an autoclave and heated at 150 °C for 24 h. The resulting material was dried and calcined at 550 °C for 4 h to produce the catalyst named SiZr.<sup>14</sup>

#### Characterization of SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst

The elemental analysis of the mixed oxide was carried out after treatment of the sample (0.5 g) with HF 40% for complete solubilization.<sup>15</sup> The amounts of Si and Zr were determined with the use of a Varian Liberty RL Series II inductively coupled plasma-optical emission spectrometer (ICP-OES).

Scanning electron microscopy (SEM) images were acquired on a Zeiss EVO50 microscope. The samples were coated with carbon using a Bal-Tec SCD-050 sputtering system. The equipment was operated at 20 keV.

The surface area was measured on a Quantachrome Nova 2200 analyzer. The infrared spectrum of the catalyst in KBr pellets was registered on a MB-100 Bomem FTIR spectrophotometer using 60 scans.

Surface acid sites were determined by infrared spectroscopy, with pyridine as a molecular probe. The materials were allowed to react with a dry pyridine atmosphere at normal pressure for 4 h. The pyridine excess was then removed under vacuum at room temperature for 10 h.<sup>16</sup>

#### Transesterification

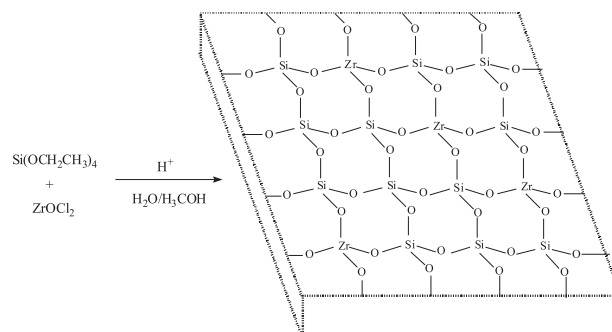
Transesterification reactions were carried out using 10.0 g of soybean oil, 1.5 g of methanol and different amounts of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst (0.1, 0.3, 0.5 and 0.7 g). The mixture was stirred at 50 °C for different periods of time.<sup>17</sup> A three-phase system was obtained, containing the solid catalyst and two liquid phases. After filtering, the upper liquid phase was separated by decantation, washed with brine, dried with anhydrous magnesium sulfate and filtered. By using a method previously published,<sup>18</sup> the recovered product was analyzed by HPLC on a Shimadzu CTO-20A chromatograph with an UV-VIS detector ( $\lambda = 205$  nm) equipped with a Shim-Pack VP-ODS column (C-18, 250 mm, 4.6 mm id).

## Results and Discussion

#### Catalyst characterization

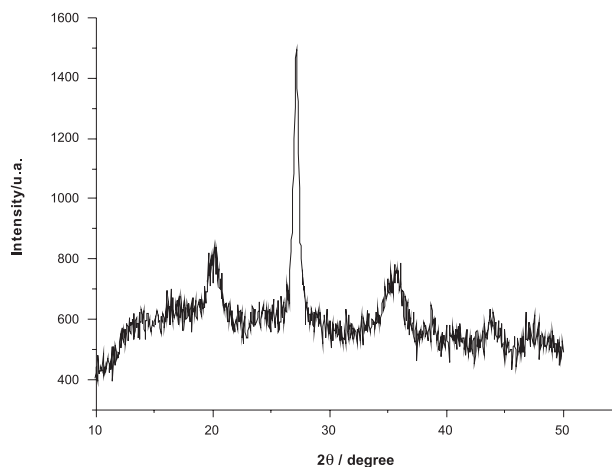
The synthesized catalyst presented a surface area which was calculated by using the BET equation for N<sub>2</sub> adsorption isotherms, giving a surface area of 135 m<sup>2</sup> g<sup>-1</sup>. ICP-OES analysis showed that the amounts of zirconium

and silicon present in the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst were in excellent agreement with the calculated composition, which was 80:20 (mol/mol). The experimental composition was 72.1:27.9 (mol/mol). The reaction to form the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst is schematically shown in Figure 1.



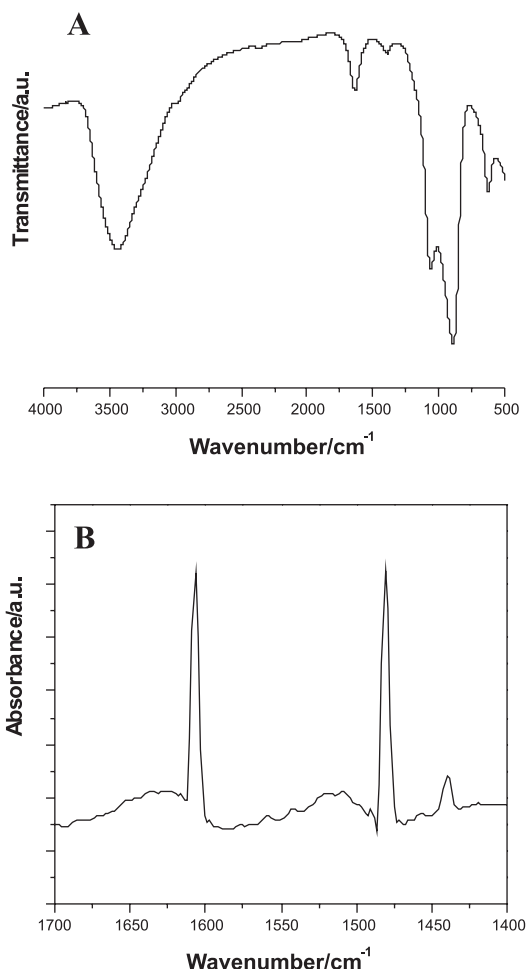
**Figure 1.** Scheme of SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst production by reaction between TEOS and ZrOCl<sub>2</sub>.

A typical XRD pattern (Figure 2) clearly shows the presence of the tetragonal phase of zirconia, assigned to peaks in  $2\theta = 22, 27$  and  $35$ .<sup>19</sup>



**Figure 2.** X-ray diffraction pattern obtained for the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst.

The FTIR spectrum (Figure 3A) presents a broad band between 3600 and 2800 cm<sup>-1</sup>, assigned to OH stretching involving two hydrogen bonds of water, to Si-OH and Zr-OH.<sup>20,21</sup> The band around 1600 cm<sup>-1</sup> is assigned to the water bending mode. The broad band at 1050 cm<sup>-1</sup> is related to stretching vibrations involving the SiO<sub>4</sub> network including Si-O, Si-O-Zr, and Si-O-Si asymmetric stretchings.<sup>20-22</sup> Other large peak at 905 cm<sup>-1</sup> is related to stretching vibrations of the Si-O and Zr-O of SiOH and ZrOH.<sup>20-22</sup> One band at 600 cm<sup>-1</sup> is assigned to O-Si-O and Zr-O-Zr bendings.<sup>20,21</sup> These characterization data shows that the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst was successfully obtained.



**Figure 3.** FTIR spectra recorded for the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst (A) and for the pyridine molecules adsorbed on the catalyst surface (B).

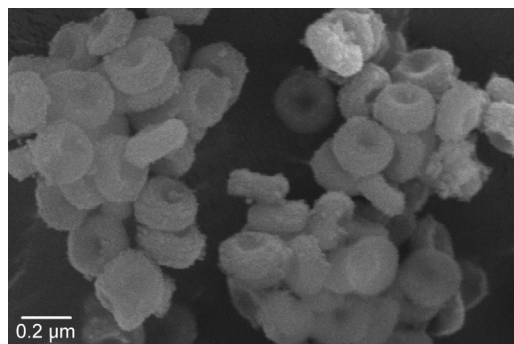
The presence of Lewis and Bronsted acid sites on the catalyst was verified by FTIR spectroscopy using pyridine as a molecular probe (Figure 3B). The FTIR spectrum presented only two new weak bands at 1606 and 1440 cm<sup>-1</sup>, which were assigned to pyridine adsorbed on a Lewis acid site.<sup>23,24</sup>

SEM images of SiO<sub>2</sub>/ZrO<sub>2</sub> were obtained in order to reveal the morphology of the catalyst particles. Figure 4 shows that the SiO<sub>2</sub>/ZrO<sub>2</sub> particles are homogeneously disperse with a particle diameter of 200 nm. This figure also shows that the particles have a donut-like morphology.

In summary, the characterization data show that the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst was obtained with success in nanometric scale.

#### *Transesterification of soybean oil catalyzed by SiO<sub>2</sub>/ZrO<sub>2</sub>*

Transesterification of soybean oil using methanol was followed in different periods of time by using different amounts of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst (Figure 5).

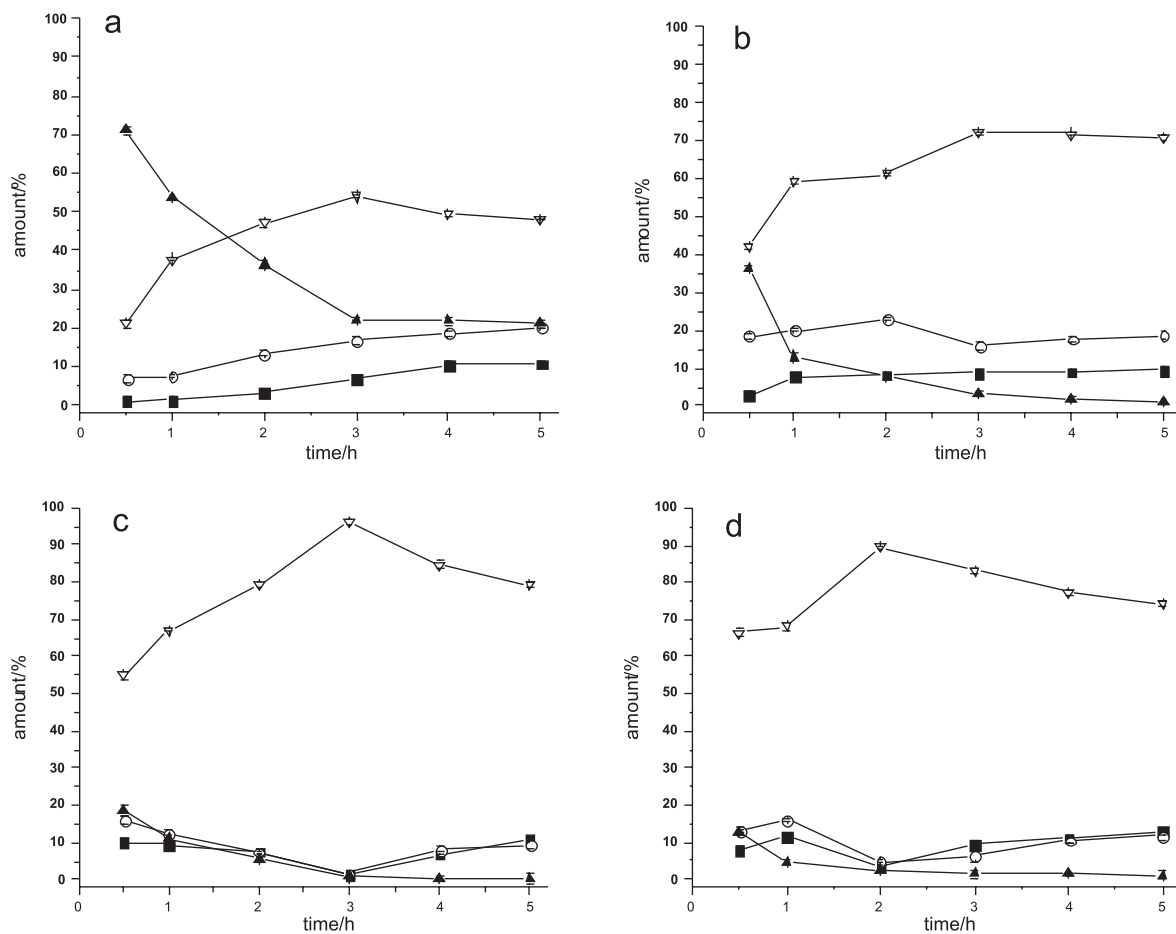


**Figure 4.** SEM image of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst.

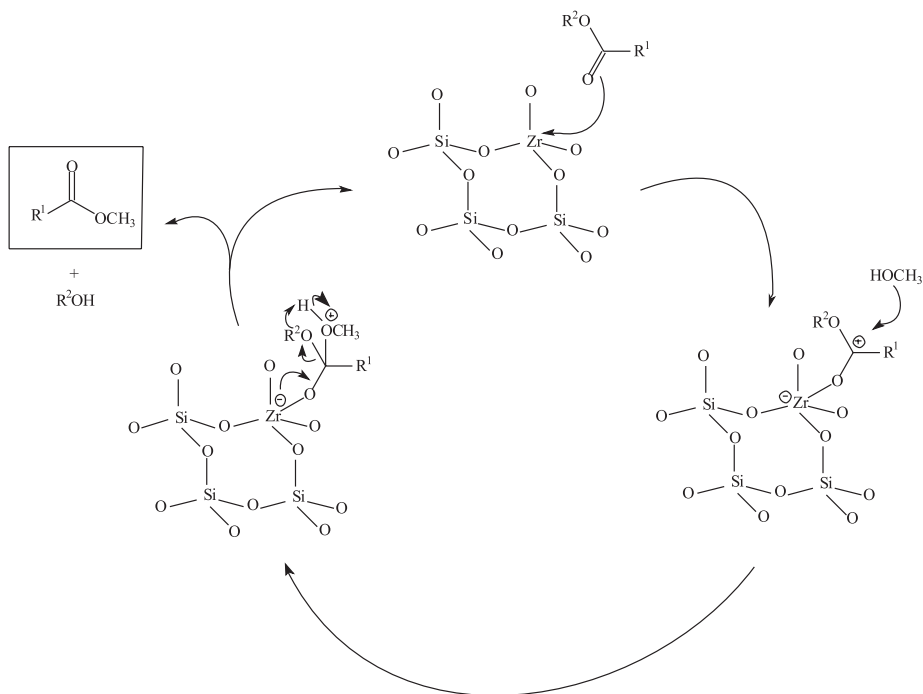
The mechanism of the conversion to biodiesel is shown in Figure 6. ICP-OES analysis confirmed the presence of 5.61 mmol of zirconium per gram of catalyst, resulting in molar ratios (oil:methanol:catalyst) of 100:400:0.5; 100:400:1.4; 100:400:2.4 and 100:400:3.4 for 0.1; 0.3; 0.5 and 0.7 g of catalyst. It is widely accepted that, using acid catalysts, the first reaction step occurs with bond formation between the carbonyl oxygen (of the vegetable oil) and the Lewis acid (in our case zirconium). This carbon is then attacked by methanol, forming a new C-O bond, which rearranges and liberates a fatty acid methyl ester (FAME).

Figure 5 shows the amounts of free fatty acid and mono-, di-, and tri-glycerides, as well as their conversion to biodiesel over a period of 5 h. The reaction yield increased with time up to 3 h, when the maximum biodiesel conversion is attained. After this time, a decrease of the methyl ester conversion was observed. Furthermore, after 3 h of reaction, the amount of fatty acid and mono-, di- and tri-glycerides increased with time together with a decrease in the methyl ester formation (Figure 5). It is also important to highlight that, using the heterogeneous catalytic system presented here, the reaction did not form soap or emulsions and the catalyst (solid phase) and desired biodiesel (upper liquid phase) were easily separated from the glycerin (lower liquid phase) at the end of the reaction. Figure 5 also shows that the best reaction condition employed 0.5 g of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst, which yielded the highest conversion (96.22 ± 1.18 %) in 3 h.

Figure 7 shows a 3-axes graph, which presents the biodiesel yield as a function of the reaction time and the amount of zirconium. This figure clearly shows that the biodiesel yield increased with time up to 2 h for the addition of 3.9 mmol of zirconium, reaching a biodiesel yield of 86.9% that decreased after this period of time. For additions of 0.6; 1.6 and 2.8 mmol of zirconium, the biodiesel yield increased with time up to 3 h, reaching 96.2 % with 2.8 mmol of zirconium. After this time, the yield decreased. This fact can be easily explained by the reversibility of the reaction through glycerolysis of the

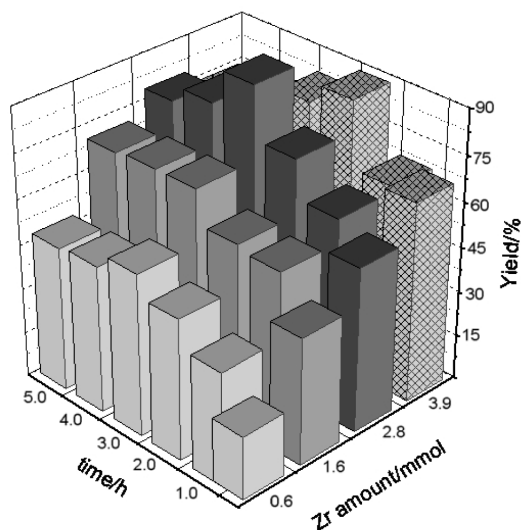


**Figure 5.** Products and yields of the transesterification reactions using 0.1 (a); 0.3; (b), 0.5; (c) and 0.7 g (d) of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst. Monoglycerides and fatty acids (■); diglycerides (○); triglycerides (▲) and biodiesel (▽).



**Figure 6.** Proposed catalytic cycle for SiZr in the transesterification of soybean oil.

methyl-fatty esters forming mono-, di- and tri-glycerides, or by hydrolysis of the methyl esters producing fatty acids, as described for other catalytic systems.<sup>10,13,25,26,27</sup>

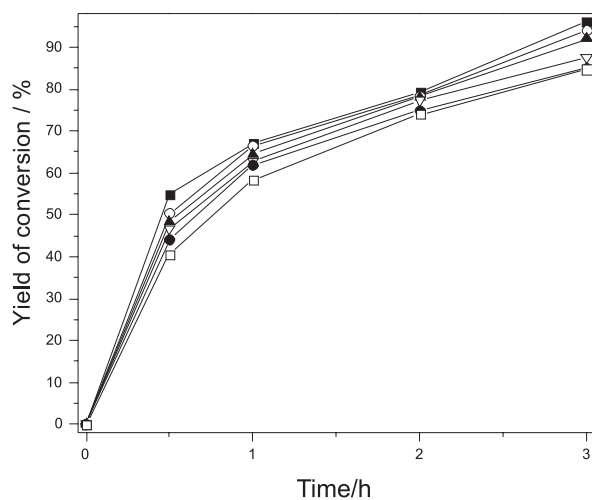


**Figure 7.** Yield of the transesterification reactions as a function of reaction time and zirconium amounts.

### Recycling studies

Results of the reuse of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst can be observed in Figure 8, which shows that the biodiesel conversion is kept practically constant after 6 catalytic cycles with SiO<sub>2</sub>/ZrO<sub>2</sub> in the transesterification of soybean oil. Therefore, the application of the SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst in this reaction to produce green fuel goes toward the key principles of Green Chemistry.<sup>28</sup>

There is one interesting paper about application of zirconia as heterogeneous catalyst for the transesterification



**Figure 8.** Conversion yields for the SiO<sub>2</sub>/ZrO<sub>2</sub> recycling experiments carried out at 80 °C for 3 h: cycle 1 (■); cycle 2 (○); cycle 3 (□); cycle 4 (▽), cycle 5 (●) and cycle 6 (▲).

of vegetable oils. Sulfated zirconia was applied to produce biodiesel at high pressure and temperatures between 85 and 150 °C. The method presented an excellent yield of 99.8 % at 2 h. However, in that case the reuse of the catalyst was limited by its fast deactivation. After 4 cycles, the yield decreased to 20%.<sup>29</sup> Other studies showed the application of sulfated zirconia as a catalyst for the reaction of vegetable oil with different alcohols. The best result was 80% of biodiesel conversion using methanol after 2 h of reaction, but in that work the catalyst deactivation was fast as well. After 3 cycles, the yield again decreased to 20%.<sup>30</sup> There is also an example of application of zirconium complexes as homogeneous catalysts to produce biodiesel. Zr(n-butoxide)<sub>x</sub>(maltolate)<sub>y</sub> complexes were applied in the transesterification of soybean oil. The experiments presented very good results, with the best conversion yield of 90% at 2 h. However, recycling studies were not done.<sup>31</sup>

### Conclusion

A synthetic method to produce a SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst has been successfully employed, forming homogeneous particles with a diameter of 200 nm. The heterogeneous catalytic system using this nanosized material proved to be a convenient route to produce biodiesel by methanolysis of soybean oil. The SiO<sub>2</sub>/ZrO<sub>2</sub> catalyst has shown to be highly efficient for transesterification, as this reaction reached 96.2% yield in biodiesel production after only 3 h of reaction. The catalyst is easily recycled, satisfying the principles of eco-friendly Chemistry.

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