INVESTIGATION OF THE HETEROGENEOUS CATALYTIC ADDITIONOF VINYL ACETATE TO AZOLES USING TRANSITION-METAL ACETATES IMMOBILIZED ONPOLY(1-VINYLAZOLES)

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The catalytic activity of acetates of various transition metals (Zn2+, Mn2+, Co2+, Ni2+, Cu2+) on poly(1-vinylazole) carriers was studied in regard to the addition reaction of vinyl acetates via aza-Markovnikov mechanism. The immobilization of homogeneous transition-metal catalysts on organic polymers has attracted increasing attention, as it enhances product yields and enables catalyst reusability, thereby reducing overall catalyst consumption. The immobilization of transition metals on polymer matrices, such as poly(1-vinylazoles), for use as catalysts in aza-Markovnikov reactions has not been previously investigated, and this study addresses that gap [1]. 1-(α-Acetoxyethyl)-3,5-dimethylpyrazole is described in the literature [2]. The compound most likely decomposes at high temperatures. It was found out that during distillation at 80-90 °C temperature under 30 mm Hg vacuum 1-(α-Acetoxyethyl)-3,5-dimethylpyrazole undergoes cleavage, resulting in the formation of acetaldehyde and 1-acetyl-3,5-dimethylpyrazole. It should be noted that 1H-imidazole reacts with vinyl acetate even in the absence of $M(OAc)_2$ catalysts, so 1-(α-acetoxyethyl)imidazole and 1-acetylimidazole are formed in approximately the 1:1 ratio. The usage of Ⓟ→$M(OAc)_2$ catalysts shifts the reaction towards the formation of 1-acetylimidazole. Notably, this method enabled the first reported synthesis of 1-(α-acetoxyethyl)-3,5-dimethylpyrazole. The suggested optimized method has a number of advantages compare to previously known methods. The products are obtained with high yields without elaborate technological solutions. Moreover, the reactions proceed at room temperature and even without mixing the reagents. The ease of separating the products from the reaction mixture is another substantial benefit of the suggested method, since the use of chromatographic methods is not required. The obtained heterogeneous catalysts proved to be reusable, maintaining catalytic activity for more than three reaction cycles without requiring intermediate purification. Moreover, the polymeric part can be also regenerated and reused.

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