Journal of Structural Chemistry, Vol. 48, Supplement, pp. S171-S183, 2007
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DFT ANALYSIS OF THE MECHANISM OF 1,2-DICHLOROETHANE DECHLORINATION ON SUPPORTED Cu–Pt BIMETALLIC CATALYSTS

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UDC 541:547.222

The reaction routes of 1,2-dichloroethane dechlorination to ethylene on discrete nanoclusters that served as models of the active sites of supported Cu–Pt catalysts were calculated. Two reaction pathways were predicted. The first route corresponds to sequential elimination of the chlorine atoms from 1,2-dichloroethane; this is a three-stage reaction that occurs via two stable intermediates (stepwise mechanism). The limiting stage is the stage that corresponds to the dissociation of the first C–Cl bond. The second channel corresponds to a simultaneous one-stage elimination of two chlorine atoms (direct mechanism). Both reaction routes are thermodynamically possible, but the stepwise process is more probable, in contrast to the process on monometallic Cu catalysts. For the stepwise process, the vibrational spectra of stable intermediates were calculated for identification of the latter. A set of spectral data characteristic for the stepwise mechanism were determined. The three-step molecular mechanism suggested for 1,2-dichloroethane dechlorination to ethylene is compared with several kinetic schemes known from the literature. Possible modifications of the reaction route that forms ethane and monochloroethane are analyzed.

Keywords: bimetallic Cu–Pt catalysts, 1,2-dichloroethane, dechlorination, DFT calculations, reaction route.

INTRODUCTION

Bimetallic systems designed for dechlorinations have aroused great interest in view of the possibility to control the activity and selectivity of catalysts by varying the concentration of the components. Realization of this possibility, however, demands thorough understanding of the molecular mechanism of the reaction. In our previous communication, we analyzed two mechanisms of 1,2-dichloroethane (1,2-DCE) dechlorination to ethylene on monometallic copper catalysts [1]. The first mechanism involves sequential three-stage dissociation of the C–Cl bonds (stepwise mechanism). The second mechanism corresponds to simultaneous one-stage elimination of two chlorine atoms from 1,2-DCE (direct mechanism). A comparison of the two reaction channels showed that the latter mechanism was most probable. However, the high activation energy and hence low activity are serious disadvantages of copper catalysts in dechlorinations. Regretfully, it is difficult to reconcile the high activity and selectivity in monometallic systems. Therefore, it is important to seek catalytic systems based on bimetallic alloys as potential catalysts for solving this problem.

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