

PREPARATION OF CuO, Co₃O₄, AND Cr₂O₃ CATALYSTS SUPPORTED BY 13X ZEOLITE

Introduction

Supported catalysts utilized in oxidative abatement of volatile organic compounds (VOCs) are usually prepared by wet impregnation method, which is both cost-effective and eco-friendly. Active sites are formed through the process of adsorption of thermally destructible salts on the selected support and their subsequent calcination. 13X zeolite is very durable material for catalyst preparation, because of its thermal stability, good mechanical strength and micro pore structure, which defines its adsorptive and chemical properties. The best catalytic activity is achieved when the content of active component reaches 10 % so in order to optimize composition of catalysts it is necessary to evaluate adsorptive nature of support, characterize active component and evaluate its distribution after calcination.

Experimental

Zeolite 13X was soaked in copper, chromium, cobalt nitrates solutions for 2 h. Concentration of solutions varied from 10 to 50 g/l. After removal of the excess solution, the resulting samples were dried for 1 h and then heated for 6 h at 450 °C. XRD analysis of dried and calcined samples showed that CuO, Co₃O₄ and Cr₂O₃ were formed as active components on the surface of zeolite. The adsorptive capacity was determined by AAS analysis. Adsorption isotherms were drawn and several models were used to describe peculiarities of the process – Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Elovich. Cross-sectional images of the samples were obtained using optical microscopy.

Results and discussion

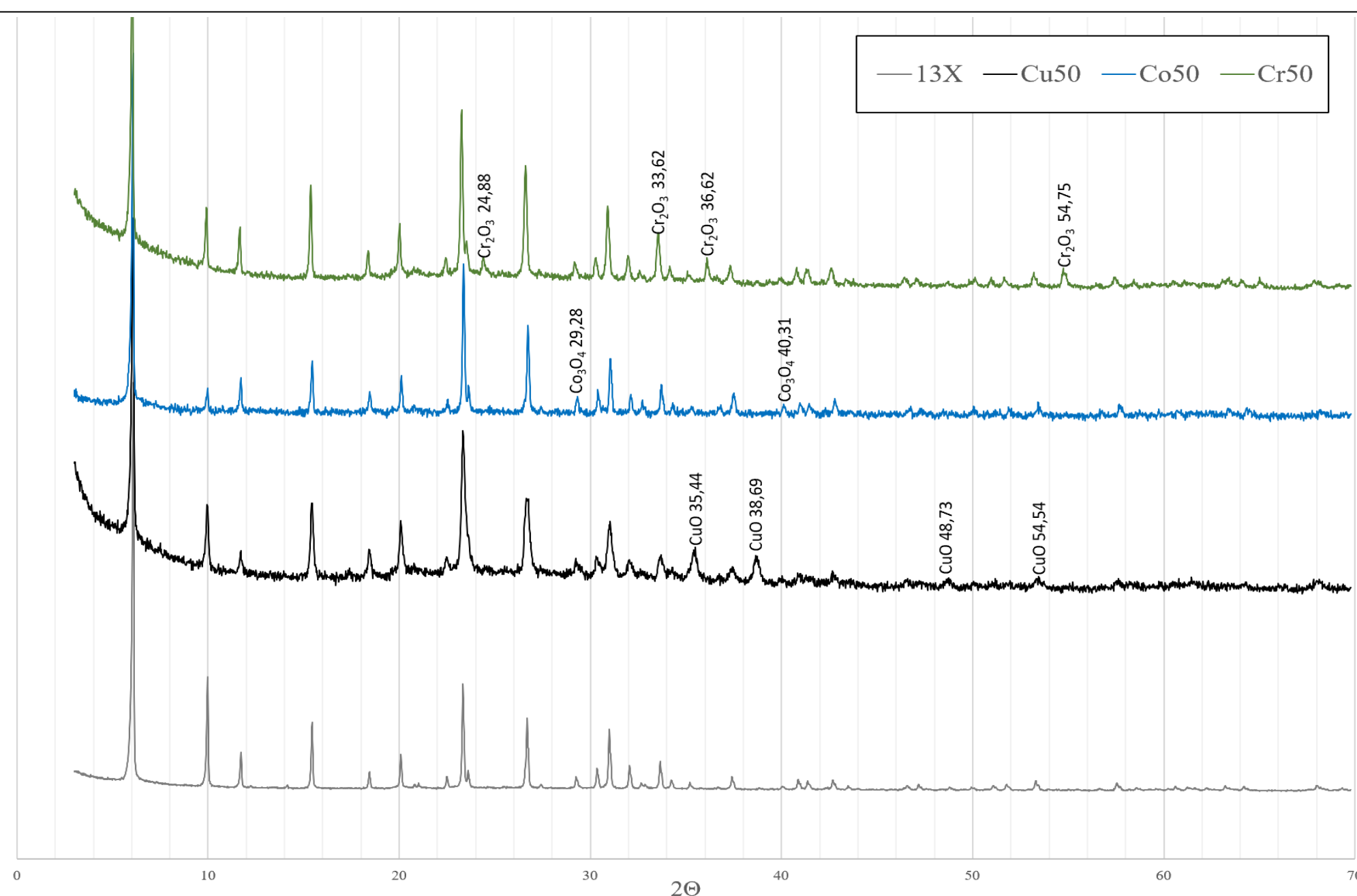


Fig. 1. Results of XRD analysis

Sample	Amount of Cu for adsorbent , mg/1g	Mass fraction of CuO, %
Cu 10	53,07	6,23
Cu 20	73,40	8,41
Cu 30	79,66	9,07
Cu 40	87,80	9,90
Cu 50	88,35	9,96

Table 1. Amount of catalitically active component in Cu samples

Sample	Amount of Co for adsorbent , mg/1g	Mass fraction of Co ₃ O ₄ , %
Co 10	54,76	6,94
Co 20	67,92	8,47
Co 30	78,11	9,62
Co 40	82,60	10,12
Co 50	85,21	10,40

Table 2. Amount of catalitically active component in Co samples

Sample	Amount of Cr for adsorbent , mg/1g	Mass fraction of Cr ₂ O ₃ , %
Cr 10	29,7	4,17
Cr 20	69,3	9,19
Cr 30	81,7	10,67
Cr 40	79,0	10,36
Cr 50	86,1	11,18

Table 3. Amount of catalitically active component in Cr samples

Table 4. Adsorption models parameters

Model	Linear form of the equation	Equation coefficients of Cu samples			Equation coefficients of Co samples			Equation coefficients of Cr samples		
		q _m	K _L	R ²	q _m	K _L	R ²	q _m	K _L	R ²
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L}$	0,4264	0,1276	0,9966	0,3919	0,1491	0,9980	0,4049	0,1424	0,9950
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	n	K _F	R ²	n	K _F	R ²	n	K _F	R ²
		3,2051	0,1149	0,953	4,0096	0,1343	0,9934	4,7710	0,1591	0,8987
Dubinin-Radushkevich	$\ln q_e = \ln q_m - \frac{(RT \ln(1 + 1/C_e))^2}{2E^2}$	q _m	E	R ²	q _m	E	R ²	q _m	E	R ²
		19,6839	733,3677	0,9911	7,0006	840,5730	0,9566	24,5915	711,4065	0,9387
Temkin	$q_e = \frac{RT}{\Delta Q} \ln C_e + \frac{RT}{\Delta Q} \ln K_T$	ΔQ	K _T	R ²	ΔQ	K _T	R ²	ΔQ	K _T	R ²
		68512459,1902	1,0032	0,9701	86304073,4132	1,0055	0,9933	44525491,6129	0,9811	0,885
Elovich	$\ln \frac{q_e}{C_e} = \ln K_E q_m - \frac{1}{q_m} q_e$	q _m	K _E	R ²	q _m	K _E	R ²	q _m	K _E	R ²
		0,1338	0,7658	0,9282	0,0937	0,8946	0,9893	0,5417	0,1178	0,3111



Fig. 2. CuO/13X from 50 g/l Cu²⁺ solution

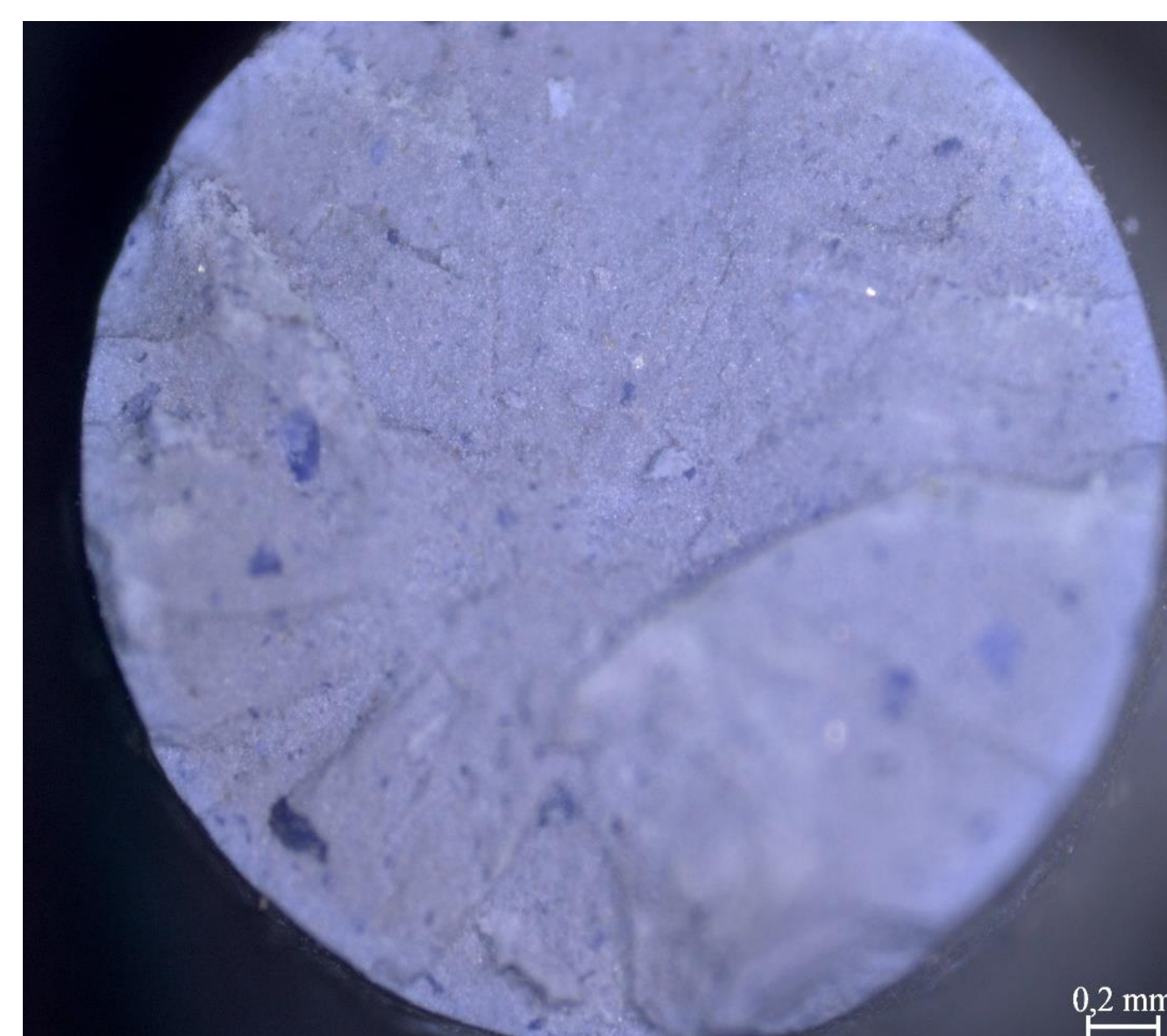


Fig. 3. Co₃O₄/13X from 50 g/l Co²⁺ solution

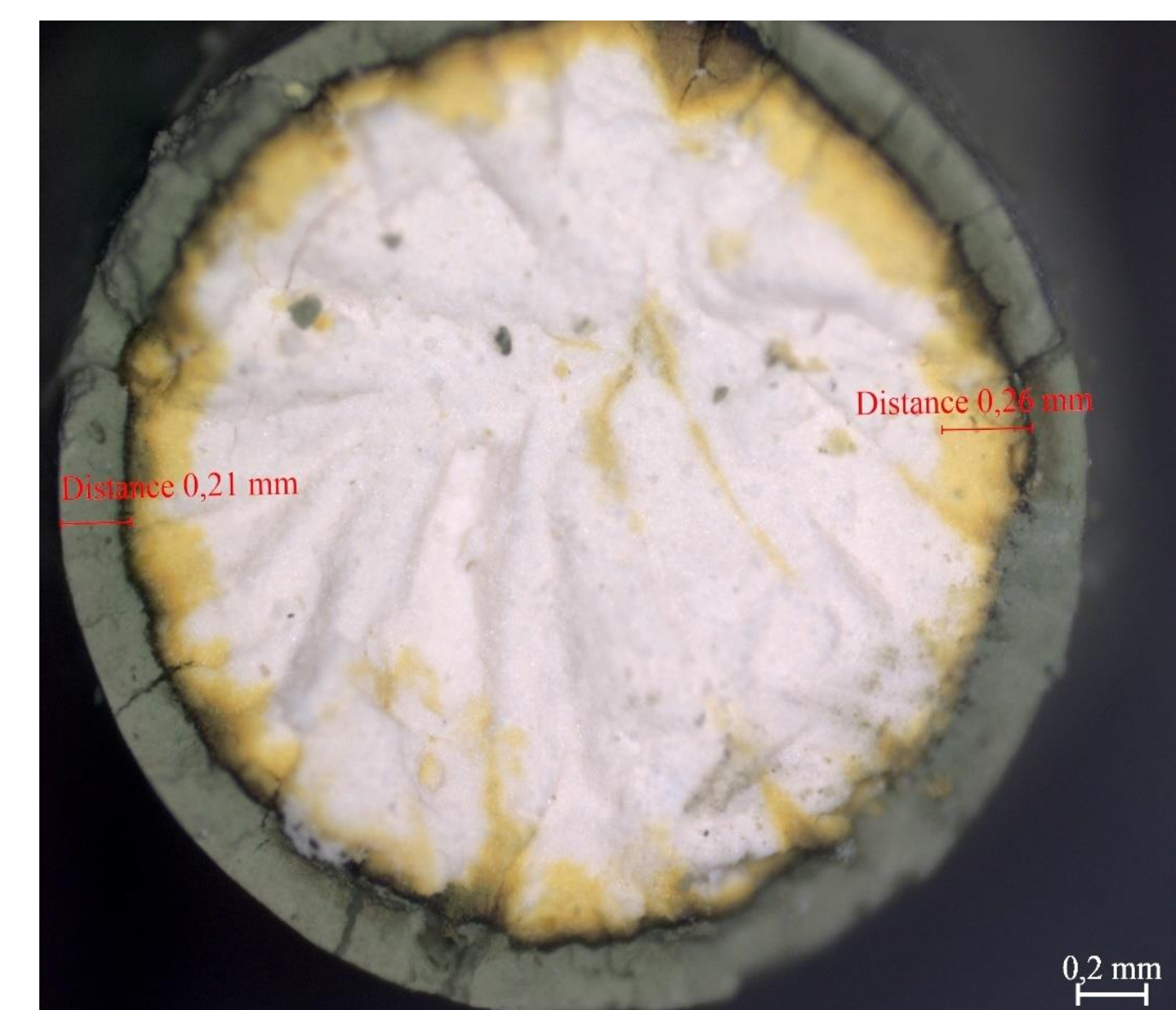


Fig. 4. Cr₂O₃/13X sample from 50 g/l Cr³⁺ solution

Conclusions

AAS analysis of solutions and calcined samples showed, that content of the oxides is in the range of 9.96 – 11.18 %. Adsorption isotherms of Cu and Cr were best described by Langmuir model, which indicated that monolayer of adsorbates were formed. Also high concentration of CuO in the outer layer of catalyst resulted in some pores being blocked with NO_x gases failing to escape and part of nitrates remaining undecomposed. In order to maximize active surface area of catalyst and optimize distribution of the oxides, adsorption of Cu and Cr should be performed in several shorter cycles with calcination step in between. Co adsorption was less affected by diffusion and with increasing concentration of the solution evenly covered all surface of zeolite. Adsorption modeling resulted in Freundlich isotherm being the best fit for Co, which indicates the formation of several layers of adsorbate and adsorption proceeding in several steps. Cross section of catalyst granule was evenly covered with no visible imperfections.

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