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HAMMETT ACIDITY FUNCTION FOR MIXED ZrO_2 - SiO_2 OXIDE AT ELEVATED TEMPERATURES

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The mixed ZrO_2 - SiO_2 oxides with different $4 \geq Zr/Si \geq 0.25$ atomic ratios have been prepared using a sol-gel method. It was shown that the concentration-strength acid site distributions on the surface of ZrO_2 - SiO_2 are caused by Zr^{4+}/Si^{4+} ratio. The ZrO_2 - SiO_2 with $Zr/Si = 0.5$ is characterized by the highest strength of acid sites ($H_0 = -11.35$). According to the IR-spectra of adsorbed pyridine, the B- and L-acid sites are present in the ZrO_2 - SiO_2 samples with $Zr/Si < 1$ whereas at $Zr/Si > 1$ only L-sites are formed. Basing on the UV-Vis diffuse reflectance spectra of adsorbed indicators, the H_0 values for ZrO_2 - $2SiO_2$ have been determined at elevated temperatures. The Hammett acidity function reaches the superacid value of $H_0 \leq -14.5$ at $T \geq 85$ °C.

INTRODUCTION

Mixed ZrO_2 - SiO_2 oxide was proposed by Standard Oil as a cracking catalyst in 1944 [1]. Soon C. Thomas [2] explained how acid sites could be formed in ZrO_2 - SiO_2 structure. The ZrO_2 - SiO_2 catalyst is used in industry for production of polytetramethylene ether from tetrahydrofuran with addition of acetic anhydride [3]. During the last years several sol-gel methods for obtaining ZrO_2 - SiO_2 have been proposed [4–8]. However, further study of the influence of Zr^{4+}/Si^{4+} ratio in ZrO_2 - SiO_2 on the concentration, type, and strength of its acid sites is of interest.

In this communication the data on an acidity of the ZrO_2 - SiO_2 samples with different Zr/Si ratios and Hammett acidity function for this oxide at elevated temperatures are presented.

EXPERIMENTAL

Zirconyl chloride octahydrate $ZrOCl_2 \cdot 8H_2O$ (ABCR GmbH & Co. KG), tetraethoxysilane (TEOS, Sigma-Aldrich) and carbamide were used as starting chemicals.

Synthesis of the samples was based on the procedure described in [8]. 322 g $ZrOCl_2 \cdot 8H_2O$ (1 g-mol) was dissolved in 1.5 l of distilled water. Water solution of silicic acid oligomers was obtained by hydrolysis of TEOS (417 g) (2 g-mol) with aqueous-alcoholic solution of HCl. After mixing these two solutions, 250 g of urea was

added at stirring. Then this solution was aged within 4 days at 90 °C. The obtained opalescent transparent gel was washed to remove Cl^- ions and then dried at 120 °C. In a similar manner the samples with ratios of $Zr/Si = 1:3, 1:1, 2:1, 3:1, 4:1, 5:1$ were synthesized. All the samples synthesized were calcined at 700 °C for 2 h in air. The marking of a sample as $ZrSi2$ means that its structure contains twice more Si^{4+} ions than Zr^{4+} .

XRD patterns of samples were recorded on a DRON-4-07 diffractometer (CuK α).

Nitrogen adsorption-desorption isotherms were obtained with using a Nova 2200e Surface Area and a Pore Size Analyzer.

Total acidity of the samples was determined by reverse titration using *n*-butylamine solution in cyclohexane with bromthymol blue as an indicator. The strength of ZrO_2 - SiO_2 acid sites was estimated by direct titration with *n*-butylamine using following indicators (Aldrich):
dicinnamalacetone ($pK_{BH^+} = -3.0$),
benzalacetophenone ($pK_{BH^+} = -5.6$),
antraquinone ($pK_{BH^+} = -8.2$),
4-nitrotoluene ($pK_{BH^+} = -11.35$).

The IR spectra of ZrO_2 - SiO_2 samples were recorded on a Specord IR-75 spectrometer. The samples were pressed into thin pellets (10–12 mg/cm²) which were placed into a quartz cell

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with water cooled KBr windows. The tablets were evacuated at 400 °C, 2 h before pyridine adsorption. A sample was cooled to 150 °C and pyridine was adsorbed. This sample was evacuated (30 min, 10⁻¹ Pa) to remove physically adsorbed pyridine, cooled to room temperature, and then its IR spectrum was recorded.

The UV-Vis diffuse reflectance spectra of 1-chloro-3-nitrobenzene ($pK_{BH^+} = -13.16$), 2,4-dinitrotoluene ($pK_{BH^+} = -13.75$), and 1-fluoro-2,4-dinitrobenzene ($pK_{BH^+} = -14.52$) indicators adsorbed on ZrO₂-SiO₂ were recorded at 20–160 °C according to the procedure described in [9].

Catalytic activity of the ZrO₂-SiO₂ samples was estimated using a test TPR reaction of 2-methyl-3-butyn-2-ol (MBOH) transformation with a mass spectrometric control of the products [10].

RESULTS AND DISCUSSION

According to the X-ray analysis (Fig. 1), all synthesized samples except 4ZrSi are amorphous what agrees with the data [4, 8]. Crystallization of tetragonal ZrO₂ is observed in 4ZrSi sample with a high content of zirconium. Also at raising Zr⁴⁺ content, the specific surface area and average diameter of mesopores for the samples decrease significantly (Table 1).

The content of acid sites in ZrO₂-SiO₂ samples reaches of maximal value at Zr:Si = 1:2 (Fig. 2) in agreement with Thomas model [2] and the data [4, 6]. The concentration of B-sites sharply decreases with increasing Zr⁴⁺ content from 1.7 mmol/g for ZrSi₂ to 0.3 mmol/g for 2ZrSi (Fig. 2). Also only ZrSi₂ sample contains strong acid sites with H₀ = -11.35 (0.2 mmol/g)

while for medium acid ZrSi and 4ZrSi the values of H₀ ≤ -5.6 (Fig. 3).

The strength of ZrO₂-SiO₂ acid sites correlates with their activity in the dehydration reaction of 2-methyl-3-butyn-2-ol (MBOH, m/e = 69) to 3-methyl-3-buten-1-yne (Mbyne, m/e = 66). The maximum rate of Mbyne formation over ZrSi₂ is observed at 45 °C and for less acid 4ZrSi – at 110 °C (Fig. 4).

The IR spectra of pyridine adsorbed on ZrSi₂ are presented in Fig. 5. The bands at 1440 and 1490 cm⁻¹ correspond to pyridine adsorbed on L-sites and 1540 cm⁻¹ – to protonated pyridine with B-sites [5, 11]. After adsorption of pyridine on 4ZrSi only band at 1437 cm⁻¹ is observed in the IR spectrum (Fig. 6) that indicates a presence of the L-sites on 4ZrSi surface.

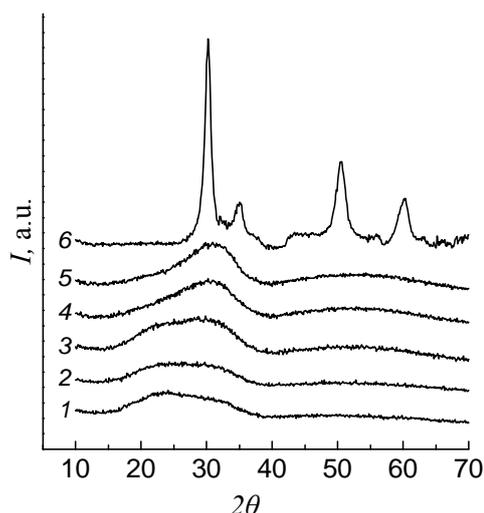


Fig. 1. XRD patterns of ZrO₂-SiO₂ samples calcined at 700°C: ZrSi₄ (1), ZrSi₃ (2), ZrSi₂ (3), ZrSi (4), 2ZrSi (5), 4ZrSi (6)

Table 1. Textural parameters and acidity of ZrSi samples

Sample	Specific surface area, m ² /g	Pore volume, cm ³ /g	Average pore diameter, nm	Total acidity	
				mmol/g	site/nm ²
ZrSi ₄	445	0.32	2.8	1.4	1.9
ZrSi ₃	420	0.30	2.8	1.5	2.2
ZrSi ₂	360	0.27	3.0	1.7	2.8
ZrSi	250	0.14	2.2	1.0	2.3
2ZrSi	180	0.10	2.2	0.3	1.0
3ZrSi	145	0.09	2.3	0.3	1.2
4ZrSi	120	0.08	2.5	0.4	2.1
5ZrSi	105	0.06	2.3	0.6	3.2

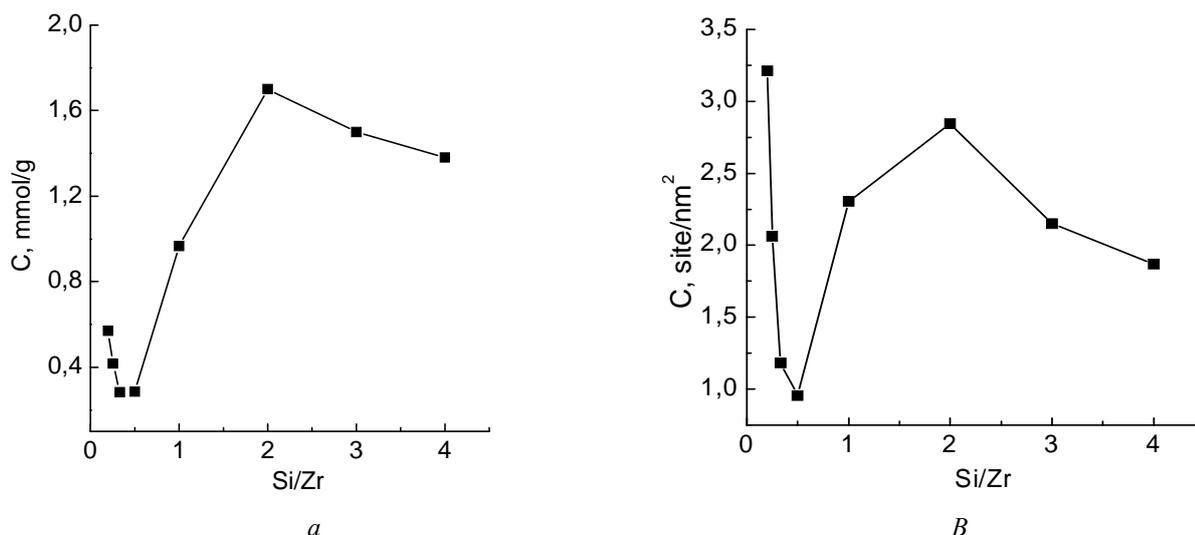


Fig. 2. Concentration of acid sites (*a* – total concentration, *b* – number of sites per 1 nm²) at different Si/Zr ratios

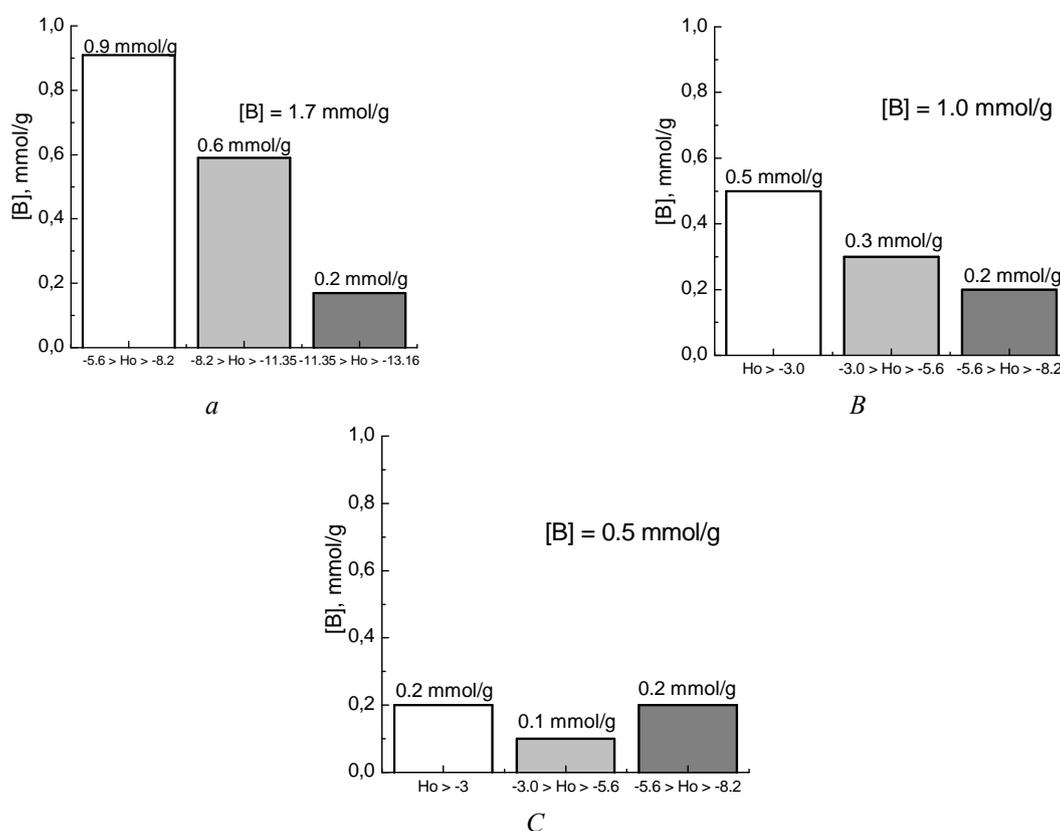


Fig. 3. Concentration-strength acid site distributions on the surface of ZrO₂-SiO₂ samples: ZrSi₂ (*a*), ZrSi (*b*), 4ZrSi (*c*)

The obtained results are agreed with the Tanabe rule [11]. At Si/Zr > 1 the difference of charges per one bond is equal to $+4/8 - 2/2 = -1/2 e^-$. This negative charge is compensated by protons forming acidic B-sites. If main component is zirconia, the difference of charge is equal to $+4/4 - 2/4 = +1/2 e^-$, and the L-sites are formed.

High acidic ZrSi₂ is capable to protonate *n*-nitrotoluene ($pK_{BH^+} = -11.35$) at room temperature, that appears in a yellowing of the sample. After adsorption of 3-nitrochlorobenzene ($pK_{BH^+} = -13.16$), the sample remains white. According to the UV-Vis diffuse reflection spectra obtained, a protonation of this indicator is observed

at $T > 50\text{ }^{\circ}\text{C}$ (Fig. 7). Taking into account the concentration-strength acid site distributions for ZrSi_2 (Fig. 3, *a*), it is possible to suppose that the B-sites with $H_0 = -11.35$ provide the first raising of an intensity of the band of protonated 3-nitrochlorobenzene at $50 - 70\text{ }^{\circ}\text{C}$, and less acidic sites ($H_0 = -8.2$) – the second raising at $80 - 140\text{ }^{\circ}\text{C}$. Similar situation is observed for 2,4-dinitrotoluene ($pK_{\text{BH}^+} = -13.75$). Namely, the strong acidic sites protonate this indicator at lower temperature, than the weak sites (Fig. 7).

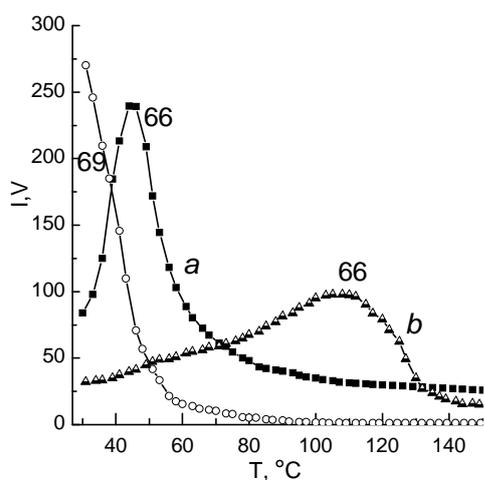


Fig. 4. TPR spectra of Mbyne ($m/e = 66$) formation from MBOH ($m/e = 69$) adsorbed on ZrSi_2 (*a*) and 4ZrSi (*b*)

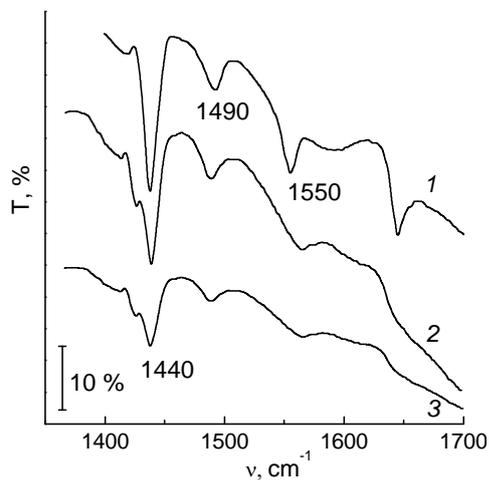


Fig. 5. IR spectra of pyridine adsorbed on ZrSi_2 before (*1*) and after sample vacuumization at 200 (*2*), $300\text{ }^{\circ}\text{C}$ (*3*)

The curves presented in Fig. 7 reflect the dependence of the concentration of protonated indicator ($[\text{BH}^+]$) on temperature in an endothermic process of a proton transfer from surface acidic sites to indicator molecules

($[\text{BH}^+] \sim \exp(-\Delta H_{\text{R}}/RT)$, at $\Delta H_{\text{R}} > 0$). On the basis of these curves, the values of Hammett acidity function $H_0 = pK_{\text{BH}^+} - \lg[\text{BH}^+]/[\text{B}]$ at $[\text{BH}^+]/[\text{B}] \approx 1$ were determined at different temperatures (Fig. 8). The increasing of H_0 values is proportional to temperature and the super acid value ($H_0 = -14.5$) is achieved at $T = 85\text{ }^{\circ}\text{C}$. It is interesting that the value of a coefficient $b = 0.06$ in the equation $-H_0 = a + bT$ is close to that earlier determined for H-Y faujasite [9].

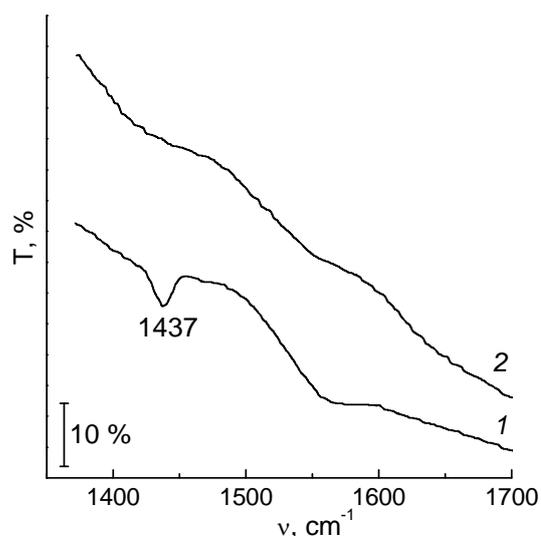


Fig. 6. IR spectra of pyridine adsorbed on ZrSi_2 before (*1*) and after sample vacuumization at $200\text{ }^{\circ}\text{C}$ (*2*)

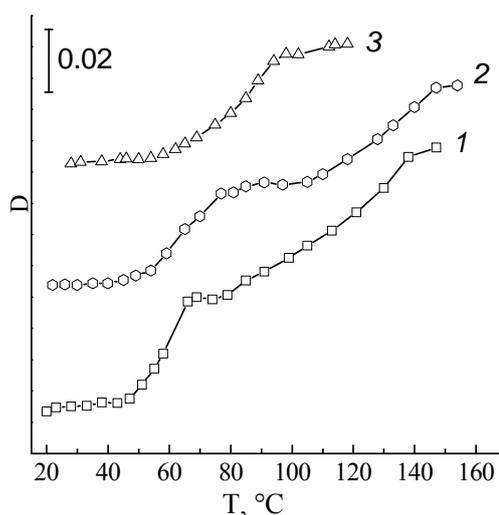


Fig. 7. Temperature dependence of optical density of absorption bands for protonated indicator forms on ZrSi_2 surface:

- 1* – 1-chloro-3-nitrobenzene (386 nm);
- 2* – 2,4-dinitrotoluene (390 nm);
- 3* – 1-fluoro-2,4-dinitrobenzene (390 nm)

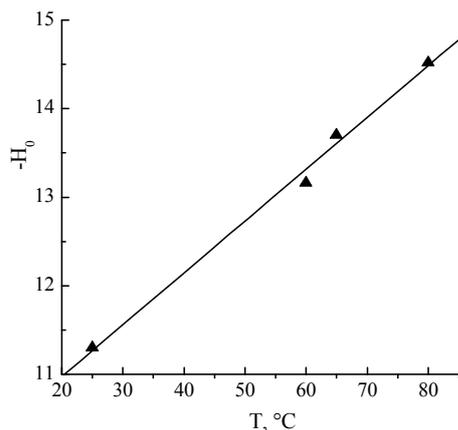


Fig. 8. H₀ values for ZrSi₂ sample at different temperatures

CONCLUSIONS

It was shown that the content and strength of acid sites on ZrO₂-SiO₂ surface are controlled by Zr⁴⁺/Si⁴⁺ ratio in the oxide matrix. At Zr/Si = 0.5 this mixed oxide is characterized by the highest strength of acid sites (H₀ = -11.35). The excess of Si⁴⁺ ions in ZrO₂-SiO₂ (Zr/Si < 1) causes the formation of B-sites while at Zr/Si > 1 only L-sites are formed. The Hammett acidity function for ZrO₂-SiO₂ reaches the superacid value of H₀ ≤ -14.5 at T ≥ 85°C.

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Функція кислотності Гаммета для змішаного $ZrO_2 - SiO_2$ оксиду при підвищених температурах

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Золь-гель методом синтезовані мішані ZrO_2-SiO_2 оксиди з атомним відношенням $4 \geq Zr/Si \geq 0.25$; визначені їхні текстурні параметри, концентрація кислотних центрів та їх розподіл за силою. На підставі ІЧ-спектрів адсорбованого піридину встановлено, що при $Zr/Si < 1$ на поверхні ZrO_2-SiO_2 переважають В-центри, а при $Zr/Si > 1$ – L-центри, що узгоджується з правилом Танабе. На основі UV-vis спектрів дифузного відбиття адсорбованих індикаторів визначені значення H_0 для ZrO_2-SiO_2 при підвищених температурах. Показано, що H_0 досягає суперкислотних значень ≤ -14.5 при $T \geq 85$ °С.

Функция кислотности Гаммета для смешанного $ZrO_2 - SiO_2$ оксида при повышенных температурах

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Золь-гель методом синтезированы смешанные ZrO_2-SiO_2 оксиды с атомным отношением $4 \geq Zr/Si \geq 0.25$; определены их текстурные параметры, концентрация кислотных центров и их распределение по силе. На основании ИК-спектров адсорбированного пиридина установлено, что при $Zr/Si < 1$ на поверхности ZrO_2-SiO_2 преобладают В-центры, а при $Zr/Si > 1$ – L-центры, что согласуется с правилом Танабе. На основе UV-vis спектров диффузного отражения адсорбированных индикаторов определены значения H_0 для ZrO_2-SiO_2 при повышенных температурах. Показано, что H_0 достигает суперкислотных значений ≤ -14.5 при $T \geq 85$ °С.