Chapter 5

Mesoporous Silicas as Basic Heterogeneous Catalysts for the Formation of Biodiesel

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ABSTRACT

The principal aspects of the production of biodiesel using heterogeneous catalysis are presented, comparing this alternative process to conventional (homogeneous) processes and evaluating the main operational parameters. The most important techniques for the preparation and characterization of silicas with basic properties are mentioned, dividing these materials into two groups with distinct properties: as-synthesized silicas, especially the M41S family, with their pores occluded with organic cations, and functionalized silicas, with accessible pores. The catalytic properties of these silicas were evaluated in transesterifications using a model reaction and vegetable oil. Finally, a brief presentation is made of other solid catalysts with basic properties that can be used in the biodiesel production reaction.

INTRODUCTION

The replacement of petroleum by renewable fuels has been widely studied and implemented in recent years. The motivation has been the growing demand for fossil fuels and the existence of limited reserves. Another issue of growing importance is concern about environmental impacts, especially due to the greenhouse effect caused by increased levels of carbon dioxide and other gases in the atmosphere.
Ethanol, biodiesel, and, more recently, biokerosene are the liquid fuels from renewable sources that have been most extensively studied and employed. The production of these biofuels involves catalytic operations: fermentative, in the case of ethanol, or chemical catalysis, in the cases of biodiesel and biokerosene.

Industrial biodiesel production began around the year 2000, and in 2014, global output was estimated at 25,000 million liters (160 million barrels) (Guo, Song & Buhainc, 2015). The process of biodiesel production involves the catalytic transesterification of triglycerides, mainly vegetable oils and to a lesser extent animal fats. Almost the entire global production of biodiesel is currently performed using homogeneous catalysis, where the main disadvantage is contamination by glycerol, a byproduct of the reaction, in which the catalyst is soluble. Consequently, homogeneous catalysts cannot normally be reused, which increases the cost of the process.

Research concerning the formation of biodiesel by heterogeneous catalysis started in 2001, using solid catalysts insoluble in the reaction medium. Since then, nearly 1,000 scientific articles and 4,000 patents have been published on this topic.

As in homogeneous transesterification, the catalysts used in heterogeneous transesterification of triglycerides possess basic sites. The most commonly used solid catalysts are alkaline earth metal oxides and, to a lesser extent, transition metal oxides and hydrotalcites. Although alkaline earth metal oxides are most active, during recycling they readily react with atmospheric carbon dioxide, leading to their deactivation.

Among the most recently reported solid catalysts with strongly basic properties are the hybrid silicas, of which there are two types: as-synthesized silicas (Kubota et al., 2004), containing caged micelles in their interiors (Figure 1a), and mesoporous silicas, with functionalized surfaces (Figure 1b).

**BIODIESEL**

**History and Importance**

Biodiesel is a fuel produced from renewable sources, consisting of alkyl esters of fatty acids derived from vegetable oils or animal fats. Unlike fossil fuels, much of the CO₂ released during its combustion is...
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