

Abstract

Formamides are valuable compounds in pharmaceutical production and organic synthesis; however, their common synthesis methods suffer from number of drawbacks including low reaction rate and contamination with heavy metals leached from a catalyst. According to several articles, these problems could be overcome by using zeolite-based catalysts. Nevertheless, the mentioned articles provide somewhat conflicting results and also lack a clear description of which centres in zeolites are catalytic active.

Therefore, we prepared a set of zeolite-based catalysts commonly described in the literature (zeolite Beta ion exchanged to H^+ and Cu^{2+} form) in order to test them as catalysts and clarify their catalytic behaviour and nature of the active sites. We chose formylation of N-methylaniline by formic acid as the model reaction for our research and performed a series of experiments under varying conditions (solvents, concentration of reactants, temperature). In contrast to the published articles, none of the investigated materials demonstrated significant catalytic activity in our experiments. Moreover, we found that the often pronounced catalyst: zeolite Beta ion-exchanged into the copper form, is unstable in the presence of formic acid, which causes leaching of copper into the reaction mixture. At the same time, we were able to prove that the reaction proceeds spontaneously in 1,4-dioxane in the absence of a catalyst and with up to 98% selectivity. Hence the question arises, whether the catalysis is even necessary to carry out this reaction.

Moreover, we found a significant dependence of the rate of uncatalysed reaction on external conditions such as ambient temperature. In light of this discovery, we have to express a concern that the authors of the published articles may not have been aware of the spontaneous course of the reaction in the collected samples and that the results presented in the literature may be greatly distorted and inconsistent with reality.

Keywords: formylation, zeolites, formamides, Beta zeolite, acid catalysis