Ru-decorated magnetic iron oxide/alumina nanocomposite catalyst for the inductively heated hydrogenation of furfural

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Highlights

- Preparation of the magnetic nanocomposite catalyst used for furfural hydrotreatment
- Induction heating-based catalysis as a way to save energy and lower costs of production
- Comparison with the conventional approach to the biomass conversion

1. Introduction

Valorization of biomass includes various biomass-derived compounds, versatile methods and chemical reactions, one of which is the hydrogenation of furfural and its conversion to furfuryl alcohol. The sole idea of furfural hydrogenation lies within the potential and the applicability of furfuryl alcohol in a number of industrial branches due to its versatility. Hence, furfuryl alcohol can be used in: monomers for the synthesis of the biopolymers, edible flavors and fragrances and fuels.[1] Conventionally, heat was being delivered to the process externally, thus heating the outer walls of the reactor first and reaching the reaction mixture through a series of conduction-convention processes. However, with the utilization of magnetic catalysts, alternating magnetic field (AMF) can be used to deliver heat directly to the catalyst surface, creating hotspots on the catalyst-reactant interface without the need to heat the whole reactor or the reaction mixture first.[2] This approach could result in lower energy consumption and faster processing time, since the magnetic nanoparticles inside of the nanocomposite catalyst can be heated up to the needed temperature point rapidly. In this work, we have prepared the nanocomposite catalyst consisting of magnetic iron oxide nanoparticles, *i.e.* the solid solution of magnetite and maghemite (Fe_3O_4), coated with alumina and decorated with catalytic Ru nanoparticles. The magnetic properties and the heating rate of the catalyst were characterized. Catalyst will be used in an experiment to determine the conversion in the furfural hydrogenation reaction. In the upcoming period, we will aim to compare the activity of the prepared nanocomposite catalyst using both induction and conventional heating to prove the hypothesis of the research. The aim is to pave the way towards the electrification of the biomass conversion processes, which would support the green transition and emphasize the advantages of the biomass use in everyday life.

2. Methods

The magnetic iron oxide nanoparticles were prepared *via* co-precipitation of Fe(II) and Fe(III) sulphates with ammonia as precursors. The suspension of precipitate then underwent a hydrothermal treatment to facilitate growth of the iron oxide nanoparticles. After the hydrothermal treatment, the product was washed multiple times to remove the sulphates from the mixture, followed by the adsorption of citrate anion in order to prepare the colloidal suspension. Iron oxide/alumina nanocomposites were prepared by adding AlN to the colloidal suspension, which was followed by annealing of solid product in an air atmosphere. That way, AlN underwent the hydrolysis to boehmite, which was then dehydrated to γ-Al_2O_3. Ruthenium nanoparticles were deposited on the surface of the nanocomposite by two methods: i) by impregnation of the nanocomposite by $RuCl_3$ followed by drying and reduction and ii) by precipitation of RuO_x nanoparticles in the aqueous suspension of the nanocomposite. Techniques used for the characterization of the material were: X-ray diffraction (XRD), vibrating sample magnetometry (VSM), transmission electron microscopy (TEM). Magnetic heating rate of the sample was performed using an aqueous suspension of the material which was subjected to the measurements at different stirrer rates and magnetic fields. The temperature of the suspension was continuously monitored throughout the duration of the test and ranged from room temperature up to about 90 °C. The synthesized material underwent its first furfural hydrogenation experiment using n-butanol as the solvent.

3. Results and discussion

It was observed that the iron oxide/alumina composite consists of two phases since there are clearly visible diffraction maximums which correspond to the γ-Al_2O_3 phase and the ones which correspond to the Fe_3O_4 spinel structures. The TEM images of the samples can be seen in Figure 1. Larger spherical particles within the sample are the iron oxide magnetic particles which are coated by “needle-shaped” structures of γ-Al_2O_3. The needles are, in fact, folded sheet alumina particles. The diameter of the iron oxide nanoparticles is roughly 10-30 nm. Under-focused TEM image unveils many spherical structures significantly smaller in size. Those are the Ru nanoparticles which were added to the iron oxide/alumina nanocomposite. Room-temperature magnetization curve of the nanocomposite shows narrow hysteresis loop which indicates the properties of soft magnets. The temperature of the magnetic nanocomposite suspension strongly depends on the stirring rate when lower AMF is applied. Upon increasing the AMF values, there seem to be a certain point at which the stirring rate no longer has a strong impact on the temperature change of the sample. Using higher AMF, the time which takes the samples to reach the highest observed temperature point was shortened to about ¼ in comparison to the low AMF experiment.

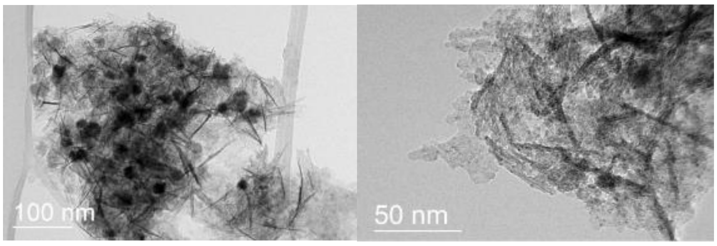

Figure 1. TEM images of the Ru-decorated iron oxide/alumina nanocomposite. Ru nanoparticles are seen as small darker dots (right).

Roughly speaking, conversion of furfural observed in the preliminary experiment was in the range between 65-85 % and strongly depended on the amplitude of applied AMF. The yield of furfuryl alcohol was observed. N-butanol reacted with some of the furfural, thus hindering the production of furfuryl alcohol and promoted the yield of reactant-solvent byproduct.

4. Conclusions

The successful preparation of the Ru-decorated iron oxide/alumina was achieved and proved using several different characterization techniques. According to the obtained magnetic measurement results, we suspect that the nanocomposite catalyst should prove successful in furfural hydrogenation *via* induction heating. Magnetic heating curves show that the catalyst under AMF heats to high temperature. The results indicate the applicability of the developed catalyst in magnetically heated hydrotreatment of furfural.

References

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Keywords

“Magnetic nanocomposite”, “Induction heating”, “Furfural”, “Hydrogenation”