111a Transesterification of Triacetin and Esterification of Acetic Acid on Tungstated Zirconia

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Currently, biodiesel is synthesized by inefficient and expensive batch processes that employ homogeneous acids and basis as esterification and transesterification catalysts, respectively. The application of heterogeneous catalysis for the synthesis of biodiesel offers significant advantages over homogeneous catalysis because it can reduce catalyst usage cost, decrease costly separation steps, and permit the use of continuous processing. Solid acid catalysts offer the advantage of being able to carry out transesterification and esterification reactions simultaneously. Although active solid acid catalysts like sulfated zirconia (SZ) and tungstated zirconia (WZ) have site activities identical to concentrated sulfuric acid, due to the lower concentration of acid sites per weight of catalyst, they are not as active on a weight basis as the liquid acid. However, they can be used at higher temperatures (>60°C) where methanol would be in the gas phase. Liquid acids present problems in the presence of multiple phases; however, solid catalysts can work efficiently in such situations. Thus, the lower activity of solid acid catalysts at typical liquid phase reaction temperatures can be corrected by operation at higher temperatures.

This paper reports on an investigation of WZ for the transesterification of triacetin (TA) (a model compound for triglycerides, TGs) and the esterification of acetic acid (HAc) (a model compound for free fatty acids, FFAs) with methanol under liquid phase conditions. Prior to reaction, the x-ray amorphous WZ samples were calcined at 400°C, 500°C, 600°C, 700°C, 800°C and 900°C under UHP flowing air for 3h. X-ray diffraction patterns were obtained for elucidation of structural characteristics. Changes in catalyst surface area were obtained using BET analysis. Temperature-programmed desorption of ammonia was used to obtain surface acidity and an estimate of the strength of the acid sites. Reactions were carried out in a well-mixed batch reactor at 60°C under atmospheric pressure using TA + MeOH, HAc + MeOH, and mixtures of TA and HAc with MeOH. Initial rate results indicated that the formation of the monoclinic phase and large zirconium oxide crystals decreased the catalyst activity. The combination of tetragonal phase of zirconia and x-ray amorphous zirconium oxide offered the best activity in the transesterification reaction. A comparison is made between the catalyst activity of WZ for esterification and for transesterification. The impact of water, produced as a byproduct of esterification, on transesterification of TA is delineated.