Nanochemistry and biotechnology

New biocomponents from hydroxyacetone: catalytic synthesis of acetonyl butyrate and 2-oxopropyl octanoate

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Etherification of monocarboxylic acids with ketoalcohols (like hydroxyacetone or acetol - this reactive ketoalcohol can be considered as useful reactant for synthesis such organic compounds as ketoesters , acetals and other oxygenates [1-3]) represents not very well-known liquid-phase reactions of considerable industrial interest due to the importance of organic ether productions. Industrially widely applied etherification and transetherification reactions are catalysed using mineral liquid acids with high catalytic activity. In fact, corrosive nature, existence of side reactions and catalysts cannot be easily separated from the reaction mixture are main problems. Solid acid catalysts are not corrosive and they can be easily reused.

Part of catalytic experiments were performed with using two rotated autoclaves (100 rpm) at 60 – 100^{0}C within 1-6 h. Typically, 15 ml of butyl acetate – acetol (or monocarboxylic acid) mixture was placed into 20 ml teflon can and 5 – 7 wt.% of a catalyst was added. Molar ration of carboxylic acid : hydroxyacetone (HA) was varied in the interval from 6:1 to 3:1. The liquid samples were analyzed on a gas chromatograph with a mass spectrometer (GC-MS, ISQ Trace GC Ultra) and with a gas chromatograph connected to a hydrogen flame ionization detector. BET surface area, pore diameter, and BJH cumulative pore volume were obtained using N_2 adsorption at−196◦C in a Quantachrome Nova 2200e Surface Area and Poze Size Analyser. Before N_2 adsorption, the catalyst samples were outgassed for 3 h at 120◦C. IR spectra were recorded using a Frontier Perkin Elmer FTIR spectrometer. Thermogravimetric analysis (TGA) was done using a Shimadzu DTG-60H to characterize the used catalysts. Under a nitrogen flow of 20 ml/min, the temperature was first stabilized at 25◦C for 30 min and then ramped to 600◦C a 10◦C/min. Scanning electron micrographs (SEM) of fresh and used catalysts were recorded using a Jeol JSM-6490LV. The acceleration voltage of 20 kV was used.

Conclusions

Synthesis of 2-oxopropyl butyrate (acetonyl butyrate) via transetherification of butyl acetate with acetol and etherification of butyric acid with hydroxyacetone was perfomed over solid acidic catalysts at an ambient argon pressure in batch reactor and autoclaves. It was found that acetol was converted into acetonyl butyrate through acid cleavage of butyl acetate and further transetherification with yield ≈50%. For the process of etherification final yield of acetonyl butyrate was reaches approximately 58% at temperature 80^{o}C in the batch reactor. Etherification of octanoic acid with hydroxyacetone over sulphoresin Dowex DR-2030 and mixed ZrO_2-SiO_2 oxide have been studied. It was found that high selectivity formation of acetonyl octanoate is observed over Dowex DR-2030 catalyst at 80^{0}C at an ambient argon pressure in batch reactor. The yield of 2-oxopropyl octanoate (acetonyl octanoate) was reaches approximately 50% .

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