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EFFECT OF DIFFERENT COBALT LOADINGS ON THE KINETIC PERFORMANCE OF COBALT-SUPPORTED ALUMINUM PILLARED CLAY TOWARDS TARTRAZINE DEGRADATION

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ABSTRACT

The 2 µm fraction of Wyoming clay rich in montmorillonite was pillared with aluminum. Obtained pillared clay was impregnated with different cobalt loadings using the incipient wetness impregnation method followed by calcination at 450 °C. The obtained materials were previously fully characterized. The synthesized materials were investigated as catalysts in catalytic oxidation of organic water pollutant, tartrazine, in the presence of Oxone®. Oxone® was a precursor of sulfate anion radicals. The effect of the different cobalt loadings on the reaction kinetics was investigated. The pseudo-first order kinetic model was found to be the most appropriate to fit the experimental data of all investigated catalysts under defined experimental conditions. The presence of Co_3O_4 as defined crystalline phase reduces the efficiency of cobalt-supported aluminum pillared clay in Oxone® activation and consequently oxidative tartrazine degradation.

INTRODUCTION

Tartrazine is a synthetic azo-dye used as a colorant in food and pharmaceutical industries to achieve yellow or green shades in sweets, juices, jams, sodas, vitamin capsules, antacids, and cosmetics [1]. Tartrazine, as azo-dye may cause allergic reactions asthma, thyroid tumors and lymphomas. Therefore, the removal of tartrazine from industrial effluents and other wastewaters is highly important.

Catalytic oxidation processes involving sulfate radicals, as strong oxidants, are broadly used for the removal of organic pollutants from wastewaters in different industries [2]. Oxone® ($KHSO_5·0.5KHSO_4·0.5K_2SO_4$) is a triple salt with potassium monopersulfate as an active component, while two other sulfur salts are inactive and do not participate in the activation reaction [3]. Its activation is necessary since the self-decomposition of Oxone® is a slow process. Catalysts containing transition metal cations were proven to be highly effective in Oxone® activation. Among investigated transition metals, cobalt was proven to be the most efficient [5]. The discharge of cobalt ions in the heterogeneous catalysts, where cobalt is supported on a solid support, is restricted. Different supports for cobalt ions have been investigated. Pillared interlayered clays (PILCs) represent materials with permanent micro and/or mesoporosity, and thermal and chemical stability with great catalytic potential. Important application of PILCs is their use as support for active catalytic phases in the preparation of supported catalysts [6].

In this work, cobalt-supported aluminum pillared catalysts with different cobalt loadings were investigated in Oxone® activated degradation of tartrazine. The influence of different cobalt loading on kinetic parameters of the decolorization process of tartrazine was followed.

EXPERIMENTAL

The fraction of clay with the particle diameters of up to 2 µm was obtained by hydroseparation of the clay purchased from The Source Clays Repository - The Clay Minerals Society, Wyoming, USA [7]. The obtained fraction was converted into homoionic Na^+ exchanged material and used for aluminum

pillaring using a previously described procedure [8] and denoted as AP. AP was impregnated with $Co(NO_3)_2$ solutions using the incipient wetness impregnation method in order for Co-supported catalysts to be obtained [9]. Different concentrations of Co^{2+} were applied (0.3, 1.0, 1.7, and 3.3 mol dm^{-3}). According to theoretical calculations, x = 1, 3, 5, and 10 wt% of cobalt were introduced in this manner into AP, respectively. After drying, the samples were calcined at 450 °C and denoted as x%CoAP.

The obtained materials were previously fully characterized by X-ray powder diffraction (XRPD), inductively coupled plasma optical emission spectroscopy (ICP-OES), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy coupled with energy dispersive X-ray spectrometry (FE-SEM/EDX), high resolution transmission electron microscopy (HR-TEM) coupled with EDX, X-ray photoelectron spectroscopy (XPS), and low temperature N_2 physisorption [10].

A 500 cm^3 Pyrex reactor thermostated using a Julabo MC 4 circular heater and equipped with a mechanical stirrer was applied in all catalytic tests. Aqueous solution of tartrazine ($C_{0,T}$ = 50 mg dm^{-3}) was stirred in the presence of 40 mg of Oxone®. In all experiments, the 10 mg of the catalyst was added to the reaction mixture 5 min after the Oxone® was introduced into the tartrazine solution. This moment was taken as the initial (0 min) moment of the reaction. With the respect to this moment, aliquots were taken at predetermined periods of time. Besides synthesized catalysts, the commercial Co_3O_4 powder (Merck) was used for comparison purpose. The amount of applied Co_3O_4 powder corresponded to the theoretical value of the highest cobalt loading. Supernatant solutions were separated from the solid phase by centrifugation at 17000 rpm for 3 min and analyzed using UV–Vis spectrophotometry (Thermo Scientific, Evolution 220 UV–Visible Spectrophotometer). The reaction temperature was 50 °C and pH was not adjusted. The peak at 426 nm indicating decolorization of the reaction solution, as the first step in the degradation process [11], was monitored and analyzed.

RESULTS AND DISCUSSION
The selected properties of catalysts are given in **Table 1.**

Table 1. Phase composition, cobalt content and some textural parameters [10]

Property	Sample			
	1%CoAP	**3%CoAP**	**5%CoAP**	**10%CoAP**
Identified phases, XRD	Mt, Q	Mt, Q	Mt, Q, Co_3O_4	Mt, Q, Co_3O_4
Co experimental [wt.%]	0.79	2.55	4.13	7.85
Co theoretical [wt.%]	1.00	3.00	5.00	10.0
$V_{0.98}$ [cm^3g^{-1}]	0.090	0.105	0.085	0.102
S_{BET} [m^2g^{-1}]	146	124	123	129

where: Mt – montmorillonite; Q – quartz, $V_{0.98}$ – total pore volume; S_{BET} – specific surface area.

XRPD analysis did not confirmed any forms of cobalt oxide in 1%CoAP and 3%Co AP samples, while cobalt in the form of Co_3O_4 was identified and confirmed using XPS in 5%CoAP and 10% CoAP. Cobalt oxide nanoparticles were evenly distributed throughout the samples, which was confirmed by the microscopic techniques coupled with EDX. The higher cobalt loading resulted in the formation of cobalt oxide agglomerates that led to larger particle sizes [10].

The ICP-OES analysis confirmed the incorporation of cobalt in all impregnated samples in approximately 80 % of the theoretically calculated values. The obtained values for total pore volume were similar for all investigated samples. On the other hand, the specific surface area was the highest for the 1%CoAP. For other catalysts, S_{BET} values were almost the same.

Data obtained in the experiments for each investigated cobalt concentration were tested with various kinetic models. The best fit was achieved with exponential model corresponding to first-order-kinetics reaction (**Figure 1**) [12].

The exponential form of the applied first order kinetics model is given in Eq. 1:

$$Y_t = X e^{-kt} + E \qquad\qquad\qquad (Eq.\ 1)$$

Where: X is the amplitude, k is the pseudo-first-order rate constant, and E is the endpoint.
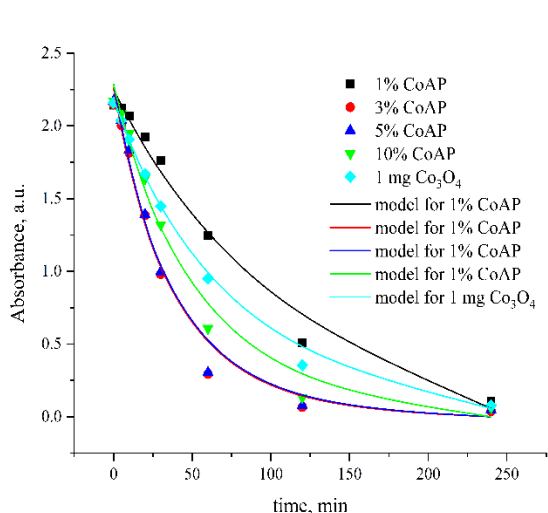

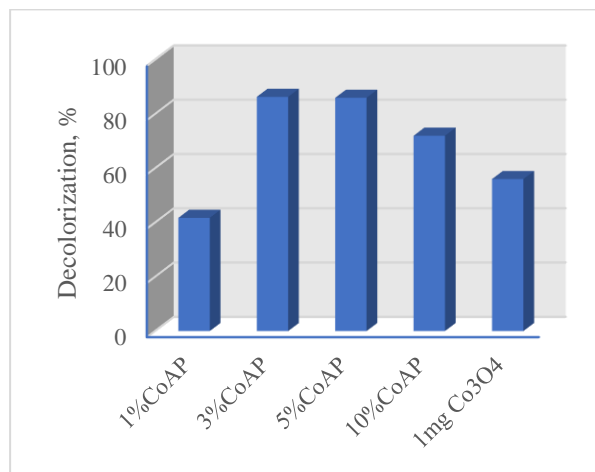**Figure 1**. Dependence of intensity of absorbance of the reaction time

Figure 2. Decolorization of tartrazine obtained for investigated samples after 60 minutes of the reaction

In **Figure 1** the symbols represent experimentally obtained values of absorbance at tartrazine characteristic peak at 426 nm, while the curves were obtained according to the model given in Eq. 1 The parameters calculated for this model are summarized in **Table 2.**

Table 2. Kinetic parameters calculated according to Eq. 1

Sample	X	k (min^{-1})	E	R^2	$\Sigma\sigma_i$
1% CoPILC	2.510	0.0086	-0.263	0.990	0.043
3% CoPILC	2.282	0.0270	-0.022	0.991	0.051
5% CoPILC	2.301	0.0271	-0.013	0.991	0.050
10% CoPILC	2.317	0.0191	-0.032	0.991	0.047
1 mg Co$_3$O$_4$	2.207	0.0138	-0.023	0.999	0.004

After 240 min of the reaction almost total decolorization occurred for all investigated catalysts. The rate of reaction was different. The reaction rate increased with the increase of the theoretical cobalt loading from 1% to 3%. With a further cobalt loading increase on 5% the reaction rate remained almost unchanged, but for the sample with 10% of cobalt the pseudo-first order kinetic constant dropped noticeably. Further decrease in degradation rate was observed for 1 mg of Co$_3$O$_4$. The obtained results indicate that the existence of Co$_3$O$_4$ resulted in a less efficient catalytic performance of the obtained catalysts. This observation is even more noticeable in **Figure 2.** where the percent of the decolorization was presented after 60 minutes of the reaction. The presence of the

small amount of the Co_3O_4 in 5%CoAP could be the explanation for the lack of the improvement of catalytic properties with an increase of the theoretical cobalt loading from 3% to 5%.

CONCLUSION

The effect of the different cobalt loadings, in cobalt-supported aluminum pillared clay, on the kinetics of the tartrazine degradation in the presence of Oxone® was investigated. The best fit for experimental data was the pseudo-first order kinetic model, for all catalysts. The presence of Co_3O_4 reduces the efficiency of cobalt-supported aluminum pillared clay in Oxone® activated tartrazine degradation. For this reason, the catalyst 5%CoAP lacked in the improvement of catalytic properties compared to the catalyst with 3% of cobalt loading.

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