Faculty of Science
Chemistry Department

Facile Synthesis and Characterization of a Thermally Stable Modified- Alumina with Tunable Catalytic Activity.

A Thesis Submitted to Faculty of Science
for
The Degree of Master of Science
Physical chemistry

Submitted by
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B.S., Chemistry, 2013

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Chemistry Department -Faculty of Science
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Basant Gamil Salib

Abstract

Name: Basant Gamil Salib

Title of thesis: Facile Synthesis and Characterization of a Thermally Stable Modified- Alumina with Tunable Catalytic Activity.

Alumina-hollow-microspheres- Graphene oxide (GO) composites with hierarchical macromesoporous structure and controllable GO loadings from 2 to 20 wt.% had been synthesized using a self-limiting hydrogel method. The composite with 5wt.% GO loading exhibited the best catalytic activity in sunflower oil transesterification, giving an oil conversion of 85.2% by using only 1.0 wt. % catalyst to oil at 60°C in traditional batch reactor. Furthermore, the same composite (GO(5wt.%)-alumina) exhibited higher oil conversion (97%) to methyl esters in autoclave reactor at 120 °C. The significant high activity of this composite toward oil conversion was attributed to that its macroporous structure facilitated the diffusion of products, and it has higher amounts of both acidic and basic oxygen functional groups than either the neat GO or alumina. In addition, GO(5wt.%)-alumina composite, also showed good water tolerance, as the oil conversion was varied from ca. 85.2 to 79.2 % in 10 h when the water content in reaction mixture was increased from 0.0 to 3.0 wt.%. The stability of this composite in liquid water at 200°C for 12 h was also examined using variety of physicochemical techniques. It is shown that the presence of GO (5wt.%) inhibited the hydration of γ-alumina to form boehmite.

Keywords: hollow spheres, alumina, graphene oxide, hierarchically, macro-mesoporous, composite, biodiesel

Summery

In the present study, self-limiting hydrogel method was used for the synthesis of hierarchical macro- mesoporous structure-hollow microsphere γ- Al_2O_3 (Al(HPS)). Structural characterization of the prepared alumina was confirmed through several techniques e.g., high-resolution *scanning electron microscope* (SEM), transmission electron microscope (TEM) and N_2 Physisorption measurements.

Different graphene oxides (GO) were prepared using different methods namely, graphite flakes of different sizes (viz., 250 and 600 μm) were oxidized using two different methods; Hummer's method with additional $KMnO_4$ and improved Hummer's method In addition, the synthesized graphene oxide samples were exfoliated either by ultrasonic or microwaves.

The choose of a suitable GO sample to modify the synthesized γ- Al_2O_3 (Al(HPS) microspheres dictated by the presence of higher amount of anchoring carboxyl groups on the surface of graphene

oxide as identified by Boehm's titration method. Graphene oxide-alumina composites (GO*X*Al(HSP) of *X* = 2.0, 5.0, 8.0, 10 and 20 wt. % in the final solid form were prepared. For aim of comparison, classical γ- Al_2O_3 (Al(CLS) was prepared by traditional precipitation method and it was modified by same weight percentages of graphene oxide where samples was designated as GO*X*(CLS).

The hydrothermal stability of g- Al_2O_3 (Al(HPS)) , GO5.0Al(HPS) and GO20Al(HPS) samples were investigated in autoclave at 200 °C for 12 h. Afterward, it was quenched in a water bath. The solid was filtered and dried, and the filtrate was saved for XRD, FT-IR and SEM analysis. Characterization results have shown that hat the presence of GO (5wt.%) inhibited the hydration of gamma-alumina to form boehmite.

The nature of GO and Al(HPS) interaction was studied via Fourier-transform infrared spectroscopy **(FT-IR)**, Ultraviolet–visible spectroscopy **(UV-Vis)** and Boehm's titration method measurements. The characterization results indicated that the formation of such GO*X*Al(HSP) composite is mediated by interaction between hydroxy groups of γ-Al_2O_3 and carboxyl groups linked on GO sheets at the edges.

The catalytic activity of various samples was examined in methanol transesterification of sunflower oil to biodiesel (SFO) where the reaction was carried out in a batch reactor. The standard reaction conditions are 1 wt. % catalyst to oil ratio, 60 °C reaction temperature, 5 h reaction time and 30:1 methanol to oil molar ratio. In addition, a series of tests were carried out over the best catalyst to identify the optimum reaction parameters (viz., temperature, time, catalyst to oil ratio (wt. %) and methanol to oil molar ratio). In the case of graphene oxide samples their performances in conversion of oil to biodiesel depends on the method of preparation. In general, the GO*X*Al(HSP) showed a higher catalytic performance in SFO than that of GO*X*(CLS). In addition, the composite of Al(HPS) modified with 5wt.% GO loading exhibited the best catalytic