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# PHYSICAL CHEMISTRY 2022

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*and*

*Borekov Institute of Catalysis Siberian Branch of  
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# KINETIC AND THERMODYNAMIC STUDY OF NICOTINE DEGRADATION BY OXONE® ACTIVATED BY COBALT BASED CATALYST

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## ABSTRACT

Acid activated montmorillonite was impregnated with  $\text{Co}^{2+}$  ions, calcined at 450 °C, and used as catalyst for Oxone® activation in catalytic oxidative degradation of nicotine. Catalytic tests were performed in temperature range from 30 °C to 60 °C in order to obtain kinetic data. Kinetic study at different temperatures showed that catalytic degradation of nicotine corresponded to the first-order kinetic model. The activation energy of the investigated degradation process was determined by applying Arrhenius equation.

## INTRODUCTION

Nicotine is usually considered as air pollutant since it is being released into the atmosphere by smoking, but many overlook the fact that nicotine dissolves in water very easily thus polluting it. Largest nicotine sources in the environment are land fields where nicotine dust from cigarette production is being disposed of, tobacco agriculture, the cigarette manufacturing industry [1] and also millions of cigarette butts as common urban litter [2]. Some of the methods used in nicotine removal from aqueous mediums are microbiological degradation, adsorption and chemical transformation [3]. In recent studies, Advanced Oxidation Processes (AOPs) as method of chemical transformation were used to investigate nicotine degradation in aqueous solutions [4]. In this work, the degradation of nicotine by Oxone® activated by cobalt impregnated acid activated montmorillonite catalyst was investigated. Effects of degradation temperature on nicotine degradation rate were analyzed, as well as degradation kinetics and thermodynamics.

## METHODS

The acid activation of montmorillonite was performed using previously described method with 4.5 M HCl [5] in order to improve textural properties of raw clay. The cobalt was introduced in the amount equal to the cation exchange capacity of acid-modified clay ( $0.693 \text{ mmol g}^{-1}$ ), using incipient wetness impregnation method [5].

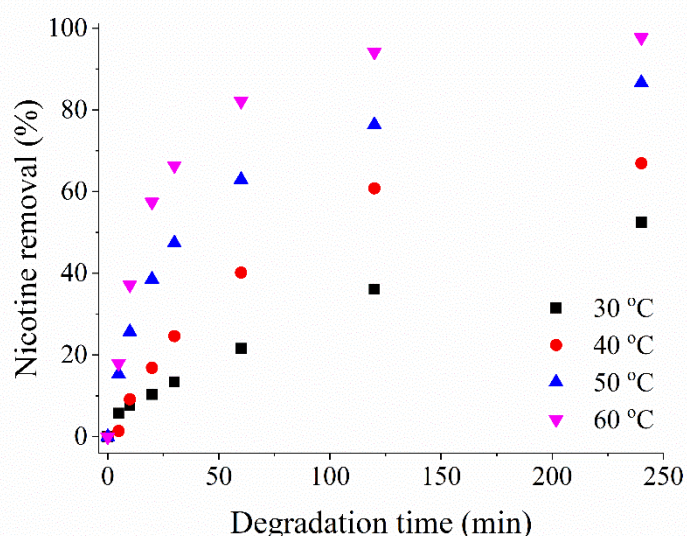
The obtained catalyst was previously fully characterized using Inductively coupled plasma (ICP), X-ray powder diffraction (XRPD), X-ray photoelectron spectroscopy (XPS), low-temperature  $\text{N}_2$  physisorption analysis, and transmission electron microscopy (TEM) [6].

Influence of the temperature on the nicotine degradation by  $1.0\text{Co}/\text{MW}_A$  was investigated under following experimental conditions:  $50 \text{ cm}^3$  of  $0.75 \text{ mmol dm}^{-3}$  nicotine solution, 0.368 mg of Oxone®, the reaction time up to 240 min, and the amount of catalyst 25 mg. Experiments were conducted in temperature range from 30 °C to 60 °C without pH adjustment. After separation of supernatant from the solid phase by centrifugation at 17000 rpm for 3 min, the solution was analyzed using a Thermo Electron Nicolet Evolution 500 UV–VIS spectrophotometer. The characteristic nicotine UV absorption peak at 261 nm was monitored.

## RESULTS AND DISCUSSION

The content of cobalt in the catalyst, expressed as CoO, was 2.17 mass %, which is 89 % of the theoretically introduced cobalt. The value of the  $d_{001}=0.97$  nm, obtained by XRPD analysis, corresponded to the collapsed smectite structure after calcination process at 450 °C. According to results of low-temperature nitrogen physisorption the following parameters for were calculated. The mesopore volume was determined to be  $0.152\text{ cm}^3\text{g}^{-1}$ , the specific surface area was  $87\text{ m}^2\text{g}^{-1}$ , and micropore volume was  $0.038\text{ cm}^3\text{g}^{-1}$ . The sample was dominantly mesoporous. The XPS analysis indicated that cobalt was in Co (II) oxidation state, while TEM microphotographs showed that dimensions of the cobalt-containing nanoparticles were approx. 5 nm [6].

The effect of temperature on nicotine degradation is presented in **Figure 1**.



**Figure 1.** Influence of temperature on catalytic degradation of nicotine.

As expected, degradation rate increased with the increase of temperature. Data obtained in the experiments for each investigated temperature were tested with various kinetic models. The best fit was achieved with exponential model corresponding to first-order-kinetics reaction [7].

Exponential form of the applied first-order kinetics model is given in Eq. 1:

$$Y_t = Xe^{-kt} + E \quad (1)$$

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

The parameters calculated for the first-order kinetics model are summarized in **Table 1**.

**Table 1.** Parameters calculated by fitting experimental data of catalytic degradation of nicotine with exponential kinetic model.

$t$ (°C)	$k$ [ $\text{min}^{-1}$ ]	$X$ [a.u.]	$E$ [a.u.]	$R^2$	$\Sigma\sigma_i$
30	$6.05 \cdot 10^{-3} \pm 9.00 \cdot 10^{-4}$	$2.09 \pm 0.17$	$1.040 \pm 0.180$	0.995	0.011
40	$1.53 \cdot 10^{-2} \pm 1.15 \cdot 10^{-3}$	$2.30 \pm 0.06$	$0.969 \pm 0.061$	0.997	0.017
50	$2.63 \cdot 10^{-2} \pm 3.20 \cdot 10^{-3}$	$2.64 \pm 0.12$	$0.580 \pm 0.096$	0.988	0.082
60	$4.26 \cdot 10^{-2} \pm 3.70 \cdot 10^{-3}$	$3.01 \pm 0.10$	$0.181 \pm 0.072$	0.993	0.067

where:  $X$ - amplitude of absorbance,  $E$  – endpoint of absorbance,  $k$  – first order kinetics rate constant,  $R^2$  – square of coefficients of correlation and  $\Sigma\sigma_i$  – sum of squared deviations.

Temperature increase was beneficial for the nicotine degradation rate. The first order rate constant ( $k$ ) increased with the increase of reaction temperature. The process kinetics showed good agreement with exponential fit with square of coefficient of correlation  $R^2 \geq 0.988$ . This confirmed the first order kinetics for catalytic degradation of nicotine at all investigated temperatures.

Arrhenius plot was used to calculate the activation energy of catalytic degradation:

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (2)$$

Where:  $k$  - first-order kinetics rate constant,  $E_a$  - the Arrhenius activation energy (kJ/mol),  $A$  - the Arrhenius factor,  $R$  - the gas constant (8.314 J/mol K) and  $T$  - the temperature (K).

The data obtained from the degradation experiments in range from 30 °C to 60 °C were used to calculate thermodynamic properties in order to better understand effect of temperature on nicotine degradation.

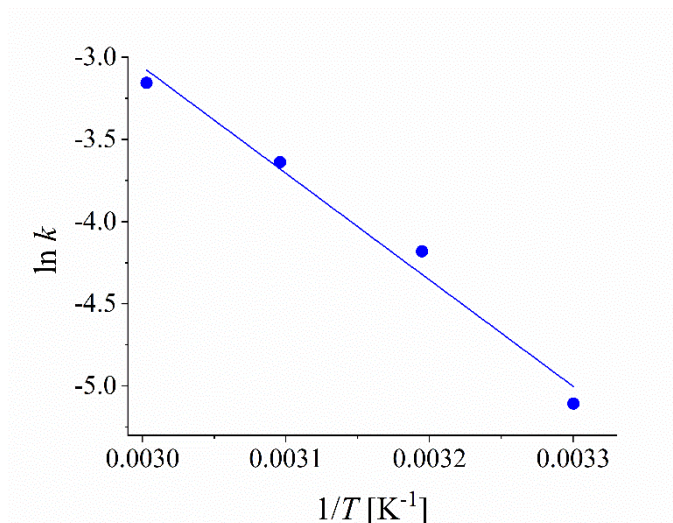
Gibbs free energy  $\Delta G^\circ$  was calculated using following equation (Eq. 3):

$$\Delta G^\circ = -RT \cdot \ln K_C \quad (3)$$

Where:  $K_C$  is the equilibrium constant, calculated as a ratio between equilibrium concentration of nicotine ( $C_e$ ), and concentration of nicotine in time  $t$  ( $C_t$ ).

Standard enthalpy  $\Delta H^\circ$  and standard entropy  $\Delta S^\circ$  were calculated from Eq. 4:

$$\ln K_C = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$



**Figure 2:** Arrhenius plot of nicotine degradation.

Thermodynamic parameters of nicotine oxidative degradation are given in **Table 2**.

**Table 2.** Thermodynamic parameters for nicotine degradation.

$T$ [K]	$\Delta S^\circ$ [kJ mol <sup>-1</sup> K <sup>-1</sup> ]	$\Delta H^\circ$ [kJ mol <sup>-1</sup> ]	$\Delta G^\circ$ [kJ mol <sup>-1</sup> ]
303	0.331	101.040	-0.250
313			-1.840
323			-5.017
333			-10.399

Negative value of  $\Delta G^\circ$  at different temperatures shows that process of nicotine degradation is spontaneous. The activation energy  $E_a$ , was obtained from slope of linear plot  $\ln k$  versus  $1/T$  (**Figure 2**) and has the value of 53.9 kJ mol<sup>-1</sup>.

## CONCLUSION

Cobalt impregnated acid modified montmorillonite was successfully applied as catalyst for Oxone® activation in the reaction of oxidative degradation of nicotine. Nicotine degradation is best described by exponential model that corresponds to first order kinetics, with squared correlation coefficients  $R^2 \geq 988$ . First-order rate constant increase with the increase of temperature. Results of the thermodynamic study indicated that nicotine degradation is a spontaneous process, endothermic process.

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