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Effect of milling on the surface functionality of $BaTiO_3$–$CaSnO_3$ ceramics

M.M. Sychov, N.V. Zakharova, S.V. Mjakin*

St-Petersburg State Institute of Technology (Technical University) 26 Moskovsky prospect 190013 St-Petersburg, Russia

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Abstract

The effect of milling in the presence of a surfactant upon the surface functionality (content of various donor–acceptor centers and corresponding functional groups) of $BaTiO_3$–$CaSnO_3$ powdered ferroelectric ceramics was studied using the selective adsorption of acid–base indicators. Milling was found to cause similar changes in the content of certain surface centers with pK_a ~7.0+x and ~7.0–x (shifted by almost the same values from the neutral point). The observed surface behavior is determined by the simultaneous formation of such centers upon bond disruption and their simultaneous shielding due to the surfactant adsorption. On the contrary, the contents of some pairs of surface centers were found to undergo opposite changes as a result of their mutual transformations. The obtained data are promising for the prediction and modification of surface functionality for various oxide based materials and other solids.

Keywords: A. Milling; Lewis centers; Brensted centers; Hydroxyls; Ceramics

1. Introduction

Non-homogeneity of the surface of solids on the chemical, structural and energy levels is determined by the presence of various structural defects and functional groups acting as active sites in adsorption processes and chemical reactions. Hence, the analysis of the composition and content of active sites on the surface allows the prediction of the properties of solids useful in such applications as catalysis, development of various composites, printed electronics, various substrates with deposited layers and especially nanotechnology.

The content of different sites, their distribution according to the ionization/dissociation constants and acidity can be measured using the adsorption of acid–base indicators with different intrinsic pK_a values as described by K.Tanabe in [1]. This method is based on L.P.Hammet's concept that the interaction of acid–base indicators with functional groups of solids proceeds with equal ratios between the activities of ionic and molecular forms of the indicator. N.B.Librovich [2] proved that this concept is valid for various compounds forming strong and symmetric hydrogen bonds. Particularly, this mechanism is observed for the interaction between acid–base indicators and solid surfaces, e.g. for the adsorption of pyrogallol red as shown by V.M.Ivanov, A.M.Mamedova in [3].

The considered method was subsequently modified by A.P. Nechiporenko et al. [4] and implemented as an efficient tool for surface characterization of various solids, including a series of our previous studies. In [5] I.V. Vasiljeva et al. used this method to reveal electron beam (EB) stimulated alternating reactions of dispersed oxide surface dehydroxylation and hydroxylation with OH groups of a certain acidity as a function of the absorbed dose. In [6] A.Ju. Shmykov et al. studied similar alternating reactions on the surface of fused silica and determined optimal conditions for its fictionalization with specific acidic hydroxyls. This kind of surface modification afforded the subsequent immobilization of an organic functional layer useful for obtaining electrochromatographic columns with improved performances. A similar

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*Corresponding author. Tel.: +7 812 3402518.
E-mail address: sergey_mjakin@mail.ru (S.V. Mjakin).

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approach was used by Vasiljeva et al. in [7] to reveal and form specific functional groups on the surface of poly(ethylene terephthalate) films providing a possibility for the deposition of *N*-vinyl pyrrolidone layers useful for the manufacture of cinematographic materials. In [8] M.M. Sychov et al. revealed electron beam stimulated mutual transformations between–Zn–S–Zn–structure and Zn–SH groups on the surface of ZnS based phosphors. The optimization of phosphor surface modification conditions in combination with a detailed characterization of its surface functionality allowed the determination of the optimal processing conditions and surface state providing the highest increase of electroluminescence efficacy. The achieved effect was determined by the surface functional transformations eliminating the undesirable Zn vacancies (electron traps) and yielding electron withdrawing centers at optimized processing parameters. The data on the detailed surface characterization of different functional materials using the considered technique and common features of their specific functionalization in order to improve their target technical performances are summarized by S.V. Mjakin et al. in [9].

The analysis of mechanisms and general trends responsible for the generation of various structural defects in the surface layer, formation and transformation of active surface sites in solids requires an adequate interpretation of the indicator adsorption data and a detailed analysis of the ratios between the contents of functional groups relating to different types. As the next step towards the understanding of these phenomena, in the present study we analyzed the evolution of donor–acceptor centers on the surface of ferroelectrics in the course of their milling in aqueous suspensions.

2. Experimental

In the present study we determined the contents of adsorption centers with different pK_a values in the range from -5 to 15 on the surface of a powdered $BaTiO_3$–$CaSnO_3$ ceramics (TBS, produced by Positron Co., St-Petersburg, Russia) before and after its milling within different time. The material was dispersed using a ball mill with the roll rotation rate 48 rpm in distilled water in the presence of Rhodia Rhodoline E983 anionic surfactant based on sodium polyacrylate. The dispersed material content C_f was 82…85 wt% and the surfactant:material ratio was $C_{s/f}$ ~0.2…0.5%. The particle size was determined by turbidimetric method according to the Russian standard 2 352-80. The specific surface of the studied materials was measured by low temperature air adsorption using a Klyachko–Gurvich method according to the Russian standard GOST 10898.4-84.

The content of donor–acceptor centers with different acid–base (donor–acceptor) properties on the milled ceramics surface was studied using the selective adsorption of acid–base indicators with intrinsic pK_a values in the range from -5 to 15. The experimental procedure described in detail in [5,10] is based on the selective indicator adsorption on surface centers with the corresponding pK_a value resulting in the change of the indicator solution optical density. Another factor contributing to the optical density change is the change of the aqueous medium acidity as a result of water interaction with the surface sites. For this reason the performed analysis involved spectrophotometric measurements (using SF-46 spectrophotometer produced by LOMO, St-Petersburg) of the following optical density (D) values:

D_0—for the initial aqueous solution of the indicator of a certain concentration,
D_1—for the same solution containing a sample of the analyzed compound of a certain weight where both the indicator adsorption and pH change affect the optical density,
D_2—for the same solution added to the solvent (water) decanted after the contact with a sample of the same weight. In this case the optical density is affected only by pH value changed due to solvent (water)–surface interaction and this factor can be eliminated in the following differential calculation.

These measurements allow the evaluation of adsorption sites with a certain pK_a value on the studied surface according to the following equation

$$q(pK_a) = \left| \frac{|D_0 - D_1|}{m_1} \pm \frac{|D_0 - D_2|}{m_2} \right| C_{ind} V_{ind} / D_0 S$$

where C_{ind} is the concentration of the indicator solution, V_{ind} is the volume of the indicator solution used in the analysis, m_1 and m_2 are weights of the samples for measuring D_1 and D_2 correspondingly, "+" sign corresponds to the case where D_1 and D_2 are oppositely changed related to D_0 ($D_1 < D_0$ and $D_2 > D_0$, i.e. the changes in optical density caused by adsorption and water-surface interaction are opposite and the decrease of optical density due to the indicator adsorption is greater than the increase due to the water-surface interaction), "–" sign corresponds to one sided optical density changes caused by both adsorption and water-surface interaction ($D_1 < D_0$ and $D_2 < D_0$, i.e. either water-surface interaction results in the decrease of the optical density or it results in the growth of this value but the decrease caused by adsorption is greater), S is the specific surface of the studied material.

The overall surface acidity was calculated as:

$$H_0 = \frac{\sum pK_a q_{Ka}}{\sum pK_a}$$

The indicators used in this study and more details of the experimental procedure are described in [8,9].

The surface of the studied material generally consists of a different Lewis and Brensted acidic and basic centers

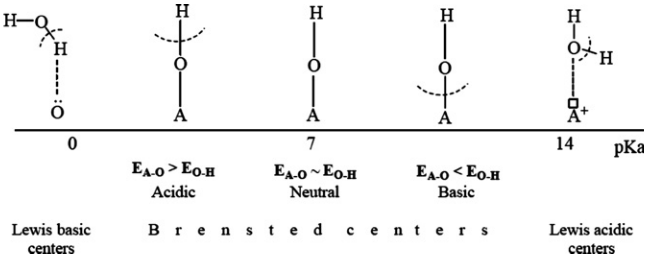


Fig. 1. Adsorption centers on a partially hydroxylated surface of a solid oxide.

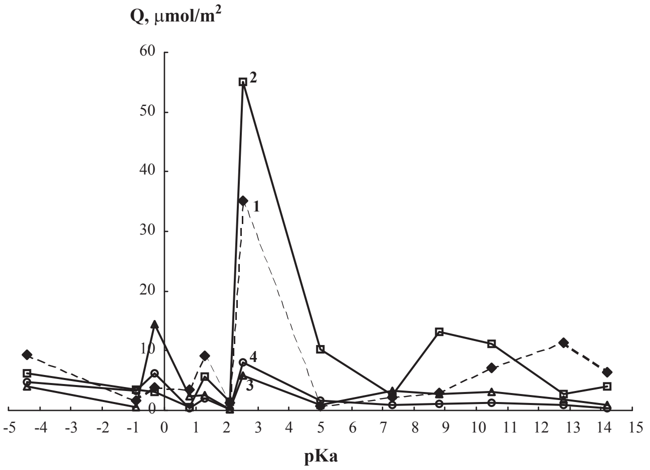


Fig. 2. Distribution of active centers on the surface of TBS as a function of the dispersion time: 1—before dispersion, 2—after interaction with the surfactant (before milling), 3—after milling within 15 min, 4–after milling within 8 h.

capable of reacting with water and acid–base indicators. The hydration of Lewis centers results in their transformation into Brensted sites such as $-A^{+}-O^{-}$–H, A–OH, A–O^{-}–H^{+} [1].

Generally, the distribution of adsorption sites on the partially hydrated (hydroxylated) surface of a solid insoluble oxide A_xO_y according to their pK_a values can be illustrated as follows (Fig. 1).

This scheme presents a qualitative interpretation of the acid–base indicator adsorption data and chemical nature of surface centers with various pK_a values.

The indicators with the lowest (usually negative) pK_a values are selectively adsorbed on Lewis basic sites possessing a free electron pair and capable of proton abstraction from water molecules [1]. In the studied material these centers are particularly represented by =BaO: and =CaO: groups. As the intrinsic pK_a of the indicators grows their selective adsorption consecutively shifts towards:

- Brensted acid sites ($pK_a = \sim 0 \div 7$) represented by ≡Ti–OH and ≡Sn–OH groups with similar octahedral coordinations and relatively high charges of the cations responsible for the relatively high M–O bond energy compared with O–H bond,

Table 1
Changes in the content of adsorption centers with different pK_a values on the surface of TBS, its average particle size and specific surface in the course of milling.

pK_a	Content of centers, μmol/m²						
	Initial sample	After the contact with the surfactant before milling	After milling within different time				
			15 min	30 min	1 h	4 h	8 h
−4.4	9.3	6.2	4.0	5.7	2.1	8.4	4.7
−0.9	1.6	3.5	0.5	4.87	3.4	2.2	3.3
−0.3	3.8	3.2	14.4	0.4	9.3	9.7	6.3
0.8	3.4	0.6	2.3	0.2	0.8	0.7	0.4
1.3	9.2	5.7	2.5	1.4	6.0	2.5	2.0
2.1	1.2	1.4	0.1	0.1	0.7	0.6	0.2
2.5	35.2	55.1	5.9	3.8	1.8	4.8	8.0
5.0	0.7	10.3	1.0	0.0	0.7	2.9	1.6
7.3	2.2	2.6	3.3	3.9	3.7	1.9	0.9
8.8	3	13.2	2.7	1.5	1.1	3.0	1.1
10.5	7.2	11.1	3.2	0.2	4.5	1.6	1.2
12.8	11.4	2.8	1.8	0.4	0.5	1.7	1.0
14.2	6.4	4.1	1.0	3.8	5.4	2.1	0.4
Σq_pK_a	106.4	136.7	56.8	30.6	44.2	43.1	32.4
Average particle size, μm	2.4	2.0	0.80		0.85	0.80	0.75
H_o	4.8	4.1	4.2	4.0	4.6	2.4	1.9
Specific surface, m²/g							
S	0.50	0.51	1.28	1.24	1.19	1.25	1.56

- Brensted basic sites ($pK_a = 7 \div \sim 14$) corresponding to –Ba–OH and –Ca–OH groups featuring with a lower cation charge and consequently weakened M–O bond compared with O–H bond,
- Lewis acidic sites ($pK_a > \sim 14$) represented by metal cations on the surface possessing a vacant orbital and capable of hydroxyl capture from water molecules.

3. Results and discussion

According to the acid–base indicator adsorption data the initial surface of the studied material (Fig. 2, Table 1) is featured with the overall acidity $H_0 = 4.8$ and contains significant amounts of Lewis acidic (pK_a 14.2), Brensted acidic (pK_a 2.5), neutral (pK_a 6.4 and 7.3) and basic (pK_a 12.8) centers.

The interaction with the surfactant itself before milling resulted in a drastic decrease in the content of strongly acidic (pK_a 0.8 and 1.3) and basic (pK_a 12.8) Brensted sites as well as in a certain drop in the content of Lewis basic (pKa −4.4) and acidic (pK_a 14.2) centers. These changes in the surface functionality indicate that the dispersant adsorption proceeds via the corresponding groups on the surface. Simultaneously, a prominent growth in the content of Lewis basic centers with pK_a −0.9 as well as Brensted acidic (pK_a 2.5 and 5.0) and basic (pK_a 8.8 and 10.5) was observed. The surface acidity slightly increased

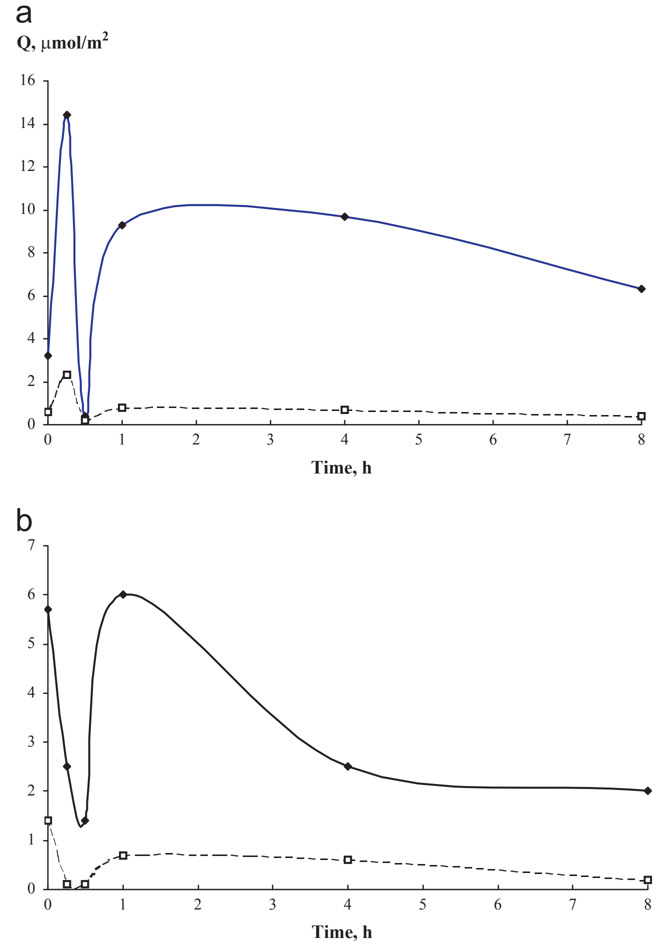


Fig. 3. Changes in the content (μmol/m^2) of adsorption centers with (a) pKa —0.3 (♦) and 0.8 (□); (b) 1.3 (♦) and 2.1 (□) in the course of milling.

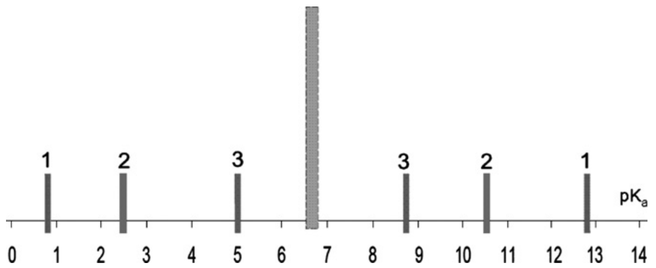


Fig. 4. Pairs of adsorption centers with pK_a values symmetrical relating to the neutral state with pK_a ~6.5–7.0: 1–1.3 and 12.8, 2–2.5 and 10.5, 3–5.0 and 8.8.

(H_o drops to 4.1 from 4.8) and no change in the specific surface area was observed.

As shown in Table 1, the subsequent milling resulted in a relatively small change in the average particle size and specific surface passing correspondingly through a maximum and minimum in about 1 h. The observed behavior suggests a certain agglomeration in about 1 h of milling followed by the gradual disintegration of agglomerates up to 8 h. The overall acidity of the surface gradually grows (H_o drops to 1.9 after 8 h of milling).

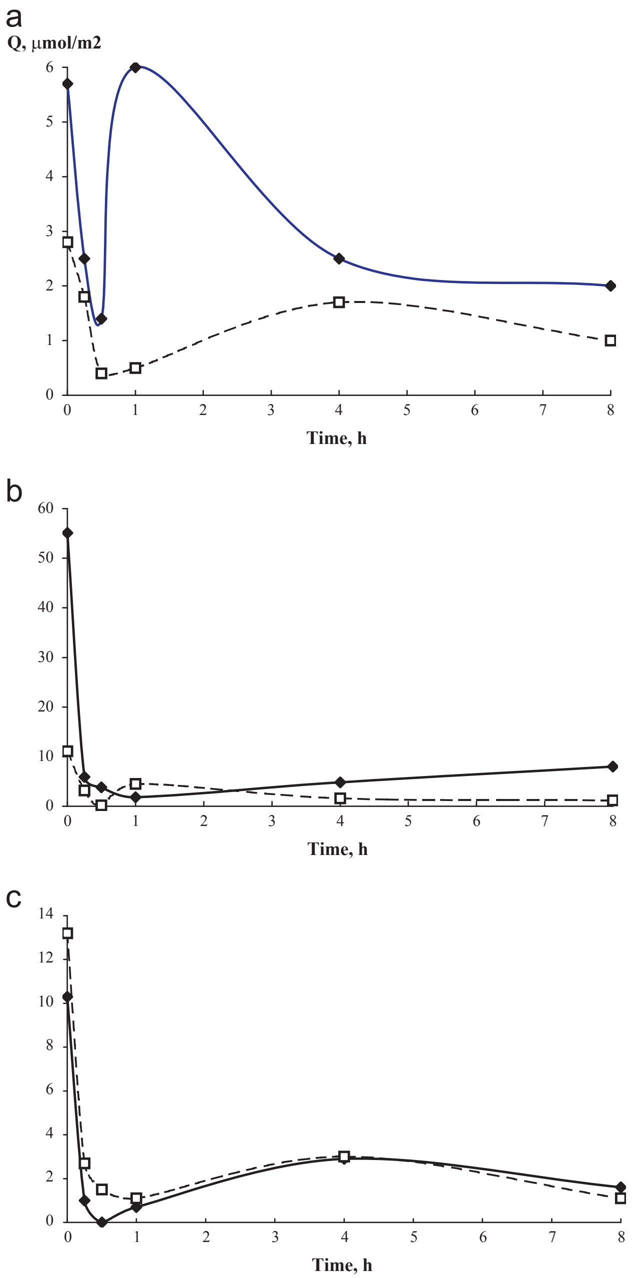


Fig. 5. Changes in the content (μmol/m^2) of adsorption centers with (a) pK_a 1.3 (♦) and 12.8 (□); (b) 2.5 (♦) and 10.5 (□); (c) 5.0 (♦) and 8.8 (□) in the course of milling.

The detailed analysis of mutual correlations between the contents of different centers allowed us to determine the following general trends:

1. Some centers with close pK_a values (-0.3 and 0.8; 1.3 and 2.1) are featured with similar change profiles (Fig. 3) with the correlation coefficient ~0.83 that is accounted for their similar chemical nature and consequently similar behavior (formation, shielding by the surfactant, etc.) in the course of milling.
2. Pairs of Brensted centers with pK_a 1.3 and 12.8, 2.5 and 10.5, 5.0 and 8.8 "symmetrical" relating to the neutral

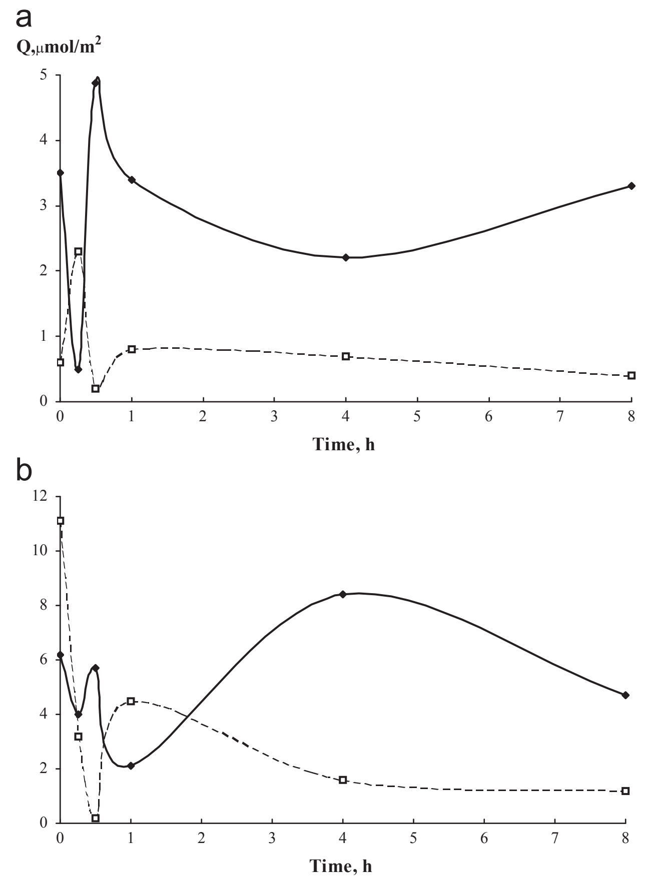
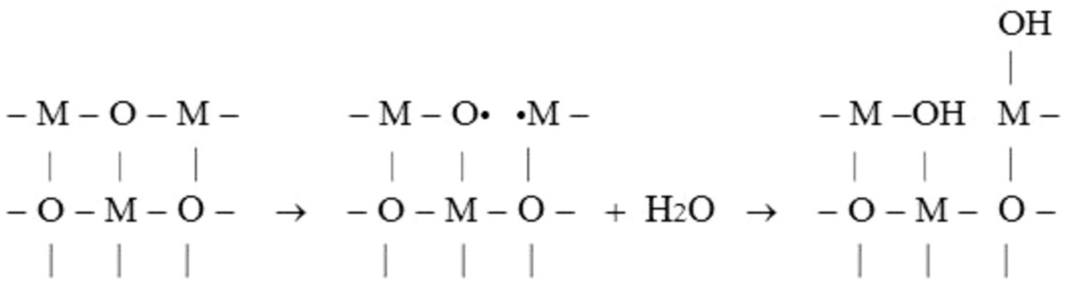


Fig. 6. Changes in the content (μmol/m^2) of adsorption centers with (a) pK_a —0.9 (◆) and 0.8 (☐); (b) -4.4 (◆) and 10.5 (☐) in the course of milling.

state with $pK_a \sim 7.0$ (Fig. 4) also undergo synchronous changes (Fig. 5).

Particularly, the simultaneous increase in their content can be determined by the mechanochemically stimulated disruption of chemical bonds on the surface yielding pairs of "complementary" centers



M = Ba, Ti, Ca, Sn

On the other hand, these pairs of Brensted and Lewis centers are adjacent to each other and probably undergo a simultaneous shielding due to the surfactant adsorption that determines the observed synchronized decrease in their content.

3. Pairs of centers with $pK_a -0.9$ and 0.8, -4.4 and 10.5 are featured with "oscillating" opposite changes (Fig. 6) that suggests their mutual transformations due to the following alternating reactions:
   (a) Lewis basic site ($pK_a < 0$) hydration to form a hydroxyl and
   (b) condensation of neighboring hydroxyls to recover the initial center according to the mechanism earlier revealed in [5,9,10].

$$\text{–M–O–M–} + H_2O \leftrightarrow \text{–M–OH} + \text{HO–M–}$$

4. Conclusion

Generally, the considered data provide an example of a detailed study of surface functionality profile changes during the mechano-chemical processing of a solid. The analysis of surface centers distribution according to their pK_a values in the course of milling using the adsorption of various acid-base indicators allowed us to reveal a series of interrelated changes in the surface functionality. Particularly, pairs of centers with pK_a values symmetrical relating to the neutral point with $pK_a \sim 7$ undergo synchronous similar changes due to their (a) simultaneous formation upon bond breaking and (b) shielding at the surfactant adsorption. The synchronized opposite changes are also observed for certain pairs of Lewis and Brensted centers suggesting their mutual transformations. Generally, the considered approach is promising for the analysis, prediction and modification of the surface properties for various heterogeneous systems such as catalysts and carriers for their supporting, fillers for composites, etc.

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