



Amine-modified silica $\text{NH}_2-(\text{CH}_2)_x-\text{SiO}_2$ ($x = 0, 2, 3$) as support for cobalt-substituted polyoxometalate $\text{TBA}_4\text{HPW}_{11}\text{CoO}_{39}$: Effect of the nature of the support on the oxidation activity

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ABSTRACT

Acidic tetra-*n*-butylammonium (TBA) salts of Keggin type transition-metal-monosubstituted polyoxometalate $\text{TBA}_4\text{HPW}_{11}\text{CoO}_{39}$ (Co-POM) have been chemically anchored to the amino-modified silica ($\text{NH}_2-(\text{CH}_2)_x-\text{SiO}_2$, $x = 0, 2, 3$) containing 40–710 μmol NH_2 -groups per 1 g of support. The interaction of Co-POM with $\text{NH}_2-(\text{CH}_2)_x-\text{SiO}_2$ was studied by DR-UV-vis spectroscopy. Spectroscopic data revealed that the type of interaction between Co-POM and support depends on the amount of anchored functional NH_2 -groups. It was found that Co-POM was attached to $\text{NH}_2-(\text{CH}_2)_x-\text{SiO}_2$ support both by the electrostatic $\text{NH}_3^+ \cdots \text{Co-POM}^-$ and dative ($\text{Si-OH} \cdots \text{Co-POM}$) bonding. Both the amount of anchored NH_2 -groups and the distance between NH_2 -group and surface of silica affect the nature of the interaction between Co-POM and surface functional groups. The increase of the amount of anchored $\text{NH}_2-(\text{CH}_2)_3$ -groups leads to decrease in the contribution of dative bonding $\text{Si-OH} \cdots \text{Co-POM}$ and an increase in the contribution of electrostatic bonding $\text{NH}_3^+ \cdots \text{Co-POM}^-$. The activity of the immobilized Co-POM was tested in benzyl alcohol oxidation with oxygen in CH_3CN medium. It was found that catalytic activity and stability of Co-POM depend on the nature of interaction between Co-POM and surface groups of support that is adjustable both by the amount of anchored functional NH_2 -groups on silica support and the distance between NH_2 -group and surface of silica.

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1. Introduction

The development of heterogeneous catalysts for the liquid-phase oxidation of organic compounds is a challenging goal [1]. Transition-metal-substituted polyoxometalates (POM) have attracted much attention as oxidation catalysts due to their unique physical-chemical properties such as thermal and hydrolytic stability, motile acidities and red-ox potentials, etc. [2,3]. One of the disadvantages of POMs utilization as homogeneous catalysts is the difficulty of their separation from reaction mixture and their inevitable loss during recycling. The attempt to heterogenization of homogeneous catalyst as alternatives to more traditional reagents and catalysts has been one area of research that has seen increasing interest. The high catalytic activity of supported systems is one of the lively motivates for heterogenization of POMs on the support surface. Substantial efforts have been done for the immobilization of POMs on the surface of supports, such as

SiO_2 , carbon, Al_2O_3 , etc. [4–9]. Unfortunately, POMs physically adsorbed on a support very easily leach into reaction solution, especially in polar medium. One mode of solving this problem is to use a support modified with functional groups such as carboxylic groups, lactam, amide, imide or amino-groups for the anchoring of POMs [10–17]. Much recent work was focused on the preparation of organically modified solid bases to heterogenization of homogeneous amine catalyst. Thus, silicates containing combinations of hydrophilic poly(ethylene oxide), hydrophobic poly(propylene oxide) and cationic quaternary ammonium groups appeared to be good supports for $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and $[\text{ZnW}_2\text{Mn}_2(\text{ZnW}_9\text{O}_{39})_2]^{12-}$ resulting in formation of active catalytic assemblies for oxydehydrogenation of dihydroanthracene with recycling possibility [13]. In Ref. [12] transition-metal-substituted polyoxometalates of the type $[\text{M}^{\text{II}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{5-}$ ($\text{M} = \text{Co}$ and Zn) and $[\text{SiW}_9\text{O}_{37}\{\text{Co}^{\text{II}}(\text{H}_2\text{O})\}_3]^{10-}$ have been successfully anchored to amino-functionalized porous silica supports. This method allowed obtaining high dispersion of the POMs, essential accessibility of active site for reagents and minimal leaching of POM. According to Ref. [11] $\text{TBA}_4\text{HPW}_{11}\text{CoO}_{39}$ and $\text{TBA}_5\text{PW}_{11}\text{CoO}_{39}$ were electrostatically bound to NH_2 - and

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NH₃⁺-groups located on the surface of mesoporous silica, correspondingly. This permits to keep activity for at least 3 catalytic cycles in selective aerobic oxidation of isobutyraldehyde due to the low loss of POMs.

In spite of amino-modified silica materials were widely used for immobilization of POMs, the effect of physicochemical properties of NH₂-modified supports on catalytic properties of POMs is less studied. The amount and the basicity of anchored functional NH₂-groups can be expected to be important in determining the strength and the nature of interaction between functional groups of support and reagents/or POMs. Thus, various NH₂-modified silica matrixes, such as SiO₂-xerogels (1.15 mmol NH₂-groups/g), MCF (2.59 mmol NH₂-groups/g), and SBA-15 (0.64 mmol NH₂-groups/g) were used for electrostatic binding of TBA₄HPW₁₁CoO₃₉ (Co-POM) in Ref. [18]. It was found that the nature of the support hardly affects the selectivity of α -pinene epoxide in α -pinene co-oxidation with isobutyraldehyde, while the effect of amount of NH₂-(CH₂)₃-groups on the selectivity was appreciable. In this paper we have synthesized (NH₂-(CH₂)_x-SiO₂, x=0, 2, 3) supports with different amounts of NH₂-groups (40–710 μ mol/g SiO₂). The proton-acceptor properties (basicity) of these amino-containing materials were investigated by IR spectroscopy with CDCl₃ as probe molecule. These NH₂-(CH₂)_x-SiO₂ samples were used for the immobilization of acidic tetra-n-butylammonium salts of Keggin type transition-metal-monosubstituted polyoxometalate TBA₄HPW₁₁CoO₃₉ (Co-POM). Catalytic properties of Co-POM/NH₂-(CH₂)_x-SiO₂ samples were tested in benzyl alcohol oxidation with oxygen.

2. Experimental

2.1. Materials

Benzyl alcohol, 3-aminopropyltriethoxysilane (APTES) and HO(CH₂)₂NH₂ were purchased from Aldrich and used without further purification. Silica Davison 952 was used as support. TBA₄HPW₁₁CoO₃₉ was synthesized by the methods described in Ref. [11]. CDCl₃ was purified under P₂O₅ with subsequent distillation. Toluene was dried over molecular sieves (4 Å), and then distilled from molten sodium metal and stored under an inert atmosphere.

2.2. Synthesis of supports and catalysts

The synthesis was performed using “break seal” techniques [19]. Prior to functionalization, silica was heated in air at 500 °C for 3 h, then placed into the quartz ampoule and dehydroxylated in vacuum at 700 °C for 3 h.

2.2.1. Synthesis of NH₂-(CH₂)_x-SiO₂ supports

Synthesis of NH₂-SiO₂ support. SiO₂ was treated with SO₂Cl₂ (SO₂Cl₂/Si-OH = 10/1 mol/mol, where [Si-OH] is the amount of OH groups per 1 g of support) for 1 h at 200 °C and dried in vacuum at 200 °C (residual pressure 0.001 Torr). Then the sample was treated by NH₃ (400 Torr) for 1 h at 400 °C and dried in vacuum for 4 h at 400 °C (residual pressure 0.001 Torr).

Synthesis of NH₂-(CH₂)₂-SiO₂ support. A weighted amount of silica (1 g) was mixed with liquid HO(CH₂)₂NH₂ (HO(CH₂)₂NH₂/[Si-OH] = 5/1 mol/mol). This mixture was heated at 150 °C for 30 h. Then NH₂-(CH₂)₂-SiO₂ was washed with toluene and dried in vacuum at 80 °C for 4 h.

Synthesis of NH₂-(CH₂)₃-SiO₂ support. A weighted amount of silica (1 g) was mixed with a liquid 3-aminopropyltriethoxysilane (0.05–1.0 mmol). This mixture was heated at 150 °C for 30 h. Then NH₂-(CH₂)₃-SiO₂ sample was washed with toluene and dried in vacuum at 80 °C for 4 h.

2.2.2. Synthesis of Co-POM/NH₂-(CH₂)_x-SiO₂ supported catalysts [10]

A sample was prepared by dissolving 0.13 g of TBA₄HPW₁₁CoO₃₉ in 15 ml CH₃CN and adding 1 g of NH₂-(CH₂)_x-SiO₂, stirring for 1 h at room temperature, filtering, washing with CH₃CN until the filtrate becomes colorless, and then drying in air at room temperature. The percentage of Co-POM on support was determined by both weight difference and elemental analysis. The Co-POM loading was about 12 wt.%. The amount of NH₂-groups was determined by titration with 0.02 M HCl aqueous solution and analytical analysis.

2.3. Physical measurements

Samples of NH₂-(CH₂)_x-SiO₂ in form of dry powders were placed into a special cell for DRIFT measurements under vacuum. The samples were exposed to saturated CDCl₃ vapor for 3 min at room temperature. IR spectra of adsorbed CDCl₃ are presented as difference spectra of the sample before and after CDCl₃ adsorption. The DRIFT spectra were recorded on a Shimadzu FTIR-8300 spectrometer with a DRS-8000 diffusion attachment in the range of 400–6000 cm⁻¹ with a resolution of 4 cm⁻¹.

The samples were placed into a special cell (0.2 cm path length) for DRS measurement. The DRS spectra were recorded on an UV-2501 PC Shimadzu spectrometer with an IRS-250A diffusion reflection attachment in the 190–900 nm range with a resolution of 2 nm.

N₂ adsorption measurements were carried out using an ASAP-2400 Micromeritics instrument.

2.4. Investigation of NH₂-(CH₂)₃-SiO₂ samples by pH titration method [20]

0.1–0.3 g of NH₂-(CH₂)₃-SiO₂ sample was dispersed in 20 ml H₂O. The mixture was titrated by 0.02 M HCl aqueous solution. The titration speed was 0.03 ml min⁻¹ to ensure diffusion of the reactant to all the active centers in the porous solid.

2.5. Catalytic test

Benzyl alcohol oxidations with O₂ in the presence of Co-POM/NH₂-(CH₂)_x-SiO₂ were carried out in autoclave for 24 h at 60 °C. Catalyst and benzyl alcohol in acetonitrile were added into autoclave and subjected to 3 atm oxygen. Benzyl alcohol and benzaldehyde were determined by GC using a gas chromatograph ‘Tsvet-500’ equipped with a flame ionisation detector and a 2 m × 3 mm column filled with SE-30. Cyclohexanol was used as an internal standard for GC.

3. Results and discussion

3.1. Structure of NH₂-(CH₂)_x-SiO₂ samples

Fig. 1 shows DRIFT spectra of SiO₂ dehydroxylated in vacuum at 700 °C before and after amino-modification. The band at 3745 cm⁻¹ attributed to terminal Si-OH groups [21] is observed in the spectrum of SiO₂ (Fig. 1, spectrum 1) and the intensity of this band decreases after a modification of silica with amino-groups. The DRIFT spectra of NH₂-(CH₂)_x-SiO₂ samples exhibit the bands in the regions of 2700–3000 cm⁻¹ and 3000–3550 cm⁻¹, which can be attributed to stretching vibrations of CH₂- and CH₃-groups [20,22] and NH₂-groups [20,21], respectively. One can see from Fig. 1 that the position of the ν_{NH} bands strongly depends on the value of x in the NH₂-(CH₂)_x-SiO₂ samples. Two bands at 3540 and 3455 cm⁻¹ are observed in spectrum of NH₂-SiO₂(70) (Fig. 1, spectrum 2). At the same time in spectra of NH₂-(CH₂)₂-SiO₂(710) and NH₂-(CH₂)₃-SiO₂(390) supports the shift of both ν_{NH} bands

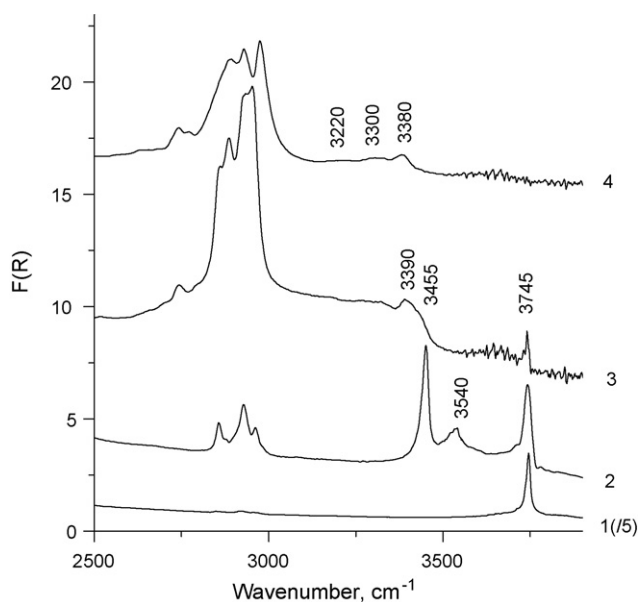
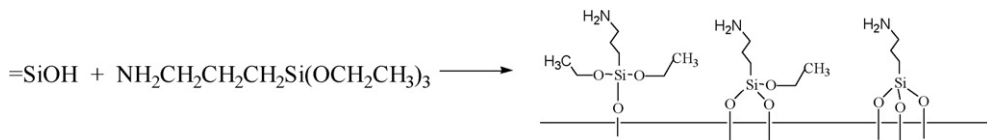


Fig. 1. DRIFT spectra of SiO₂ (1), NH₂-SiO₂(70) (2), NH₂-(CH₂)₂-SiO₂(710) (3) and NH₂-(CH₂)₃-SiO₂(390) (4).

to the lower frequency region was observed (Fig. 1, spectra 3 and 4, respectively), i.e. the longer the distance between NH₂-group and surface of silica, the larger the shift of the ν_{NH} bands to low frequency region. Interestingly, NH₂-SiO₂(70) mainly possesses terminal NH₂-groups, while NH₂-(CH₂)₂-SiO₂(710) and NH₂-(CH₂)₃-SiO₂(390) samples have both terminal NH₂-groups and hydrogen-bonded NH₂-groups (-NH₂···HO-Si, -NH₂···H₃C- and -NH₂···NH₂-) [23].

The effect of the amount of NH₂-groups on the surface of silica has been studied for silica modified with 3-aminopropyltriethoxysilane (NH₂-(CH₂)₃-SiO₂ samples). It has been shown by IRS [20], ¹H and ¹³C NMR MAS [24] that APTES is immobilized on the silica via chemical interaction of ethoxy-groups of APTES with Si-OH groups of silica (Eq. (1)):



As emerges from Fig. 2, the grafting 3-aminopropyltriethoxysilane to silica favours the decrease of intensity of the band at 3745 cm⁻¹. Simultaneously new bands appear in region of stretching vibrations of the NH₂-groups (3000–3550 cm⁻¹). The intensities of ν_{NH} bands increase with increase of the amount of APTES.

According to Ref. [21], silica dehydroxylated at 700 °C contains 1.15 μmol Si-OH groups per m² of SiO₂. Therefore silica used for the preparation of NH₂-(CH₂)_x-SiO₂ samples contains 300 μmol OH groups per g. Based on these data it can be calculated that in NH₂-(CH₂)₃-SiO₂(40) and NH₂-(CH₂)₃-SiO₂(90) samples the amount of NH₂-functional groups anchored is lower than the amount of free Si-OH groups remained in the surface of silica after dehydroxylation at high temperature (see C_{OH}/C_{NH₂} values in Table 1). As emerges from spectra 2 and 3 in Fig. 2, the intensity of the band at 3745 cm⁻¹ attributed to terminal Si-OH groups sharply decreases and intensity of the ν_{NH} bands at 3380 and 3300 cm⁻¹ increases for NH₂-(CH₂)₃-SiO₂(40) and NH₂-(CH₂)₃-SiO₂(90) samples, respectively. The intensities of ν_{NH} bands are higher for NH₂-(CH₂)₃-SiO₂(270) and NH₂-(CH₂)₃-SiO₂(390) samples than

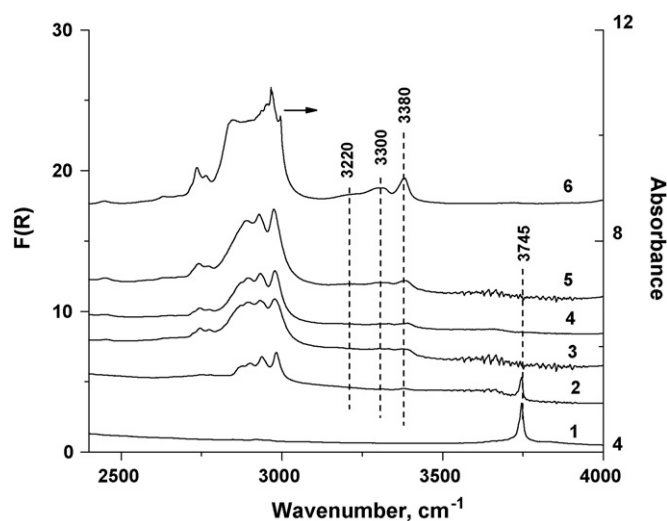


Fig. 2. DRIFT spectra of SiO₂ (1), NH₂-(CH₂)₃-SiO₂(40) (2), NH₂-(CH₂)₃-SiO₂(90) (3), NH₂-(CH₂)₃-SiO₂(270) (4), NH₂-(CH₂)₃-SiO₂(390) (5) and UV-vis spectrum of APTES (liquid) (6).

that for NH₂-(CH₂)₃-SiO₂(40) and NH₂-(CH₂)₃-SiO₂(90) (compare spectra 4 and 5 with spectra 2 and 3 in Fig. 2). This phenomenon is very likely caused by the appearance of hydrogen-bonded NH₂-groups due to the interaction of NH₂-groups with Si-OH groups (-NH₂···HO-Si), because in the case of NH₂-(CH₂)₃-SiO₂(270) and NH₂-(CH₂)₃-SiO₂(390) samples the amount of NH₂-groups anchored is comparable with the amount of Si-OH groups.

The textural analysis of NH₂-(CH₂)₃-SiO₂ samples indicates that 3-aminopropyltriethoxysilane was effectively grafted onto the silica surface. As one can judge from Fig. 3, the specific surface area, pore volume and pore diameter decrease with the increase in the amount of APTES grafted. This phenomenon may be explained by a result of blocking of some pores by grafted NH₂-(CH₂)₃-groups. Taking into account that one aminopropylsilane covers approximately 50 Å² [25] we estimated the surface area covered by the organic layer on the surface of samples (S_{APTES}). It was found that

the increase of the amount of APTES grafted leads to the linear increase of the S_{APTES}/S_{sample} ratio (Fig. 3A), that can indicate monolayer coverage of silica surface by 3-aminopropyltriethoxysilane. Therefore, the blocking of pores leads to decrease in the average pore diameters of the samples and the formation additional pores with small diameter (Fig. 3D).

3.2. Base properties of NH₂-(CH₂)_x-SiO₂ samples

Base properties of NH₂-(CH₂)_x-SiO₂ samples have been studied by IR spectroscopy with CDCl₃ probe molecule. CDCl₃ is a soft probe molecule for basic sites such as amines, ketones, oxides, base zeolites [23,26–29]. Spectra of CDCl₃ adsorbed on the pure SiO₂ and NH₂-(CH₂)₃-SiO₂ samples with different amounts of anchored NH₂-groups are shown in Fig. 4. A gas phase frequency ν_{C-D} of CDCl₃ is equal to 2268 cm⁻¹ [26,27]. This frequency becomes lower (ν_{C-D} 2265 cm⁻¹) after adsorption of CDCl₃ on the silica (Fig. 4, spectrum 1). According to Ref. [27] this band is attributed to the complex of CDCl₃ with Si-OH groups. The DRIFT spectra of NH₂-(CH₂)₃-SiO₂ samples exhibit the absorption bands in

Table 1
Spectral characteristics (ν_{C-D}) of NH_2 -groups for $NH_2-(CH_2)_x-SiO_2$ samples and parent silica support according to adsorption of $CDCl_3$ probe molecule.

Sample	Amount of NH_2 ($\mu mol g^{-1}$)	C_{OH}/C_{NH_2} ($mol mol^{-1}$)	ν_{C-D} (cm^{-1})	$\Delta\nu_{C-D}$ (cm^{-1})	PA ($kJ mol^{-1}$)
$CDCl_3$	–	–	2268	–	–
SiO_2^a	–	–	2265	3	733
APTES	–	–	2197	71	941
$NH_2-SiO_2(70)$	70	4.3	2255	13	829
$NH_2-(CH_2)_2-SiO_2(710)$	710	0.4	2215	53	919
$NH_2-(CH_2)_3-SiO_2(40)$	40	7.5	n.d. ^b	–	–
$NH_2-(CH_2)_3-SiO_2(90)$	90	3.3	2206	62	932
$NH_2-(CH_2)_3-SiO_2(200)$	200	1.5	2206	62	932
$NH_2-(CH_2)_3-SiO_2(270)$	270	1.1	2203	65	935
$NH_2-(CH_2)_3-SiO_2(390)$	390	0.8	2200	68	938

^a SiO_2 was dehydroxylated in vacuum at 700 °C for 3 h.

^b Not determined.

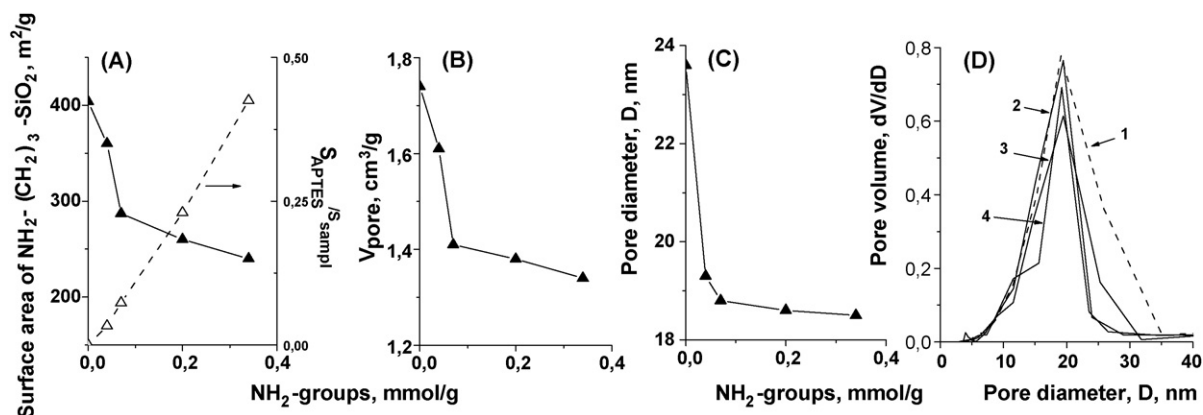


Fig. 3. Effect of NH_2 -groups content on the specific surface area and the change of APTES surface area based on the specific surface area (S_{APTES}/S_{sample} ratio) (A), pore volume (B) pore diameter (C) and pore-size distribution plots from N_2 adsorption experiments (D): SiO_2 (1), $NH_2-(CH_2)_3-SiO_2(40)$ (2), $NH_2-(CH_2)_3-SiO_2(70)$ (3) and $NH_2-(CH_2)_3-SiO_2(340)$ (4) samples.

the regions of 2190–2210 cm^{-1} and 2230–2260 cm^{-1} . The band at 2247 cm^{-1} can be attributed to the complex of $CDCl_3$ with ethoxy-groups of APTES, that is in a good agreement with spectrum of $Si(OEt)_4-CDCl_3$ solution (Fig. 4, spectra 7 and 8). The bands in the region of 2190–2210 cm^{-1} can be attributed to the interaction between $CDCl_3$ and NH_2 -groups. The position of these bands depends on the amount of immobilized APTES. The increase of the amount of APTES leads to the low frequency shift. Probably the change of nature of interaction of NH_2 -groups with functional groups of support causes this shift. It is worth to note that the spectrum of $NH_2-(CH_2)_3-SiO_2(390)$ is similar to the spectrum of the mixture of APTES and $CDCl_3$ (Fig. 4).

Interestingly, the NH_2 -groups remoteness from surface of silica support affects the position of the ν_{C-D} band in spectra of $NH_2-(CH_2)_x-SiO_2$ samples (Table 1). The longer the distance between NH_2 -group and surface of silica, the larger the bands shift to low frequency region.

The strength of NH_2 -groups was calculated from shift of ν_{C-D} band using Eq. (2) [26–28]:

$$\log \Delta\nu_{C-D} = 0.0066 \times PA - 4.36 \quad (2)$$

where PA is proton affinity, $kJ mol^{-1}$. Calculated PA values of $NH_2-(CH_2)_x-SiO_2$ samples are presented in Table 1. Proton affinity for SiO_2 is equal to 733 $kJ mol^{-1}$. As shown in Table 1, for NH_2-

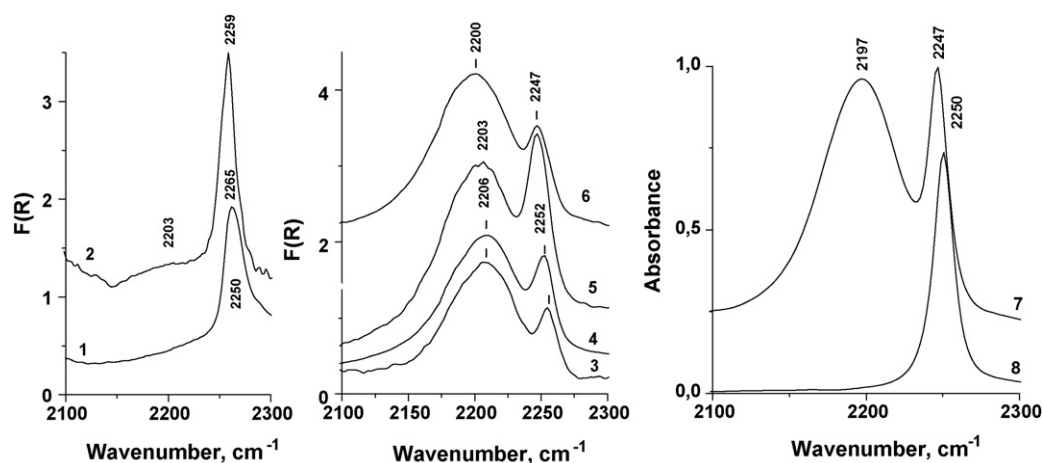


Fig. 4. DRIFT spectra of $CDCl_3$ adsorption on SiO_2 (1), $NH_2-(CH_2)_3-SiO_2(40)$ (2), $NH_2-(CH_2)_3-SiO_2(90)$ (3), $NH_2-(CH_2)_3-SiO_2(200)$ (4), $NH_2-(CH_2)_3-SiO_2(270)$ (5), $NH_2-(CH_2)_3-SiO_2(390)$ (6), APTES: $CDCl_3$ 1:1 (mol/mol) (7) and $Si(OEt)_4: CDCl_3$ 1:1 (mol/mol) (8).

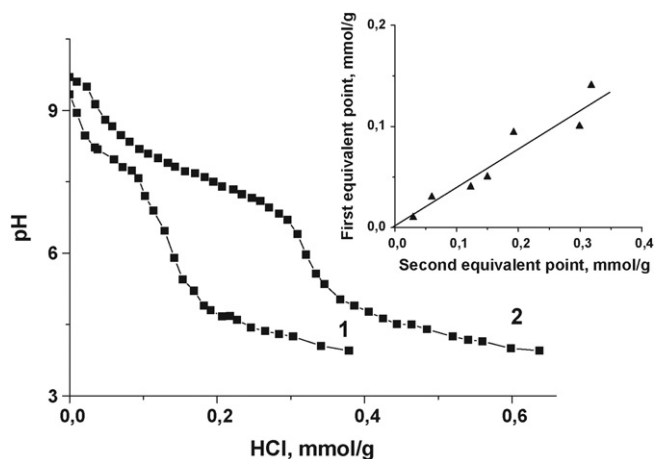
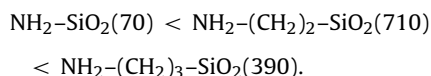


Fig. 5. Titration curves obtained for $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2(140)$ (1) and $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2(340)$ (2) samples with adding 0.02 M HCl. The titration speed was 0.03 ml min^{-1} . Inset: Correlation between first equivalent point and second equivalent point determined by titration of $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ samples.

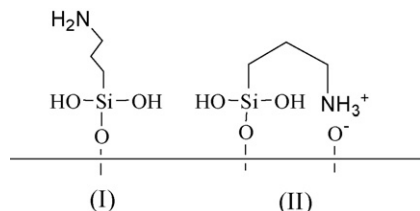
modified SiO_2 support the range of PA value is $829\text{--}940 \text{ kJ mol}^{-1}$. As emerges from the data presented in Table 1, the PA value increases with the increase of the value of x in the $\text{NH}_2-(\text{CH}_2)_x-\text{SiO}_2$ samples in the following order:



PA increases with growth of APTES amount and runs up to PA value of the mixture of APTES and CDCl_3 . The increasing of the basicity of $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ with the increase of the amount of APTES anchored is likely caused by the decreasing effect of free Si-OH groups.

In all likelihood, one of the main reasons is the change of the nature of interaction of NH_2 -groups with silica support. Thus, the higher the amount of APTES anchored on the surface of support, the lower amount of unreacted free Si-OH groups. These interchanges are accompanied by the decrease of the contribution of hydrogen-bonded NH_2 -groups ($-\text{NH}_2 \cdots \text{HO-Si}$). Moreover, the longer the distance between NH_2 -group and surface of silica, the weaker the interaction between NH_2 - and Si-OH groups, and therefore, the higher the PA value.

Direct titration of $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ samples by 0.02 M HCl allows determining two types of basic sites on the surface of solid. As shown in Fig. 5, two successive pH jumps are observed in the characteristic titration curves of $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ samples. The first one with a constant of proton exchange (K_H^0) 9.4–9.6 and second one with a K_H^0 6.7–7.0 are ascribed to protonation of the free amino-groups (I) and the protonation of the zwitterion-like species (II), correspondingly [19]:



As can be seen from Fig. 5, the increase in amount of APTES grafted on silica leads to the linear correlation between these two equivalent points. This shows that these two type of amino-groups co-exist in the surface of $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ samples with a constant (I)/(II) ratio, which is about 1:2.

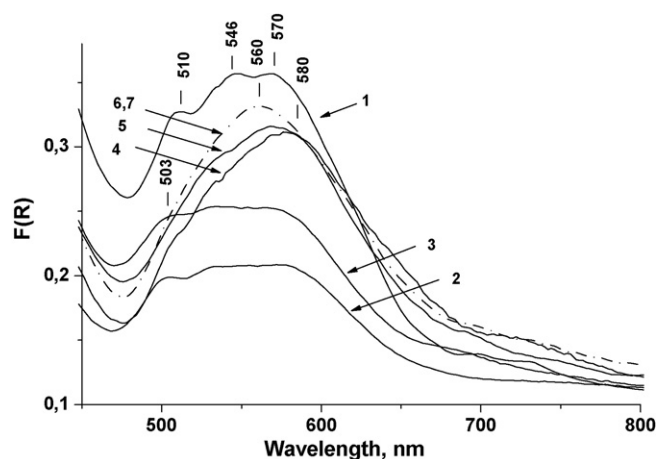


Fig. 6. DR-UV-vis spectra of $\text{TBA}_4\text{HPW}_{11}\text{CoO}_{39}$ (solid) (1), Co-POM/SiO_2 (2), $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(40)$ (3), $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(90)$ (4), $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(200)$ (5), $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(270)$ (6), $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(390)$ (7).

3.3. Preparation and investigation of $\text{Co-POM/NH}_2-(\text{CH}_2)_x-\text{SiO}_2$

The interaction between $\text{TBA}_4\text{HPW}_{11}\text{CoO}_{39}$ and $\text{NH}_2-(\text{CH}_2)_x-\text{SiO}_2$ support was studied by DR-UV-vis spectroscopy. DR-UV-vis spectra of $\text{TBA}_4\text{HPW}_{11}\text{CoO}_{39}$ salt and Co-POM immobilized on pure SiO_2 and $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ samples are presented in Fig. 6.

The bands at 570, 546 and 510 nm are observed in spectrum of Co-POM (Fig. 6, spectrum 1). The band at 570 nm and a small shoulders at 510 nm are attributed to $d-d$ electron transition (${}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{1g}$) for octahedral Co^{II} coordination with six oxygen bound ligands [13,29]. Other bands appeared due to the distortion of crystalline structure of Co-POM . Changes of the ligand-field band in the 450–750 nm region are observed after supporting Co-POM on SiO_2 and $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ support. The shift of bands ($510 \rightarrow 503 \text{ nm}$, $570 \rightarrow 580 \text{ nm}$ and $546 \rightarrow 531 \text{ nm}$) and lines spreading are observed in spectra (Fig. 6). The shape of the spectrum of $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(40)$ is almost the same as that of Co-POM/SiO_2 , indicating the similar character of interaction between Co-POM and both supports (Fig. 6, spectra 2 and 3). Co-POM is datively linked to support in both samples. It is believed that this dative bond forms by means of interaction $\text{Si-OH} \cdots \text{Co-POM}$ due to the high amount of free Si-OH groups on the surface of $\text{NH}_2-(\text{CH}_2)_3-\text{SiO}_2(40)$ sample with the lowest amount of anchored NH_2 -groups (Table 2) [12]. The shape of spectra of $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2(90\text{--}390)$ samples changes significantly with increasing amount of anchored NH_2 -groups (Fig. 6, spectra 4–7). One broad line in the region of 570–531 nm is observed in the spectrum of all samples, which is also observed in the spectra of five-coordination high spin complexes of cobalt (II) [30]. It is reasonable to expect that the change in symmetry of cobalt ion is due to the formation of electrostatic bonding $\text{NH}_3^+ \cdots \text{Co-POM}^-$. The increase of APTES amount leads to hypsochromic shift of band from 580 to 560 nm. The observed shift can point to the re-allocation of electron density in heteropoly anion, because the value of shift proportionate to the change of the electron density distribution in Co-POM molecule [31]. The changes in spectra of $\text{Co-POM/NH}_2-(\text{CH}_2)_3-\text{SiO}_2$ samples with the change of amount of APTES grafted on silica can be attributed to the alteration of the character of interaction of Co-POM with surface functional groups, because the increase in the amount of APTES results in the decrease of $C_{\text{OH}}/C_{\text{NH}_2}$ ratio and increase of $\text{NH}_2/\text{Co-POM}$ ratio, simultaneously (Table 2).

A series of impregnation experiments were performed to estimate the effect of distance between NH_2 -group and surface of

Table 2
Benzyl alcohol oxidation with oxygen in the presence of Co-containing systems^a.

Catalyst ^b	C_{OH}/C_{NH_2} (mol mol ⁻¹)	$NH_2-/Co-POM$ (mol mol ⁻¹)	C_{BzOH}/C_{NH_2} (mol mol ⁻¹)	$C_6H_5CH_2OH$ conversion (%)	Selectivity of C_6H_5CHO (mol.%)
Without catalyst	–	–	–	<1	n.d.
SiO ₂	–	–	–	<1	n.d.
NH ₂ –(CH ₂) ₃ –SiO ₂ (270)	1.1	–	28.6	<1	n.d.
Co-POM ^c	–	–	–	8	100
Co-POM/NH ₂ –SiO ₂ (70)	4.3	1.7	111.1	13	100
Co-POM/NH ₂ –(CH ₂) ₂ –SiO ₂ (710)	0.4	17.7	11.0	10	100
Co-POM/NH ₂ –(CH ₂) ₃ –SiO ₂ (40)	7.5	1.0	200.0	8 (3) ^d	100 (100) ^d
Co-POM/NH ₂ –(CH ₂) ₃ –SiO ₂ (90)	3.3	2.2	90.9	10	100
Co-POM/NH ₂ –(CH ₂) ₃ –SiO ₂ (270)	1.1	6.7	28.6	22	100
Co-POM/NH ₂ –(CH ₂) ₃ –SiO ₂ (390)	0.8	9.7	20.0	22 (21) ^d	100 (100) ^d
Co-POM ₉ /NH ₂ –(CH ₂) ₃ –SiO ₂ (500)	0.6	12.5	15.6	20	98

^a Reaction conditions: 0.13 M C₆H₅CH₂OH in 3 ml CH₃CN, 3 atm oxygen, 50 mg catalyst, 60 °C, 24 h.

^b 0.12 g Co-POM was supported on 1 g of NH₂–(CH₂)_x–SiO₂.

^c 5 mg Co-POM.

^d Catalyst was re-used in the second catalytic cycle.

silica. Spectra of Co-POM supported on NH₂–(CH₂)_x–SiO₂ are shown in Fig. 7. As will readily be observed, the shape of spectra depends on the nature of support. Thus, the shape of spectra of Co-POM supported on SiO₂, NH₂–SiO₂(70), NH₂–(CH₂)₃–SiO₂(40) is similar (compare Fig. 7, spectrum 4 and Fig. 6, spectra 2 and 3) that is likely due to the preferential dative bond formed by means of Si–OH...Co-POM interaction. At the same time spectra of Co-POM/NH₂–(CH₂)₂–SiO₂(710) and Co-POM/NH₂–(CH₂)₃–SiO₂(90–270) exhibit the bands at 526 and 560 nm (Fig. 7, spectrum 3 and Fig. 6, spectra 4–6), respectively. It may be suggested that the increase in the distance between NH₂-group and surface of silica results in decreasing of the contribution of dative bonding Si–OH...Co-POM and increasing of the contribution of electrostatic bonding NH₃⁺...Co-POM[–], simultaneously.

3.4. Oxidation of benzyl alcohol with oxygen

The catalytic activity of Co-POM/NH₂–(CH₂)_x–SiO₂ for the aerobic oxidation of benzyl alcohol was evaluated and compared with the catalytic properties of the homogeneous Co-POM. The results are presented in Table 2. In the absence of catalyst the conversion of C₆H₅CH₂OH is very low (<1%). In the presence of Co-POM the conversion of benzyl alcohol is 8%. Benzaldehyde is the main oxidation product. The immobilization of Co-POM on NH₂–(CH₂)_x–SiO₂ favours the increase in the conversion of C₆H₅CH₂OH (Table 2).

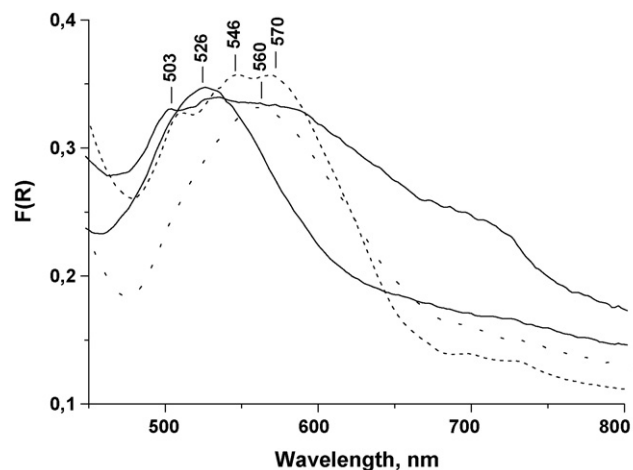


Fig. 7. DR-UV-vis spectra of TBA₄HPW₁₁CoO₃₉ (solid) (1), Co-POM/NH₂–(CH₂)₃–SiO₂(270) (2), Co-POM/NH₂–(CH₂)₂–SiO₂(710) (3), and Co-POM/NH₂–SiO₂(70) (4).

As seen from Table 2, the catalytic activity of Co-POM/NH₂–(CH₂)_x–SiO₂ systems strongly depends on the amount of NH₂-groups and distance between NH₂-group and surface of silica. Thus, the increase in the amount of anchored NH₂–(CH₂)₃-groups up to 270 μmol of NH₂-groups per 1 g of SiO₂ ($C_{OH}/C_{NH_2} = 1.1$ mol mol⁻¹ and $C_{BzOH}/C_{NH_2} = 28.6$ mol mol⁻¹) resulted in an increase of the oxidation activity for benzyl alcohol (Table 2). The further increase of the amount of anchored NH₂–(CH₂)₃-groups tended to level off the benzyl alcohol conversion. Interestingly that conversion of benzyl alcohol over Co-POM/NH₂–(CH₂)₃–SiO₂ is higher than that over Co-POM/NH₂–SiO₂ and Co-POM/NH₂–(CH₂)₂–SiO₂ catalysts. These may have several explanations. First, it is necessary to mention that the nature of interaction between Co-POM and surface functional groups strongly depends on the type of NH₂-precursor and amount of NH₂-groups grafted on the silica surface. Thus, we may conclude that the lower the amount of free Si–OH groups, i.e. the lower C_{OH}/C_{NH_2} ratio, the higher catalytic activity of Co-POM/NH₂–(CH₂)₃–SiO₂. Note that this assumption is feasible for one-type systems. For systems with different types of NH₂–(CH₂)_x-groups we can believe that the shorter the distance between NH₂-group and surface of silica, i.e. the lower the x value, the lower the catalytic activity due to increasing of Si–OH...Co-POM interaction and the decrease of contribution of electrostatic bonding NH₃⁺...Co-POM[–]. The effect of amine additions (α-piperidine and pyridine) on activity was already demonstrated for aerobic oxidation of benzyl alcohol over Co^{II}/NaY system [32]. The addition of small amount of pyridine caused an increase in the oxidation activity for benzyl alcohol up to 0.006 pyridine/benzyl alcohol mole ratio. The further addition of pyridine tended to level off the yield of benzaldehyde. This phenomenon was related with the formation of Co^{II}–pyridine (or piperidine) complex within the large cavities of NaY zeolite and blocking of active sites for reagents adsorption. Moreover, amino-groups can be considered as a poisonous additive of Si–OH groups for reagents adsorption, which facilitate the sorption-desorption processes of reagents [33]. The effect of the amount of anchored NH₂–(CH₂)₃-groups on the selectivity of α-pinene epoxide in α-pinene co-oxidation with isobutyraldehyde over Co-POM/NH₂–(CH₂)₃–SiO₂ was observed in Ref. [18]. Unfortunately, the effect of NH₂–(CH₂)₃-groups content on the selectivity of benzaldehyde was negligibly in our case.

It is worth noting that basicity and amount of NH₂-groups influence on the stability of catalytic system. It was demonstrated that Co-POM/NH₂–(CH₂)₃–SiO₂(390) sample kept its activity during two catalytic cycles (Table 2). At the same time the activity of Co-POM/NH₂–(CH₂)₃–SiO₂(40) sample was low in the second run. Leaching of Co-POM is one of the reasons for the loss of the activity.

According to elemental analysis of Co-POM/NH₂-(CH₂)₃-SiO₂ (40) 1.7 mg of Co-POM (34% from total amount of Co-POM) was leached into solution during the reaction. This loss of Co-POM may be due to the low amount of NH₂-groups and weak basic sites on the surface of catalyst (Table 1).

4. Conclusion

The amino-modified silica (NH₂-(CH₂)_x-SiO₂, x = 0, 2, 3) have been synthesized and characterized by DRIFT spectroscopy. The proton-acceptor properties of NH₂-(CH₂)_x-SiO₂ were investigated by DRIFT spectroscopy using CDCl₃ adsorption as probe molecule. Two types of surface functional groups were identified on the surface of supports. There are isolated Si-OH and hydrogen-bonded NH₂-groups (-NH₂...HO-Si). It was demonstrated that the amount of NH₂-groups and the distance between NH₂-group and surface of silica affect the basicity of NH₂-groups. The increase in the amount of NH₂-groups and/or distance between NH₂-group and surface of silica leads to increase in the basicity of NH₂-groups.

The Co-containing polyoxometalate TBA₄HPW₁₁CoO₃₉ was chemically immobilized on NH₂-(CH₂)_x-SiO₂ type of supports. DR-UV-vis spectroscopic data indicate that the character of interaction between Co-POM and support depends on type of functional groups. The increase in amount of NH₂-groups and distance between NH₂-group and surface of silica favours the formation of electrostatic bonding NH₃⁺...Co-POM⁻. The activity of the immobilized Co-POM was tested in benzyl alcohol oxidation with oxygen in CH₃CN medium. It was found that catalytic activity of Co-POM depends on the nature of interaction between Co-POM and surface groups of support that is adjustable by both the distance between NH₂-group and surface of silica and amount of NH₂-groups on silica.

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References

- [1] K.H.J. Buschow, R.W. Cahn, M.C. Flemings, B. Ilshner, E.J. Kramer, S. Mahajan, P. Veyssi ere (Eds.), *Encyclopedia of Materials: Science and Technology*, Wiley, 2001.
- [2] V. Kozhevnikov, *Catalysis by Polyoxometalates. Catalysis for Fine Chemical Synthesis*, vol. 2, Wiley, UK, Chichester, 2002, p. 201.
- [3] M.T. Pope, A. Muller (Eds.), *Polyoxometalate Chemistry from Topology via Self-assembly to Applications*, Kluwer, 2001.
- [4] W. Yue, Y. Xingkai, Y. Xiangguang, W. Xinping, C. Wenling, H. Yucai, *Ind. Eng. Chem. Res.* 35 (1996) 2546–2560.
- [5] N.Y. He, C.S. Woo, H.G. Lee, *Appl. Catal. A: Gen.* 281 (2005) 167–178.
- [6] R.J.J. Jansen, H.M. van Veldhuizen, H. Van Bekkum, *J. Mol. Catal.* 107 (1996) 241–253.
- [7] K. Nowinska, R. Formaniak, W. Kaleta, A. Waclaw, *Appl. Catal. A: Gen.* 256 (2003) 115–123.
- [8] A.M. Khenkin, R. Neumann, A.B. Sorokin, A. Tuel, *Catal. Lett.* 63 (1993) 189–192.
- [9] L. Xu, E. Boring, C.L. Hill, *J. Catal.* 195 (2000) 394–405.
- [10] W. Kaleta, K. Nowinska, *Chem. Commun.* (2001) 535–536.
- [11] O.A. Kholdeeva, M.P. Vanina, M.N. Timofeeva, R.I. Maksimovskaya, T.A. Trubitsina, M.S. Mel'gunov, E.B. Burgina, J. Mrowiec-Bialon, A.B. Jarzebski, C.L. Hill, *J. Catal.* 226 (2004) 363–371.
- [12] B.J.S. Johnson, A. Stein, *Inorg. Chem.* 40 (2001) 801–808.
- [13] M. Cohen, R. Neumann, *J. Mol. Catal. A: Chem.* 146 (1–2) (1999) 291–298.
- [14] R. Neumann, H. Miller, *J. Chem. Soc. Chem. Commun.* (1995) 2277–2278.
- [15] D. Kumar, C.C. Landry, *Micropor. Mesopor. Mater.* 98 (2007) 309–316.
- [16] H. Kim, J.C. Jung, P. Kim, S.H. Yeom, K.-Y. Lee, I.K. Song, *J. Mol. Catal. A: Chem.* 259 (2006) 150–155.
- [17] M. Hasik, W. Turek, E. Stochmal, M. Lapowski, A. Pron, *J. Catal.* 147 (1994) 544–551.
- [18] N.V. Maksimchuk, M.S. Melgunov, Yu.A. Chesalov, J. Mrowiec-Bialon, A.B. Jarzebski, O.A. Kholdeeva, *J. Catal.* 246 (2007) 241–248.
- [19] L.R. Fisher, *J. Phys. E: Sci. Instrum.* 4 (1971) 608–612.
- [20] M. Etienne, A. Walcarius, *Talanta* 59 (2003) 1173–1188.
- [21] L.T. Zhuravlev, *Colloids Surf. A: Physicochem. Eng. Aspects* 173 (2000) 1–38.
- [22] L.M. Sverdlov, M.A. Kovner, E.P. Krainov, *Vibrational Spectra of Polyatomic Molecules*, Nauka, Moscow, 1972 (in Russian).
- [23] V.N. Panchenko, V.A. Pozimienko, E.A. Paukshtis, V.A. Zakharov, *Russ. J. Inorg. Chem.* 54 (11) (2009) 1798–1803.
- [24] H. Juvaste, E.I. Iiskola, T.T. Pakkanen, *J. Mol. Catal. A: Chem.* 150 (1999) 1–9.
- [25] E.F. Vansant, P. Van der Voort, K.C. Vrancken, *Characterisation and Chemical Modification of the Silica Surface*, Elsevier, The Netherlands, 1995.
- [26] F.L. Slejko, R.S. Drago, D.G. Brown, *J. Am. Chem. Soc.* 94 (1972) 9210–9216.
- [27] E.A. Paukshtis, N.S. Kotsarenko, L.G. Karakchiev, *React. Kinet. Catal. Lett.* 12 (1979) 315–319.
- [28] H. Knozinger, S. Huber, *J. Chem. Soc., Faraday Trans.* 94 (1998) 2047–2059.
- [29] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113–252.
- [30] T.J.R. Weakley, *J. Chem. Soc., Dalton Trans.* 3 (1973) 341–346.
- [31] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam/Oxford/New York/Tokyo, 1984.
- [32] S. Truruya, H. Miyamoto, T. Sakae, M. Masai, *J. Catal.* 64 (1980) 260–271.
- [33] Z.G. Zhao, L.H. Zhang, Y. Lin, *J. Colloid Interface Sci.* 166 (1994) 23–28.