

IR-Spectroscopic Study of Adsorption of Aminoazoles on Oxide Catalysts of Biginelli Reaction

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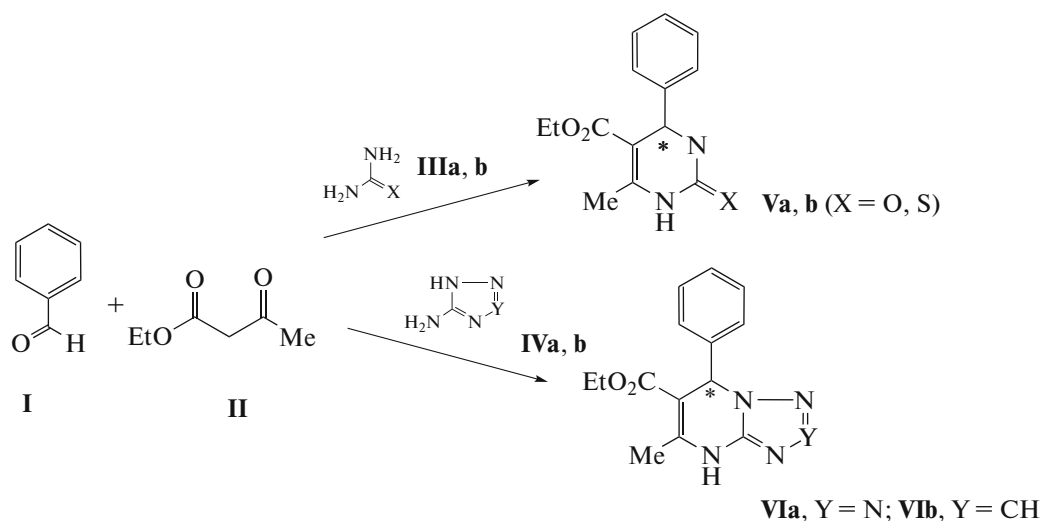
Abstract—Adsorption of 5-aminotetrazole and 3-aminotriazole on the surface of nanosized oxides of Al and Si–Ti, which are catalysts of the Biginelli reaction with the participation of aminoazoles, have been studied using the method of IR spectroscopy. It has been shown that 5-aminotetrazole and 3-aminotriazole interact with the Brønsted base centers on the oxide surface, with the behavior of aminoazole in the Biginelli reaction being determined by the coordination.

Keywords: IR spectroscopy, Biginelli reaction, catalysts, nanosized oxides of metals and silicon, aminoazoles, adsorption

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Metal oxides are widely used as catalysts in organic synthesis both in industry and in laboratory practice [1]. Review [2] considered the applications of oxides of metals and silicon in the condensation reactions, reactions with the formation of C–N and C–O bonds and in multicomponent reactions. The latter includes the Biginelli reaction (Scheme 1) with the participa-

tion of aldehyde (**I**), a CH-active compound (**II**), and an NH-active compound, which is urea (**IIIa**), thiourea (**IIIb**) [3] or aminoazoles (**IVa** and **IVb**) [4]. Substituted dihydroazolo[1,5-a]pyrimidines of type **VIa** and **VIb**, which are of interest as distant analogues of purines and nucleosides, possess a wide spectrum of biological activities [5–7].



Scheme 1. The Biginelli reaction.

The catalysts for the classical Biginelli reaction, which involves urea or thiourea, are well known. These are mineral and Lewis acids (e.g., $\text{BF}_3\text{-OEt}_2$) in combination with salts of transition metals [8], FeCl_3

[9], InCl_3 [10], $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ [11], lanthanides or copper triflate [12, 13]. Sometimes, this reaction is carried out in the presence of metal oxides: aluminum oxide supported on molybdenum oxide [14], palladium

Table 1. The influence of the nature of the catalyst and solvent on the yield of compound **VIa** at 22–23°C (according to HPLC data)

No.	Order of reagent loading	Catalyst	S_{sp} , m ² /g	Solvent	Reaction time	Yield VIa , %	Yield VII , %	
1	I + II + IVa	–	–	EtOH	40 h	<3	<3	
2			–	CH ₃ CN		<3	<3	
3			–	THF		7 days	8	<3
4			–				12	<3
5		Morpholine	–		20		4	
6		CF ₃ COOH	–		5		<3	
7		SiO ₂	266		0.2		<3	
8		ZnO	46		<3		<3	
9		Al ₂ O ₃	197		5		<3	
10		TiO ₂	250		4		<3	
11		MgO	394		15		<3	
12		SiO ₂ –ZrO ₂	179		12		<3	
13		SiO ₂ –MgO	279		18		<3	
14		SiO ₂ –TiO ₂	220	20	4			
15		I + II , after 30 min + IVa		SiO ₂ –TiO ₂	25	9		

oxide [15], or nanosized zirconium oxide [16]. We have studied nanosized oxides of aluminum, copper, zinc, and titanium as catalysts in the Biginelli reaction [17]. It has been shown that the observed increase in the reaction chemoselectivity is associated with activation of benzaldehyde (**I**), acetoacetic ester (**II**) and urea (**IIIa**) under conditions of their sorption on the surface of nanosized oxide catalyst [17, 18].

Substituted dihydroazolo[1,5-a]pyrimidines of type **VIa** and **VIb** are mostly synthesized under heating (90–150°C) using mineral or organic acids (e.g., sulfamic [19] or toluenesulfonic acid [20]), N,N,N,N-tetrabromobenzene-1,3-disulfonamide [21], as well as Lewis acids [19] as catalysts. Only one work is known [22] in which the compound **VIb** was synthesized at room temperature using ionic liquid [Bmin]BF₄ as a catalyst.

The search for new catalysts that allow the synthesis of substituted dihydroazolo[1,5-a]pyrimidines without heating is an important problem, since such catalysts can be useful in the development of stereoselective methods of synthesis [23]. Stereoselective synthesis of compound **Va** at a room temperature in the presence of nanooxides Al₂O₃, SiO₂–TiO₂ and SiO₂–ZrO₂ was described in [24, 25].

In the present work, we studied catalysts for the synthesis of dihydroazolopyrimidines **VIa** and **VIb** at room temperature. The sorption of aminoazoles **IVa** and **IVb** on the surface of Al₂O₃ and SiO₂–TiO₂ nano-

oxides, which contain active centers of different natures [18–25], was investigated by IR spectroscopy. These results were used to explain the different behavior of aminoazoles in the Biginelli reaction, as well as the different catalytic activity of oxides Al₂O₃ and SiO₂–TiO₂ in this reaction.

MATERIALS AND METHODS

Reagents

Reagents produced by Lancaster were used in the experiments, including urea (99%), benzaldehyde (99%), 5-aminotetrazole monohydrate (97%), anhydrous 3-aminotriazol (98%), and acetoacetic ester (99%, Acros Organics).

Synthesis of Catalysts

Individual nanosized oxides of titanium, silicon, aluminum, zinc, and magnesium were prepared by the sol–gel method [26]. Double nanooxides SiO₂–ZnO₂ (3 : 1), SiO₂–MgO (3 : 1) and SiO₂–TiO₂ (3 : 1) were prepared in a similar way by mixing sols at a predetermined ratio with subsequent drying at 100–150°C to constant mass. The values of the specific surface area (S_{sp}) of the studied samples are given in Table 1.

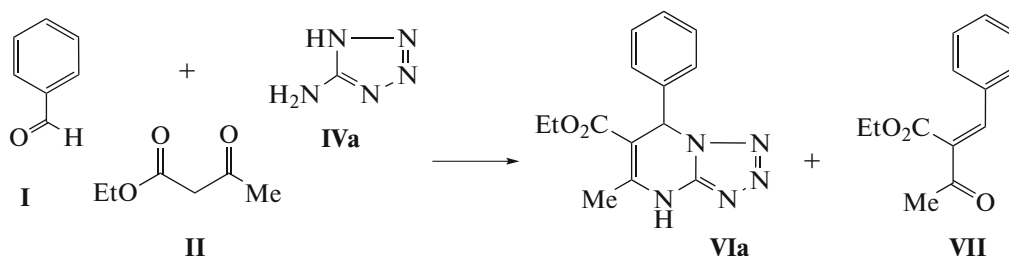
Methods for Analysis of Catalysts

The melting points were measured using a Boetius heating microstage (Germany) without further adjustment of the results. Diffuse reflectance spectra of the samples in the powder state were recorded on a Spectrum One IR-Fourier spectrometer (Perkin Elmer, United States) equipped with an automatic diffuse reflectance attachment. The diffuse reflectance spectrum was converted to Kubelka–Munch units using Spectrum software. The addition of the spectra was performed using the Spectral Calculator program implemented in Spectrum, which allows estimation of the contribution of each component in the spectral picture. The ^1H NMR spectra were recorded using an AVANCE DRX-400 spectrometer (Bruker, Germany) with an operating frequency of 400.13 MHz (internal standard TMS). The elemental analysis was carried out on an EA 1108 CHN-analyzer (Carlo Erba Instruments, Italy).

Study of the Catalytic Action of Nanooxides in the Biginelli Reaction

The Biginelli reaction was carried out in a tetrahydrofuran (THF) with a molar ratio of aldehyde : acetoacetic ester (AAE) : aminoazole : metal nanooxide = 1 : 2 : 1 : 0.1. The reaction mass was stirred at a temperature of 22–25°C for 7 days and then was evaporated.

The obtained crude product was analyzed by ^1H NMR and high-performance liquid chromatography (HPLC) on an Agilent 1200 chromatograph (Agilent Technologies, USA, a Chiralpak AD-H column (Daicel Chemical Industries, Japan), the eluent $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (35 : 65), at a wavelength of 285 nm). The contents of target compound **VI** and chalcone **VII** (Scheme 2) in the reaction mass were determined according to the HPLC data on the same column using the method of absolute calibration.



Scheme 2. Products of the Biginelli reaction with the participation of 5-aminotetrazole.

Study of the Adsorption of Aminoazoles

Adsorption of aminoazoles on nanooxides of metals or silicon was carried out from methanolic solutions of the sorbate (at the sorbate : sorbent molar ratio of 1 : 3) followed by removal of the solvent.

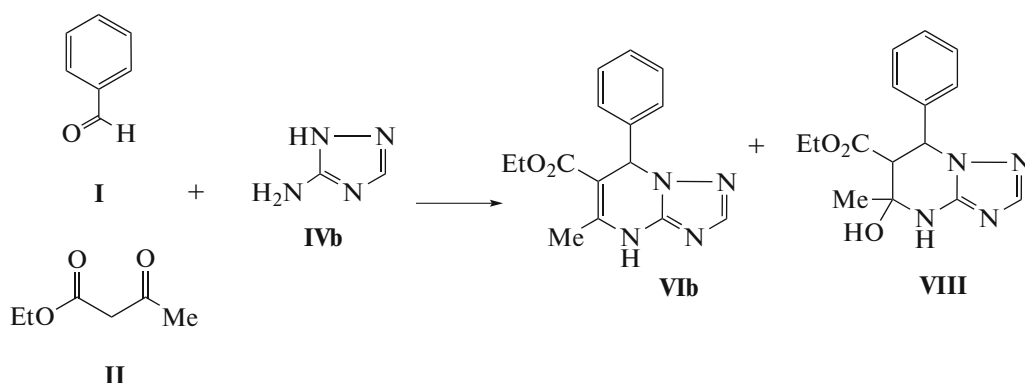
RESULTS AND DISCUSSION

Similar to the classical Biginelli reaction (synthesis of compounds **Va** and **Vb**), which does not occur at room temperature in the absence of a catalyst [27], benzaldehyde (**I**), AAE (**II**) and 5-aminotetrazole (**IVa**) according to the ^1H NMR and HPLC data practically do not interact among themselves at 22–23°C during a reaction time of 40 h (Table 1, no. 1). Replacing the ethanol and acetonitrile solvents with tetrahydrofuran results in an increase of **VIa** yield up to 8% (Table 1, no. 2 and 3). Some further increase in the product yield is observed with an increase of the reaction time from 40 h to 7 days (Table 1, no. 4). The reaction mass always contains the intermediate chalcone **VII**, which is produced by the interaction of benzaldehyde with AAE. If CF_3COOH is replaced by morpholine, the yield of **VIa** increases to 20% (Table 1, no. 5).

We also studied the influence of the nature of nanosized oxides (SiO_2 , Al_2O_3 , ZnO , MgO , TiO_2 , $\text{SiO}_2-\text{ZrO}_2$, SiO_2-MgO , $\text{SiO}_2-\text{TiO}_2$) on the yield of products. These oxides have a high specific surface area (from 46 to 394 m^2/g) and contain particles ranging in size from 10 to 80 nm. It turned out that in the presence of MgO , the reaction proceeds more selectively than in the presence of SiO_2 , ZnO , TiO_2 and Al_2O_3 (compare nos. 7–10 and 11 in Table 1). The best results were achieved using mixed nanooxides SiO_2-MgO and $\text{SiO}_2-\text{TiO}_2$.

A delay in adding aminoazole **IVa** for 30 min increases the yield of **VIa** up to 25%. Therefore, $\text{SiO}_2-\text{TiO}_2$ can be recommended as a catalyst for the stereoselective synthesis of compound **VIa**.

Dihydrotriazolopyrimidine (**Vib**) is practically not formed under the conditions of multicomponent synthesis at room temperature in THF in the absence of catalysts (Scheme 3). The main product is triazolotetrahydropyrimidine (**VIII**). The reaction is stopped at this stage and the cleavage of the water molecule does not occur [28]. A similar result is also observed in the presence of nanooxides Al_2O_3 or $\text{SiO}_2-\text{TiO}_2$.



Scheme 3. Products of the Biginelli reaction with participation of 3-aminotriazole.

Thus, at room temperature nanosized $\text{SiO}_2\text{-TiO}_2$ catalyzes the Biginelli reaction with the participation of 5-aminotetrazole (Table 1, no. 14) and don't catalyzes the same reaction with the participation of 3-aminotriazole (Table 2, no. 5).

To clarify the causes of the different behaviors of aminoazoles in interaction with benzaldehyde and AAE, and also different catalytic activities of nanosized Al_2O_3 and $\text{SiO}_2\text{-TiO}_2$, we studied the sorption of 5-aminotetrazole and 3-aminotriazole on the surface of nanosized Al_2O_3 and $\text{SiO}_2\text{-TiO}_2$ by IR-spectroscopy.

It is known that Lewis acid sites of nanosized oxides of metals and silicon are positively charged metal (silicon) atoms, whereas the Brønsted acid sites are the hydrogen atoms of the OH groups. In turn, the Brønsted base sites are the oxygen atoms of nanooxide and carboxylate groups of carbon dioxide sorbed on the catalyst surface [29].

According to the elemental analysis data, 5-aminotetrazole (**IVa**) is a monohydrate. Its IR spectrum (Fig. 1, spectrum 1) indicates the presence of the hydroxonium ion H_3O^+ , as evidenced by a fairly intense absorption in the $2768\text{--}2502\text{ cm}^{-1}$ ($\nu_{\text{H}_3\text{O}^+}$) range and at 1781 cm^{-1} ($\delta_{\text{as, H}_3\text{O}^+}$) [30]. This indicates considerable acidity of the NH group of the ring. According to the calculation results [31], absorption bands at 1450 , 1158 , 1064 and 996 cm^{-1} are related to

the vibrations of the tetrazole ring. In addition, the rocking vibrations of NH_2 groups also contribute to these vibrations. The position and relative intensity of the observed bands mostly coincide with data of [31]. The band at 1298 cm^{-1} was assigned to vibrations of the N-N=N group (by analogy with the findings of [31, 32]). A large number of bands in the region of the stretching vibrations of NH_2 (3478 and 3368 cm^{-1}) and NH groups (3338 cm^{-1}) and the presence of the split band of the deformation vibrations of the NH_2 groups (1640 and 1661 cm^{-1}) indicate the existence of an amino-imino tautomeric equilibrium [33], which is not observed using the methodology described in [31] for the preparation of samples in tablets with KBr.

The interaction of 5-aminotetrazole monohydrate with aluminum nanooxide results in disappearance of the absorption bands related to the oxonium ion because the oxide takes a water molecule from 5-aminotetrazole (Fig. 1, spectrum 2). Absorption bands that correspond to the stretching vibrations of NH- and NH_2 groups are clearly visible against the background of the water stretching vibration band of nanooxide at 3484 cm^{-1} ; in comparison with the spectrum of initial 5-aminotetrazole, the number of these bands decreases upon sorption. The absorption bands that correspond to the deformation vibrations of amino groups become more narrow and the band of the NH groups shift from 1590 to 1601 cm^{-1} . At the same time, the bands of the tetrazole ring exhibit significant changes: the 1064 cm^{-1} band splits into two (1068 and 1049 cm^{-1}) and the bands at 1158 and 1298 cm^{-1} shift to 1143 to 1265 cm^{-1} , respectively. These changes have been observed earlier in IR-spectroscopic studies of dihydrated 5-aminotetrazole [34]. The splitting and shift of the bands of the tetrazole cycle indicate a distortion of the molecule [35]. On the other hand, the observed changes of the spectral characteristics of aluminum oxide concern only the absorption band of carboxylate groups which is formed upon due to the sorption of CO_2 from the air on the oxide surface: the 1419 and 1465 cm^{-1} bands disappear and a band at 1451 cm^{-1} appears. This may

Table 2. The influence of the nature of the catalyst on the yield of compound **VIb** at $22\text{--}23^\circ\text{C}$ in the THF environment (according to ^1H NMR data)

No.	Catalyst	Yield VIb , %	Yield VIII , %
1	—	Traces	40
2	CF_3COOH	Traces	48
3	Morpholine	10	8
4	Al_2O_3	Traces	5
5	$\text{SiO}_2\text{-TiO}_2$	Traces	20

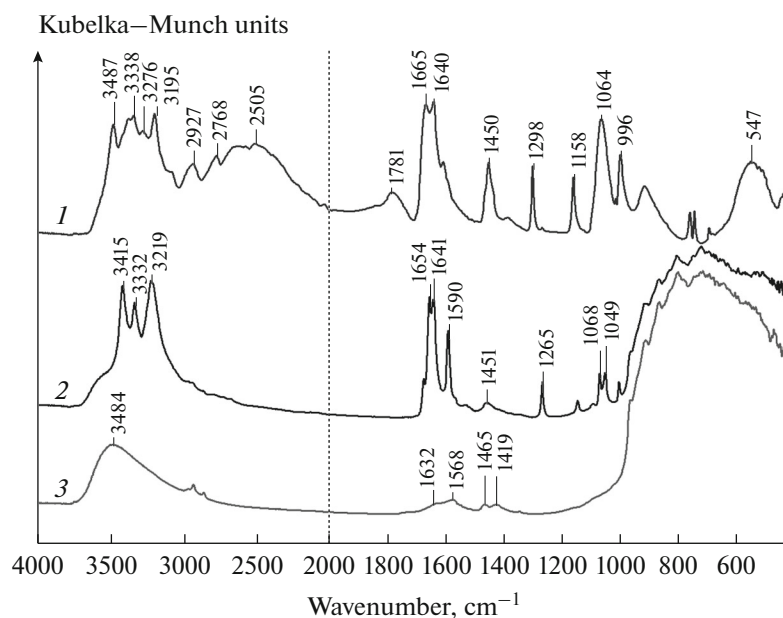
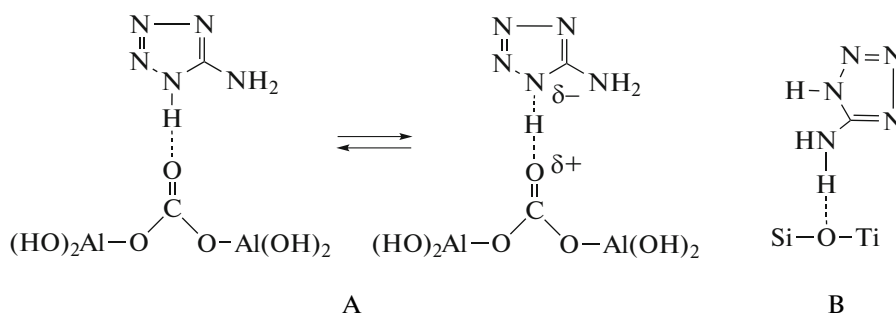


Fig. 1. The IR spectra of (1) monohydrate of 5-aminotetrazole, (2) monohydrate of 5-aminotetrazole sorbed on aluminum nanooxide, and (3) aluminum nanooxide.

indicate that the sorption of 5-aminotetrazole occurs by coordination of the NH group of the tetrazole ring mainly on the oxygen atoms of carboxylate groups of carbon dioxide (Scheme 4, A).

The sorption of 5-aminotetrazole on the surface of the $\text{SiO}_2\text{-TiO}_2$ composite also leads to destruction of the oxonium ion. In addition, the splitting of the deformation vibration band of the NH_2 group disappears: instead of the doublet at 1641 and 1668 cm^{-1} there is only one band at 1651 cm^{-1} . The spectrum also shows a band at 1454 cm^{-1} related to the vibrations of the tetrazole cycle, the remaining bands of this cycle are not seen against the background of the absorption of the composite. In the region of the stretching vibrations of N–H bonds (3500–3000 cm^{-1}) the number of bands decreases (Fig. 2). Such changes in the absorp-

tion of the stretching and deformation vibrations of amino groups imply that the equilibrium is shifted towards the tautomeric amine form and that the NH_2 group interacts with the surface of the composite at a higher energy of the complex system of intermolecular hydrogen bonds (IMHB) in the sorbate–sorber system than in the initial aminoazole. This is confirmed by the changes in the oxide spectrum: the shift of Si–O–Ti and Si–O–Si bands (from 1068 and 947 to 1082 and 955 cm^{-1} , respectively), which may be due to the interaction of the oxygen atom in these groups with 5-aminotetrazole (Scheme 4, A). Upon the coordination of the NH_2 group with the surface of the composite, the NH group of the ring remains free, which allows its participation in the Biginelli reaction (Scheme 4, B).



Scheme 4. The proposed coordination of 5-aminotetrazole on nanooxides Al_2O_3 (A) and $\text{SiO}_2\text{-TiO}_2$ (B).

Thus, the manner of 5-aminotetrazole coordination on the surface of Al_2O_3 and $\text{SiO}_2\text{-TiO}_2$ nanoo-

xides is different: in the first case, the proton of the NH group of the tetrazole cycle interacts with the sur-

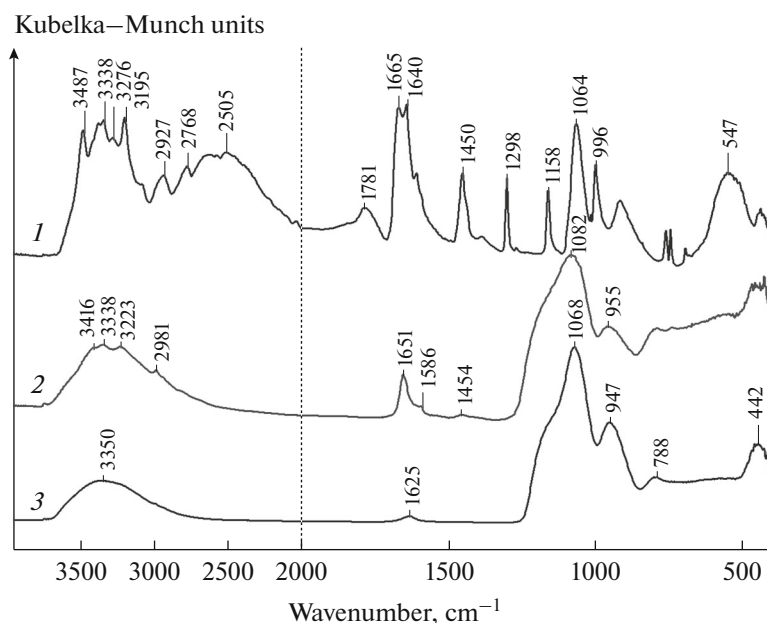
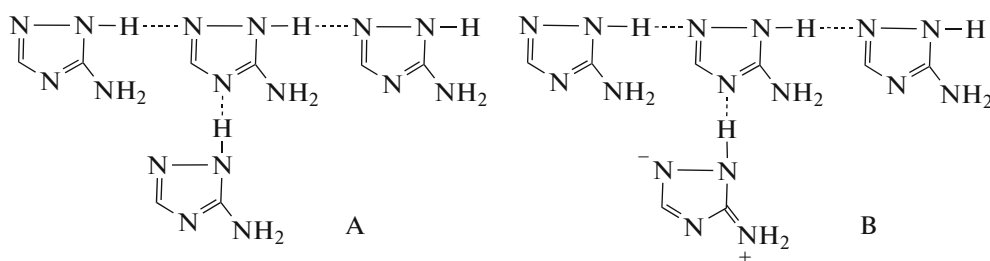


Fig. 2. The IR spectra of (1) dihydrate of 5-aminotetrazole, (2) dihydrate of 5-aminotetrazole sorbed on $\text{SiO}_2\text{-TiO}_2$ nanooxide, and (3) $\text{SiO}_2\text{-TiO}_2$ nanooxide.

face, while in the second case it is the proton of the NH_2 group. Correspondingly, in the first case the NH group is blocked, while in the second case it is free. This explains the effectiveness of $\text{SiO}_2\text{-TiO}_2$ nanooxide in contrast to Al_2O_3 nanooxide in the Biginelli reaction with the participation of 5-aminotetrazole.

The IR spectrum of 3-aminotriazole (which, according to the elemental analysis data, is anhydrous) in the $2725\text{--}2771\text{ cm}^{-1}$ range shows the bands that

correspond to the stretching vibrations of a strongly associated NH group (Fig. 3). The absorption band at 1639 cm^{-1} is due to the deformation vibrations of the NH_2 group. The band at 1593 cm^{-1} corresponds to the vibrations of the $\text{C}=\text{N}$ bond of the triazole cycle, while the bands due to vibrations of the five-membered cycle are below 1400 cm^{-1} [36]. Apparently, the formation of IMHB of the $\text{NH}\dots\text{N}$ type with high energy is characteristic for 3-aminotriazole (Scheme 5, A).



Scheme 5. The proposed coordination of 5-aminotriazole due to the formation of IMHB in (A) the absence and (B) presence of nanooxide $\text{SiO}_2\text{-TiO}_2$.

When 3-aminotriazole is sorbed on aluminum oxide (Fig. 3), absorption bands in the $1419\text{--}1445\text{ cm}^{-1}$ region, which correspond to the vibrations of carboxylate groups of the oxide, disappear; this suggests that these groups are replaced by the sorbate interacting with the oxygen atoms of the surface.

The absorption bands that correspond to the stretching vibrations of NH and NH_2 groups are seen against the background of the broad band at 3350 cm^{-1} due the stretching vibrations of water of nanooxide. The NH and NH_2 bands practically do not change

after the sorption of 3-aminotriazole. The absorption bands due to the deformation of NH bonds of triazole are superimposed on the deformation bands of water in the $1500\text{--}1650\text{ cm}^{-1}$ range, and the sorption practically does not affect the shape of the spectrum. This indicates that the system of strong IMHB is preserved. It can be assumed that 3-aminotriazole molecules are adsorbed physically and settle in a flat manner on the surface of Al_2O_3 .

The 3-aminotriazole molecules settle in a similar way in the case of sorption on the surface of $\text{SiO}_2\text{-}$

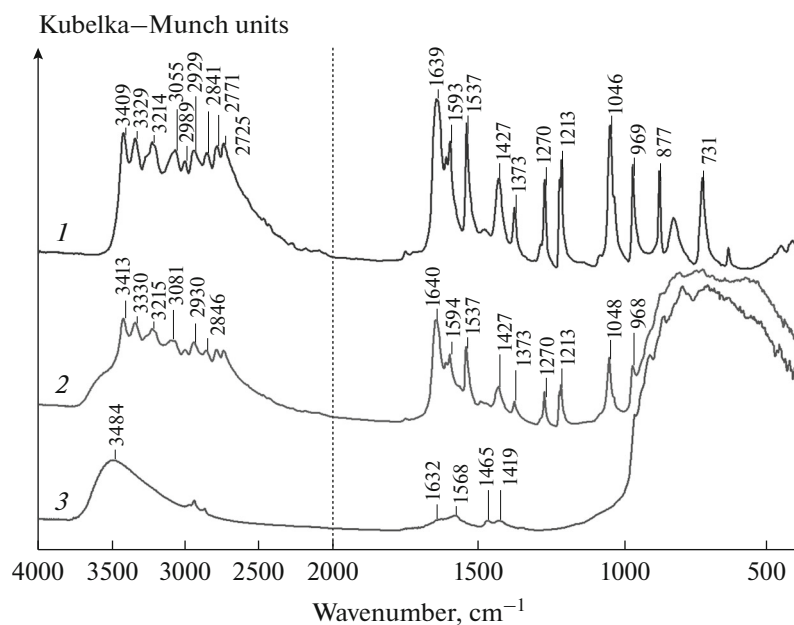


Fig. 3. The IR spectra of (1) 3-aminotriazole, (2) 3-aminotriazole sorbed on Al_2O_3 nanooxide, and (3) nanooxide of aluminium.

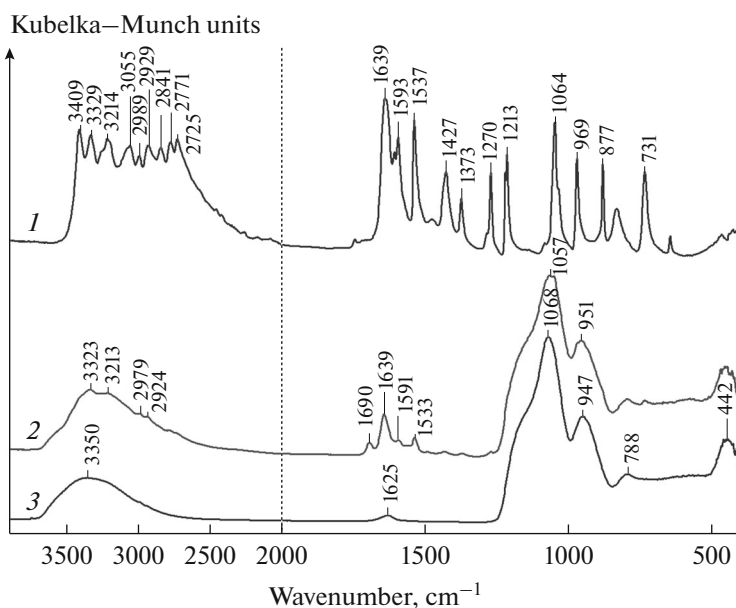


Fig. 4. The IR spectra of (1) 3-aminotriazole, (2) 3-aminotriazole sorbed on $\text{SiO}_2\text{-TiO}_2$ nanooxide, and (3) $\text{SiO}_2\text{-TiO}_2$ nanooxide.

TiO_2 composite (Fig. 4). In contrast to the sorption on Al_2O_3 , the IMHB system is somewhat disturbed. This conclusion is supported by the decrease in the intensity of the bands in the 2700–3000 cm^{-1} region and by the redistribution of the intensities of the bands due to the stretching vibrations of N–H bonds in the 3408–3335 cm^{-1} range, which can be seen against the background of the band of water of nanooxide at 3350 cm^{-1} . The band that appears at 1690 cm^{-1} should be assigned to the vibrations of exocyclic $\text{C}=\text{NH}_2^+$ of the tautomeric imine form [36–38], i.e., one part of the molecules is in the amine form and the other part is in the

tautomeric imine form (Scheme 5, B). The maxima of the absorption bands that correspond to the vibrations of the Si–O–Si and Si–O–Ti bonds are shifted from 1068 to 1057 cm^{-1} and from 947 to 951 cm^{-1} , respectively. The O atoms of these are apparently involved in the sorption of 3-aminotriazole.

Thus, the different catalytic activities of Al_2O_3 and $\text{SiO}_2\text{-TiO}_2$ nanooxides in the Biginelli reaction with the participation of 5-aminotetrazole may be explained by the feature of the coordination of 5-aminotetrazole molecule on the surface. On the surface of Al_2O_3 5-aminotetrazole is coordinated by the NH

group of tetrazole cycle, which is accompanied its passivation, whereas on the $\text{SiO}_2\text{-TiO}_2$ surface it is coordinated by the NH_2 group; thus, the NH group of aminoazole remains free and can participate in the reaction. The 3-aminotriazole molecules settle in a flat manner on the surface of Al_2O_3 and $\text{SiO}_2\text{-TiO}_2$ nanooxides and are bound with each other by IMHB, which constrains the participation of the NH group of the tetrazole cycle in the reaction. This explains the lack of catalytic activity of Al_2O_3 and $\text{SiO}_2\text{-TiO}_2$ nanooxides in the Biginelli reaction with the participation of 3-aminotriazole.

The results of the present study of the IR spectra of sorbed aminoazoles **IVa** and **IVb** allow us to recommend nanosized $\text{SiO}_2\text{-TiO}_2$ (3 : 1) as a promising catalyst for the Biginelli reaction with the participation of 5-aminotetrazole at room temperature.

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