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Stability of waste-based zeolite supported CaO catalyst for bio-diesel production from waste oily feedstocks

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Waste-based zeolite supported CaO catalyst (20CaO/ZM_{FA}) was synthesized by ultrasound-assisted impregnation from alcoholic suspension. Zeolite was previously synthesized from lignite coal fly ash (FA) by alkali activation in miniature rotating autoclave reactors (6.25 M NaOH, 260 °C, 4 h), whereas CaO was prepared by chicken eggshell (ES) calcination (900 ºC, 4 h). The final catalyst was obtained by precursor calcination at 550 °C, 4 h. The obtained catalyst was used for catalyst stability tests (reusability and leaching) in transesterification (methanol/oil molar ratio of 12/1, catalyst concentration of 4 wt%, and temperature of 60 °C) of three types of oily feedstocks, fresh sunflower oil (SFO), waste cooking oil (WCO) and model thermal treated (230 °C, 5 days) sunflower oil (SFO_{TT}). The concentration of triacylglycerols (TAGs) and fatty acid methyl esters (FAMEs) was determined by GC and HPLC, respectively. The 20CaO/ZM_{FA} exhibited high activity (FAME content > 96.5 % for 180 min) in the transesterification of all three oily feedstocks. The stability tests are shown that catalyst is stable even in four reaction cycles for SFO and WCO, whereas the Ca^{2+} leaching was significantly lower compared to similar catalytic systems.

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Scope

Waste-based zeolites present promising material in many sustainable processes in the fields of renewable energy and environmental improvement, as well as highly efficient catalysts, catalyst supports, adsorbents, and ion-exchangers [1]. On the other hand, supported CaO-based catalysts are very prosperous for the transesterification of different oily feedstocks, non-edible and waste edible (cooking, frying, and restaurants oils) to biodiesel [2]. It is estimated that the production of such oil in European countries varies between 100,000 – 700,000 tons per year. Biodiesel produced from WCO has numerous advantages (reducing biodiesel production costs by 60-90%, a zero CO_2 emission, reducing environmental pollution and high cost for wastewater treatment). The high presence of FFA (higher than 3%), water, and other impurities in waste oil is the main threat to base catalysts, whereby the source should be previously treated to be esterified and purified [3]. During frying, oil changes its physicochemical properties, whereby viscosity and density increases due to polymers and dimmers formation and molecular mass and iodine value decrease. Since the most alkaline earth metal-based catalysts have shortcomings for biodiesel production from waste oils, it is advantageous to develop a complex heterogeneous catalytic system that can simultaneously catalyze both reactions esterification and transesterification.

In the present study, the stability of waste-based zeolite from coal fly ash supported CaO catalyst in transesterification of three types of oily feedstocks was studied.

Results and discussion

The obtained 20CaO/ZM_{FA} catalyst was fully structural, morphological, and textural characterized in our previous study [2]. The catalyst exhibits significant activity in the transesterification of different oily feedstocks. Moreover, was active and stable even in four reaction cycles for fresh SFO and WCO with a slight decrease in activity after the third

cycle (Fig. 1a).

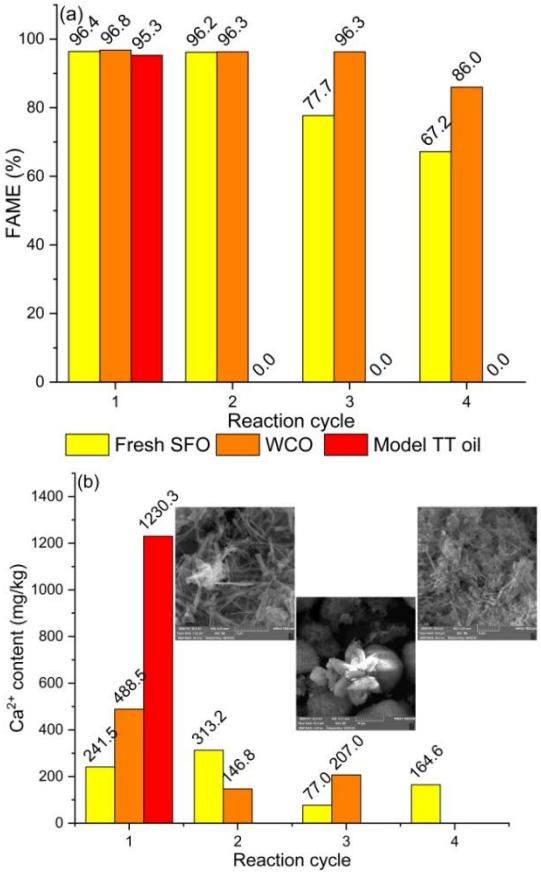

Fig. 1: (a) reusability study (b) leaching test (inset – SEM micrographs of spent catalyst)

However, in the case of model SFO_{TT}, the catalyst was active only in the first reaction cycles. It can be ascribed to significant changes in chemical composition due to decomposition (polymers and dimers formation) of essential TAGs present in fresh vegetable oil (Table 1).

Table 1. Chemical composition of different oily feedstocks

Oil/FA	SFO	WCO	SFO_{TT}
	mol %		
C16:0	6.51	8.85	8.5
C18:0	3.14	4.12	4.22
$C18:1_{cis}$	35.87	30.74	42.39
$C18:1_{trans}$	0.00	0.00	0.73
$C18:2\text{-}9_{cis},12_{cis}$	54.07	53.89	39.79
$C18:2_{trans}$	0.07	0.67	3.91
$C18:3_{cis}$	0.04	0.05	0.00
C20:0	0.19	0.19	0.25

The conducted leaching study is shown that Ca^{2+} leaching into the reaction mixture varies from 77.0 to 313.2 mg kg^{-1} for fresh SFO and from 146.8 to 488.5 mg kg^{-1} for WCO, whereas in the case of model SFO_{TT} the leaching was higher even four times. It can be seen that the changes in the Ca^{2+} content do not correlate with reaction cycles, whereby the decrease in activity could be explained not only by the loss of active species but also by the deposition of products on the catalyst surface (see SEM micrographs in Fig. 1b).

Conclusion

Waste-based zeolite supported CaO catalyst can be used successfully in the transesterification of waste oily feedstocks with different composition. In the case of fresh SFO and WCO, the catalyst can be used in four reaction cycle with a slight decrease in activity, whereas in the case of model thermal treated oil the catalyst was active only in the first cycle due to the significantly impaired initial composition caused by severe thermal treatment. On the other hand, the decrease in activity also could be attributed to blockages of active species with reaction products deposition.

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