Catalytic Compositions Based on Chlorides of *d* Metals and Natural Aluminosilicates for the Low-Temperature Sulfur Dioxide Oxidation with Air Oxygen

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Samples of natural bentonite and clinoptilolite modified with copper(II), iron(III), and palladium(II) were characterized by both X-ray phase and the Fourier transform infrared spectral methods. The activity of monometallic compositions $M_iL_j/S(M = Co(II), Fe(III),$ and $Pd(II); L = NO_3^-, Cl^-,$ and $SO_4^{2-}; S = $ N-CLI or N-Bent) in the reaction with sulfur dioxide was found to depend on the nature of both a metal ion and a support. For bimetallic compositions Cu(II)–Fe(III) and Cu(II)–Pd(II) based on the natural aluminosilicates, a certain synergism in the action of metals forming these pairs towards the reaction of sulfur dioxide oxidation with oxygen was determined.

1. Introduction

In spite of the fact that there are some works [1, 2] concerning sulfur dioxide, the most widespread atmospheric pollutant, abatement in air, this problem remains relevant as before because the recent metal and oxide catalysts (except for those containing manganese oxides [3]) are active only at high temperatures and are not suitable for application at ambient temperature. Some salts of *d* metals such as iron, copper, manganese, and cobalt dissolved in water [4] are able to oxidize sulfur dioxide at its concentrations of $10^{-7} \div 10^{-6}$ mol/l at room temperature. We would like to notice that the simultaneous presence of two metal ions may cause their simple additive action (for Mn(II)–Ni(II) [5]), their synergetic action (for Mn(II)–Fe(III), Mn(II)–Co(II) [6], and Cu(II)–Fe(III) [7]), or the inhibition of their action (for Mn(II)–Cr(III) [5]). The detailed kinetic and thermodynamic analysis of numerous data on the liquid phase sulfur(IV) oxidation in the equilibrium mixture $SO_{2aq}-HSO_3^- -SO_3^{2-}$ as well as the possible theoretic interpretation of synergetic action of *d* metal ions in this process are reported in works of Ermakov et al. [8–10], Golodov [11], and some former but still relevant papers [5–7].

It is well-known that the reactivity of metal ions can be altered by their anchoring on different supports but there are only few works [2, 12, 13] investigating compositions thus obtained in their reactions with sulfur dioxide. Such compositions consist of $Co^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}$ or Ag^+ and such supports as zeolites (clinoptilolite [2] and NaY [13]). These compositions have no catalytic activity and, after certain periods of time, SO_2 concentration at

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the reactor outlet attains its initial value. The only information on the catalysts consisting of metal complexes anchored on natural minerals for sulphur dioxide oxidation with air oxygen is presented in our earlier work [14].

The aim of this work was to find conditions under those mono- and bimetallic compositions anchored on natural aluminosilicates, i.e. bentonite and clinoptilolite, show their catalytic performance in the reaction of low-temperature sulphur dioxide oxidation with air oxygen.

2. Experimental

Such compositions as M_iL_j/S (S = N-Bent and N-CLI; M = Cu^{2+}, Fe^{3+}, Pd^{2+}; L = Cl^-, NO_3^-, and SO_4^-), and $CuCl_2 - M_iL_j/S(M = Fe^{3+}$ or $Pd^{2+})$ were prepared by a method of incipient wetness impregnation of natural bentonite (Dashukovskoye deposit, Ukraine) and natural clinoptilolite (Sokirnitskoye deposit, Ukraine) with aqueous-alcoholic solutions of corresponding salts. The samples thus obtained were dried in air at $20\,°C$ till constant weight.

The X-ray diffraction phase analysis was carried out on a Siemens D500 diffractometer (CuK_α radiation, $\lambda = 1.54178$ Å) with a secondary beam graphite monochromator [14, 15].

Infrared analysis was carried out using a Fourier transform infrared spectrometer (PerkinElmer FT-IR spectrometer) with resolution of 4 cm^{-1} [14, 15].

A gas–air mixture (GAM) with SO_2 concentration of $150\,mg/m^3$ was obtained by mixing a purified air flow and a flow of pure SO_2 in a special mixer. Initial and final sulphur dioxide concentrations, $C_{SO_2}^{in}$ and $C_{SO_2}^f$, respectively, were measured using a 667EKh08 electrochemical gas analyzer (made by "Analitpribor", Ukraine) with the minimal detectable SO_2 concentration of 2 mg/m^3.

The kinetics of sulphur dioxide removal by the compositions under study was investigated using a gas flow setup with a fixed-bed glass reactor temperature-controlled at 293 K. The relative humidity of the GAM, φ_{GAM}, was kept at 76%. The weight of each sample under study was 10 g. The volume flow rate w of the GAM (1 l/min), the linear velocity U of the GAM (4.2 cm/s), and the ratio between the average grain size of aluminosilicate samples $\overline{d}_g$ (0.75 mm) and an inner diameter of the reactor met the requirements for the regime of ideal displacement and the reaction proceeding in the kinetic region.

3. Results and discussion

3.1. Results of physicochemical study of the supports and compositions based on them

X-ray phase analysis shows that the main phase of natural bentonite is montmorillonite characterized by the following values of X-ray spectral parameters 2θ and (d [Å]): 5.739° (15.540), 19.743° (4.493), 35.830° (2.504), 61.710° (1.501). Besides the main phase, natural bentonite contains α-quartz and calcite. The polyphase composition of N-Bent is confirmed by data of its Fourier transform infrared (FT-IR) spectrum containing absorption bands at 3692, 3622, 1036, 915, 876, 519, and 468 cm^{-1} characteristic of montmorillonite structural groups and also the shoulders of amorphous SiO_2 at 1163 and 1096 cm^{-1}, the bands of α-quartz at 799, 779, and 695 cm^{-1} and the band of calcite at 1421 cm^{-1}. Very low concentrations of metal salts (10^{-7}-10^{-5} mol/g) in the compositions are not able to create some evident changes both in X-ray and FT-IR spectra.

The pure clinoptilolite phase in natural clinoptilolite is identified based on three base reflections at 2θ and (d [Å]): 9.856° (8.959), 22.416° (3.963), 30.057° (2.970). Impurity phases are α-quartz, mordenite, and Fe_2O_3. It should be noted that for compositions based on clinoptilolite as well as for those based on bentonite there are no changes induced by anchored metal salts. However, the IR spectra of N-CLI change as a result of Cu(II) and Pd(II) salts anchoring. These alterations are observed in the region of vibrations characteristic of OH groups bound to adsorbed water molecules (the shift from 3444 to 3427 cm^{-1}) and vibrations characteristic of Brønsted OH groups in Si(OH)Al bridges (the shift from 3625 to 3618 cm^{-1}). Such alterations could be explained by formation of surface metal complexes.

3.2. Results of kinetic study

Compositions based on both aluminosilicates were tested in the reaction of SO_2 oxidation with air oxygen. In the case of bentonite based monometallic compositions M_iL_j/N-Bent, where M = Fe(III), Cu(II), Pd(II) and L = NO_3^-, Cl^-, SO_4^{2-} it was found that their activity in the reaction with sulphur dioxide depended on the nature of both metal and anion. As an example, the influence of anion was demonstrated for Fe(III) salts. Figure 1 shows curves $C_{SO_2}^f$ vs. time (τ) obtained as a result
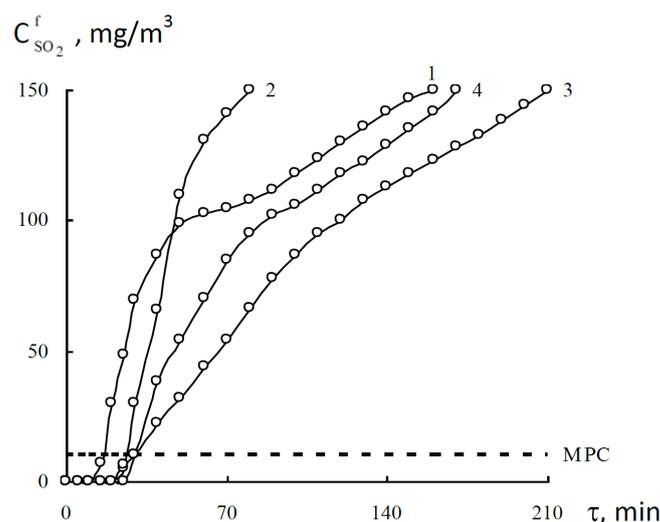

Fig. 1. Time dependence of $C_{SO_2}^f$ in the course of sulfur dioxide removal from air with N-Bent (1), $Fe(NO_3)_3$/N-Bent (2), $FeCl_3$/N-Bent (3), and $Fe_2(SO_4)_3$/N-Bent (4) ($C_{Fe(III)} = 1.0 \times 10^{-6}$ mol/g).

of GAM passing throw fixed beds of N-Bent and Fe(III) containing monometallic compositions based on it.

Analyzing the experimental data, we use kinetic and stoichiometric reaction parameters: τ_0, τ_{MPC}, $\tau_{1/2}$, and Q_{exp}. τ_0 is a period of time when SO_2 is completely removed from GAM, i.e. when $C_{SO_2}^f = 0$; τ_{MPC} is a time of protective action, i.e. a period of time from experiment beginning up to the moment when $C_{SO_2}^f$ achieves the maximum permissible concentration of sulphur dioxide equal to 10 mg/m^3; $\tau_{1/2}$ is a half-conversion time, i.e. a period of time from experiment beginning up to the moment when $C_{SO_2}^f$ became equal to $0.5C_{SO_2}^{in}$; Q_{exp} is an amount of SO_2(mol) entering into the reaction during a total period of testing.

It is obvious that all kinetic curves presented have portions characterized by the complete removal of SO_2 and then $C_{SO_2}^f$ goes up and becomes equal to $C_{SO_2}^{in}$. All kinetic and stoichiometric reaction parameters mentioned above increase in the order N-Bent(1) < Fe(NO$_3$)$_3$/N-Bent < FeCl$_3$/N-Bent < Fe$_2$(SO$_4$)$_3$/N-Bent. Kinetic curves for bentonite anchored Cu(II) and Pd(II) salts are similar to those presented in Fig. 1. The most active compositions of these metals are $CuCl_2$/N-Bent and $PdCl_2$/N-Bent. By varying a concentration of copper(II) chloride in $CuCl_2$/N-Bent from 1.5×10^{-5} to 2.9×10^{-4} mol/g, we have found that τ_{MPC} increases from 25 to 55 min and Q_{exp} rises from 1.13×10^{-5} to 2.81×10^{-5} mol of SO_2. For $PdCl_2$/N-Bent, τ_0, τ_{MPC}, $\tau_{1/2}$, and Q_{exp} parameters are practically unchanged when palladium(II) concentration increases from 1.5×10^{-6} to 6.8×10^{-6} mol/g, however, these parameters are higher than for N-Bent. Interestingly, the parameters became lower than for N-Bent when $C_{Pd(II)} > 6.8 \times 10^{-6}$ mol/g.

As for mono- and bimetallic N-Bent based compositions (Fig. 2 and Table I), all of they demonstrate rather high adsorption properties towards sulfur dioxide and some of them (5, 7, and 8) show certain periods of time when $C_{SO_2}^f$ is constant that is characteristic of a steady state mode.
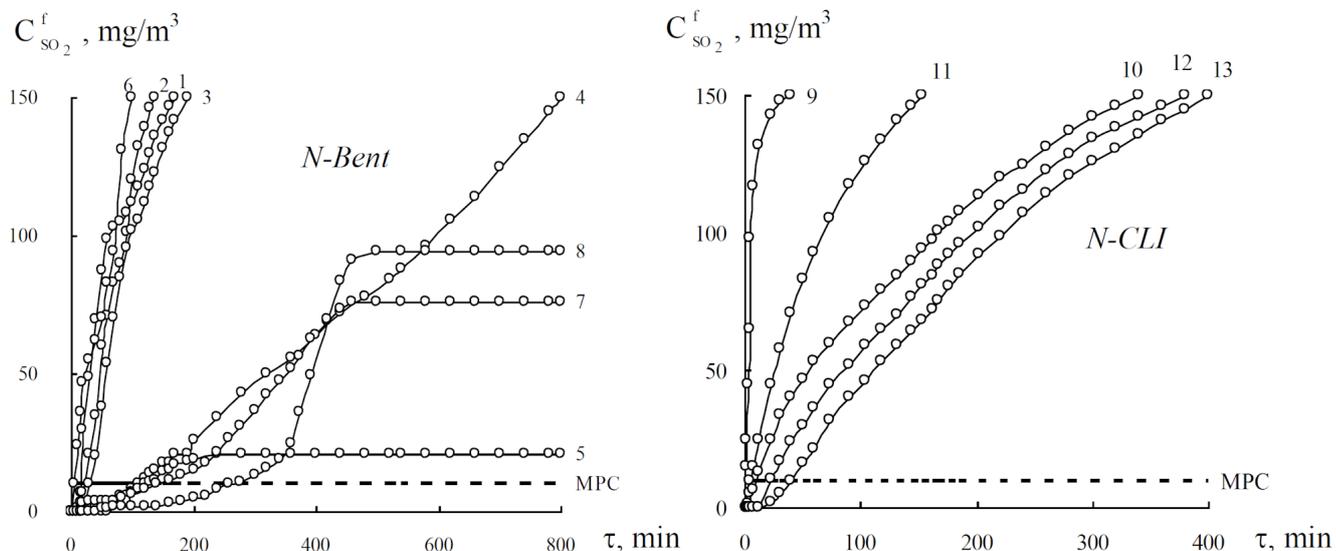

Fig. 2. Time dependence of $C_{SO_2}^f$ characteristic of sulfur dioxide removal with N-Bent (1) and N-CLI (9) as well as its oxidation with air oxygen over CuCl$_2$/N-Bent (2), FeCl$_3$/N-Bent (3), CuCl$_2$–FeCl$_3$/N-Bent (4), CuCl$_2$–FeCl$_3$–KCl/N-Bent (5), K$_2$PdCl$_4$/N-Bent (6), CuCl$_2$–K$_2$PdCl$_4$/N-Bent (7), CuCl$_2$–K$_2$PdCl$_4$–KCl/N-Bent (8); CuCl$_2$/N-CLI (10), K$_2$PdCl$_4$/N-CLI (11), CuCl$_2$–K$_2$PdCl$_4$/N-CLI (12), CuCl$_2$–K$_2$PdCl$_4$–KCl/N-CLI (13).

TABLE I

Parameters of sulfur dioxide removal from air with natural aluminosilicates as well as its oxidation with air oxygen over compositions containing d metal chlorides and based on these natural supports $C_{Pd(II)} = 2.72 \times 10^{-5}$, $C_{Cu(II)} = 5.9 \times 10^{-5}$, $C_{Fe(III)} = 1.0 \times 10^{-6}$ mol/g, $t = 20\,°C$, $C_{SO_2}^{in} = 150$ mg/m^3.

Composition number*	Composition	τ_0 [min]	τ_{MPC} [min]	$\tau_{1/2}$ [min]	$Q_{exp} \times 10^4$ [mol SO$_2$]	K_s
1	N-Bent	10	15	35	1.11	-
2	CuCl$_2$/N-Bent	15	25	55	1.20	-
3	FeCl$_3$/N-Bent	25	30	65	1.57	-
4	CuCl$_2$–FeCl$_3$/N-Bent	30	110	460	10.20	2.0
5	CuCl$_2$-FeCl$_3$–KCl/N-Bent	60	120	-	16.30**	2.2
6	K$_2$PdCl$_4$/N-Bent	1	5	30	0.77	-
7	CuCl$_2$–K$_2$PdCl$_4$/N-Bent	5	140	440	12.30**	4.7
8	CuCl$_2$–K$_2$PdCl$_4$–KCl/N-Bent	40	260	420	12.10**	8.7
9	N-CLI	-	-	5	0.09	-
10	CuCl$_2$/N-CLI	4	10	110	2.60	-
11	K$_2$PdCl$_4$/N-CLI	2	5	45	1.02	-
12	CuCl$_2$–K$_2$PdCl$_4$/N-CLI	12	25	145	3.20	1,7
13	CuCl$_2$–K$_2$PdCl$_4$–KCl/N-CLI	12	40	170	3.80	2,7

* composition numbers coincide with numbers of curves in Fig.2

** the experiment was stopped in 800 min

Making a comparison between the two aluminosilicates under study (Fig. 2 and Table I), one can see that the kinetics of SO$_2$ adsorption from GAM by natural clinoptilolite (curve 9) is quite different compared with that for natural bentonite (curve 1), i.e., for N-CLI, in contrast to N-Bent, there is no period of time when SO$_2$ removal is complete, τ_0, and the total amount of SO$_2$ adsorbed by N-CLI (0.9×10^{-5} mol) is much less than that in the case of N-Bent.
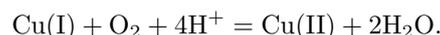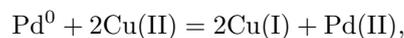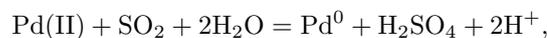
For palladium(II) and copper(II) monometallic compositions based on N-Bent and N-CLI, kinetic curves are similar: at the beginning, τ_0 portions of curves are present and a consequent gradual increase in $C_{SO_2}^f$ up to $C_{SO_2}^{in}$ takes place. A similar shape of kinetic curves for SO_2 adsorption by M^{n+}/N-CLI compositions (M^{n+} = Zn^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, Ag^+, Ca^{2+}, Li^+, Na^+, K^+) obtained by the ion-exchange method was described earlier [2]. It is evident (Table I) that τ_0 and τ_{MPC} parameters for $CuCl_2$/N-CLI are lower than those for $CuCl_2$/N-Bent, whereas these parameters do not change and are the same for Pd(II)/N-CLI and Pd(II)/N-Bent. Interestingly, $\tau_{1/2}$ and Q_{exp} parameters for M^{2+}/N-CLI are higher than those for M^{2+}/N-Bent (M^{2+} = Cu^{2+}, Pd^{2+}).

In the case of bimetallic compositions based on the two aluminosilicates, the kinetic curves characterized by the presence of τ_0 portions and consequent gradual increases in $C_{SO_2}^f$ up to $C_{SO_2}^{in}$ are also observed for bimetallic compositions 12 (Cu(II)–Pd(II)/N-CLI) and 13 (in fact, composition 12 doped with chloride ions) as well as for bimetallic composition 4 ($CuCl_2$–$FeCl_3$/N-Bent) (Fig. 2). Compositions 4, 12, and 13 are much more active (i.e. their reaction parameters are noticeably higher) than their monometallic counterparts but they do not demonstrate a steady-state mode of sulfur dioxide oxidation. N-Bent based bimetallic compositions 5, 7, and 8 show that the reaction kinetics substantially differed from that for bimetallic composition 4, 12, and 13. As can be seen from Fig. 2, kinetic curves demonstrating the behavior of compositions 5, 7, and 8 show long portions with $C_{SO_2}^f$ = const characteristic of a steady-state mode and indicating the true catalytic process of sulfur dioxide oxidation. Notably, composition 5 containing additional chloride ions ($C_{KCl} = 6.8 \times 10^{-6}$ mol/g) shows the true catalytic action in contrast to composition 4 not containing additional chloride ions. At the same time, additional chloride ions worse the catalytic action for composition 8 (SO_2 oxidation level decreases) as compared with composition 7. For the Cu(II)–Pd(II)/N-CLI compositions, additional chloride ions in composition 13 (Cu(II)–Pd(II)/N-CLI) make it slightly more active than composition 12 (Table I) although both compositions do not show a true catalytic behavior.

It is evident that all bimetallic compositions based on both N-Bent and N-CLI show the explicit synergetic action of two metal ions. This is confirmed by values of their synergetic factors, K_s, (calculated as a ratio of τ_{MPC} for each bimetallic system to the sum of τ_{MPC} for corresponding monometallic systems) which are higher than 1 (Table I).

In our opinion, the observable synergetic effect can be explained as follows. When a supported composition is comprised of a single metal ion and a support, the interaction of this ion with sulfur dioxide results in the reduction of the metal ion. Its reoxidation by air oxygen is a very slow process if it takes place at all. In contrast

to that, for some metal ion pairs, e.g. Fe(III)–Cu(II) and Pd(II)–Cu(II), such a process occurs: a reduced metal ion (a catalyst) can be rapidly oxidized with the second metal ion (a cocatalyst). The cocatalyst, in its turn, due to its lower redox potential can be rapidly reoxidized with air oxygen. Thus, a scheme of the catalytic process under study can be considered as that comprised of three stages, e.g. for Pd(II)–Cu(II) [16]:

$$Pd(II) + SO_2 + 2H_2O = Pd^0 + H_2SO_4 + 2H^+,$$

$$Pd^0 + 2Cu(II) = 2Cu(I) + Pd(II),$$

$$Cu(I) + O_2 + 4H^+ = Cu(II) + 2H_2O.$$

This scheme is similar to the scheme of well-known Wacker process used for oxidation of ethylene and carbon monoxide.

Differences in the action of Pd(II)–Cu(II) compositions based on bentonite and clinoptilolite confirm our viewpoint [16, 17] that the nature of the support substantially influences the process of surface complexing and therefore the catalytic activity of metal complexes formed by metal ions on different supports.

4. Conclusions

Bimetallic compositions $CuCl_2$–M_iCl_j/S (M is Fe(III) or Pd(II) and S is N-Bent or N-CLI) obtained by us showed certain dependences of their activity in the reaction with sulfur dioxide on the nature of the metal ion and support. All bimetallic compositions under study show certain synergism in action of two d metal ions towards SO_2 oxidation (some of them show the true catalytic action). For Cu(II)–Pd(II) compositions based on the two natural aluminosilicates, at the same metal ions and their concentrations, their synergetic factors depend on the nature of the support.

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