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Book of Abstracts (poster)

Effects of preparation conditions on the catalytic activity of chicken eggshell catalysts for the transesterification of oils to biodiesel

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Eggshell based catalysts were synthesized by calcination (600 and 900 °C, 4 h) of raw and re-hydration (RH) modified (RH-temperature of 80 °C, S/L ratio of 1/5, and RH-time of 6 h) eggshell. After RH-treatment, the sample underwent calcination at 600 °C, 4 h. Obtained catalysts were characterized by XRD, SEM, N₂-physisorption, and Hg-porosimetry, whereas the catalytic activity was analyzed in a batch reactor (reaction temperature of 60 °C, sunflower oil/methanol molar ratio of 1/12, and catalyst concentration of 4 wt.%). The concentration of fatty acid methyl esters (FAMES) was determined by HPLC. The reaction has reached equilibrium (FAME > 97%) with re-hydrated catalyst for 1.5 h, whereas with catalyst calcined at 900 °C for 4 h.

1. Scope

CaO-based catalysts are known as highly active, easily accessible and low price catalytic materials and are widely used for the transesterification of vegetable oils to biodiesel [1]. Catalysts, derived from biological resources as raw waste materials such as egg, oyster or clam shells may be suitable sources of calcium, which can be easily converted into CaO. The catalytic activity of such materials generally depends on the catalyst preparation conditions [2, 3]. In the present study, the influence of thermal activation by calcination and re-hydration involving calcination-hydration-dehydration-calcination steps on the activity of the catalysts derived from the raw chicken eggshell (ESR) in the transesterification of the sunflower oil to biodiesel were studied.

2. Results and discussion

XRD patterns showed (Fig. 1) that the ESR is converted into active form at 900 °C, whereas modified calcined form is converted at 600 °C. The hysteresis loop

corresponds to type III (Fig. 2), characteristic for the non-rigid aggregate of plate-like structure (SEM micrograph). Textural properties and catalyst activity of prepared catalysts presented in Table 1 show that thermal and re-hydration treatment lead to significant improvement in the porous structure (specific surface and pore diameter).

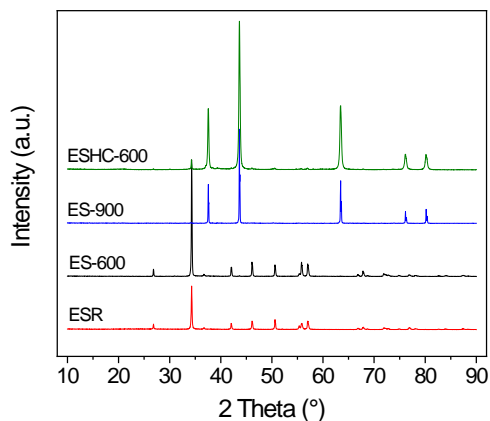


Figure 1. XRD patterns of synthesized catalysts

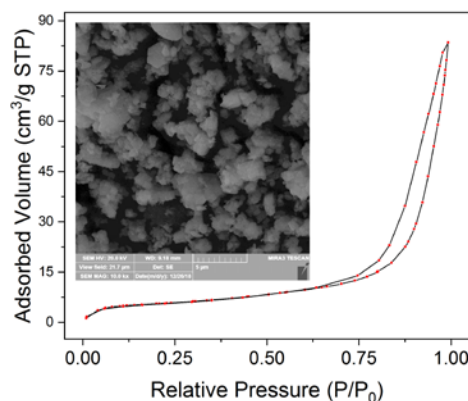


Figure 2. BET adsorption-desorption isotherms and SEM micrographs of ESHC-600

Table 1. Textural properties and activity of prepared catalysts from chicken eggshell

Sample	ESR	^a ES-600	^b ES-900	^c ESHC-600
<i>Textural properties</i>				
^d S _{BET} (m ² /g)	<1	-	<1	19.3
^e D _{p,av,BJH} (nm)	8.7	-	28.0	17.0
^f V _{p,BJH} (mm ³ /g)	0.9	-	0.7	121.2
^g P (vol.%)	29.8	27.0	55.2	73.6
<i>Catalytic activity</i>				
^h FAME (%)	0.0	0.0	46.5	97.4

^{a,b}ES-t-eggshell calcined at 600 and 900 °C; ^cESHC-600-eggshell calcined at 900 °C-re-hydrated-calcined at 600 °C; ^dS_{BET}-specific surface; ^eD_{p,av,BJH}-average pore diameter; ^fV_{p,BJH}-pore volume; ^gP-porosity; ^hFAME (%) after 1.5h.

3. Conclusions

Non-active carbonate form obtained from eggshell can be converted to the active oxide form by means of a thermal treatment. However, thermal treatment combined with re-hydration leads to catalysts with more favourable structural and morphological properties and with a significant improvement in the catalytic activity. The high FAME concentration (>97%) is achieved with ES-900 and ESHC-600 catalysts for different reaction time, 4 and 1.5 h, respectively.

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