Electronic spectra of organic bases adsorbed on the surface of the vanadium-phosphoric catalyst

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The electronic spectra of basic indicators adsorbed on the dehydroxylated vanadium-phosphoric catalyst were studied. It has been found that the molecules of 4-aminoazobenzene, 4-(4'-tolylazo)-2-methylaniline, 4-phenylazodiphenylamine, and 4-nitroaniline are adsorbed in the ionized acid form while 2-nitroaniline as a basic indicator is not adsorbed in the conjugated acid form. The acidity strength of the surface adsorption centres thus revealed is attributed to the Lewis centres.

Исследовались электронные спектры основных индикаторов, адсорбированных на дегидроксилированном ванадиево-фосфорном катализаторе. Обнаружено, что молекулы 4-аминоазобензола, 4-(4'-толилазо)-2-метиланилина, 4-фенилазодифениламина и 4-нитроанилина адсорбируются в ионизованной кислой форме, в то время как 2-нитроанилин как основной индикатор уже не адсорбируется в сопряженной кислой форме. Таким образом определенная сила кислотности поверхностных адсорбционных центров приписана льюисовым центрам.

The catalysts on the base of some compounds containing vanadium and phosphorus belong among efficacious contact catalysts of the partial oxidation of n-butane to maleic anhydride [1]. The study of the adsorption centres of these catalysts appears to be interesting from the viewpoint of deeper elucidation of that process.

In paper [2] dealing with the adsorption of ammonia on $VOPO_4$ and $(VO)_2P_2O_7$ the existence of acid adsorption centres of the Brönsted and Lewis type has been evidenced. In this paper, we investigate the electronic absorption spectra of some basic indicators adsorbed on the dehydroxylated vanadium--phosphoric catalyst and thus contribute to better knowledge of acid properties of its surface.

Experimental

The investigated vanadium-phosphoric catalyst with the ratio $n(V) : n(P) = 1 : 1.2$ was prepared by the method described in paper [3]. It was treated by two hours' evacuation

at 760 K before the adsorption of indicators. 4-Aminoazobenzene (AAB; $pK_a = 2.8$), 4-(4'-tolylazo)-2-methylaniline (TAMA; $pK_a = 2.0$), 4-phenylazodiphenylamine (PAD-PA; $pK_a = 1.5$), 4-nitroaniline ($pK_a = 1.1$), and 2-nitroaniline ($pK_a = -0.2$) (products of Aldrich Chemical Company) were used as molecular probes. Other chemicals used were anal. grade reagents. The values of pK_a for AAB and TAMA are stated in literature [4, 5] and employed because of the colour transition yellow (basic form)—red (conjugated acid form). According to [6], the value of pK_a valid for PADPA refers to the colour transition yellow (basic form)—purple (conjugated acid form). The pK_a values of nitroanilines have been taken from literature [4].

The dehydroxylation of the investigated catalyst was investigated by infrared spectroscopy. The samples were pressed into tablets with planary density of $7.5 \, mg/cm^2$ and subjected to measurement. The infrared spectra were recorded with a spectrometer Perkin—Elmer 577 equipped with a vacuum cell.

The electronic spectra of the basic indicators adsorbed on the surface of the vanadium-phosphoric catalyst were examined in the wavelength region 250 nm—600 nm with a spectrophotometer PU 8800 UV VIS (Philips) completed by the equipment for measurement of diffusion reflection. The adsorption of indicators took place in a vacuum cell through the gaseous phase at temperatures up to 393 K.

Results and discussion

The surface state of the catalyst prior to adsorption of indicators was investigated by infrared spectroscopy which showed that the evacuation of sample at 300 K brought about extinguishing of the band at $\bar{\nu} = 1620 \, cm^{-1}$. We attribute this band to bending vibrations in molecules of the physically adsorbed water.
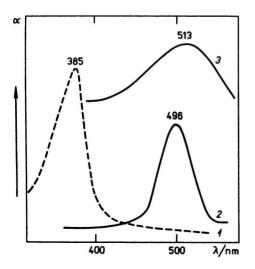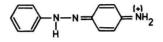

Fig. 1. Spectra of 4-aminoazobenzene:
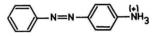1. in hexane; 2. in 30% H_2SO_4; 3. adsorbed on the vanadium-phosphoric catalyst.

Further evacuation at 500 K results in an intensity decrease of the broad absorption band with the maximum at $\bar{v} = 3400$ cm^{-1} which may be assigned to stretching vibrations in the superficial —OH groups. This band disappears after two hours' evacuation at 760 K.

The electronic spectra of indicators were investigated in solutions as well as in the adsorbed state. Fig. 1 represents the electronic spectra of AAB dissolved in hexane, in 30% solution of sulfuric acid, and adsorbed on the catalyst. According to [5], the following forms of AAB exist in acid media of varying strength
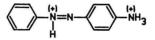
<p style="text-align:center">quinoid form with maximum at $\lambda = 495$ nm</p>

<p style="text-align:center">ammonium form with maximum at $\lambda = 325$ nm</p>
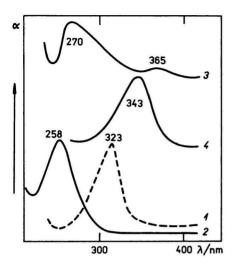
<p style="text-align:center">two-charge form with maximum at $\lambda = 430$ nm</p>

It follows from these facts that AAB is adsorbed on the surface of the vanadium--phosphoric catalyst in the acid quinoid form.

TAMA gives in nonpolar medium an absorption band with the maximum at the wavelength $\lambda = 380$ nm. An absorption band at the wavelength $\lambda = 493$ nm was observed in the medium of 30% sulfuric acid. After adsorption of TAMA on the vanadium-phosphoric catalyst, a broad absorption band with the maximum at $\lambda = 514$ nm appears in its electronic spectrum. On the basis of these facts and similarity between the structures of TAMA and AAB, we may draw the conclusion that TAMA is adsorbed on the investigated sample in the acid quinoid form.

The electronic spectrum of PADPA in nonpolar medium shows a band at $\lambda = 388$ nm while a band at $\lambda = 532$ nm appears if the medium of 30% sulfuric acid is used. After adsorption of PADPA on the vanadium-phosphoric catalyst, a broad absorption band of the indicator was observed at $\lambda = 546$ nm. According to [7], the physical adsorption of PADPA manifests itself by absorption of radiation in the wavelength region 400—450 nm while the chemisorption shows

itself in the region 540 nm. Thus it follows that PADPA is adsorbed on the surface of the vanadium-phosphoric catalyst in the ionized acid form.

Fig. 2. Spectra of 4-nitroaniline:
1. in isooctane; 2. in 30 % H_2SO_4; 3. adsorbed on the vanadium-phosphoric catalyst; 4. in isooctane—ethanol mixture.
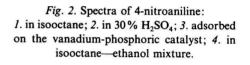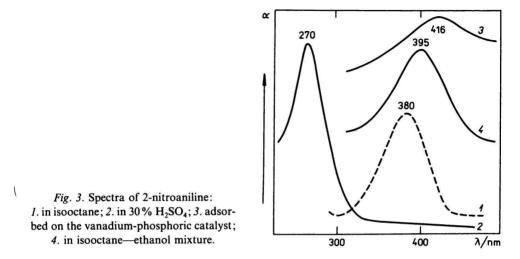
Fig. 2 shows the positions of the band corresponding to $n(NH_2) \rightarrow \pi(NO_2)$ charge transfer [8] in 4-nitroaniline dissolved in isooctane, dissolved in 30 % sulfuric acid, and adsorbed on the vanadium-phosphoric catalyst. The influence of the polar medium which is not able significantly to transfer 4-nitroaniline from the basic form into the conjugated acid ionized form is to be seen in the electronic spectrum of 4-nitroaniline dissolved in an isooctane—ethanol mixture. The spectrum of 4-nitroaniline adsorbed on the catalyst shows absorption bands at $\lambda = 270$ nm and $\lambda = 365$ nm. We assign the first absorption band which vanishes in the course of subsequent adsorption of water vapour to an $n \rightarrow \pi$ transition in the acid ionized form of the indicator. The poorly intensive absorption band at $\lambda = 365$ nm the intensity of which increases in the course of subsequent water adsorption is to be assigned to an $n \rightarrow \pi$ transition in the physically adsorbed nonionized molecules of 4-nitroaniline. On the basis of these facts, we may deduce that 4-nitroaniline is predominantly adsorbed on the vanadium-phosphoric catalyst in the ionized acid form. The influence of water on the adsorbed indicators has been discussed in [9].

The positions of $n(NH_2) \rightarrow \pi(NO_2)$ electron transitions in the molecules of 2-nitroaniline dissolved in isooctane, dissolved in 30 % sulfuric acid, dissolved in an isooctane—ethanol mixture, and adsorbed on vanadium-phosphoric catalyst are represented in Fig. 3. The spectral records show that 2-nitroaniline as a basic indicator is not adsorbed on the investigated surface in the conjugated acid form. The influence of the polar surface of catalyst on the adsorbed

molecules of 2-nitroaniline is observable in the bathochromic shift in $n \to \pi$ transitions in the adsorbed molecules of indicator with respect to $n \to \pi$ transitions in the molecules of indicator dissolved in nonpolar medium [8].

Fig. 3. Spectra of 2-nitroaniline: 1. in isooctane; 2. in 30 % H_2SO_4; 3. adsorbed on the vanadium-phosphoric catalyst; 4. in isooctane—ethanol mixture.

The strength of acid adsorption centres of a solid acid may be valuated according to the smallest pK_a value of the basic indicator which has been ionized in the course of adsorption on the investigated solid substance [9].

For instance, the dehydroxylated vanadium-phosphoric catalyst was still able in the course of adsorption to transform 4-nitroaniline ($pK_a = 1.1$) from the basic form into the conjugated acid ionized form. The strength of acidity of the superficial adsorption centres of the investigated catalyst which has been estimated on the basis of the state of surface prior to adsorption of indicators may be attributed to the Lewis acid centres.

References

1. Brutovský, M. and Gerej, Š., *Collect. Czechoslov. Chem. Commun. 47*, 403 (1982).
2. Rozhkova, E. V. and Kuznetsov, V. A., *Ukr. Khim. Zh. 47*, 1036 (1981).
3. Brutovský, M., *CSc. Thesis*. Akad. Nauk SSSR IFCH L. V. Pisarzhevskogo, Kiev, 1984.
4. Tanabe, K., *Tverdye kisloty i osnovaniya*, pp. 13—42. Mir, Moscow, 1973.
5. Sivalov, E. G., Vasiľev, N. G., and Ovcharenko, F. D., *Kinet. Katal. 22*, 1590 (1981).
6. Antipina, T. V., Bulgakov, O. V., and Yushenko, V. V., *Kinet. Katal. 9*, 196 (1968).
7. Leftin, H. P. and Hobson, M. C., *Kataliz*, pp. 40—41. Mir, Moscow, 1967.
8. Zubareva, N. A., Kiselev, H. V., and Lygin, V. N., *Kinet. Katal. 18*, 241 (1977).
9. Kotsarenko, N. S., Karakchiev, L. G., and Dzisko, V. A., *Kinet. Katal. 9*, 158 (1968).

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