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The influence of the solvent nature on glyoxal disproportionation in glycolic acid using Sn-MFI zeolite as a catalyst

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Recently, the metal-containing high-silica zeolites have gained a significant interest as heterogeneous catalysts for liquid-phase processes [1-4]. Such materials are used as catalysts for keto-alco transformation, including isomerization of ketoalcohols [5], disproportionation of α-dicarbonyls [2], MPV-type reactions [3], alkene epoxidation [4], cycloketone-lactone oxidation [6]. The main advantages of these catalysts are a homogeneity of their active centers and a microporous structure that cause high selectivity in the abovementioned processes. According to the literature, the tetrahedrally coordinated tin cation in the zeolite lattice acts as an active center [7]. The intramolecular glyoxal (GLY) disproportionation into glycolic acid is the most selective and irreversible reaction which may be carried out over Sn-containing MFI-type catalysts. Ohshima et. al. [8] proved that the reaction mechanism passes through a hydride shift. There is an information about the opportunity of GLY disproportionation reaction to occur using different proton solvents such as alcohols (methanol, ethanol, and butan-1-ol) [2]. The present work is focused on the influence of water–acetonitrile binary mixture on the GLY disproportionation kinetics with the Sn-MFI-140 used as the most active and selective catalyst amongst the obtained mesoporous silica-based tin-incorporated zeolite materials.

Batch catalytic tests were carried out under argon cushion in the 40 cm^3 thick-walled glass vials dipped in a heating stirrer at 343 K. The vials were loaded with 0.3 ml of 1M glyoxal solution prepared from 40 %wt. glyoxal (Sigma-Aldrich), 10 mg of the Sn-MFI catalyst (Si/Sn = 140), and 29.7 ml binary solvent with a different molar ratio. The glyoxal/tin ratio was 259 in the final reaction mixture. In reaction products glycolic acid (GA) was isolated by high-performance liquid chromatography (HPLC) in a Shimadzu LC-20C system equipped with a Phenomenexe Rezex ROA-H+ column heated at 313 K and a UV detector at 210 nm using an aqueous eluent of 0.005 M H_2SO_4 (pH 2.30) flowing at 0.9 cm^3 min^{-1}. Glyoxal was determined by addition of Girard-T reagent in a 0.5 M H_3PO_4 water solution. After derivatization, GLY-Girard-T adduct was isolated by the high-performance liquid chromatography (HPLC) in a Shimadzu LC-20C system equipped with a Zorbax SB-Aqua column heated at 303 K and a UV detector at 295 nm using an aqueous eluent of 0.005 M H_2SO_4 (pH 2.30) flowing at 1.0 cm^3 min^{-1}.

It was shown that the reaction of GLY disproportionation to glycolic acid on the Sn-MFI-140 catalyst occurs quantitatively. The rate of GLY transformation in water–acetonitrile binary mixture rises with the increase in the concentration of acetonitrile in the mixture and depends on the dielectric constant of the system. The maximal rate is observed for the water–acetonitrile molar ratio of 1/8. The effective rate constant logarithm for glyoxal disproportionation to glycolic acid is straightened in the Kirkwood equation coordinates, which evidences on the presence of non-specific interactions between the solvent and the activated complex.To study the influence of the adsorption of glyoxal and glycolic acid the experiments on GLY and GA adsorption on the surface of the studied catalyst have been carried out. Unlike glycolic acid, glyoxal adsorption was observed in both solvents. The adsorption degree of GLY in acetonitrile was 32 times higher than in water. The tentative scheme of glyoxal transformation into glycolic acid over the tin-containing active site will be discussed.

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