

## Adsorption-desorption properties of clinoptilolites and the catalytic activity of surface Cu(II)–Pd(II) complexes in the reaction of carbon monoxide oxidation with oxygen

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Adsorption-desorption properties of natural and acid-modified clinoptilolite (N-CLI and H-CLI, respectively) with respect to Cu(II) and Pd(II) have been studied. It has been found that an acid-thermal treatment (3M HNO<sub>3</sub>, T = 373 K, 6 h) of N-CLI weakens the palladium bonding to the H-CLI-6 surface with a fraction of weakly bound palladium(II) of 71.2 % and this alone determines the activity of the K<sub>2</sub>PdCl<sub>4</sub>–Cu(NO<sub>3</sub>)<sub>2</sub> / H-CLI-6 catalyst during carbon monoxide oxidation. The bonds that copper(II) forms with the H-CLI-6 surface can be divided into weak (30 %), medium-strength (40 %), and strong (30 %) ones, however, the contribution of weakly bound copper(II) amounts to only 4 % of the K<sub>2</sub>PdCl<sub>4</sub>–Cu(NO<sub>3</sub>)<sub>2</sub> / H-CLI-6 catalytic activity.

Adsorption-desorption of copper(II) and palladium(II) / Natural and acid-modified clinoptilolite / Catalyst for carbon monoxide oxidation

### Introduction

Adsorption-desorption properties of natural sorbents with respect to palladium(II) and copper(II) ions affect significantly both the mechanism of formation of the surface Pd(II)–Cu(II) complex and the catalytic activity of the latter in the reaction of carbon monoxide oxidation [1]. Even though a number of works [2-8] have dealt with Pd(II) and Cu(II) adsorption by natural clinoptilolites, neither the adsorption properties of their acid-modified samples (H-CLI), nor Pd(II) and Cu(II) desorption in case of their simultaneous presence on the clinoptilolite surface, have been studied. However, these data can give important information about the affinity of Cu(II) and Pd(II) complexes for the adsorption sites of N-CLI and H-CLI and, consequently, about the effect of this characteristic on the catalytic properties of Cu(II)–Pd(II) complexes.

In this work, we aim to elucidate the correlation between the adsorption-desorption properties of natural and acid-modified clinoptilolite and the catalytic activity of Cu(II)–Pd(II) complexes anchored to those supports in the reaction of carbon monoxide oxidation.

### Experimental

In the study, we used commercial natural clinoptilolite from the Sokyryntsy deposit (Transcarpathian region, Ukraine) with the following chemical composition (wt.%): SiO<sub>2</sub> – 71.5, Al<sub>2</sub>O<sub>3</sub> – 13.1, Fe<sub>2</sub>O<sub>3</sub> – 0.9, TiO<sub>2</sub> – 0.5, CaO – 3.44, MgO – 0.68, K<sub>2</sub>O–Na<sub>2</sub>O – 3.03, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mass ratio 5.5, pH of its aqueous extract 8.5, and specific surface S<sub>sp</sub> 50-65 m<sup>2</sup>/g.

*Modification of clinoptilolite.* The acid-thermal modification of N-CLI was carried out as follows: 50 g of the initial zeolite (grain size – 0.5-1.0 mm) was placed into a flask with a backflow condenser, 3M nitric acid (100 mL) was added, and the content was then boiled for 6 h and washed thoroughly till the reaction for NO<sub>3</sub><sup>-</sup> ions was negative. The sample (H-CLI-6) was then air-dried at 383 K till constant weight. According to [9], the specific surface of the acid-modified Transcarpathian clinoptilolite is 39 m<sup>2</sup>/g (as determined by water adsorption), whereas the natural form of the zeolite has a specific surface of 59 m<sup>2</sup>/g [2,9].

The X-ray phase analysis (CuKα radiation) showed that the N-CLI and H-CLI-6 samples were crystalline and the clinoptilolite phase they contained

was identified based on  $2\theta$  values ( $9.84^\circ$ ,  $22.45^\circ$ , and  $23.60^\circ$ ).

N-CLI and H-CLI-6 samples dried till constant weight were used to obtain the surface copper-palladium complexes Cu(II)-Pd(II)/N-CLI and Cu(II)-Pd(II)/H-CLI-6, respectively. Reference samples were obtained by impregnating each support (10 g) with an aqueous solution containing set amounts of  $K_2PdCl_4$  and  $Cu(NO_3)_2$ . Wet reference samples were kept for 20-24 h in covered Petri dishes at 293 K and then dried at 383 K till constant weight.

Model samples intended to demonstrate how the method of copper(II) or palladium(II) desorption affect the catalyst activity were prepared by a separate impregnation procedure that included the following alternating steps: (i) impregnation of the samples (N-CLI or H-CLI-6) with a  $Cu(NO_3)_2$  or  $K_2PdCl_4$  solution; (ii) desorption of Cu(II) or Pd(II) with water at 293 K, or with nitric acid (1:1) at 293 K, or with boiling nitric acid (1:1); and (iii) impregnation of the samples from the second step with a  $K_2PdCl_4$  solution after desorption of copper(II), or with a  $Cu(NO_3)_2$  solution after desorption of palladium(II).

*Testing the catalytic activity of the samples.* The catalytic activity of the samples in the reaction of CO oxidation was tested in a thermostatic flow-through installation at 293 K in a reactor with a fixed catalyst bed (as described in [1]). The catalyst samples were tested at the initial CO concentration of  $300 \text{ mg/m}^3$ , the linear velocity ( $U$ ) of gas-air mixture (GAM) flow was  $4.2 \text{ cm/s}$ , and the constant relative humidity of GAM ( $\varphi_{\text{GAM}}$ ) 76 %.

The reaction rate  $W$  was calculated by the formula:

$$W = \frac{w(C_{\text{CO}}^{\text{in}} - C_{\text{CO}}^{\text{f}})}{m_c}, \text{ mol/(g}\cdot\text{s)}$$

where  $w = 1.67 \times 10^{-2}$  is the volume flow rate of the GAM (L/s),  $C_{\text{CO}}^{\text{in}}$  and  $C_{\text{CO}}^{\text{f}}$  are the initial and final CO concentrations (mol/L), respectively, and  $m_c$  is the mass of the catalyst sample (g).

The experimental amount of oxidized CO ( $Q_{\text{exp}}$ ) was determined based on the experimental function  $\Delta C_{\text{CO}}^{\text{f}}$  vs.  $\tau$ . The yield of CO conversion in the steady-state mode ( $\eta_{\text{ss}}$ , %) and the stoichiometric coefficient ( $n$ ) per 1 mole of Pd(II) were calculated by the formulas

$$\eta_{\text{ss}} = \frac{(C_{\text{CO}}^{\text{in}} - C_{\text{CO}}^{\text{f}})}{C_{\text{CO}}^{\text{in}}} \cdot 100, \%; \quad n = Q_{\text{exp}}/Q_{\text{Pd(II)}}$$

where  $Q_{\text{Pd(II)}}$  is the amount of palladium(II) present in the sample.

*Adsorption-desorption studies.* 1 g of natural or acid-modified clinoptilolite ( $d_g = 0.75 \text{ mm}$ ) was placed into a glass flask containing 100 mL of Cu(II) nitrate solution of set concentration. Sorption was performed at 298 K in the intensive shaking mode for 4 h. The value of the adsorption of Cu(II) ions was determined as the difference between their

concentrations before and after the sorption (the latter value took into account Cu(II) concentrations in wash waters) and was related to the mass of the adsorbent. The concentration of Cu(II) ions in the solutions (from 0.25 to  $10 \mu\text{g/mL}$ ) was determined by atomic absorption spectrophotometry (AAS) using a "Saturn" atomic absorption spectrophotometer.

The method of desorption of Pd(II) and Cu(II) ions from the surface of the supports was used to estimate the relative bond strength between these ions and the adsorption centers. Desorption of Pd(II) and Cu(II) ions from the  $K_2PdCl_4$ - $Cu(NO_3)_2$ /N-CLI (CAT-1) and  $K_2PdCl_4$ - $Cu(NO_3)_2$ /H-CLI-6 (CAT-2) samples was performed under static conditions by varying the type of desorbent (eluent) and the temperature and time of sample treatment. The concentration of desorbed Pd(II) and Cu(II) ions in the solutions was determined by atomic absorption spectrophotometry using an AAS-1N atomic absorption spectrophotometer (Carl Zeiss, Jena) with a propane-butane-air flame. The interfering matrix effect of the solution was solved by the method of standard addition with background correction. In particular, the wavelength of the resonance radiation in the palladium(II) concentration measurements was  $247.6 \text{ nm}$  with a background correction at  $\lambda = 246.7 \text{ nm}$ ; the copper(II) concentration was determined at  $\lambda = 324.8 \text{ nm}$  with a background correction at  $\lambda = 323.1 \text{ nm}$ . The error on the Pd(II) and Cu(II) determinations was  $\pm 5 \%$ .

## Results and discussion

As shown by previous experiments, N-CLI and H-CLI-6 samples selectively adsorbed Cu(II) from  $K_2PdCl_4$ - $Cu(NO_3)_2$  binary solutions in the pH range 3.5-6.0. Similar results have been obtained when natural and acid-modified basalt tuffs were used as adsorbents [1]. The data in [7,8] were evidence for the absence of palladium(II) adsorption by clinoptilolite from nitrate solutions at pH 3.2 or chloride solutions ( $C_{\text{Cl}} = 2.5 \times 10^{-2} \text{ mol/L}$ ) at pH 2-6. Based on those data, we studied Cu(II) adsorption by N-CLI and H-CLI-6 samples only from nitrate solutions (Fig. 1a). All the isotherms of the copper(II) adsorption were similarly shaped, suggesting practically the same adsorption mechanism. However, the adsorption of Cu(II) by the H-CLI-6 sample was appreciably smaller because of the lack of some adsorption sites, mainly  $Al^{3+}$ , caused by the acid-thermal treatment of the clinoptilolite. Evidence for partial dealumination of Transcarpathian clinoptilolite during the process of acid treatment was presented in [9]. Copper(II) adsorption by N-CLI and H-CLI-6 samples takes place in weak-acid environment and is characterized by a decrease in pH of the solutions approximately by one unit in the range of equilibrium copper(II) concentrations ( $C_{\text{eq}}$ ) from  $4.0 \times 10^{-5}$  to  $30 \times 10^{-5} \text{ mol/L}$  (Fig. 1b). The pH values remain practically unchanged at  $C_{\text{eq}} > 30 \times 10^{-5} \text{ mol/L}$ .

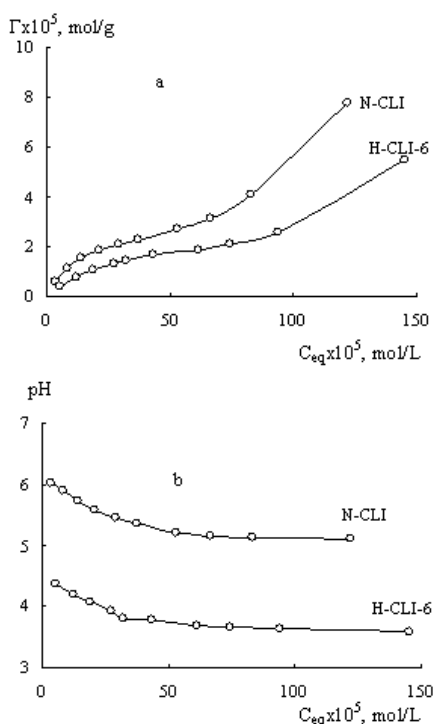
It should be noted that the increase in pH of the solution after copper(II) adsorption is 1.6 unit larger for N-CLI as compared to H-CLI-6. This is due to the release of  $H^+$  ions from the cation-exchanging sorbent complex into the solution during  $Cu^{2+}$  sorption on H-clinoptilolite.

The analysis of the adsorption isotherms was carried out using a linear form of the Langmuir equation

$$\frac{C_{eq}}{\Gamma_{Cu^{2+}}} = \frac{1}{\Gamma_{\infty}K} + \frac{1}{\Gamma_{\infty}}C_{eq} \quad (1)$$

where  $C_{eq}$  is the equilibrium  $Cu^{2+}$  concentration (mol/L);  $\Gamma_{Cu^{2+}}$  is the specific  $Cu^{2+}$  adsorption at the equilibrium  $Cu^{2+}$  concentration;  $\Gamma_{\infty}$  is the maximum value of the specific  $Cu^{2+}$  adsorption that corresponds to monolayer filling of the adsorbent surface with  $Cu^{2+}$  ions (mol/g); and  $K$  is the constant characterizing the  $Cu^{2+}$  affinity to the adsorbent (L/mol).

Equation (1), the parameters and correlation coefficient,  $R^2$ , of which are listed in Table 1, is valid at  $C_{eq} < 40 \times 10^{-5}$  mol/L for both N-CLI and H-CLI-6 supports. One can see that the Langmuir equation describes conveniently the experimental results of the  $Cu^{2+}$  adsorption by N-CLI and H-CLI-6 samples ( $R^2$  values close to 1) and that the acid-thermal modification of clinoptilolite produces a decrease of the  $\Gamma_{\infty}$  and  $K$  parameters.



**Fig. 1** Isotherms of copper(II) adsorption from aqueous solutions of copper(II) nitrate by samples of natural and acid-modified clinoptilolite (a). The dependence of pH equilibrium values on  $C_{eq}$  (b).

The results of this study suggest that the copper(II) adsorption proceeds *via* an ion-exchanging mechanism in the range of low  $C_{eq}$  values. This conclusion is in agreement with literature data [4-7,10,11].

Multiplicity and inhomogeneity of adsorption sites ( $\equiv AlOH$ ,  $\equiv SiOH$ ,  $Si(OH)Al$ ) in clinoptilolite as well as competition between  $Cu(II)$  and  $Pd(II)$  ions for active adsorption sites cause inequality in strength of bonds formed by these metal ions with the surface. The fractions of weak and strong bonds between the metal ions and adsorption sites can be determined by a desorption method. As a rule, weak and medium-strength bonds between the metal ions and surface functional groups are disrupted at 293 K with water and with acids, respectively. Strong bonds break down only with acids at 373 K (by boiling) [12].

The data obtained by studying  $Cu(II)$  and  $Pd(II)$  desorption from  $K_2PdCl_4-Cu(NO_3)_2/N-CLI$  (CAT-1) and  $K_2PdCl_4-Cu(NO_3)_2/H-CLI-6$  (CAT-2) samples are presented in Table 2. By varying the desorbent (eluent) type ( $H_2O$ ,  $HCl$ , or  $HNO_3$ ), the time of desorbent contact with the sample, and the temperature (293 or 373 K), the following results were obtained. Palladium(II) was not desorbed by water from the CAT-1 sample at 293 K. The use of acids ( $HCl$ ,  $HNO_3$ ) as desorbents indicated that regardless of the type of acid, its concentration, or the contact time, the yield of palladium(II) desorption at 293 K is 71.2 %, and total desorption occurs at 373 K. The absence of palladium(II) desorption with water at 293 K is due to the fact that the metal ions on a natural clinoptilolite surface exist in the form of poorly soluble hydrolyzed species. On the other hand, for the CAT-2 sample, acid modification of the support results not only in changing of the palladium(II) form but also in weakening of the bonding to the surface. Meanwhile, the yield of palladium(II) desorption with  $HCl$ ,  $HNO_3$ , and  $H_2O$  at 293 K is ~70 % as before modification. This indicates that palladium(II) forms preferably weak bonds with the acid-modified clinoptilolite surface in the presence of copper(II) in the CAT-2 sample. The fraction of the bonds palladium(II) forms with the surface that are strong is ~30 %, and this part of palladium can be desorbed only by boiling in nitric acid (1:1).

Copper(II) desorption exhibits a number of differences as compared to palladium(II) desorption. For instance, only 7 % of copper(II) was desorbed from the CAT-1 sample with water at 293 K. The desorption increases to 30-32 % when  $HCl$  and  $HNO_3$  are used (note that in this case the yield of copper(II) desorption is not affected by the contact time). Copper(II) is desorbed nearly completely (~78 %) by boiling in acids. According to the results presented in Fig. 1a and Table 1, the adsorption parameters and, especially, copper(II) affinity to the adsorbent, decrease as a result of the acid modification of clinoptilolite. Hereupon, the desorptivity (the desorption degree) of copper(II) from the CAT-2

**Table 1** Characteristic parameters ( $\Gamma_{\infty}$ ,  $K$ ) and the correlation coefficient ( $R^2$ ) for the experimental data corresponding to the Langmuir equation.

System	Parameters of the Langmuir equation		$R^2$
	$\Gamma_{\infty} \times 10^5$ , mol/g	$K \times 10^{-3}$ , L/mol	
Cu(NO <sub>3</sub> ) <sub>2</sub> / N-CLI	3.20	6.49	0.99
Cu(NO <sub>3</sub> ) <sub>2</sub> / H-CLI-6	2.10	3.60	0.99

**Table 2** The results of the study on Pd(II) and Cu(II) desorption from K<sub>2</sub>PdCl<sub>4</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O / N-CLI and K<sub>2</sub>PdCl<sub>4</sub>-Cu(NO<sub>3</sub>)<sub>2</sub> / H-CLI-6 samples.

Sample Component concentration, $\mu\text{g/g}$	Desorbent (eluent)	Contact time, min	Temperature, K	Pd(II) desorbed			Cu(II) desorbed		
				$\mu\text{g/g}$	$\times 10^5$ , mol/g	wt. %	$\mu\text{g/g}$	$\times 10^5$ , mol/g	wt. %
Pd(II)-Cu(II) / N-CLI $C_{\text{Pd(II)}} = 1442$ ; $C_{\text{Cu(II)}} = 1842$ (CAT-1)	H <sub>2</sub> O	60	293	0	0	0	130	0.2	7.05
	1.5M HCl	25	293	1026	1.1	71.2	586	0.9	31.8
	1.5M HCl	15	373	1440	1.4	100	1806	2.8	97.8
	HNO <sub>3</sub> (1:1)	15	293	1026	1.1	71.2	570	0.9	30.9
	HNO <sub>3</sub> (1:1)	60	293	1026	1.1	71.2	600	0.9	32.5
	HNO <sub>3</sub> (1:2)	15	293	1026	1.1	71.2	570	0.9	30.9
	HNO <sub>3</sub> (1:2)	60	293	1026	1.1	71.2	600	0.9	32.6
	HNO <sub>3</sub> (1:1)	15	373	1440	1.4	100	1796	2.8	97.5
Pd(II)-Cu(II) / H-CLI-6 $C_{\text{Pd(II)}} = 1442$ ; $C_{\text{Cu(II)}} = 3747$ (CAT-2)	H <sub>2</sub> O	30	293	1020	1.1	70.7	1100	1.9	29.3
	1.5M HCl	30	293	1018	1.1	70.7	2605	4.5	69.5
	1.5M HCl	15	373	1026	1.1	71.2	3740	5.9	100
	HNO <sub>3</sub> (1:2)	30	293	1026	1.1	71.2	2610	4.5	69.6
	HNO <sub>3</sub> (1:1)	15	373	1440	1.4	100	3742	5.9	100

sample at 293 K increases substantially: it is equal to 29.3 % and 69.5 % for desorption with water and acids, respectively. Total copper(II) desorption can be achieved by boiling in HCl or HNO<sub>3</sub>. Since the degree of copper(II) desorption at 293 K with water and with acids is different, it can be concluded that the fractions of weak and medium-strength bonds are ~30 % and ~40 %, respectively.

It is worth comparing the results of the Cu(II) and Pd(II) adsorption-desorption with those obtained from testing the CAT-1 and CAT-2 samples in the reaction of CO oxidation with oxygen. The reference samples were prepared by the standard procedure, whereas the model ones were obtained by alternating impregnation and desorption steps. It is notable that the K<sub>2</sub>PdCl<sub>4</sub>-Cu(NO<sub>3</sub>)<sub>2</sub> / N-CLI sample is not active in the reaction of carbon monoxide oxidation and this is in agreement with the results obtained for other unmodified natural sorbents: basalt tuffs, mordenite, and montmorillonite [13]. Only the K<sub>2</sub>PdCl<sub>4</sub>-Cu(NO<sub>3</sub>)<sub>2</sub> / H-CLI-6 catalyst obtained by acid-thermal modification of the natural clinoptilolite sample enabled CO oxidation in a steady-state mode (Figs. 2 and 3, curve 1). Judging by the stationary final concentration of carbon monoxide,  $C_{\text{CO}}^f$  (mg/m<sup>3</sup>), the yield of CO conversion is only 53 % (Table 3), *i.e.* not high enough, even when the Pd(II) concentration is twice that of CAT-2 (Table 2). According to [1], a twofold increase of the Pd(II)

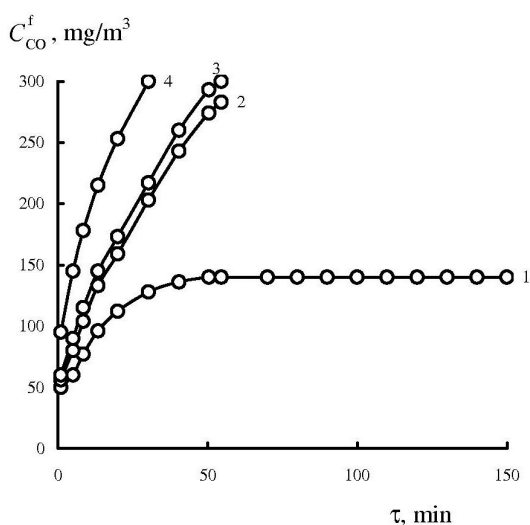
concentration in the tested samples did not affect the degree of desorption.

Based on the data obtained from testing the model catalyst samples subjected to desorption of palladium(II) (Fig. 2) and copper(II) (Fig. 3) in the reaction of CO oxidation with oxygen, as well as from an analysis of the kinetic ( $W_{\text{ss}}$ ,  $C_{\text{CO}}^f$ ,  $\eta_{\text{ss}}$ ) and stoichiometric ( $Q_{\text{exp}}$ ,  $n$ ) parameters of the reaction (Table 3), the following conclusions can be drawn. The samples lose their catalytic activity after palladium(II) desorption with water and acids, as judged from the absence of steady-state portions in the kinetic curves; the final CO concentration quickly equalizes with the initial one (300 mg/m<sup>3</sup>); and the stoichiometric coefficient decreases from 3.2 to 0.2. Since water and acids desorb equal amounts of palladium(II) (Table 2), the kinetic curves 2 and 3 practically match.

The features determined for the copper(II) desorption from the CAT-2 sample are also confirmed by kinetic studies (Fig. 3). The catalyst sample loses 29.3 % of copper(II) after desorption with water at 293 K and thereby retains  $4.0 \times 10^{-5}$  mole of Cu(II) per 1 g of the catalyst. This amount is sufficient to maintain steady carbon monoxide oxidation, the degree of CO conversion was only 4 % lower, and the other reaction parameters changed only insignificantly (Table 3). This indicates that copper(II) weakly bound

**Table 3** The results of testing  $K_2PdCl_4-Cu(NO_3)_2/H-CLI-6$  samples in the reaction of CO oxidation with oxygen after separate Pd(II) and Cu(II) desorption  $C_{Pd(II)} = 2.72 \times 10^{-5}$ ;  $C_{Cu(II)} = 5.9 \times 10^{-5}$  mol/g.

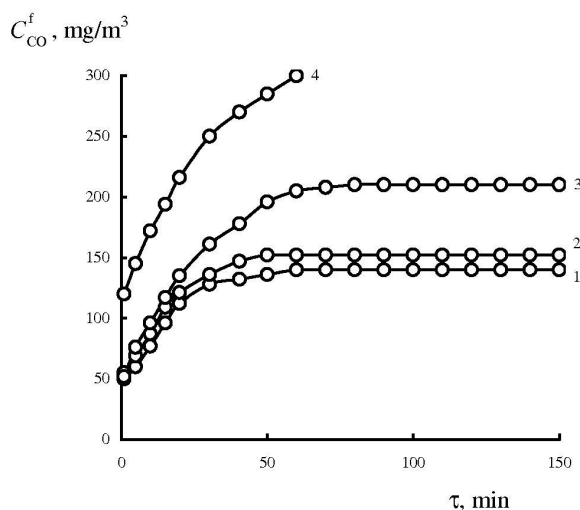
Conditions of desorption	$W_{ss} \times 10^9$ , mol/(g·s)	$C_{CO}^f$ , mg/m <sup>3</sup>	$\eta_{ss}$ , %	$Q_{exp} \times 10^4$ , CO moles	$n$
Reference samples	9.6	140	53	8.59	3.2
Pd(II) desorption					
H <sub>2</sub> O (293 K)	–	300	–	1.55	0.6
HNO <sub>3</sub> (1:1) (293 K)	–	300	–	1.45	0.5
HNO <sub>3</sub> (1:1) (373 K)	–	300	–	0.55	0.2
Cu(II) desorption					
H <sub>2</sub> O (293 K)	8.9	152	49	7.97	2.9
HNO <sub>3</sub> (1:1) (293 K)	5.4	210	30	5.53	2.0
HNO <sub>3</sub> (1:1) (373 K)	–	300	–	0.95	0.3

**Fig. 2** Time dependence of the activity of  $K_2PdCl_4-Cu(NO_3)_2/H-CLI-6$  samples in the carbon monoxide oxidation with oxygen under different conditions of palladium(II) desorption: 1 – reference sample; 2 – desorption with water at 293 K; 3 – desorption with nitric acid (1:1) at 293 K; and 4 – desorption with nitric acid (1:1) at 373 K.

to the surface does not sensibly affect the catalyst activity. It is copper(II) forming medium-strength and strong bonds with the H-CLI-6 surface (their fraction is approximately 70 %) that contributes the most to the total reaction rate. The sample loses 69.5 % of copper(II) after its desorption with nitric acid at 293 K. Residual copper ( $1.4 \times 10^{-5}$  mol/g) is sufficient to maintain the steady-state regime of the reaction (Fig. 3, curve 3). Despite a 23.5 % decrease of  $\eta_{ss}$ , as compared with the reference test, the process remains catalytic in nature, and the stoichiometric coefficient is equal to 2 towards the end of the test. In the case of quantitative copper(II) desorption, curve 4 (Fig. 3) demonstrates a change in the kinetics of the interaction of palladium(II) with carbon monoxide,

resulting in reduction of palladium(II) to  $Pd^0$  (visually observable).

Taking into consideration the obtained data, it can be suggested that the formation of a surface Cu(II)-Pd(II) complex, which is the one most active in the carbon monoxide oxidation, proceeds according to the following scheme. A support, acid-modified clinoptilolite, plays the role of a polydentate ligand [14,15] and selectively adsorbs copper(II) aqua complexes; whereas palladium(II), which, relying on the protonic acidity of the surface of the support (pH ~5), is most likely present in the form of its hydroxo chloride complex [16], is bound to the copper(II) ions *via* a water molecule. The palladium(II) ions, which are strongly bound to the support surface, either have low activity in the reaction of CO oxidation with oxygen, or do not participate in the reaction at all.

**Fig. 3** Time dependence of the activity of  $K_2PdCl_4-Cu(NO_3)_2/H-CLI-6$  samples in the carbon monoxide oxidation with oxygen under different conditions of copper(II) desorption: 1 – reference sample; 2 – desorption with water at 293 K; 3 – desorption with nitric acid (1:1) at 293 K; and 4 – desorption with nitric acid (1:1) at 373 K.



## Conclusions

It has been found that Cu(II) adsorption by N-CLI and H-CLI-6 samples from copper(II) nitrate solutions at equilibrium concentrations ranging from  $4 \times 10^{-5}$  to  $40 \times 10^{-5}$  mol/L can be described by a Langmuir equation; acid-thermal modification of clinoptilolite results in a decrease of its characteristic parameters,  $\Gamma_{\infty}$  and  $K$ .

Palladium(II) and copper(II) have been found to be strongly hold on to the natural clinoptilolite surface and that causes the absence of catalytic activity in carbon monoxide oxidation in the case of the  $K_2PdCl_4-Cu(NO_3)_2$  / N-CLI sample.

The acid-thermal modification of N-CLI results in a change of its surface properties that affect the nature of the interactions of the metal ion with the adsorption sites. It is typical of palladium(II) to form mainly (~70 %) weak bonds with the H-CLI-6 surface and it is the weakly bound palladium(II) that generally determines the activity of the  $K_2PdCl_4-Cu(NO_3)_2$  / H-CLI-6 catalyst in the carbon monoxide oxidation. Copper(II) forms weak (30 %), medium-strength (40 %), and strong (30 %) bonds with the H-CLI-6 surface. However, the contribution of weakly bound copper(II) in the CAT-2 catalyst activity amounts only to 4 %.

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