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HOMOGENEOUS OXIDATION OF CYCLOHEXANE CATALYZED BY COORDINATION COMPOUNDS OF COPPER (II), AMMONIA AND NAPHTHOIC ACIDS

Various copper compounds form a vast variety of catalytic systems which are widely applied in homogeneous and heterogeneous catalysis. Cu-containing catalysts are attractive because of versatile redox properties of this metal, its natural abundance, relatively low cost, low toxicity [1].

Copper salts are capable of catalyzing the oxidation of cyclohexane to give cyclohexanol and cyclohexanone. This reaction is an important step in the production of caprolactam. The industrial process of oxidation of cyclohexane by air in presence of cobalt naphthenate is carried out under sufficiently rigid conditions: at temperature of 120–160°C and pressure of 1–2 MPa. Nevertheless, the conversion of the initial hydrocarbon to the alcohol and ketone does not exceed 5%. At the same time some metal–organic coordination compounds of copper allow cyclohexane oxidation under mild conditions with total product yield of 15% [2].

Two novel coordination copper compounds presented in this paper, $[\text{Cu}(\text{NH}_3)_2(\text{naphthalene-2-carboxylate})_2]$ (1) and $[\text{Cu}(\text{NH}_3)_2(\text{naphthalene-2,6-dicarboxylate})]_n$ (2), were obtained by self-assembly reactions of copper (II) nitrate, ammonia, 2-naphthoic acid or 2,6-naphthalenedicarboxylic acid, correspondingly. Compound 2 is a coordination polymer, which was formed due to bifunctionality of the carboxylic acid. The complexes were isolated as stable, aqua-soluble microcrystalline products and were characterized by IR spectroscopy and single-crystal X-ray diffraction (Figure 1). Compounds 1 and 2 were used as homogeneous catalysts for the mild oxidation of cyclohexane. The reaction was carried at 50°C under atmospheric pressure in aqueous acetonitrile medium using H_2O_2 as an oxidant both in the presence of acid promoter (CF_3COOH) and without it. The kinetics of cyclohexanol and cyclohexanone formation was studied by measuring their concentrations in the reaction mixture with the gas-liquid chromatography method: *Agilent 7820A* with the *FID* detector and capillary column *BP20/SGE* (30 m × 0.22 mm × 0.25 μm), helium as a carrier gas.

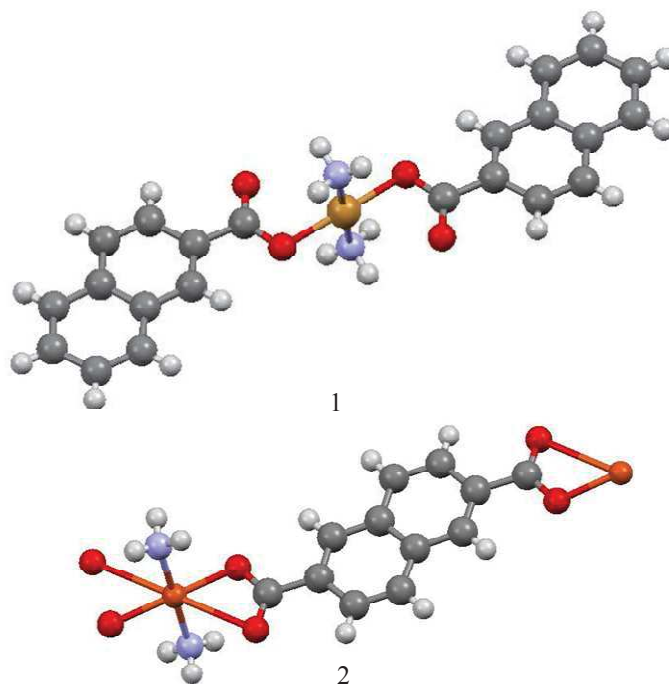


Figure 1 - Structural fragment of complexes 1 and 2

It was found that:

- the reaction does not run without an acid promoter; in the presence of both (1) and (2), the conversion of cyclohexane to the alcohol and ketone does not exceed 1%;

- the maximum conversion of cyclohexane to the alcohol and ketone was 15% and 22% in the presence of trifluoroacetic acid for the reactions catalysed by complexes 1 and 2, correspondingly. The promoter activates the catalysts via partial protonation of ligands, facilitates protons transfer, and enhances the oxidation properties of H_2O_2 ;

- cyclohexanol is predominantly formed in the beginning of the reaction, however, after 2 h the ketone to the alcohol ratio reaches 1:2 in the reaction mixture.

- after 4 h the yield of cyclohexanol decreases slightly. This is probably explained by the drastic oxidation of cyclohexane.

REFERENCES

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