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Catalytic activity of Pd(II) and Cu(II) complexes anchored to natural and pre-modified bentonite in the oxidation of carbon monoxide

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The influence of different methods of pre-modification (thermal, hydrothermal, and acid-thermal) of natural bentonite on the catalytic activity of bentonite-anchored palladium(II) and copper(II) complexes in low-temperature oxidation of carbon monoxide has been studied. The contributions of weakly and strongly bound Pd(II) and Cu(II) forms to the total activity of the catalysts were evaluated by two methods, desorption of the metal ions and a kinetic method.

Desorption of palladium(II) and copper(II) / Natural and pre-modified bentonite / Catalysts for carbon monoxide oxidation

Introduction

For the first time, Ukrainian natural bentonites have been used as supports for anchoring palladium(II) and copper(II) complexes. Depending on the origin of the bentonite, such supported metal complexes have different catalytic properties in the reaction of carbon monoxide oxidation. When the reaction proceeded in a steady-state mode, the maximum carbon monoxide oxidation yield (87 %) was observed for natural bentonite from the Gorbske deposit. However, the carbon monoxide concentration at an outlet of the catalyst bed was higher than its maximum permissible concentration in the working area ($MPC_{CO} = 20$ mg/m^3) [1]. From our experience, we know that the catalytic activity can be improved by activation (pre-modification) of a natural sorbent, changing the physicochemical properties of its surface and a nature of the bonds formed by the palladium(II) and copper(II) ions with the adsorption sites.

Because of the large number and the inhomogeneous distribution of the adsorption sites of natural and acid-pre-modified basalt tuff [2] and clinoptilolite [3], the bonds formed by palladium(II) and copper(II) with the surface sites differ in strength, and this factor affects the catalytic activity of the anchored metal complexes.

It should be noted that bentonites, similarly to other natural sorbents, are selective with respect to metal ions: the origin of the bentonite affects the position of Cu(II) in the order of selectivity [4-6]. Adsorption of palladium(II) was not studied in the above-mentioned works. This fact can be due to some difficulties characteristic of the investigation of palladium(II) adsorption with natural sorbents: influence of a nature of palladium(II) precursors and pH of the medium, as well as palladium(II) hydrolysis taking place already at pH > 1. For instance, palladium(II) cannot be adsorbed on the surface of clinoptilolite, neither from nitrate solutions at pH 2, nor from chloride solutions at pH 2-6 ($C_{Cl^-} = 2.5\times10^{-2}$ mol/g) [7,8]. In principle, the conditions for palladium(II) adsorption and preparation of Pd(II)-Cu(II)/$\overline{S}$ catalysts ($\overline{S}$ are supports of natural origin such as clinoptilolite, mordenite, basalt tuffs, tripolis, bentonites, *etc.*) are not the same [9]. Therefore, to evaluate the contributions of weakly and strongly bound Pd(II) and Cu(II) forms to the catalytic activity of anchored palladium(II) and copper(II) complexes in the oxidation of carbon monoxide, it is recommended to combine two investigation methods *i.e.* desorption of the metal ions and a kinetic method (testing of catalyst samples in the reaction) [2,3].

The aim of this work was to ascertain how the methods used for pre-modification of bentonite affect the desorption of palladium(II) and copper(II) ions and the activity of Pd(II)-Cu(II)/$\overline{\text{S}}$ catalysts (where $\overline{\text{S}}$ is bentonite, either natural or pre-modified by different methods) in the oxidation of carbon monoxide.

Experimental

In this study, natural bentonite from the Gorbske deposit (Trans-Carpathian region, Ukraine) with the following chemical composition, converted to main oxides (wt.%): SiO_2 – 50.0; Al_2O_3 – 18.5; Fe_2O_3 – 7.6, was used. Investigation of the natural bentonite sample (N-Bent) by X-ray diffraction showed that, besides the main phases, *i.e.* montmorillonite and α-quartz, it contained contaminant phases such as cristobalite, kaolinite, and calcite [1].

Pre-modified bentonite samples were prepared as follows:

- Thermally pre-modified bentonite (300-Bent) was prepared by calcination of N-Bent at 573 K for 1 h.
- Hydrothermally pre-modified bentonite (H_2O-Bent) was prepared by boiling 50 g of N-Bent in 100 ml of distilled water for 1 h, subsequent filtration and air-drying at 383 K till constant weight.
- Acid-thermally pre-modified bentonite (H-Bent-1) was prepared by boiling 50 g of N-Bent in 100 ml of 1M nitric acid in a flask with a backflow condenser for 1 h and subsequent thorough washing with distilled water till negative reaction for NO_3^- ions. Then, the moist particles were air-dried at 383 K till constant weight.

Samples of N-Bent and bentonite, pre-modified by the above methods (M-Bent denoting 300-Bent, H_2O-Bent or H-Bent-1) and dried at 383 K till constant weight, with a particle size of 0.5-1.0 mm, were used to prepare Cu(II)-Pd(II)/N-Bent and Cu(II)-Pd(II)/M-Bent.

Reference samples were obtained by impregnating each support (10 g) with an aqueous solution containing prescribed amounts of K_2PdCl_4, $Cu(NO_3)_2$ and KBr. The wet reference samples were kept for 20 h in covered Petri dishes at 293 K and then dried at 383 K till constant weight.

Model samples, intended to demonstrate how a particular method of copper(II) or palladium(II) desorption affects the catalyst activity, were prepared by a separate impregnation procedure that included the following, alternating steps: (i) impregnation of the support sample (N-Bent or M-Bent) with $Cu(NO_3)_2$ 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) repeated impregnation of the samples from the second step with K_2PdCl_4 solution after desorption of copper(II), or with $Cu(NO_3)_2$ solution after desorption of palladium(II).

Desorption studies

Desorption of Pd(II) and Cu(II) from the K_2PdCl_4-$Cu(NO_3)_2$-KBr/N-Bent(M-Bent) samples was performed under static conditions, varying the type of desorbent, temperature and time of the 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 handled by the method of standard addition with background correction. The wavelength of the resonance radiation for the measurements of the palladium(II) concentration was 247.6 nm with a background correction at $\lambda = 246.7$ nm; the copper(II) concentration was determined at $\lambda = 324.8$ nm with a background correction at $\lambda = 323.1$ nm. The error on the determination of Pd(II) and Cu(II) was ±5%.

Testing the catalytic activity

The catalytic activity in the oxidation of CO was tested in a temperature-controlled flow-through installation at 293 K in a reactor with a fixed catalyst bed. The catalyst samples were tested at an initial CO concentration of 300 mg/m^3; the linear velocity (U) of the gas-air mixture (GAM) flow was 4.2 cm/s, and the constant relative humidity of the GAM (φ_{GAM}) was 76 %.

The reaction rate W was calculated by the formula:

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

where $w = 1.67\times10^{-2}$ is the volume flow rate of the GAM (L/s), C_{CO}^{in} and C_{CO}^{f} are the initial and final CO concentrations (mol/L), respectively, and m_c is the mass of the catalyst sample (g).

The amount of oxidized CO (Q_{exp}) was determined based on the experimental function ΔC_{CO}^{f} *vs.* τ. The degree of CO conversion in the steady-state mode (η_{ss}, %) and the stoichiometric coefficient (n) per 1 mole of Pd(II) were calculated by the formulas:

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

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

Results and discussion

The kinetic curves shown in the C_{CO}^{f} *vs.* τ plot in Fig. 1 describe the process of low-temperature oxidation of carbon monoxide with atmospheric oxygen over Pd(II)-Cu(II)-Br$^-$/$\overline{\text{S}}$ catalysts ($\overline{\text{S}}$ is N-Bent or M-Bent). Characteristic properties of these catalysts, which require the simultaneous presence of palladium(II) and copper(II), are optimal physicochemical and structural-adsorption properties of their supports, enabling carbon monoxide oxidation in a steady-state mode (*i.e.* at C^{f}_{CO} independent of time). The degree of CO conversion in the steady-state mode was taken as a measure of the activity of the catalysts.

Fig. 1 shows that the profiles of the kinetic curves are similar: initially, C^{f}_{CO} decreases, then the steady-state mode is reached. For example, when N-Bent is used as support, the reaction starts to proceed in the steady-state mode after 20 min. During this period, C^{f}_{CO} has decreased from 65 to 38 mg/m^3.

Similar results were observed for hydrothermally pre-modified bentonite. For these two catalysts, C^{f}_{CO} in the steady-state mode exceeds MPC_{CO}. Thermal and acid-thermal pre-modification of bentonite increases the activity of the anchored palladium(II) and copper(II) complexes: constant C^{f}_{CO} is attained in 10 min and is lower than MPC_{CO}.

Parameters characterizing the oxidation of carbon monoxide over catalysts of the same composition, but differing by the state of the bentonite (natural or pre-modified by one of the above methods), are presented in Table 1. For all these catalysts, the stoichiometric coefficient *n* exceeded 4 at the moment the experiment was interrupted (after 150 min), confirming the catalytic character of the reaction. The reaction rate and the degree of carbon monoxide conversion in the steady-state mode, W_{ss} and η_{ss}, respectively, depend on the state of the support and increase in the following order: N-Bent < H_2O-Bent < 300-Bent < H-Bent-1.

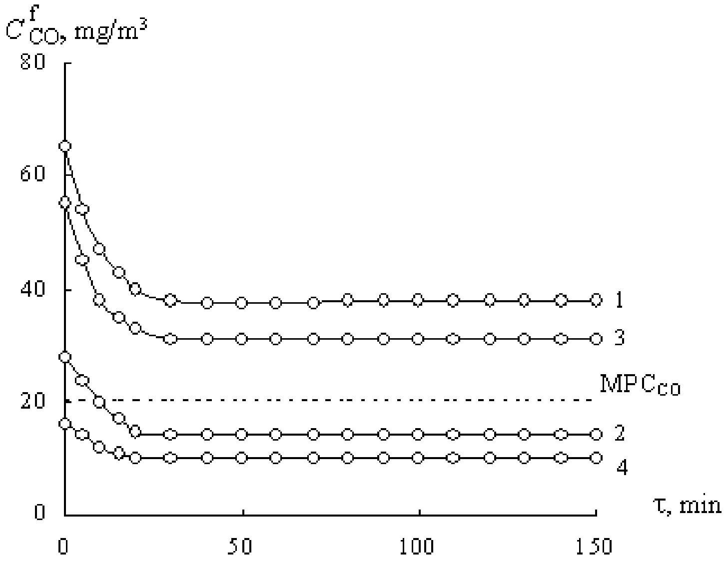

Fig. 1 Time dependence of the final concentration of CO, C^{f}_{CO}, during the oxidation of carbon monoxide with oxygen over Pd(II)-Cu(II) catalysts based on natural (curve 1) and pre-modified bentonite (curves 2-4): 1 – N-Bent, 2 – 300-Bent, 3 – H_2O-Bent, 4 – H-Bent-1.
$C_{Pd(II)} = 2.72\times10^{-5}$, $C_{Cu(II)} = 2.9\times10^{-5}$, $C_{KBr} = 1.02\times10^{-4}$ mol/g; C^{in}_{CO} = 300 mg/m^3; T = 293 K.

Table 1 Parameters (see text) of K_2PdCl_4-$Cu(NO_3)_2$-KBr/N-Bent(M-Bent) catalyst samples in the oxidation of carbon monoxide. $C_{Pd(II)} = 2.72\times10^{-5}$, $C_{Cu(II)} = 2.9\times10^{-5}$, $C_{KBr} = 1.02\times10^{-4}$ mol/g.

Support	$W_{ss}\times10^9$, mol/(g×s)	C^{f}_{CO}, mg/m^3	η_{ss}, %	$Q_{exp}\times10^4$, CO moles	*n*
N-Bent	15.72	38	87.3	13.4	4.12
300- Bent	17.16	14	95.3	14.7	5.41
H_2O- Bent	16.14	31	89.6	13.8	5.07
H-Bent-1	17.40	10	96.6	14.9	5.47

The desorption method was used to elucidate how the different methods of support pre-modification affect the fractions of palladium(II) and copper(II) ions weakly and strongly bound to the bentonite surface. As a rule, weak bonds between the metal ions and the bentonite surface can be disrupted at 293 K with water, whereas bonds of medium-strength and strong bonds break down with acids at 293 K and 373 K (during boiling), respectively. The degree of desorption does not depend on the nature of the acid (HCl, HNO_3) [2,3], however, it is greatly affected by the chemical and mineralogical composition of the support.

The data obtained by studying Cu(II) and Pd(II) desorption from catalysts containing natural or pre-modified bentonite as support are summarized in Table 2. Desorption was carried out with water at 293 K for 15 min and with boiling nitric acid for 30 and 60 min. Analysis of the results leads to the following conclusions: in the case of palladium(II) desorption with water the degree of desorption is relatively high (35-43 wt.%), in other words, the fraction of palladium(II) that is weakly bound to the bentonite surface is in the range from 35 to 43 wt.%. Depending on the pre-modification method, the degree of desorption increases as follows: 300-Bent ≈ H_2O-Bent < N-Bent < H-Bent-1. The difference in the degree of desorption for the first three samples is only 3 wt.%. A considerable change was observed for the acid-pre-modified bentonite. After boiling in a nitric acid solution for 30 min, the desorption degree of palladium(II) had increased by 20 wt.% for N-Bent, 300-Bent, and H_2O-Bent, and by 10 wt.% for H-Bent-1. The desorption degree increased even more when the boiling lasted 60 min; however, 35-40 wt.% of Pd(II) remained in the catalyst sample.

Since the pH of the suspension of the bentonite samples changes from 6.7 for N-Bent, H_2O-Bent, and 300-Bent to 5.8 for H-Bent-1, one may deduce that in the latter case, according to the distribution diagrams [10], part of palladium(II) exists in insoluble form, as $Pd(OH)_2$. A high content of palladium(II), 22 wt.%, remaining on acid-pre-modified basalt tuff, has been reported earlier [2].

As seen from Table 2, the method of pre-modification of bentonite slightly affects the desorption degree of copper(II): it varies from 26.9 to 34.5 wt.% for desorption with water. In the case of desorption with boiling nitric acid for 30 min, the desorption degree increases up to 80 wt.% (H-Bent-1), and copper(II) is completely desorbed in the case of boiling in nitric acid for 60 min.

Thus, one may conclude that the fraction of palladium(II) that is weakly bound to the surface of both natural and pre-modified bentonite is higher than that of copper(II). The definition “strongly bound palladium(II)” is rather relative because of the partial formation of poorly soluble $Pd(OH)_2$, which cannot be desorbed even on boiling in nitric acid for 60 min.

The results of the measurements of palladium(II) and copper(II) desorption are compared with data obtained from testing Pd(II)-Cu(II)/N-Bent(M-Bent) catalyst samples prepared by both the standard procedure (reference samples) and the alternating impregnation procedure (model samples), described in the section Experimental. The dependences obtained from testing the reference and model samples are presented graphically only for the H-Bent-1 support (Fig. 2). Data for the other supports are listed in Table 3. The kinetic study shows that the profiles of the kinetic curves of the reference samples do not change after desorption of palladium(II) (Fig. 2a) or copper(II) (Fig. 2b). The presence of steady-state portions in the kinetic curves in all of the cases proves that residual amounts of Pd(II) or Cu(II) are sufficient to provide a catalytic effect, *i.e.* proceeding of the oxidation of CO in the steady-state mode.

Table 2 The results of Pd(II) and Cu(II) desorption from K_2PdCl_4-$Cu(NO_3)_2$-KBr/N-Bent(M-Bent) catalyst samples. $C_{Pd(II)} = 2.72\times10^{-5}$, $C_{Cu(II)} = 2.9\times10^{-5}$ mol/g.

Support	Desorbent	Contact time, min	Temperature, K	Pd(II) desorbed		Cu(II) desorbed	
				$\times10^5$ mol/g	wt.%	$\times10^5$ mol/g	wt.%
Pd(II)–Cu(II)/ N-Bent	H_2O	15	293	1.05	38.48	0.78	26.89
	HNO_3(1:1)	30	373	1.61	59.29	2.07	71.31
	HNO_3(1:1)	60	373	1.79	65.88	2.9	100
Pd(II)–Cu(II)/ 300-Bent	H_2O	15	293	0.96	35.36	0.83	28.62
	HNO_3(1:1)	30	373	1.46	53.74	2.15	74.14
	HNO_3(1:1)	60	373	1.51	55.47	2.9	100
Pd(II)–Cu(II)/ H_2O-Bent	H_2O	15	293	0.96	35.36	0.85	29.31
	HNO_3(1:1)	30	373	1.61	59.29	2.09	72.07
	HNO_3(1:1)	60	373	1.79	65.88	2.89	100
Pd(II)–Cu(II)/ H-Bent-1	H_2O	15	293	1.19	43.68	1.00	34.5
	HNO_3(1:1)	30	373	1.46	53.74	2.3	79.3
	HNO_3(1:1)	60	373	1.51	55.47	2.9	100

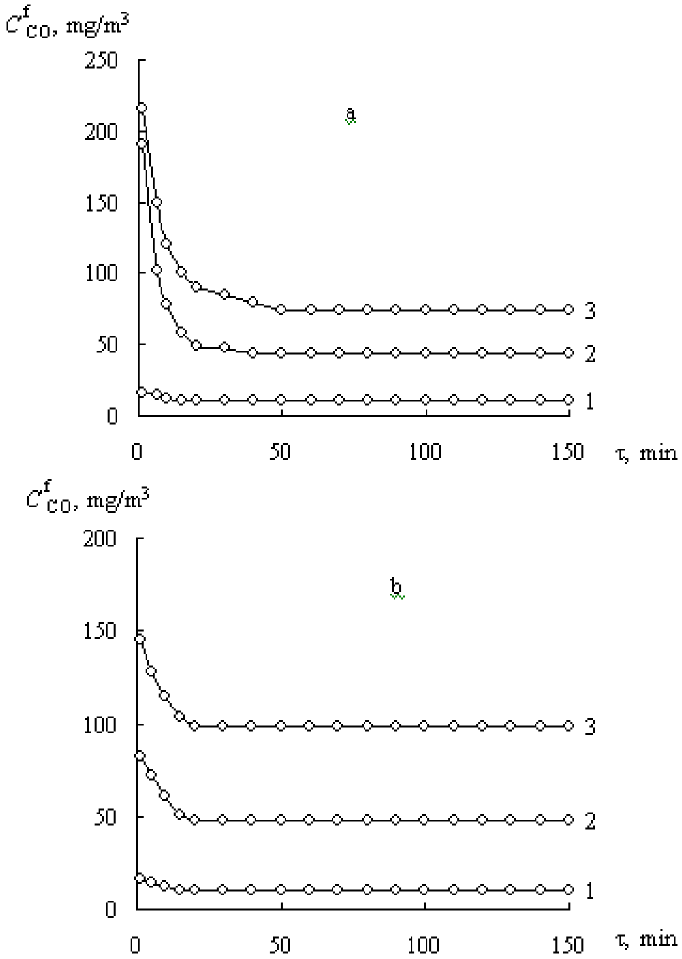

Fig. 2 Time dependence of the final CO concentration in a K_2PdCl_4-$Cu(NO_3)_2$-KBr/H-Bent-1 sample in the process of oxidation of carbon monoxide with oxygen under different conditions of desorption of palladium(II) (a) and copper(II) (b): 1 – reference sample; 2 – desorption with water at 293 K; 3 – desorption with nitric acid at 373 K for 30 min.

The following conclusions may be drawn: (i) desorption of palladium(II) by both methods causes a more significant increase of C^{f}_{CO} than desorption of copper(II), both at the very beginning of the reaction under study and in the steady-state mode, except for the H-Bent-1 support. Such a behavior is predictable because palladium(II) is indeed responsible for the coordination and activation of the carbon monoxide molecule [11]; (ii) a significant difference in C^{f}_{CO} is observed (Fig. 2a) after palladium(II) desorption from the K_2PdCl_4-$Cu(NO_3)_2$-KBr/H-Bent-1 catalyst at the beginning of the reaction, which can be an evidence of prevailing desorption of palladium(II) located on the external surface of the support. The contents of palladium(II) and copper(II) remaining after desorption of these ions with water and nitric acid, as well as the difference (decrease) in catalytic activity between the reference and the corresponding model samples ($\Delta\eta_{ss}$) are presented in Table 3. The initial palladium(II) and copper(II) contents in the reference samples were taken as 100 wt.% and the remaining amounts were calculated based on this value. The methods used for pre-modification of bentonite considerably affect the activity of the catalyst samples under study, and $\Delta\eta_{ss}$ was used to evaluate the contributions of weakly and strongly bound forms of palladium(II) and copper(II) to the catalytic activity.

Analyzing the data presented in Table 3, the following conclusions can be drawn. In spite of the fact that the values of the Pd(II) content remaining after removal with water (desorption of weakly bound palladium(II)) are very similar for all the catalyst samples, the values of the decrease of their catalytic activity are very different, especially for K_2PdCl_4-$Cu(NO_3)_2$-KBr/H-Bent-1. Desorption of palladium(II) with nitric acid leads to breakage of bonds, both weak and strong ones, with the bentonite surface, therefore the $\Delta\eta_{ss}$ values, except for the N-Bent anchored samples, are higher by ~12 % than for desorption with water.

Table 3 Comparative results of desorption of palladium(II) and copper(II) ions and testing of K_2PdCl_4-$Cu(NO_3)_2$-KBr/N-Bent(M-Bent) catalyst samples in the reaction of carbon monoxide oxidation $C_{Pd(II)} = 2.72\times10^{-5}$, $C_{Cu(II)} = 2.9\times10^{-5}$, $C_{KBr} = 1.02\times10^{-4}$ mol/g.

Desorption conditions	Content, wt.%		C^{f}_{CO}, mg/m^3	η_{ss}, %	$\Delta\eta_{ss}$, %
	Pd(II)	Cu(II)			
N-Bent					
Reference sample	100	100	38	87.3	0
Pd(II) desorption					
H_2O (293 K)	61.52	100	220	26.7	60.6
HNO_3 (1:1) (373 K)	40.71	100	226	24.7	62.6
Cu(II) desorption					
H_2O (293 K)	100	73.1	104	65.3	22.0
HNO_3 (1:1) (373 K)	100	28.9	150	50.0	37.3
300-Bent					
Reference sample	100	100	14	95.3	0
Pd(II) desorption					
H_2O (293 K)	64.64	100	153	49.0	46.3
HNO_3 (1:1) (373 K)	46.26	100	176	41.3	54.0
Cu(II) desorption					
H_2O (293 K)	100	71.38	68	77.3	18.0
HNO_3 (1:1) (373 K)	100	25.86	117	61.0	34.3
H_2O-Bent					
Reference sample	100	100	31	89.6	0
Pd(II) desorption					
H_2O (293 K)	64.64	100	148	50.7	38.9
HNO_3 (1:1) (373 K)	40.71	100	200	33.3	56.3
Cu(II) desorption					
H_2O (293 K)	100	70.69	100	66.7	22.9
HNO_3 (1:1) (373 K)	100	27.93	160	46.6	43.0
H-Bent-1					
Reference sample	100	100	10	96.6	0
Pd(II) desorption					
H_2O (293 K)	56.32	100	43	85.7	10.9
HNO_3 (1:1) (373 K)	46.26	100	74	75.3	21.3
Cu(II) desorption					
H_2O (293 K)	100	65.5	48	84.0	12.6
HNO_3 (1:1) (373 K)	100	20.7	98	67.3	29.3

The desorption of copper(II) differs from the desorption of palladium(II) (Table 2). After desorption with water, the residual of copper(II) is higher than the residual of palladium(II). This means that the fraction of weakly bound copper(II) is lower than that of palladium(II). Removal of weakly bound copper(II) decreases the catalytic activity of the samples by only 12-23 %. The residual of copper(II) after desorption with nitric acid for 30 min is in the range from 20.1 to 28.9 wt.%, *i.e.* it decreases considerably due to breakage of weak and strong bonds. $\Delta\eta_{ss}$ varies from 29.3 % for H-Bent-1 to 43 % for H_2O-Bent. The order of magnitude of the activity decrease after desorption of palladium(II) and copper(II) is similar to the order of magnitude of the catalytic activity of the reference samples, except for the H_2O-Bent based samples. In all of the cases, the more active the catalyst, the less its activity decreases after palladium(II) or copper(II) desorption.

Conclusions

It has been found that the catalytic activity of bentonite-anchored palladium-copper complexes depends on the state of the support and increases in the following order: N-Bent < H_2O-Bent < 300-Bent < H-Bent-1. In the latter two cases, the catalysts purify air to CO concentrations lower than MPC_{CO}.

It has been confirmed that the combination of two research methods, *i.e.* desorption of metal ions under different conditions and testing of the catalysts in the oxidation of carbon monoxide, is advisable for the evaluation of the contribution of Pd(II) and Cu(II) forms that are weakly and strongly bound to the surface of natural and differently pre-modified bentonites.

Moreover, it has been found that acid-thermally pre-modified bentonite contains the highest fraction of palladium(II) and copper(II) forms that are weakly bound to the surface, 43.68 and 34.5 wt.%, respectively, whereas desorption of these forms reduces the catalytic activity by only 10.9 and 12.6 %, respectively. This can indicate that palladium(II) and copper(II) forms strongly bound to the bentonite surface considerably contribute to the activity of the catalyst in the oxidation of carbon monoxide.

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