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Catalytic cracking of crude soybean oil on Beta nanozeolites

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ABSTRACT

The global economic and population growth has significantly increased the demand for fuels. On the other hand, the strictness of environmental legislation and the depreciation of fossil fuel reserves have motivated the research for alternative energy sources. With this purpose, the preparation and characterization of catalysts based on Beta nanozeolites were described in this work, aiming to find active and selective catalysts to produce biofuels through the cracking of crude soybean oil. The samples were prepared by using different organosilanes such as phenylaminopropyltrimethoxysilane (PHAPTMS), phenyltrimethoxysilane (PHMTS) and aminopropyltriethoxysilane (APTES) to functionalize the Beta zeolite seeds. The silanized seeds produced solids with smaller crystallites, more framework aluminum and different textural and acidic properties as compared to the Beta nanozeolite prepared without organosilane. APTES produced the solid with the smallest crystallites while PHAPTMS produced the sample with the highest external area, the differences being related to agglomeration of nanoparticles, generating voids related to the size of organosilane chains. The catalysts showed different selectivities during the cracking of crude soybean oil, depending on the organosilane used in the preparation. This finding was related to the different acidic properties and to the different particles size and porosity of the solids. The Beta nanozeolite obtained without any organosilane produced more gaseous compounds (C2–C4), due to the largest percentage of strong acidic sites, whereas those obtained with organosilanes were more selective to liquid hydrocarbons. The sample prepared with APTES was the most active and selective to hydrocarbons in the range of gasoline, diesel and kerosene, because of its smallest crystallite size and low acidity, as well as to the agglomeration of nanoparticles, which facilitates the hydrogen transfer reactions. Moreover, the sample prepared with PHMTS was the most selective to hydrocarbons in the gasoline range (C5–C11) while that obtained with PHAPTMS was the most selective to oxygenates. These changes were related to the combined effects of crystallite sizes, porosity and acidity on the catalytic properties of the solids, in the different pathways of the complex reaction network of cracking of soybean oil. It was shown that different organosilanes allowed tailoring the catalytic properties of Beta nanozeolites to produce biofuels or chemicals for several applications.

1. Introduction

Currently, most of the energy consumed worldwide is mainly provided by fossil fuels (coal, oil and natural gas) with some contribution from hydroelectric and nuclear sources as well as from wind and biomass. In recent years, the energy consumption has increased drastically, due to both population growth and economic development, which have led to an increasing dependence on non-renewable natural resources [1]. However, the large use of fossil fuels has contributed significantly to climate changes due to emissions of carbon (CO_x), sulfur (SO_x) and nitrogen (NO_x) oxides, besides other compounds (including organics), produced during the fuel combustion [2].

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As a consequence of the strictness of environmental legislation and of the forecast oil decline or exhaust [3,4], an increase of fuel and chemical products obtained from renewable sources such as biomass and other agricultural sources (e.g., vegetable oils) is expected. Therefore, several routes have been investigated for converting vegetable oils into biofuels or chemicals, such as pyrolysis, gasification, transesterification, catalytic cracking and hydrocracking [1]. Among these methods, the catalytic cracking at high temperatures seems to be very promising, producing fuel oil fractions similar to petroleum fractions (gaseous hydrocarbons, gasoline, kerosene and diesel) with negligible sulfur content, nitrogen and heavy metals [2,5]. In this process, various factors affect the composition of the products like the reaction conditions (time, temperature, space velocity and others) as well as the kind of catalyst [6–10].

Several acidic catalysts are active in the cracking of vegetables oils but the solid catalysts, instead of liquids, have been preferred due to environmental restrictions. Among them, acidic solids such as zeolites have been largely used due to their properties, which can be controlled during preparation, like porosity, size of crystals and acidity [11,12]. Therefore, several papers have been addressed [6–10] to the catalytic cracking of vegetable oils, carried out on a variety of zeolite catalysts under different reaction conditions. Nevertheless, the presence of only micropores in these solids imposes limitations in the diffusion of reactants or bulky products. The slow transport of reactants and products in the micropores of zeolites usually results in a long residence time favoring undesired reactions [13], such as coke formation which continuously deactivate the zeolite by the poisoning of active sites or by the blockage of micropores [14].

A promising solution to overcome the drawback of diffusion limitation in zeolites is the decrease in crystal size, from micrometer to nanometer scale [15–21]. In nanocrystals, the diffusion paths are decreased, facilitating the reactants access to the active sites and the product output from the catalyst [16,22]. For most cases, the zeolite nanocrystals are prepared using a homogeneous solution or a gel containing an aluminosilicate with (or without) a template, generally in the absence of alkaline cations, under hydrothermal conditions. In these methods, low crystallization temperatures are used in order to favor the nucleation instead of the crystal growth and thus a colloidal suspension of discrete particles of zeolite with sizes of 100 nm is obtained [15]. Other methods involve the synthesis of the zeolite in a confined space, by the use of an inert matrix or of amphiphilic organosilanes to generate steric hindrance to crystals growth [18–20]. Serrano et al. [17] described a promising method for the preparation of nanozeolites, in which the seeds of zeolite were functionalized by an organosilane to prevent the crystals growth during zeolite crystallization. After the crystallization step, the solid was calcined for the removal of the organosilane, forming aggregates of zeolite nanocrystals. The synthesis with organosilanes generally occurs in two stages: in the first one, the precrystallization occurs, in which there is the formation of zeolite seeds to be functionalized with the organosilane molecules. In the second step, the functionalized seeds go on crystallization, forming the zeolite structure [18].

Despite the great potential of this method, there are few studies concerning the synthesis conditions and the nature of organosilanes used for preparing nanostructured Beta zeolite by seed functionalization [17,20,23]. However, several works [20,23–29] carried out with different kinds of zeolites have shown that the time and temperature of precrystallization step and the nature and concentration of organosilane determine the properties of the catalysts. It is well-known [24,25,28,29], for instance, that the nature of organosilane plays a vital role on the textural and acidic properties of hierarchical zeolites. Since organosilanes have high affinity for silicates and aluminosilicates species, as well as for protozeolitic units and zeolite crystallites, they can easily be anchored to silicate species and nanoparticles by reacting via silanol groups, producing organic–inorganic composites. During calcination, these composites produce hierarchical zeolites with mesoporosity directly related to the voids occupied by organosilane species. As a large number of organosilanes with different sizes, configuration and chemical nature is available, it is expected that the mesoporosity of hierarchical zeolites can be tailored by using different types of organosilanes. On the other hand, the secondary surface represents a discontinuity of the crystalline framework, in which the silicon and aluminum atoms show a lower T atom connectivity, as compared to the positions inside the channels, which have a high concentration of silanol groups. As a consequence, these solids often have behavior and properties between those of conventional zeolites and amorphous aluminosilicates, such as the nature and strength of acidic sites, the hydrophobic or hydrophilic character, the confinement effect, the shape selectivity and the hydrothermal stability [20,25,30]. The differences in these properties frequently result in different catalytic performances [20,25–30].

In the present work, Beta nanozeolites were prepared by the functionalization of seeds with different organosilanes (phenylaminopropyltrimethoxysilane, phenyltrimethoxysilane and aminopropyltriethoxysilane), aiming to obtain active and selective catalysts for the cracking of crude soybean oil to produce biofuels. It is expected that the differences in the textural and acidic properties can result in improved catalytic properties. To the best of our knowledge, among these organosilanes only phenylaminopropyltrimethoxysilane was used to prepare Beta nanozeolites, which in turn have not been evaluated in the cracking of soybean oil yet [17,20].

2. Experimental

2.1. Reagents and chemicals

Aerosil 200 fumed silica (Degussa, purity 100%), aluminum sulfate (Aldrich, 100% purity), tetraethylammonium hydroxide (Aldrich, aqueous solution 35 wt%), phenylaminopropyltrimethoxysilane (Aldrich, 100% purity), phenyltrimethoxysilane (Aldrich, 97% purity) and aminopropyltriethoxysilane (Aldrich, 98% purity) were used for samples preparation in this work.

2.2. Preparation of Beta nanozeolites

The nanozeolites were prepared by the functionalization of Beta zeolite seeds with different organosilanes, using a method based on the work of Serrano et al. [17]. The seeds gel ($30TEAOH/50SiO_2/Al_2O_3 1/1000H_2O$) was obtained by mixing two solutions: the first one was prepared by dissolving aluminum sulfate (0.66 g) in water (9.8 mL) while the second solution was obtained by dissolving 3.0 g of Aerosil silica in 12.60 g of an aqueous solution (35 wt%) of tetraethylammonium hydroxide (TEAOH). After homogenization, the gel was kept under stirring for additional 4 h. The mixture was maintained under hydrothermal treatment at 140 °C, for 24 h to allow the formation of seeds of Beta zeolite.

The produced seeds were then functionalized with different organosilanes: phenylaminopropyltrimethoxysilane (PHAPTMS), phenyltrimethoxysilane (PHTMS) and aminopropyltriethoxysilane (APTES), which were used in a molar percentage of 5% relative to the total amount of silicon in the seeds gel. The seeds and the organosilane were mixed in a Parr reactor, where the reaction of functionalization took place at 90 °C, for 3 h, under stirring.

After the functionalization step, the seeds were transferred to an autoclave and kept in an oven at 140 °C, for 48 h, to crystallize. After