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Valorization of glycerol in the presence of carbon catalysts

ABSTRACT

The submitted doctoral dissertation aimed at detailed research on the development of novel heterogeneous carbon-based catalysts for selected glycerol valorization processes, including the esterification of glycerol with acetic acid, the etherification of glycerol with tert-butyl alcohol, and the glycerolysis of urea, all leading to valuable chemical compounds. This topic is of particular importance due to the need for efficient management of glycerol, a by-product in the biodiesel production process, which is currently on the market in significant excess, potentially threatening the profitability of the biodiesel industry. The main purpose of the work was to establish the relationship between the physicochemical properties of the obtained samples and their catalytic activity in the selected glycerol valorization processes. The most significant findings are summarized in the doctoral dissertation, which includes a series of five thematically related scientific articles (P1–P5) along with appropriate commentary.

Article P1 presents the results of the glycerol esterification process with acetic acid. The reaction was carried out in the presence of thermally reduced graphene oxide (TRGO) functionalized with various agents, such as sulfuric acid, in situ generated diazonium salt (BDS), or phosphoric acid, serving as catalysts. Physicochemical analyses of the samples confirmed that the applied modifications were effective, leading to a significant increase in the total acidity of the TRGO due to the introduction of S-, O-, and/or P-containing functional groups onto its surface. It was demonstrated that the type of surface groups had a key impact on glycerol esterification with acetic acid. Specifically, the esterification process was most efficient in the presence of catalysts containing strongly acidic groups, i.e., $-SO_3H$ functionalities. The BDS-modified TRGO exhibited the best catalytic performance in the process, attributed to the high content of sulfonic groups, and maintained its catalytic activity for at least four reaction cycles.

Etherification of glycerol with tert-butyl alcohol over fibrous carbon catalysts is discussed in scientific articles P2, P4, and P5.

The P2 article shows the results of using carbon fibers (CF) obtained through the CCVD process from ethylene or isobutane and modified with H_2SO_4 or BDS. It was found that sulfonation with BDS was a more effective method for introducing sulfur-containing

moieties into the CF structure compared to modification with sulfuric acid. Furthermore, it was demonstrated that the carbon fibers produced from ethylene were more susceptible to functionalization than those from isobutane. The BDS-modified materials, which presented the highest functionalization degree with -SO_3H groups, worked most effectively in the tested process. However, due to the variable structure of the samples (i.e., the presence of fibers with different diameters and a small number of carbon nanotubes), it was not possible to clearly determine the impact of the initial carbon type on the functionalization of CF and their activity in the tested reaction.

In the subsequent stages of work, commercial carbon nanotubes (CNT) were used to prepare functionalized catalysts for the etherification of glycerol with tert-butyl alcohol. These samples had a uniform structure, which facilitated a more accurate assessment of the results, and the outcomes are presented in articles P4 and P5. Additionally, an attempt was made to increase the CNTs' susceptibility to functionalization through their mechanical pretreatment (using a ball mill). This method positively impacted the efficiency of sulfur incorporation into the carbon structure by fragmenting CNT bundles and breaking individual fibers, thereby generating new edges susceptible to functionalization. Furthermore, adding glucose to carbon nanotubes during their modification with H_2SO_4 improved CNTs' functionalization, as a carbonaceous matter derived from glucose and deposited onto the CNT acted as a "glue" for the introduced groups. The most effective method of modification of CNT was the use of BDS, which introduced a significant amount of sulfur in the form of -SO_3H groups into the carbon structure. In the presence of the most active samples (selected CNT modified with BDS), glycerol conversion and yields of the desired tert-butyl ethers exceed those obtained with a commercial catalyst Amberlyst-15. Importantly, these CNT samples retained their activity over several reaction cycles. It was demonstrated that sulfonic groups are crucial for the etherification of glycerol with tert-butyl alcohol. However, the presence of oxygen-containing species also had a positive effect on the reaction, most likely due to the increased hydrophilicity of the materials, which facilitated the adsorption of reagents on the catalyst surface and enabled their contact with active sites.

Article P3 presents the development of novel carbon-based catalysts for the glycerolysis of urea to glycerol carbonate (GC). Systems consisting of oxides of selected metals (Ba, Cr, Mg, and Zn) deposited on carbon fibers (CF) obtained from LPG gas via the CCVD process were prepared in this study. All the catalysts were active in the urea glycerolysis, however, the catalytic results varied slightly between the samples. These differences were most likely due to variations in the distribution of acid-base groups within the materials. It was also

shown that the use of oxidized carbon support (CF) in the reaction positively impacted the process, significantly increasing the selectivity to GC compared to the reaction without a catalyst. The reaction conditions were optimized for the best-working sample, i.e., ZnO/CF. Two methods of removing ammonia (by-product) from the reaction medium were also presented: passing inert gas (Ar) through the reactor or through the reaction mixture. It was demonstrated that the latter method significantly reduces side reactions.