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Nonaqueous synthesis of SrO nanopowder and SrO/SiO_2 composite and their application for biodiesel production via microwave irradiation

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ABSTRACT

SrO/SiO_2 composite was synthesized in a few minutes by reacting Strontium acetylacetonate in benzyl alcohol with mm size SiO_2 beads using microwave radiation under argon atmosphere. The current work illustrates the optimization of a one-stage method whereby *Nannochloropsis* microalgae is converted to biodiesel using direct transesterification by microwave irradiation, the SrO/SiO_2 serving as a base catalyst. Microwave radiation accelerates the disruption of the microalgae cells, and eases the release of oil. The SrO/SiO_2 has been characterized by thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), scanning electron micrograph (SEM) and dynamic light scattering (DLS). The activity of the catalyst particles in the transesterification reaction was studied using ^1H NMR spectroscopy. The catalyst was reused for six cycles without appreciable loss in catalytic activity and the biodiesel yield of the *Nannochloropsis* microalgae was measured.

1. Introduction

The demand for energy and its resources continues to rise due to, among other reasons, population growth and urbanization. Since 1973 energy resources have doubled in developed countries, but the demand still exceeds this value [1]. As a result, there is increasing interest in developing alternative energy resources, which include hydrogen cells [2], solar energy [3], and wind power [4].

Biodiesel, which is made from renewable biological sources, has gained importance as an alternative transportation fuel. Biodiesel consists of fatty acid methyl esters (FAME). The most common way to produce biodiesel is to transesterify triglycerides of vegetable oil, or of the lipid phase obtained from algae. The transesterification is performed by reacting the oil with alcohol in the presence of an alkali or acid catalyst. Many types of alkaline earth metal oxide catalysts can catalyze the transesterification reaction. One of the most active catalysts among the alkaline earth metal oxides is SrO. SrO can catalyze many chemical reactions, such as the oxidative coupling of methane, nitroaldol reactions, mixed Tishchenko reactions and selective oxidation of propane [5–7]. SrO is insoluble in vegetable oil, methanol, and fatty acid methyl ester. Despite the low surface area of SrO [8] there are other factors that are responsible for the high catalytic activity of SrO. Factors such as alkalinity, and acid/base sites of alkaline earth metal oxides also affect the catalytic activity [8]. In previous reports we have shown that the transesterification of tryglicerides in supermarket oils (corn oil, canola oil etc.) or cooked oil into biodiesel can be completed in 10 s when the reaction is conducted in a domestic microwave oven under stirring using commercial SrO as catalyst [1]. Microalgae could also be converted to biodiesel in a similar process but at a slower rate. It took 5 min to completely convert a *Nannochloropsis* microalgae into biodiesel [9]. It was expected that if the micron sized catalytic commercial particles would be replaced by nanosized particles of SrO, further acceleration of the transeterification would be achieved. If this process of combining MW radiation and SrO were to reach commercialization, the SrO NPs would have to be anchored on a solid support. Coating a solid support such as SiO_2 with SrO nanoparticles would be the best option for catalyzing the transesterification reaction in a continuously operating reactor. SrO coated SiO_2 particles answer the concern that nano materials not be scattered in the environment and permit the utilization of the catalyst in a continuous reaction.

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The current paper reports the synthesis of SrO nanoparticles (Nps). The synthesis is performed in the presence of mm size SiO_2 beads and the Nps of SrO deposited on the surface of the silica spheres. Among the different synthetic approaches developed in the last few years, nonaqueous or nonhydrolytic processes were particularly successful and were adopted by us for the preparation of nanosized TiO_2 [10]. Therefore the same non aqueous process using MW radiation was applied for nanosized SrO particles synthesis. The synthesis of SrO NPs results in good yields, and high crystallinity, as noted previously by others [11–15]. However, the microwave technique results in an immense reduction of the reaction time, completing the synthesis of SrO NPs in 5 min.

Furthermore, the use of MW has already been demonstrated to be a suitable deposition technique for anchoring NPs on solid supports [16–20]. In the synthetic approach, the SrO/SiO_2 composite was prepared by reacting strontium acetylacetonate and benzyl alcohol in the MW oven in the presence of silica beads. In this nonaqueous reaction, benzyl alcohol is used as a solvent and a ligand at the same time [10], and as mentioned above, the reaction is completed within a few minutes. Nanoparticles of pure SrO, which were prepared in the absence of the silica beads have never been prepared previously by microwave radiation. They were prepared by other synthetic methods, usually as a composite, on alumina, titania and more [21,22].

The synthesis of the SrO/SiO_2 nanoparticles involved the dispersion of the precursor in benzyl alcohol containing SiO_2 beads (Scheme 1) followed by microwave heating for a short reaction time.

- In the absence of SiO_2, a SrO powder composed of the oxide NPs is obtained.

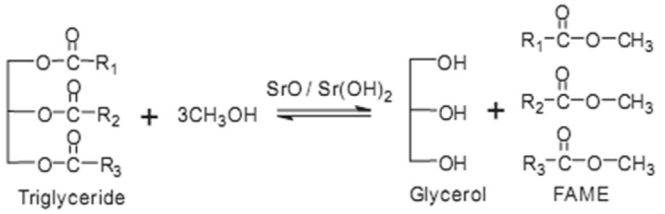
Though transesterification is usually performed under conventional heating recently, performing the reaction under microwave heating has also been reported [23,24]. In these reports conventional alkali homogenous catalysts were employed. However, the use of KOH or NaOH as the alkaline catalyst has some drawbacks [25–28]. In the current work we explore the optimization of biodiesel production, probing the combination of the microwave (MW) irradiation of oil (soybean oil) or N*anochloropsis* algae and MW using nanosized SrO or the SrO/SiO_2 as catalyst. The transesterification reaction is represented in Scheme 2. The catalytic reaction takes place on the surface of the catalyst, and therefore the replacement of a micron size catalyst by nanomertic catalyst in the present work could offer a significant advantage. This is demonstrated for microalgae containing a lipid content of more than 30% of dry biomass (see Scheme 3).

The nano catalysts SrO and SrO/SiO_2 were synthesized according to Scheme 1. Microwave radiation accelerates the disruption of the microalgae cells, and the release of the oil. SrO/SiO_2 as a base catalyst can be separated from the reaction mixture and reused.

2. Experimental section

2.1. Materials

Strontium acetylacetonate (>99.9%), silica gel orange and benzyl alcohol (99.8%, anhydrous) were obtained from Sigma-Aldrich.



Scheme 2. The transesterification reaction.

Crude dried solid *Nannochloropsis* was obtained from the Seambiotic Company.

2.2. Synthesis of strontium oxide nanoparticles and SrO nanoparticles supported on silica beads (SrO/SiO_2)

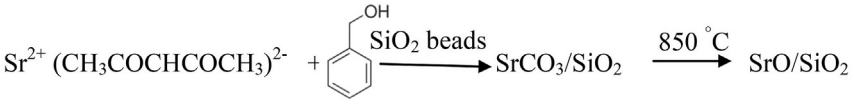
In a typical preparation, 500 mg of Strontium acetylacetonate were added to 50 mL of benzyl alcohol under vigorous stirring at room temperature. The mixture was introduced into the microwave oven under an argon atmosphere, with stirring, for 5 min (SrO is sensitive to air). The microwave reaction was conducted without cooling and a temperature of 363 K was measured pyrometrically at the end of the reaction.

The resulting suspensions were centrifuged and the precipitate was thoroughly washed twice with acetone. The collected material, a white-yellow powder was annealed at 850 °C for 3 h. A white powder was obtained at the end of the annealing process.

The supported catalyst, SrO/SiO_2, was also prepared under microwave irradiation. The optimized weight ratio of Sr:Si is 2:1. Typically, 0.5 g of silica beads and 1 g of strontium acetylacetonate were dissolved in 50 mL of benzyl alcohol. The synthesis was performed in a similar way to the process adopted for SrO nanoparticles. SrO/SiO_2 is obtained as a white product.

2.3. Two-stage method for biodiesel production from the Nannochloropsis microalgae using microwave and SrO or SrO/SiO_2 nanoparticles as catalyst

A two-stage method was carried out on the microalgae biomass of *Nannochloropsis* for biodiesel production; namely, extraction of the lipidic material in the first stage, followed by transesterification. Both stages were conducted using microwave heating and SrO or SrO/SiO_2 as catalyst. Crude dried *Nannochloropsis* (1 g) was mixed with methanol-chloroform (1:2 v/v) for oil extraction using a microwave oven which was operated for 5 min at 70% power (cycle mode of 21 s on and 9 s off). After extraction the chloroform-methanol phase containing the extracted oil was separated from the microalgae powder by filtration, and the solvent was evaporated. The weight of oil obtained from each sample was determined. For the transesterification of the extracted microalgae oil, a mixture of methanol-chloroform (1:2 v/v) and SrO or SrO/SiO_2 catalyst (0.3 or 0.6 g, respectively), were used under microwave irradiation for 2 min. The samples were then centrifuged and filtered to separate the methanol-chloroform phase containing the FAME (fatty acid methyl esters) from the glycerol and the catalyst. The methanol and chloroform were evaporated in a rotary



Scheme 1. General reaction scheme displaying the metal complex precursor, the solvent, the experimental condition and the resulting SrO/SiO_2 nanoparticles.