Adsorption of benzene on the $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst

L. D. Asnin,* A. A. Fedorov, and Yu. S. Chekryshkin

Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences,
13 prosp. Lenina, 614990 Perm, Russian Federation.
Fax: +7 (343 2) 12 6237. E-mail: cheminst@mpm.ru

Adsorption of benzene on the $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts was studied in the temperature interval from 443 to 493 K and at partial pressures of the adsorbate ranging from 1 to 400 Pa. The adsorption isotherms were plotted. The isosteric heats and various entropy characteristics of adsorption were determined. Mobility of benzene in the adsorption layer is restricted compared to the model of ideal dimeric gas. The adsorbed amounts of benzene and chlorobenzene are compared.

Key words: adsorption, benzene, chlorobenzene, vanadium pentaoxide, alumina.

The problem of characterization of active sites of vanadium oxide catalysts is of interest for many researchers. Adsorption of chlorobenzene (CB) and benzene on the $\gamma\text{-}Al_2O_3$ support and catalysts of deep oxidation of the chloroaromatic compounds $CuCl_2/\gamma\text{-}Al_2O_3$ and $V_2O_5/\gamma\text{-}Al_2O_3$ has previously[1—4] been studied. IR spectroscopic and thermodesorption studies showed that the high-temperature adsorption of benzene on the vanadium-aluminum oxide catalyst occurred to form a σ-complex due to the dissociation of the C—H bond.[5] It was assumed in several works that benzene favors reduction of vanadium during adsorption on the vanadium oxide catalysts.[5—8] It was of interest to study the thermodynamics of adsorption equilibrium in the benzene—$V_2O_5/\gamma\text{-}Al_2O_3$ and CB—$V_2O_5/\gamma\text{-}Al_2O_3$ systems.

Experimental

The V_2O_5 (5%) catalyst on $\gamma\text{-}Al_2O_3$, whose synthesis has previously[4] been described, was used. The specific surface area of the catalyst determined by the method of nitrogen desorption was 115 $m^2\ g^{-1}$. The true density obtained picnometrically using the toluene method[9] was 3.6 $g\ cm^{-3}$. The pore volume found from an increase in the weight of the samples pre-dried at 473 K after saturation with benzene vapors in a desiccator at room temperature was 0.8 $cm^3\ g^{-1}$.

Adsorption isotherms were determined chromatographically[10] in helium in the temperature interval from 443 to 493 K. Experimental details have been described previously.[4] Benzene (reagent grade) distilled above freshly calcined zeolite NaA was used for measurements.

The relative error of determination of the excessive amount adsorbed (Γ) and partial pressure of the adsorbate (p) did not exceed 5%. The error of calculation of the isosteric heat of adsorption (q_{st}) decreased monotonically with an increase in Γ: from 5 kJ mol^{-1} for $\Gamma = 0.9 \cdot 10^{-10}$ mol m^{-2} to 2 kJ mol^{-1} for $\Gamma \geq 35 \cdot 10^{-10}$ mol m^{-2}. The q_{st} value was calculated from the linear plot of ln$p$ *vs.* inverse temperature at the specified Γ. The error of calculation of the entropy characteristics of adsorption was 7 J mol^{-1} K^{-1}.

Results and Discussion

On introducing V_2O_5 on the support a remarkable (28%) decrease in the surface area of the catalyst was observed (the specific surface area of the support was 160 $m^2\ g^{-1}$). It is most likely that the vanadium particles are adsorbed on the support surface and structured to prevent the access into micropores. Probably, these structures are not dimeric, although, as follows from the published data,[11—14] they are not yet the crystalline phase. The concentration of V_2O_5 on the support surface calculated per V^{5+} ion was 4.8 μmol m^{-2}. Accepting that for the compact monolayer the concentration of V^{5+} is[13] 13 μmol m^{-2}, we obtain the degree of filling 0.37. In reality, it can be lower due to the possibility of the volume pore filling and polylayer adsorption of the VO_x particles.

The adsorption isotherms of benzene on the catalyst under study are presented in Fig. 1. Their shape differs insignificantly from that of the linear plots and are well (with the determination coefficient $r^2 > 0.999$) approximated by the equation of the Freundlich adsorption isotherm $\Gamma = Cp^{1/n}$, where p is the partial pressure of the adsorbate, and C and n are the temperature-dependent coefficients. The plot of the n parameter *vs.* T in the temperature interval under study can be described by the equation $n(T) = 533/T$ ($r^2 = 0.96$).

The plot of q_{st} of benzene *vs.* Γ (Fig. 2) coincides within the experimental error with the similar plot ob-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 845—847, April, 2003.

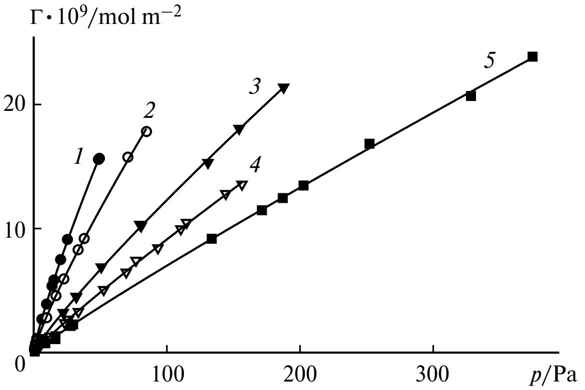

Fig. 1. Adsorption isotherms of benzene (points) at 443 (*1*), 453 (*2*), 473 (*3*), 483 (*4*), and 493 K (*5*). The isotherms calculated using the Freundlich equation are shown by solid lines.

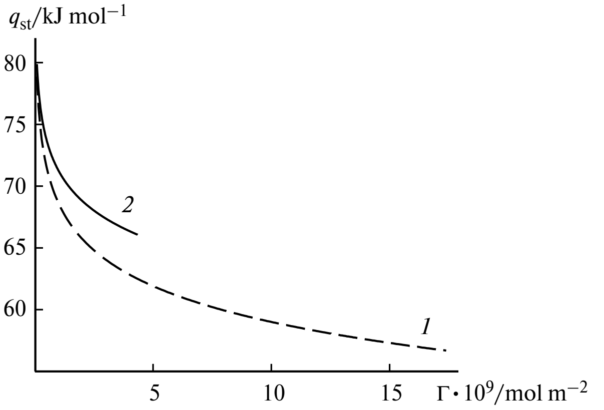

Fig. 2. Isosteric heats of adsorption (q_{st}) of benzene (*1*) and chlorobenzene (*2*) on $V_2O_5/\gamma\text{-}Al_2O_3$ as a function of the amount adsorbed (Γ). The data refer to temperature intervals of 443—493 K (benzene) and 463—513 K (chlorobenzene) inside which q_{st} is independent of *T*.

tained on the support,[2] *i.e.*, the modification of the $\gamma\text{-}Al_2O_3$ surface by 5% vanadium oxide does not result in the appearance of adsorption sites which are more active toward benzene.

Comparison of the $q_{st}(\Gamma)$ plots for CB [4] and benzene on $V_2O_5/\gamma\text{-}Al_2O_3$ (see Fig. 2) shows that they are close at the coverages under study (this interval for CB is narrower than that for benzene) and, meanwhile, tend to deviate with an increase in the degree of filling. Note that although the difference between q_{st} of benzene and CB on the support is small[2] but still more noticeable than that on $V_2O_5/\gamma\text{-}Al_2O_3$, being 6—12 kJ mol^{-1} depending on the amount adsorbed. Thus, V_2O_5, when introduced in the amounts lower than a half monolayer capacity of the support, levels out a weak difference in the energies characterizing adsorption of benzene and CB on $\gamma\text{-}Al_2O_3$.

The quantitative characteristics of adsorption of the adsorbates on $V_2O_5/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$ can be obtained from the adsorption isobars (Fig. 3). As can be seen, CB is better adsorbed on $V_2O_5/\gamma\text{-}Al_2O_3$ than benzene. Since the heats of adsorption of the adsorbates are close, the enhanced adsorption of CB is evidently related to the fact that at the same temperature its saturation vapor pressure is lower than that of benzene. The adsorption capacity of the supported catalyst toward benzene (calculated per surface unit) is higher than that of Al_2O_3.

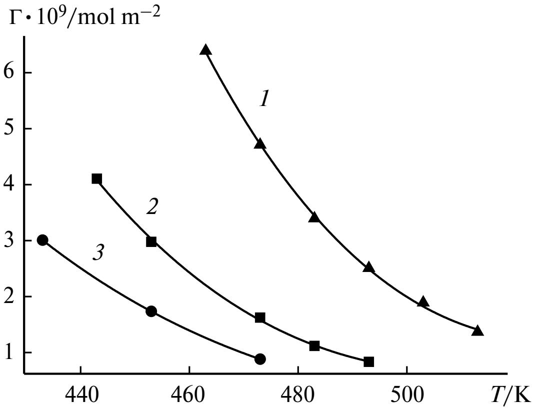

Fig. 3. Adsorption isobars of chlorobenzene on $V_2O_5/\gamma\text{-}Al_2O_3$ (*1*), benzene on $V_2O_5/\gamma\text{-}Al_2O_3$ (*2*), and benzene on $\gamma\text{-}Al_2O_3$ (*3*) at $p = 10$ Pa.

Once q_{st} is known, one can calculate the change in the differential excessive entropy during adsorption $\Delta\bar{S}^s = -q_{st}/T'$, where T' is the temperature to which the q_{st} value is referred; here $T' = 488$ K. In the case where adsorption obeys the equation of the Freundlich isotherm, one can go from the differential entropy to the change in the averaged-molar entropy ($\Delta\tilde{S}^s$) using the expression[15] $\Delta\tilde{S}^s = \Delta\bar{S}^s + R[n(T') + T'n'(T')]$, where $n'(T')$ is the derivative of the $n(T)$ function at the point T', and R is the universal gas constant. Comparison of the experimental $\Delta\tilde{S}^s$ values with $\Delta\tilde{S}^s{}_{theor}$ calculated from the model of ideal dimeric gas[16] gives some data on the behavior of molecules in the adsorption layer. For this purpose, it is convenient to use the function $D = |\Delta\tilde{S}^s| - |\Delta\tilde{S}^s{}_{theor}|$, which characterizes the degree of mobility loss of the adsorbate molecules in the adsorption layer. The $\Delta\tilde{S}^s{}_{theor}$ value is calculated using the formula[16]

$$-\Delta\tilde{S}^s{}_{theor} = R\ln(\Gamma/c) + R[0.5 + \ln(2\pi mkT/h^2)^{0.5}], \qquad (1)$$

where c is the adsorbate concentration in the equilibrium gas phase, m is the weight of the adsorbate molecule, h is the Planck constant, and k is the Boltzmann constant.

As can be seen from the data in Fig. 4, the degrees of mobility loss (D) for benzene and CB are higher than zero. This indicates that molecules in the adsorption layer are less mobile than molecules described by the model of ideal dimeric gas. The decrease in the D values of the adsorbed molecules with an increase in Γ is explained by the fact that the molecules, which were first to adsorb on the most active sites of the surface are stronger localized

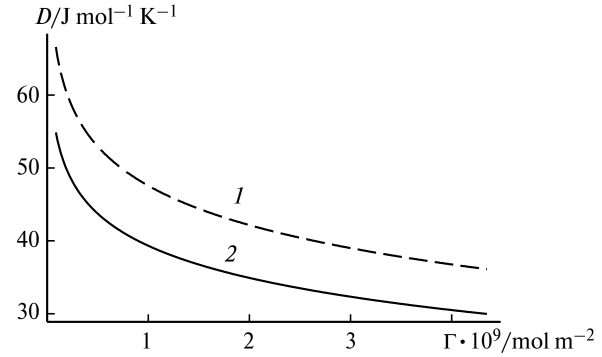

Fig. 4. Degree of mobility loss (D) as a function of the amount adsorbed of benzene (*1*) and chlorobenzene (*2*) on $V_2O_5/\gamma\text{-}Al_2O_3$ at $T = 488$ K.

than the molecules adsorbed from the next portions of the adsorbate. As the amount adsorbed increases, the properties of the adsorption layer approach those of the ideal dimeric gas. The D function decreases with retardation. The D function decreases sharply with an increase in Γ to ~10^{-10} mol m^{-2}, whereas with the further increase in Γ, the degree of mobility loss decreases fairly weakly. Therefore, the number of sites to which the adsorbate molecules are attached on the catalyst and support surface[2,3] for a relatively long time is very small (~10^{-2}% surface).

The plots of the D functions for benzene and CB run parallel, but the D value is higher for benzene. Analysis of the data in Table 1 and in a similar table published previously[4] shows that D(benzene) > D(CB) due to the difference in $\Delta\tilde{S}_{\text{theor}}$ of the adsorbates. This difference, in turn, is related to the fact that the term $R\ln(\Gamma/c)$ in the right part of Eq. (1) for benzene is by ~10 J mol^{-1} K^{-1} lower than that for CB. The second term of this equation differs insignificantly for the adsorbates (215.7 and 217.2 J mol^{-1} K^{-1} for benzene and CB, respectively). Taking into account that the isosteric heats of adsorption of the adsorbates coincide, we can explain the lower Γ/c ratio for benzene by a higher pressure of the saturated benzene vapor.

Table 1. Entropy characteristics of benzene adsorption on $V_2O_5/\gamma\text{-}Al_2O_3$ ($T = 488$ K)

$\Gamma\cdot10^9$ /mol m^{-2}	$-\Delta\tilde{S}^{s}$	$-\Delta\tilde{S}^{s}_{\text{theor}}$
	J mol^{-1} K^{-1}	
0.09	161.6	95.0
0.44	147.8	93.7
0.87	141.8	93.2
1.74	135.9	92.7
3.48	130.0	92.1
8.70	122.1	91.4
17.4	116.1	90.8

Mobility of adsorbed molecules is known to increase with temperature. The temperature, above which the adsorption layer is formally similar to the ideal dimeric gas, can be estimated using the temperature plot of the exponent in the equation of the Freundlich isotherm. When the temperature increases, the power dependence between Γ and p is degenerated to a linear plot. In the transition point $n(T) = 1$.

The temperature in the transition point (T_{tr}) is 533 K for the benzene—$V_2O_5/\gamma\text{-}Al_2O_3$ systems. Using this value, one can estimate the order of the upper limit for the activation energy (E_a) of surface diffusion. The E_a value should be lower than the energy per degree of freedom of the forward movement at the temperature T_{tr}, *i.e.*, $0.5RT_{\text{tr}}$, which is ~2 kJ mol^{-1}.

According to the thermodynamic characteristics, benzene adsorption on the $V_2O_5(5\%)/\gamma\text{-}Al_2O_3$ catalyst is similar to the adsorption of CB. The observed differences are related to a higher saturation vapor pressure of benzene. This confirms the conclusion[17] that, when the V_2O_5 concentration in the V_2O_5/Al_2O_3 catalyst does not exceed 10%, the type of acidity of the support remains unchanged but the distribution of acid-site strengths becomes more uniform, although the fraction of weak sites increases. This explains, most likely, why the isosteric heats for benzene and CB adsorption on $V_2O_5/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$ are close.

The authors thank R. M. Yakushev for determination of the specific surface areas.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-96405Ural).

References

1. A. A. Fedorov, Yu. S. Chekryshkin, and N. G. Shadrina, *Zh. Prikl. Khim.*, 1998, **71**, 1828 [*Russ. J. Appl. Chem.*, 1998, **71**, No. 11 (Engl. Transl.)].
2. L. D. Asnin, A. A. Fedorov, and Yu. S. Chekryshkin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 65 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 68].
3. L. D. Asnin, Ph. D. (Chem.) Thesis, Institute of Technical Chemistry, Ural Branch, RAS, Perm, 2002, 159 pp. (in Russian).
4. L. D. Asnin, A. A. Fedorov, Yu. S. Chekryshkin, and R. M. Yakushev, *Zh. Prikl. Khim.*, 2001, **74**, 1417 [*Russ. J. Appl. Chem.*, 2001, **74**, No. 9 (Engl. Transl.)].
5. I. V. Davidenko, A. A. Davydov, Yu. I. Pyatnitskii, Yu. V. Belokopytov, and A. G. Agazade, *Zh. Fiz. Khim.*, 1991, **65**, 164 [*Russ. J. Phys. Chem.*, 1991, **65**, No. 1 (Engl. Transl.)].
6. R. S. G. Ferreira, P. G. P. de Oliveira, and F. B. Norohna, *Appl. Catal., B: Environ.*, 2001, **29**, 275.
7. I. K. Badalova and L. N. Vorob´ev, *Uzb. Khim. Zh.* [*Uzbek Chem. J.*], 1991, No. 1, 30 (in Russian).
8. I. K. Badalova and L. N. Vorob´ev, *Uzb. Khim. Zh.* [*Uzbek Chem. J.*], 1990, No. 6, 38 (in Russian).

9. Zh. F. Galimov, G. G. Dubinina, and M. M. Masagutov, *Metody analiza katalizatorov neftepererabotki* [*Methods of Analysis of Oil Processing Catalysts*], Khimiya, Moscow, 1973, p. 49 (in Russian).
10. A. V. Kiselev and Ya. I. Yashin, *Gazo-adsorbtsionnaya khromatografiya* [*Gas Adsorption Chromatography*], Nauka, Moscow, 1967, 256 pp. (in Russian).
11. *Vanadievye katalizatory okisleniya geterotsiklicheskikh soedinenii* [*Vanadium Catalysts of Oxidation of Heterocyclic Compounds*], Ed. M. V. Shimanskaya, Zinatne, Riga, 1990, p. 48 (in Russian).
12. M. A. Vuurman, I. E. Wachs, and A. M. Hirt, *J. Phys. Chem.*, 1991, **95**, 9928.
13. I. E. Wachs, G. Deo, B. M. Weckhuysen, A. Andreini, M. A. Vuurman, M. de Bour, and M. D. Amiridis, *J. Catal.*, 1996, **161**, 211.
14. I. E. Wachs and B. M. Weckhuysen, *Appl. Catal., A: General*, 1997, **157**, 167.
15. L. D. Asnin, A. A. Fedorov, and Yu. S. Chekryshkin, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 175 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 178 (Engl. Transl.)].
16. A. A. Lopatkin, *Zh. Fiz. Khim.*, 1997, **71**, 916 [*Russ. J. Phys. Chem.*, 1997, **71**, No. 5 (Engl. Transl.)].
17. D. V. Spiridonova, E. A. Fokina, K. N. Spiridonov, and O. V. Krylov, *Kinet. Katal.*, 1977, **18**, 1495 [*Kinet. Catal.*, 1977, **18**, No. 5 (Engl. Transl.)].

Received November 4, 2002;
in revised form January 5, 2003