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ADSORPTION OF WATER VAPOUR BY NATURAL AND CHEMICALLY MODIFIED CLINOPTILOLITE AND MORDENITE SAMPLES

T.L. Rakytskaya [1]*, T.A. Kiose [1], A.S. Truba [1], A.A. Ennan [2],
R.M. Dlubovskiy [2], V.Ya. Volkova [1]

[1] Mechnikov National University of Odessa, Faculty of Chemistry
2 Dvoryanskaya Str., Odessa, 65082, Ukraine
[2] Physicochemical Institute of Environment and Human Protection
3 Preobrazhenskaya Str., Odessa, 65026, Ukraine

Water vapour adsorption-desorption properties of natural clinoptilolite (N–CLI) and mordenite (N-MOR) samples (Trans-Carpathian region, Ukraine), their acid modified forms, H–CLI–6 and H-MOR-6, and catalysts for both CO oxidation, Pd(II)-Cu(II)/H-CLI-6 and Pd(II)-Cu(II)/H-MOR-6, and ozone decomposition, $MeCl_2$/N-CLI (Me = Cu, Co, Mn), have been studied. All adsorption isotherms at $p/p_s < 0.4$ are described by BET equation with correlation coefficient $R^2 = 0.99$. The activity of the catalysts depends on water content in samples.

INTRODUCTION

Significant information about properties of natural sorbents and their chemically modified forms can be obtained from study of water vapour adsorption-desorption. Clinoptilolite and mordenite demonstrated the enhanced adsorption capacity at low values of the water vapour relative pressure, p/p_s [1, 2]. This allows for wide use of these sorbents as effective air dryers [3]. It has also been shown that mordenite adsorbs less water vapour than clinoptilolite, for instance, the respective adsorption value for MOR and CLI at $p/p_s = 0.4$ are 6.66 and 7.98 mmol/g [2]. However, it is clear that adsorption properties of natural sorbent samples somewhat differ subject to their origin. Thus, clinoptilolite from Turkey adsorbs only 6.25 mmol of water vapour per 1 g at $p/p_s = 0.4$ [4]. Moreover, adsorption capacity values of basalt tuff samples mined from different occurrence depths of the same deposit are different [5]. Researches on water vapour adsorption by acid-modified clinoptilolite samples have not been systematic, and they have been carried out under varying sample pretreatment conditions such as using different kinds and concentrations of acid, changing duration and temperature of treatment, and employing different fractions of sorbent [2, 4]. This makes the comparison of known results and obtaining consistent correlations very problematic.

Both natural and acid-modified clinoptilolites and mordenites are used as supports for metal-complex compounds in production of catalysts for ozone decomposition [6, 7] and carbon monoxide oxidation with air oxygen [8, 9]. The activity of these catalysts significantly depends on water content in the sorbent samples. Therefore, the data on water vapour adsorption by natural and chemically modified sorbents must be taken into consideration when choosing supports for optimising production methods and application conditions of metal-complex catalysts used for air purification from CO and O_3 at enhanced humidity.

The aim of the present study is to determine the parameters of water vapour adsorption by natural and acid-treated clinoptilolites and mordenites and their samples modified with metal-complex compounds. The effect of water adsorption values on the activity of catalysts for both carbon monoxide oxidation with air oxygen and ozone decomposition will be assessed.

EXPERIMENTAL

Samples of natural clinoptilolite from Sokirnitsa and mordenite from Lipcha (Trans-Carpathian region, Ukraine) were used in the

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* corresponding author *TLR@onu.edu.ua*

work. The samples were identified based on X-ray phase analysis data (a Siemens D500 diffractometer). Natural clinoptilolite and mordenite were found to be polyphase minerals with main phase content at approximately 70 %. The identification of clinoptilolite and mordenite was done relying on four baselines at $2\theta = 9.84°$, 22.46°, 22.80°, and 30.07° (d, Å = 8.987, 3.958, 3.900, and 2.972) and at $2\theta = 9.74°$, 22.28°, 25.65°, and 27.66° (d, Å = 9.079, 3.990. 3.473, and 3.225), respectively. The presence of quartz impurities was determined ($2\theta = 26.74°$, d = 3.334 Å). The quartz line was more intense in clinoptilolite than in mordenite XRD patterns. Weak lines of α-Fe_2O_3 phase are apparent at $2\theta = 35.64°$ and 40.907° (d, Å = 2.519 and 2.053). The results of identification of N-CLI and N-MOR agree well with previously published data [10].

Clinoptilolite and mordenite samples were modified in accordance with the following procedure: 50 g of natural zeolite of a specific fraction (0.5–1.0 mm) were placed in a flask with a backflow condenser, 100 mL of 3M HNO_3 were added, then the flask content was boiled for 6 h. After boiling, the samples were washed with water until a nitrate test gave negative result. The acid-treated samples were air-dried at 383 K until constant weight.

Clinoptilolite and mordenite, both natural and acid-modified, were used for supporting metal-complex compounds according to the incipient wetness impregnation method. The procedure was as follows: 10 g of support of a specific fraction (0.5–1.0 mm) were impregnated with 4 mL of a solution with given component ratios. The obtained wet mass was dried in the air at 383 K until constant weight. Compositions of samples are presented in Table 1.

Table 1. Compositions of clinoptilolite and mordenite samples with metal-complex compounds supported on them

Sample		Content, $C_{Me(II)}\cdot10^5$, mol/g			
		Pd(II)	**Cu(II)**	**Co(II)**	**Mn(II)**
I	K_2PdCl_4-$Cu(NO_3)_2$-KBr^*/H-CLI-6	2.7	5.9	–	–
II	K_2PdCl_4-$Cu(NO_3)_2$-KBr^*/H-MOR-6	2.7	2.9	–	–
III	$CuCl_2$/N-CLI	–	12.0	–	–
IV	$CoCl_2$/N-CLI	–	–	12.0	–
V	$MnCl_2$/N-CLI	–	–	–	12.0
VI	$MnCl_2$/N-CLI	–	–	–	0.12

*KBr content is $1.02\cdot10^{-4}$ mol/g

Samples I and II were tested in low-temperature carbon monoxide oxidation according to the recently described procedure [8]. Samples III–VI were tested in ozone decomposition according to [7].

Water vapour sorption by samples of natural and chemically modified clinoptilolite and mordenite was studied in a vacuum assembly thermostatted at 294 ± 0.2 K equipped with a McBain–Bakr quartz spring balance. Samples weighing 0.1–0.2 g were dried first at 383 K. They were evacuated by a fore pump and an oil-vapour vacuum pump for several hours. The residual pressure of 0.13–0.013 Pa was monitored by a VIT-2M ionization-thermocouple vacuum gauge Water vapour puffing was performed after samples had reached constant weight. The partial pressure of carrier gas was measured using a U-tube mercury manometer with an accuracy of ±2.6 Pa. The equilibration time was 24 h. Both a change in the sample weight as a result of sorption and a change in position of U-tube mercury manometer level were measured with a KM-6 cathetometer with an accuracy of ±2 %.

RESULTS AND DISCUSSION

Isotherms of water vapour sorption-desorption by samples of natural and acid-modified clinoptilolite (*a, b*) and mordenite (*d, e*) are equiformal to those of K_2PdCl_4-$Cu(NO_3)_2$-KBr/H-CLI-6 (*c*) and K_2PdCl_4-$Cu(NO_3)_2$-KBr/H-MOR-6 (*f*) catalysts for low-temperature carbon monoxide oxidation with air oxygen (Fig. 1). The adsorption-desorption isotherms of the clinoptilolite- and mordenite-based samples are equiformal too. However, the adsorption values at all p/p_s values are higher for N-MOR, H-MOR and the catalyst samples. The adsorption values for N-CLI and N-MOR at $p/p_s = 0.4$ are almost 2-fold lower than previously reported [2, 4]. Hysteresis loops of capillary condensation are observed for all samples under study. The difference between values of adsorption and desorption isotherm branches, Δ*a*, is negligible for natural N-CLI (*a*) and N-MOR (*c*) and acid-modified H-CLI-6 (*b*) and H-MOR-6 (*d*) samples to the extent that their adsorption and desorption curves are practically congruent. Conversely, the hysteresis loops of Pd(II)-Cu(II) catalysts have larger Δ*a* and extend to abnormally low p/p_s values. Moreover, the hysteresis loop of Pd(II)-Cu(II)/H-CLI-6 catalyst is open. This behaviour may be caused not only by substantial changes in clinoptilolite structure but also by chemical transformations of catalyst components. The latter is supported by our observation that, during vacuum treatment, Pd(II)-Cu(II)/H-CLI-6 samples turned the colour typical of palladium black, which did not disappear after long-term air-exposed storage of the catalyst. Testing of the sample in the reaction of carbon monoxide oxidation with air oxygen showed that it lost its catalytic activity [11].

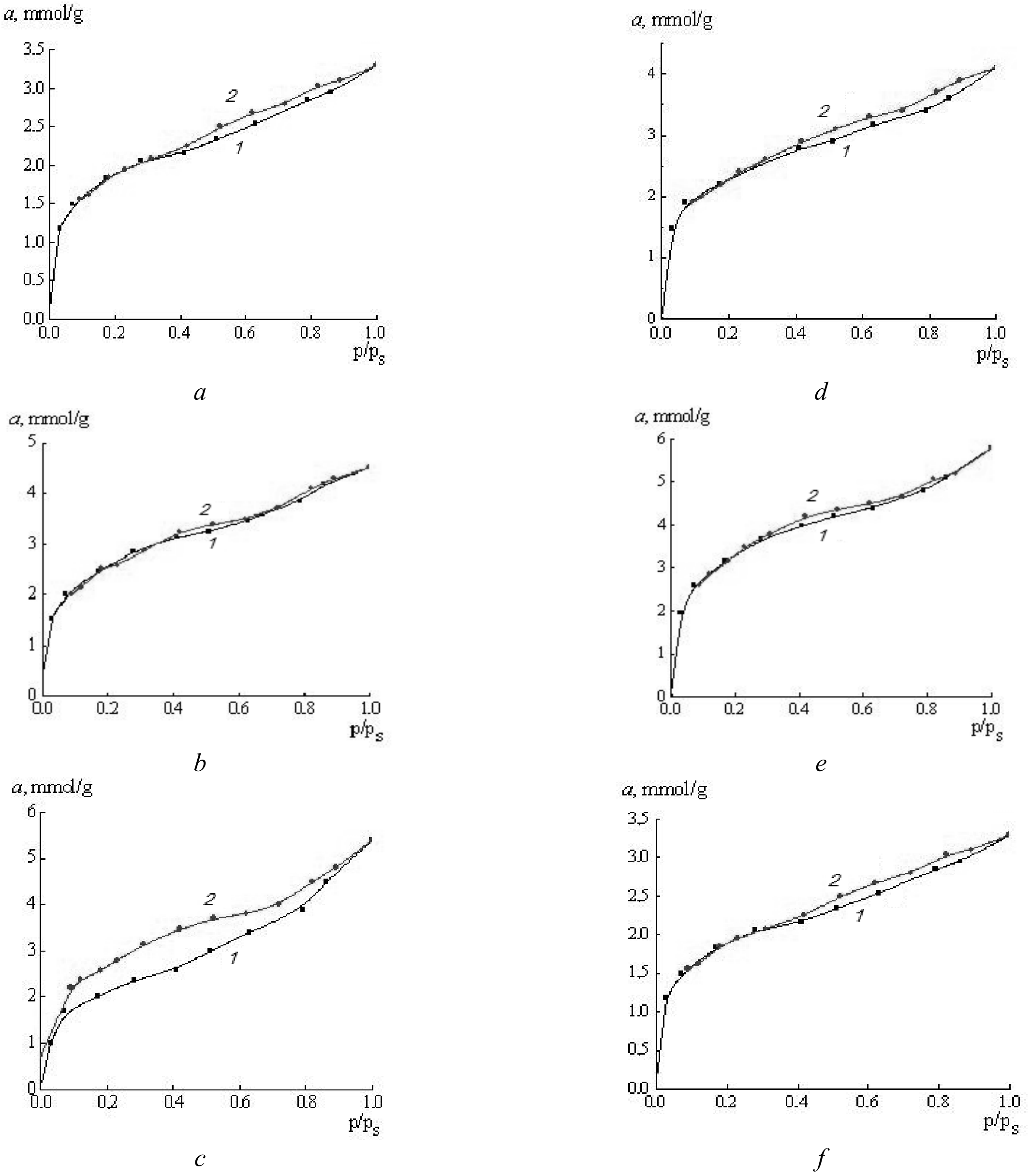

Fig. 1. Isotherms of water vapour adsorption (*1*) and desorption (*2*) by samples of natural and modified clinoptilolite and mordenite: N-CLI *(a)*, H-CLI *(b)*, Pd(II)-Cu(II)/H-CLI-6 *(c)*, N-MOR *(d)*, H-MOR*(e)*, Pd(II)-Cu(II)/H-MOR-6 *(f)*

Samples of $MeCl_2$/N-CLI (Me = Cu, Co, Mn) catalysts for ozone decomposition are characterized by similar adsorption-desorption isotherms at $C_{MeCl_2} = 1.2 \cdot 10^{-4}$ mol/g. A hysteresis loop of a $MnCl_2$/N-CLI sample abnormally extends down to $p/p_s < 0.1$ with Δa of 0.4 mmol/g at $p/p_s = 0.4$ (Fig. 2). A hysteresis loop of a $MnCl_2$/N-CLI catalyst sample with lower manganese chloride content ($1.2 \cdot 10^{-6}$ mol/g) (curve *2*) is narrower ($\Delta a = 0.24$ mmol/g), but still exceeds the width of the hysteresis loop of native clinoptilolite ($\Delta a = 0.06$ mmol/g). This progression indicates a substantial contribution of hydration of exchangeable cations to the adsorption-desorption equilibrium [1].

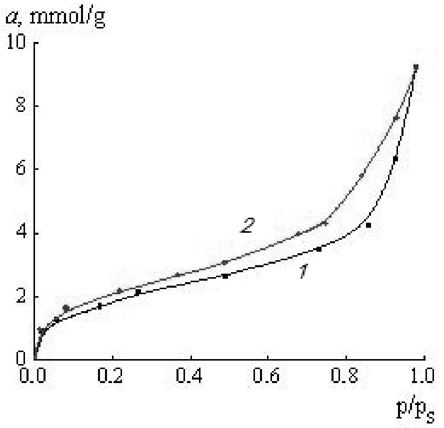

Fig. 2. Water vapour adsorption (*1*) and desorption (*2*) isotherms for $MnCl_2$/N-CLI at $C_{Mn} = 1.2 \cdot 10^{-4}$ mol/g

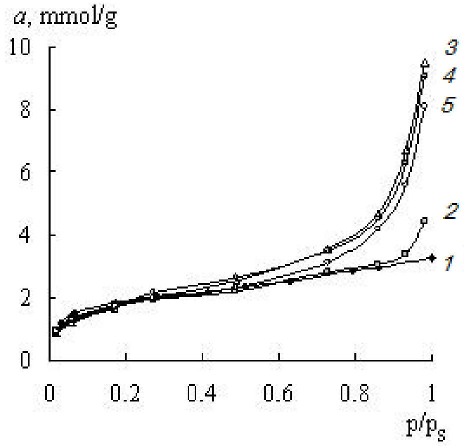

Fig. 3. Comparative water vapour adsorption isotherms for samples of N-CLI (*1*) and $MeCl_2$/N-CLI, where $MeCl_2$ are: *2* – $MnCl_2$ ($C_{Me} = 1.2 \cdot 10^{-6}$ mol/g); *3* – $MnCl_2$; *4* – $CoCl_2$; *5* – $CuCl_2$ ($C_{Me} = 1.2 \cdot 10^{-4}$ mol/g for three latter)

A similar conclusion can be drawn from a comparative analysis of water vapour sorption isotherms for N-CLI and $MeCl_2$/N-CLI (Me = Cu, Co, Mn) samples (Fig. 3) at $C_{MeCl_2} = 1.2 \cdot 10^{-4}$ mol/g (curves *3*, *4*, and *5*) and $C_{MeCl_2} = 1.2 \cdot 10^{-6}$ mol/g (curve *2*). An increase in water vapour adsorption in comparison with that on clinoptilolite is observed in the case of high contents of Cu(II), Co(II), and Mn(II) chlorides already at $p/p_s = 0.4$ whereas at $C_{MeCl_2} = 1.2 \cdot 10^{-6}$ mol/g it is observed just at $p/p_s > 0.85$.

The sorption isotherms were analyzed using Brunauer-Emmett-Teller (BET) equation for polymolecular adsorption. The linear form of BET equation is

$$\frac{p/p_s}{a(1-p/p_s)} = \frac{1}{a_m \cdot C} + \frac{C-1}{a_m \cdot C} \cdot \frac{p}{p_s}, \tag{1}$$

where a is the adsorption value at equilibrium relative pressure, p/p_s; a_m is the monolayer volume; C is a constant characterizing the heat of adsorption for the first layer.

Equation 1 fits all adsorption isotherms obtained at $p/p_s < 0.4$ with correlation coefficient, R^2, of 0.98–0.99. Parameters of BET equation are summarized in Table 2.

Additionally, the adsorption heat for the first layer, Q_1, was calculated using the following approximate relationship from [12]

$$C \approx e^{\frac{Q_1 - Q_L}{RT}}, \tag{2}$$

where Q_L is the water condensation heat ($Q_L = 135.9$ J/mol [13]).

Equation 2 can be rewritten in a more convenient form as follows:

$$RTlnC = Q_1 - Q_L. \tag{3}$$

A number of conclusions can be drawn from the values of the adsorption parameters. The adsorption value is higher for mordenite- than that for clinoptilolite-based samples. The monolayer volume, a_m, increases in acid-treated samples compared to native ones and slightly decreases in the samples supporting catalyst components, Pd(II) and Cu(II). Values of the monolayer volume were similar among all tested $MeCl_2$/N-CLI samples, and they were only insignificantly different from those of N-CLI.

C (Q_1) decreases in sequences N-CLI > H-CLI-6 > Pd(II)-Cu(II)/H-CLI-6, N-MOR > H-MOR-6 > Pd(II)-Cu(II)/H-MOR-6, and N-CLI > $MeCl_2$/N-CLI. The C values decrease in sequence Co > Mn > Cu when metal content is 1.2·10^{-4} mol/g. The *C* value is higher in the $MnCl_2$/N-CLI samples with $MnCl_2$ content of 1.2·10^{-6} mol/g but it is still lower than the *C* value of N-CLI. The *C* values for the chemically modified clinoptilolite-based samples are close to literature data [4].

Thus, owing to chemical modification of natural sorbents, the energy of interaction of water molecules with their surfaces decreases. It is worth noting that the adsorption value at $p/p_s \rightarrow 1$, a_∞, increases considerably in $MeCl_2$/N-CLI samples compared to native clinoptilolite samples only when the content of Cu(II), Co(II), or Mn(II) chloride is high. S_{sp} values calculated from water vapour adsorption greatly exceed those measured by the method of thermal desorption of argon [12, 13].

Table 2. Structural-adsorption characteristics of natural and chemically modified clinoptilolite and mordenite

Sample	BET equation constants		a_∞, mmol/g	Q_1, кJ/mol	S_{sp}, m^2/g
	a_m, mmol/g	C			
N-CLI	1.53	133.4	3.30	12.09	99.5
H-CLI-6	2.13	85.2	4.50	11.01	138.7
Pd(II)-Cu(II)/H-CLI-6	1.80	52.3	5.40	9.82	117.2
N-MOR	1.82	210.9	4.10	13.22	118.3
H-MOR-6	2.73	89.2	5.80	11.11	177.5
Pd(II)-Cu(II)/H-MOR-6	2.69	74.4	6.30	10.67	174.9
$CuCl_2$/N-CLI	1.51	68.4	8.10	10.46	98.2
$CoCl_2$/N-CLI	1.60	43.9	9.20	9.38	105.3
$MnCl_2$/N-CLI (1.2·10^{-4} mol/g)	1.54	48.6	9.50	9.62	100.1
$MnCl_2$/N-CLI (1.2·10^{-6} mol/g)	1.49	93.5	4.42	11.21	96.9

The catalytic activity of metal-complex compounds supported on porous supports in redox reactions with CO, PH_3, SO_2 and O_3 depends significantly on the water content in catalyst samples [14, 15]. In processes of catalytic purification of the air with high moisture content, catalysts become poisoned by virtue of the water vapour adsorption and lose their activity. The activity of the catalysts can be completely or partially restored by dehydration. In the case of supported metal-complex catalysts, the dehydration is carried out at the temperatures ranging from 383 to 403 K. Some examples of influence of the water adsorption on the activity of catalysts for CO oxidation and ozone decomposition are presented below.

Catalyst samples I and II (Table 1) were tested in the reaction of carbon monoxide oxidation with air oxygen at the initial CO concentration (C^{in}_{CO}) of 300 mg/m^3, temperature of 293 K, the relative humidity of a gas-air mixture (GAM) of 65 %, and the GAM linear velocity (U) of 4.2 cm/s. Typical time dependence curves of carbon monoxide final concentration (C^{f}_{CO}) for the two catalyst series are shown in Fig. 4.

Catalyst samples I-a.d. and II-a.d. were dried at 383 K for 3 h and then air-dried at the relative humidity of 65 %. The water contents in I-a.d. and II-a.d. samples were 2.22 and 2.56 mmol/g, respectively. According to the data presented in Table 2, these values are close to the monolayer volume for these samples. Samples denoted as I-0.03 and II-0.03, were prepared similarly to I-a.d. and II-a.d. but extra amount of water was added to each of the samples leading to an increase in their water content by 0.03 g/g (1.67 mmol/g).

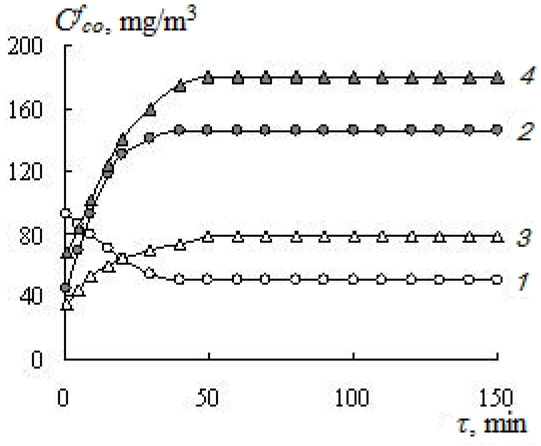

Fig. 4. Time dependences of C^{f}_{CO} at different water contents in catalyst samples under conditions presented in Table 3: *1* – I-a.d., *2* – I-0.03, *3* – II-a.d., *4* – II-0.03

All kinetic curves in Fig. 4 have portions where C^f_{CO}, the reaction rate (W), the reaction rate constant (k_I), and the CO oxidation level (η) are constant over an extended period of time regardless of the water contents in the samples. Based on reaction quantitative characteristics presented in Table 3, it can be concluded that, under steady-state conditions, the increased water content in the samples is linked to higher final CO concentration. The CO oxidation level is ca. 30 % lower in the samples with higher water content.

Possible mechanisms of the influence water has on the activity of supported Pd(II)-Cu(II) catalysts have been considered elsewhere [14].

Samples III-VI (Table 1) of $MeCl_2$/N-CLI catalysts (Me = Cu, Co, Mn) were tested in the reaction of ozone decomposition. The results for the catalysts with Me = Cu, Co have been published earlier [6, 7] Here, the data on the kinetics of ozone decomposition by $MnCl_2$/N-CLI samples at low ($1.2\cdot10^{-6}$ mol/g) and high ($1.2\cdot10^{-4}$ mol/g) Mn(II) chloride content are presented (Fig. 5).

Table 3. Effect of the water content in Pd(II)-Cu(II) catalysts on parameters of the reaction of CO oxidation with air oxygen

Catalyst sample	Water content, mmol/g	$W_{st}\cdot10^9$, mol/(g·s)	k_{Ist}, s^{-1}	$C^f_{CO\ st}$, mg/m^3	η_{st}, %
Pd(II)-Cu(II)/H-CLI-6 catalyst					
I-a.d.	2.22	14.9	2.6	51	83
I-0.03	3.89	9.3	1.1	145	52
Pd(II)-Cu(II)/H-MOR-6 catalyst					
II-a.d.	2.56	13.3	2.0	78	74
II-0.03	4.23	7.2	0.7	180	40

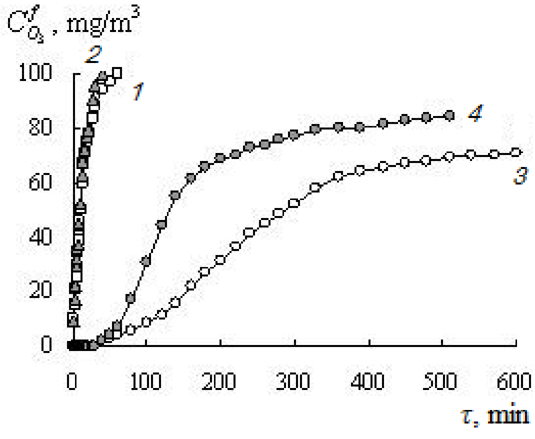

Fig. 5. Time dependence of $C^f_{O_3}$ in the ozone decomposition by $MnCl_2$/N-CLI samples:
1 – initial;
2 – dehydrated ($C_{Mn(II)} = 1.2\cdot10^{-6}$ mol/g);
3 – initial;
4 – dehydrated ($C_{Mn(II)} = 1.2\cdot10^{-4}$ mol.g)
($C^{in}_{O_3}$ = 100 mg/m^3)

The kinetics of the reaction is significantly different for air-dried samples with low Mn(II) content (curve *1*) compared to those with high Mn(II) content (curve *3*). It is clear that ozone decomposition over the former stops ($C^f_{O_3} = C^{in}_{O_3}$) after 60 min, whereas the latter starts to decompose ozone in the steady-state regime after 400 min. $C^f_{O_3}$ remained constant for at least 400 min more (data not shown) until the experiment was terminated at 1000 min. No changes in sample appearance were observed in the case of the former catalyst sample, whereas the latter sample changed its colour to that characteristic of MnO_2 after being in contact with ozone for an extended period of time. This oxide form of manganese was retained strongly on clinoptilolite and could not be removed from the surface with water, what agreed with the data on the use of manganese oxide form of clinoptilolite for wastewater treatment [1].

A possible cause of the decrease in activity of the catalysts is blockage of their active sites with water the catalysts adsorb from the humid ozone-air mixture. It was demonstrated by dehydration of the samples at 383 K for 3 h that the catalysts with low and high Mn(II) content stored 0.17 and 2.3 mmol/g of water, respectively. The latter value is 1.5-fold higher than the monolayer volume for the sample (Table 2). Dehydrated samples were tested again in the reaction of ozone decomposition (Fig. 5).

In the case of the sample with low manganese content, dehydration had little or no effect on the activity (compare curves *1* and *2*). On the other hand, the dehydrated sample with $C_{MnCl_2} = 1.2 \cdot 10^{-4}$ mmol/g (curve *4*) entered the steady-state regime of the reaction sooner than the initial sample, albeit its activity was 15 % lower. However it is obvious that dehydration has a potential to be used to regenerate these catalysts.

Besides blocking active sites of the catalyst, water molecules can displace chloride ions from the inner coordination sphere of a manganese ion to the outer sphere. It not only alters the metal complex composition but also significantly decreases the activity of the supported metal-complex redox catalyst [14, 15]. Furthermore, long-time exposure of such an altered catalyst with high Mn(II) content to ozone results in the following reaction on the clinoptilolite surface: $Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + 2H^+ + O_2$. This causes irreversible formation of a new catalyst, the oxide form of manganese, with catalytic activity lower than that of the metal-complex catalyst. Thus, the presence of manganese dioxide in the dehydrated catalyst sample can explain its faster entering the steady-state regime and a lower rate of the reaction of ozone decomposition, i.e. a more rapid catalytic activity loss.

CONCLUSIONS

Natural clinoptilolite, N-CLI, and mordenite, N-MOR, their acid-modified forms, H-CLI-6 and H-MOR-6, as well as low-temperature catalysts for both carbon monoxide oxidation with air oxygen, Pd(II)-Cu(II)/H-CLI-6 and Pd(II)-Cu(II)/H-MOR-6, and ozone decomposition $MeCl_2$/N-CLI (Me = Cu, Co, Mn), are characterized by non-uniform structure with predominantly transient pores. Water molecules can interact with a support surface and catalyst components causing a decrease in *C* parameter in BET equation in the following sequences N-CLI > H-CLI-6 > Pd(II)-Cu(II)/H-CLI-6, N-MOR > H-MOR-6 > Pd(II)-Cu(II)/H-MOR-6, and N-CLI > $MeCl_2$/N-CLI.

A substantial contribution of hydration of exchangeable cations to the adsorption-desorption equilibrium has been shown. In the case of the catalysts of ozone decomposition ($MeCl_2$/N-CLI), the samples with high Cu(II), Co(II), and Mn(II) chloride content of $1.2 \cdot 10^{-4}$ mol/g demonstrated the elevated water vapour adsorption compared to the native support at as low as p/p_s of 0.4. The vapour adsorption of the samples with $MnCl_2$ content of $1.2 \cdot 10^{-6}$ mol/g exceeded the native support at as low as $p/p_s = 0.85$.

The increase in the water content in samples of metal-complex compounds supported on natural and acid-modified supports results in the decrease in their catalytic activity in the redox transformations of carbon monoxide and ozone. It has been shown that the samples of Pd(II)-Cu(II) catalysts supported on H-CLI-6 or H-MOR-6 are the more active in the reaction of carbon monoxide oxidation the closer their water content is to the monolayer volume. $MnCl_2$/N-CLI catalyst for ozone decomposition with low Mn(II) content becomes completely inactive adsorbing only 0.17 mmol of water per 1 g in the course of an experiment but the activity was restored to its initial values after dehydration of the sample. The sample with high Mn(II) content adsorbs 2.3 mmol of water per 1 g retains some of its catalyst activity over a long period of time. Its dehydration only partially restores its activity owing to the change in the active form of manganese.

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Адсорбція парів води природними і хімічно модифікованими зразками клиноптилоліту та морденіту

Т.Л. Ракитська, Т.О. Кіосе, А.С. Труба, А.А. Еннан, Р.М. Длубовський, В.Я. Волкова

Одеський національний університет імені І.І. Мечникова, хімічний факультет
вул. Дворянська, 2, Одеса, 65082, Україна, TLR@onu.edu.ua;
Фізико-хімічний інститут захисту навколишнього середовища і людини
вул. Преображенська, 3, Одеса, 65026, Україна

Вивчено адсорбцію парів води зразками природного клиноптилоліту (N–CLI) і морденіту (N–MOR) (Закарпатська обл., Україна), їх кислотно-модіфікованими формами H–CLI–6, H–MOR–6, а також каталізаторами окиснення CO Pd(II)-Cu(II)/H-CLI-6 і Pd(II)-Cu(II)/H-MOR-6 та розкладу озону $MeCl_2$/N-CLI (Me = Cu, Co, Mn). Всі ізотерми адсорбції в області $p/p_s < 0.4$ описуються рівнянням БЕТ з коефіцієнтом кореляції $R^2 = 0.99$. Активність каталізаторів залежить від вмісту в них води.

Адсорбция паров воды природными и химически модифицированными образцами клиноптилолита и морденита

Т.Л. Ракитская, Т.А. Киосе, А.С. Труба, А.А. Эннан, Р.М. Длубовский, В.Я. Волкова

Одесский национальный университет имени И.И. Мечникова, химический факультет
ул. Дворянская, 2, Одесса, 65082, Украина, TLR@onu.edu.ua
Физико-химический институт защиты окружающей среды и человека
ул. Преображенская, 3, Одесса, 65026, Украина

Изучена адсорбция паров воды образцами природного клиноптилолита (N–CLI) и морденита (N–MOR) (Закарпатская обл., Украина), их кислотно-модифицированными формами H–CLI–6, H–MOR–6, а также катализаторами окисления CO Pd(II)-Cu(II)/H-CLI-6 и Pd(II)-Cu(II)/H-MOR-6 и разложения озона $MeCl_2$/N-CLI (Me = Cu, Co, Mn). Все изотермы адсорбции при $p/p_s < 0.4$ описываются уравнением БЭТ с коэффициентом корреляции $R^2 = 0.99$. Активность катализаторов зависит от содержания в них воды.