**Study on the deactivation of the CaO containing catalysts used in transesterification of sunflower oil with methanol**

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**Highlights**

* CaO based catalysts were prepared by mechanochemical treatment.
* 3CaO·SiO2 mixed oxide showed better stability than CaO·ZnO.
* Deactivation was caused mainly by adsorbed organic compounds on active sites.

**1. Introduction**

The synthesis of biodiesel, a mixture of fatty acid methyl esters (FAME), applying heterogeneous catalytic process could solve most of the economic and environmental drawbacks of the conventional homogeneous process. Solid catalyst can be easily separated from the reaction mixture, regenerated and reused, what make the biodiesel synthesis cost-effective and also enables the continuous process development [1]. However, one of the main problems associated with solid catalysts is their deactivation, caused by poisoning of active sites, leaching of active component into the reaction mixture, or structural change of the catalyst.

CaO based catalysts, CaO·ZnO and 3CaO·SiO2 mixed oxide prepared by mechanochemical treatment and subsequent calcination exhibited excellent activity in transesterification of sunflower oil at 60 °C [3-5]. In this work, stability and deactivation of these CaO based catalysts was studied and compared to the activity and deactivation of pure CaO. The possibility to reuse the catalysts in consecutive runs was examined, as well as the leaching of the active component of the catalyst in the reaction mixture. The characterization of catalysts after reaction was performed in order to find out the cause of deactivation.

**2. Methods**

The fresh and reused catalysts were characterized by XRD, TGA/DSC, FTIR, SEM/EDX and base strength using Hammett indicator method. The details on the preparation of catalysts and the used instruments for their characterization are described elsewhere [2-4]. The methanolysis of sunflower oil was carried out in a 250 ml three-necked glass flask with a condenser and magnetic stirrer at 60 °C, methanol to oil molar ratio of 10:1 and 2 wt% of catalyst based on oil weight.

**3. Results and discussion**

The results showed that CaO·ZnO catalyst could be reused only 2 times without losing its activity, while already in the third cycle the FAME yield declined to 47%, and in fourth cycle the catalyst was practically not active (Figure 1). 3CaO·SiO2 showed better stability, maintaining very good activity and high FAME yield, above 97%, for 4 cycles. For comparison, the activity of pure CaO decreased in four consecutive runs [5]. To evaluate leaching of the active component, the catalyst sample was placed in contact with methanol under reaction conditions. After the catalyst was removed by filtration, methanol was mixed with the fresh sunflower oil. When CaO·ZnO was used, FAME yield was 0.21%, revealing negligible leaching of active component, while for 3CaO·SiO2 FAME were not detected. This finding confirmed the stabilization of CaO by the presence of another phase, since CaO, when used as pure compound, is partially dissolved in methanol [1].

The FTIR spectra of fresh and 4-times used 3CaO·SiO2 catalysts are very similar, indicating the stability of the catalyst during its use in transesterification of sunflower oil, and only negligible adsorption of organic compounds on the catalyst surface (Figure 2). XRD patterns of reused CaO·ZnO revealed only peaks assigned to ZnO, while peaks corresponding to CaO were not observed, indicating that they were blocked by products or intermediates. FTIR analysis confirmed the presence of organic compounds on the surface of CaO·ZnO catalyst.

 

**Figure 1.** Number of repeated use.

**Figure 2.** FTIR spectra of fresh and used catalysts.

**4. Conclusions**

3CaO·SiO2 catalyst showed good stability in transesterification of sunflower oil, while drop of activity occurred already in the third reuse cycle when CaO·ZnO catalyst was used. The observed catalyst deactivation was probably the result of active site blockage by adsorbed organic compounds from the reaction mixture.

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