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on Fundamental and Applied Aspects of
Physical Chemistry

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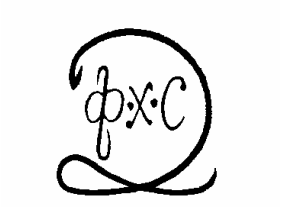

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COBALT-DOPED ALUMINA CATALYSTS IN CATALYTIC OXIDATION OF TARTRAZINE INDUCED BY OXONE®

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ABSTRACT
In this work cobalt-doped alumina catalysts were synthetized using the sol-gel method. The calcination temperatures were 500 °C, 1000 °C and 1100 °C and the catalysts were denoted as CoA-500, CoA-1000 and CoA-110, respectively. The obtained catalysts were tested as Oxone® activators for the degradation of tartrazine azo-dye. The influence of the mass of catalyst and the reaction temperature was investigated. The catalyst mass and temperature increase were beneficial for the dye degradation rate. All three catalysts were found to be effective for tartrazine degradation in the presence of Oxone®.

INTRODUCTION
Cobalt-based catalysts are widely studied and applied in different processes. Cobalt nitrate and cobalt acetate are the most commonly used precursors in the preparation of the cobalt-based catalysts. These catalysts are usually prepared via impregnation on various oxide supports, such as Al_2O_3, SiO_2 or TiO_2 [1]. The cobalt-based catalysts have been largely used as oxidation catalysts in numerous environmental applications [2].

One of the applications of the cobalt-based catalysts is the activation of Oxone® ($2KHSO_5 \times KHSO_4 \times K2SO_4$) in order to generate $SO_4^{\cdot -}$ radicals effective in the oxidative degradation of different organic pollutants in wastewaters [3]. Azo-dye tartrazine is mostly used in the food industry. The presence of tartrazine in wastewater may cause serious health problems. Therefore, the removal of tartrazine from industrial effluents can be regarded as a highly important goal [4].
In this work cobalt-doped alumina catalysts were used for the Oxone® "activation" in the catalytic oxidation of tartrazine dye as a water pollutant.

EXPERIMENTAL
The sol-gel method was used for the preparation of the Co(II)-doped alumina composites. Aluminum alkoxide was used as the precursor for boehmite sols. Aluminum isopropoxide was hydrolyzed at 80 °C in an excess amount of water. The hydrolysis was followed by a peptization with the appropriate amount of HNO_3 in order for a stable colloidal sol to be formed. The sol was kept at a constant temperature and under reflux conditions for a desired time, during which most of the alcohol evaporated [5]. In order for the Co/Al composite to be obtained, $CoNO_3x6H_2O$ was added to a freshly prepared sol, in the amount that provides 40 mass% of Co with respect to Al. The doped boehmite sol was then gelled for 24 hours at 40 °C, and subsequently at 100 °C for another 24 hours. The gels were calcined at 500 °C, 1000 °C and 1100 °C for 5 h. These temperatures were selected in order for different structural phases of alumina (γ,δ-θ and α) to be obtained, with the goal of determining their catalytic diversity and selecting the most active phase. The obtained samples were denoted as CoA-500, CoA-1000 and CoA-1100, where Co stands for cobalt, the A stands for alumina and the number refers to the calcination temperature.

Catalytic tests were performed by stirring an aqueous tartrazine solution ($C_{0,dye}$=50 mg dm^{-3}) in the presence of 0.130 mmol of Oxone®. The tests were conducted in a 500 cm^3 Pyrex reactor thermostated using a Julabo MC 4 circular heater and equipped with a mechanical stirrer. The

following experimental parameters were investigated. The effect of the mass of the catalyst was investigated for CoA-500 catalyst in the range from 5 mg to 100 mg and at the reaction temperature of 30 °C. The effect of temperature was monitored for all three catalysts (CoA-500, CoA-1000 and CoA-1100) in the range from 30 °C to 60 °C. The moment of adding Oxone® to the reaction mixture was taken as the initial (0 min) moment of the reaction. With respect to this moment, aliquots were taken at the predetermined periods of time. Supernatant solutions were separated from the solid phase by centrifugation at 17000 rpm for 3 min and analyzed using the UV–Vis spectrophotometry (Thermo Scientific, Evolution 220 UV–Visible Spectrophotometer). The peak at 426 nm, indicating the decolorization of the solution, was monitored and analyzed.

RESULTS AND DISCUSSION

The sol-gel method was used for the synthesis of the Co/Al composites. The impregnation with cobalt, performed after the synthesis of alumina, could be an alternative synthesis method, which would provide catalysts with lower contents of Co. However, the impregnation was not chosen, mainly because a lower leaching of cobalt was intended to be achieved, and leaching usually occurs as a problem in this type of catalyst synthesis. ICP measurements showed that leaching was in the order of magnitude of ppb, which is acceptable. Another advantage of the applied synthesis method is that it results in a higher dispersity and more homogeneous distribution of cobalt comparing with those in impregnated samples. This leads to a better exposure of the catalytically active sites.

The influence of the mass of the catalyst was investigated for CoA-500 in the mass range from 5 mg to 200 mg (200 cm^{-3} of 50 mg dm^{-3} tartrazine solution; 40 mg of Oxone®; T=30 °C, reaction time of up to 240 min) (Fig.1). With the increase of the mass of the catalyst the degree of decolorization increased. For the mass of 100 mg a plateau, related to nearly 100% of decolorization, was reached after only 5 minutes. On the other hand, for the lowest mass, the total decolorization was not reached within the investigated time (240 minutes). For further investigations, a lower mass of catalyst was chosen for the monitoring of the occurrence and disappearance of other degradation products, detectable by UV–Vis spectra (Fig. 2).

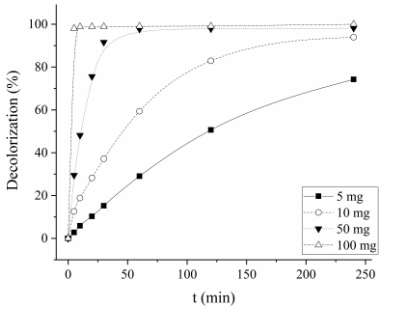

Figure 1. Influence of mass of catalyst CoA-500 on decolorization of tartrazine

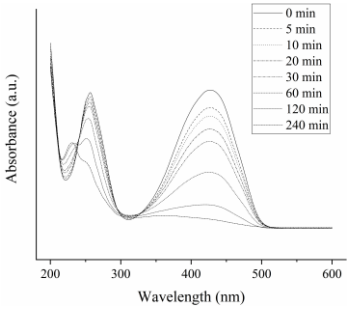

Figure 2. UV–Vis spectra for catalytic tests with 10 mg of the CoA-500 at 30 °C

The mass of the catalysts of 10 mg was chosen for the experiments conducted in order for the temperature influence on the efficiency of the catalysts to be investigated. Three catalysts: CoA-500, CoA-1000 and CoA-1100 were tested (Fig. 3). The rate of the decolorization of tartrazine under the investigated conditions was the highest for CoA-500 and the lowest for CoA-1100, for all investigated temperatures. Temperature increase was beneficial for the dye decolorization rate. Under the investigated conditions, the total decolorization was achieved in the case of the reaction conducted at 60 °C for all three catalysts. In the case of CoA-500, almost complete decolorization was achieved after 240 min for all temperatures. On the other hand, for CoA-1100, the decolorization at 30 °C was much slower, and almost linear

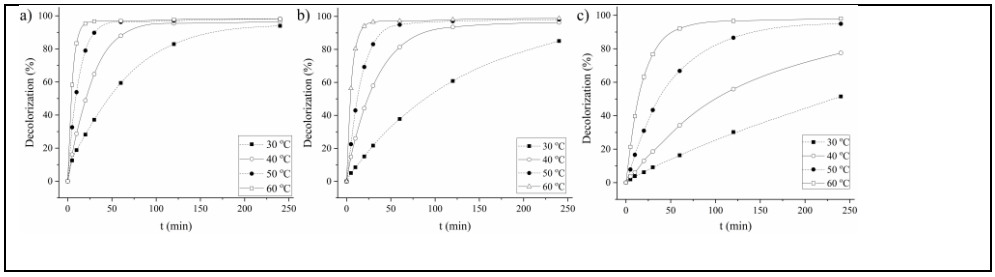

Figure 3. Decolorization of tartrazine solution at different temperatures using: a) CoA-500, b) CoA-1000 and c) CoA-1100

with time. Only 50% of the decolorization of the tartrazine was completed after 240 minutes.The results of the catalytic tests indicate that the gamma phase of the alumina was the most active in this reaction, under the selected test reaction conditions.

CONCLUSION

CoA-500, CoA-1000 and CoA-1100 were synthesized using the sol-gel method and tested as catalysts in a tartrazine solution decolorization. The role of the catalysts was to activate Oxone®, thus yielding $SO_4^{\cdot -}$ radical that act as oxidizing species. The influence of the catalyst mass and temperature was investigated. The increase of temperature and the mass of the catalyst was beneficial for the reaction. Although CoA-500 catalyst was found to be the most active in the investigated reaction, all three catalysts were efficient. The cobalt-doped alumina materials were found to be promising catalysts in the Oxone® initiated tartrazine decolorization.

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