Study of the surface properties of silicon and calcium oxygen compounds

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The acid-base surface state of samples of the silicon oxide and calcium oxygen compounds was investigated. Adsorption of freon on calcium compounds has been studied. Adsorption data were compared with the acid-base surface properties of calcium oxygen compounds. To estimate the expected freon adsorption on the calcium compound surfaces, approximated to the conditions of the troposphere, experiments were carried out with samples exposed to air for a long time.

Introduction

Atmosphere is a complicated system, in which the majority of chemical reactions occur simultaneously. Therefore, some consequences of the measures on prevention of the stratospheric ozone depletion are of concern.[1] The knowledge accumulated in atmospheric chemistry on the behavior of different chemicals in lower layers of the atmosphere clearly show that active use of fluorine-chlorine-hydrocarbons of $CHFCl_2$ (freon-21) and CHF_2Cl (freon-22), which are less dangerous for ozonosphere, instead of ozone-destroying $CFCl_3$ (freon-11) and CF_2Cl_2 (freon-12) will lead to fast increase of the products of their oxidation in the near-ground air.

Solid aerosol in the atmosphere has a complicated chemical composition. The known phase components of aerosol are metal oxides (aluminum, magnesium, calcium, iron, titanium, zinc, tin), as well as calcium hydroxide, calcium carbonate, silicon dioxide, silicates. Processes of dark adsorption on these molecules can be an effective channel for removing organic pollutions from the atmosphere.

The purpose of this work was revealing and studying the adsorption of freon-22 on compounds of silicon and calcium oxygen.

Experiment

The following samples were taken for the study: calcium oxide (pure), the state standard 8677-76, a specific surface of 5 m^2/g; calcium hydroxide, the state standard 9262-77, a specific surface of 11 m^2/g; calcium carbonate, technical conditions 6-09-895-77, a specific surface of 3 m^2/g; silicon oxide obtained in laboratory conditions of the Institute of Catalysis SB RAS, a specific surface of 500 m^2/g; silica with a specific surface of 212 m^2/g.

Adsorption measurements were carried out by the volume method at a vacuum setup.[2] Freon-22 was selected as the adsorbent. The Pirani manometer, calibrated by oxygen with a correction coefficient of 1.4 for freon, was used for measurement of the partial pressure. The samples were preliminary vacuum-processed for 9 hours at the room temperature. All experiments were carried out at the room temperature as well.

The methods of pH-metry, Hammet indicator adsorption, and potentiometric titration were used for the study of the acid-alkaline properties. The following procedure of the Ph-metric study of powders was used for investigation of the surface total acidity: 10 ml of bidistilled water were injected into the potentiometric cell, a sample portion of 0.2 g was poured after stabilization of the glass electrode potential with a simultaneous switching-on of the stop-watch. The suspension was continuously mixed by the magnetic mixer. Weak organic acids and alkalines, the colors of molecular and ion forms of which are different, were used as the acid-alkaline indicators. The technique for investigations of the surface acidity by the indicator method is described in detail in Ref. 3. Adsorption of indicators was carried out not only in water medium, but also in dimethylformamide (DMFA).

Potentiometric titration of suspension was carried out by means of the ionometer ESL-43-07 with glass and argentum-chloride flux electrodes, the titrant was delivered automatically. The sample portion of 0.2 g was suspended in 1 ml of 0.1 normal solution of HCl with addition of 19 ml of 0.1 normal solution of KCl and titrated by 0.1 normal solution

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of KOH. Also, the sample was suspended in 0.1 ml of 0.1 normal solution of KOH with addition of 19 ml of 0.1 normal solution of KCl and titrated by 0.1 normal solution of HCl. Titration of solutions free of the sample was carried out in the same way. Mixing was executed by a glass mixer with a rate of 100–150 turns per minute. The pH value of the isoion state (pHiis) was determined from the crossing point of the titration curves of the examined suspension and the sample-free solution.

Discussion of the results

Isoterms of adsorption for the samples of calcium oxide, hydroxide, and carbonate have the shape of isoterm of I type upon the Brunauer classification and are described by the Freindlich equation, i.e., are linearized in the coordinates $\ln a - \ln P$ (a is the equilibrium value of adsorption, measured at the equilibrium pressure P). When considering interaction of calcium compounds with freon-22 (from the adsorption data), the reactivity decreases in the sequence oxide-hydroxide-carbonate, that is also confirmed by thermodynamic calculation using the data of the IVTANTERMO database.

We judged about the state of the sample surfaces using the results of studying their alkaline properties.

The pH magnitude of the isoion state can be estimated by the shape of the kinetic curves, which was approximately determined from the equilibrium value of the time dependence of pH. In the case of calcium oxide and hydroxide, pHiis are equal to 12.1 and 12.2, respectively. This value for calcium carbonate is equal to 9.3. The data of pH-metry are in agreement with the results of indicator analysis. The band of intermediate intensity at $\text{p}K_\text{a} = -0.29$, corresponding to the main Lewis centers, is observed in spectra of distribution of the adsorption centers (DAC), which is absent for samples of calcium carbonate.

Indicator method allows determining the local acidity and gives more complete idea about situation on the surface. Four bands can be selected, which describe active centers on surfaces of samples of calcium oxide, hydroxide and carbonate in acid ($\text{p}K_\text{a} = -0.29 \div 1.3$; $2.5 \div 4.1$), alkaline ($\text{p}K_\text{a} = 10.5 \div 12.8$), and neutral ($\text{p}K_\text{a} = 6.45 \div 7.1$) ranges.

The strong Bronsted acid and alkaline centers are better pronounced in the DAC spectra of the samples of calcium oxide and hydroxide than the weak ones. The strong Bronsted acid centers in calcium carbonate are present in greater concentration than alkaline ones. This is also in agreement with the data of the pH-metry.

If to compare spectra in water medium with spectra in DMFA, the following differences can be noticed. The band with $\text{p}K_\text{a} = -0.29$ in DMFA for calcium oxide and hydroxide is more intense than in water medium, which is caused by adsorption of water on Lewis alkaline centers according to the acid mechanism.

When passing from DMFA to water, the intensity of peaks in the acid range (1.3–2.5) significantly decreases, and slightly increases in the alkaline range (10.5–12.8). In this case, water leads to amplification of alkaline properties and significant decrease of acid ones. This is explained by more acid properties of water in comparison with DMFA. Thus, the surfaces of the considered compounds are of the alkaline character.

The acidity of the surface of the compounds under investigation was also determined after adsorption and desorption of freon-22. In this case, the suspension curves lie a few higher than those of initial samples. Value of pHiis for calcium oxide, hydroxide, and carbonate were 12.2, 12.5, and 9.5, respectively. The increase of the pHiis values corresponds to the increase of intensity of the band at $\text{p}K_\text{a} = -0.29$ in DAC spectra. The DAC spectrum after adsorption and desorption of freon-22 on calcium oxygen compounds demonstrates the concentration increase of the centers in the acid range and the decrease in the alkaline range. This can be explained by formation of surface compounds (CaF_2, $CaCl_2$) on the samples under study, which have acid properties. The degree of the filling, calculated from the adsorption data, is $1 \cdot 10^{-2}$, hence, fluorides and chlorides formed on the surface weakly affect the change of the surface total acidity. The data of pH-metry bear evidence of the surface reduction.

Thus, the acidity of the surface changes under the effect of two competing processes: reduction in vacuum and, perhaps, formation of more acid calcium fluoride and calcium chloride compounds on the surface as the result of interaction of oxide compounds with freon-22. The pH-metry, determining the total acidity, bear witness to the dominating effect of the surface reduction in vacuum.

Silicon oxide and silica were studied by the methods of pH-metry, spectrometry, and potentiometric titration. The kinetic curves of the time dependence of the suspension pH throughout the range lie lower than the neutral line, that is the evidence of weakly acid character of the samples of silicon oxide and silica. The method of potentiometric titration was used for more precise determination of pH. The data obtained show similar results on pHiis.

Four bands can be selected for silicon oxide, which describe the active centers both in acid ($\text{p}K_\text{a} = 1 \div 3$, $5 \div 6$) and alkaline ($\text{p}K_\text{a} = 7 \div 8$, $9 \div 12$) range. A large difference in energy of links Si–O and O–H provides for a strong acidity to the center observed in the spectrum at $\text{p}K_\text{a} = 2.3 \div 3.4$. The adsorption centers at $\text{p}K_\text{a} = 7.3$ have a neutral character, the energy of links Si–O and O–H for them are approximately equal. Maximum at $\text{p}K_\text{a} = -0.29$ is related with the adsorption of water molecules by the acid mechanism on the main Lewis centers of the type $\equiv \text{Si–O}^{-} \cdots \text{H}^{\delta+}\text{–OH}^{\delta-}$. Maximum at $pK_a = 10.5$ is caused by the presence of the alkaline groups of OH-centers on the surface of silicon oxide formed by the appearance on the surface of edges of the type $-\,Si(OH)_3$ which have long and weak link Si–O. This provides for alkaline properties to their hydroxyl groups and easy removability under vacuumization. When considering the acid-alkaline properties in a non-water medium, the shift of peaks responsible for Bronsted ($pK_a = 10.5$) and Lewis ($pK_a = -0.29$) centers to the range of greater pK_a values, as well as the decrease of peaks of acid centers are observed.

Thus, the qualitative consideration has shown that samples with more strong alkaline surface properties (calcium oxide and hydroxide) have a high reactivity with respect to freon-22.

References

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