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Adsorption-Order Dependence of the Numbers of Spins of Coexisting Two Radical Species on an HY Type Zeolite

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Synopsis. The number of spins of coexisting two-radical species on an HY-type zeolite (HY) in the absence of a solvent were independently determined with electron paramagnetic resonance spectroscopy. The coexistence of both donors and acceptor molecules on HY gave rise to the increasing numbers of both cations and anion radicals and to their adsorption-order dependence. The numbers of coexisting cations and anion radicals were independent of, while their maximal numbers of spins were dependent on, the spin-generating abilities of the donors and acceptors. Furthermore, a small enhancement of radicals and a remarkable adsorption-order dependence arose in a solvent-free ternary system comprising HY and either two donors or two acceptors.

We have determined the number of spins generated in a solvent (heptane)-free system comprising an HY-type zeolite (HY) and single or two organic compounds.[1] The number of spins increased with the passage of time, and finally attained a constant number of spins (CNS) at adsorption equilibrium. The CNS value of the binary (HY-organic) system was reversible and linear to the amount of adsorption.[1,2] This suggested the importance of the presence of adsorption equilibrium. Although each CNS value of coexisting two-radical species produced on HY during contact with a solution was nonlinear to the amount of adsorption, it was still independent of the order of adsorption. On the other hand, each CNS value of a solvent-free HY-two organic system became dependent on the adsorption order.[1] In all cases, the CNS values and their time courses were dependent on the calcination temperature of HY and the electron-donating or -accepting characteristics of the organic molecules.[1]

An independent determination of the values of CNS of the solvent-free HY-two organic system might be a convenient example for a quantitative discussion of this adsorption-order dependence. We thought that this kind of nonlinearity and the adsorption-order dependence might reflect some of the roles of the presence of nonequilibrium states and that an independent and quantitative determination of the CNS values would prompt the discovery of some new factors necessary either for improving the reproducibility of physicochemical data of relatively complicated systems, or for elucidating the solid acidity or basicity on the HY surface.[1] We, therefore, attempted to determine with electron paramagnetic resonance (EPR) spectroscopy the CNS values of the coexisting two-radical species on HY, using a solvent-free system comprising either HY and two donors, HY and two acceptors, or HY, a donor, and an acceptor and ranging in the content of each organic compound from 0.1 to 1.0 times the maximal amount of adsorption/g-HY ($A_{\max}$). Eventually, the adsorption-order dependence was connected with the electron-donating or -accepting characteristics of adsorbate molecules.

Experimental

Materials. An HY was obtained by calcining an NH_4^+-exchanged Y-type zeolite (Si/Al=1.90) at 650 °C. The purification of perylene (PE), naphthalene (NA), tetracyanoethylene (TCNE), and 1,3-dinitrobenzene (DNB) has been previously described.[1]

Procedure. A solvent-free HY-two organic ternary system was obtained by impregnating HY with a given volume of a heptane solution (0.1 mol dm^{-3}) of the first organic compound (a constant amount ($A_{\max}$) of adsorption), followed by drying under reduced pressure (ca. 2 Pa), soaking again with a given volume of a heptane solution (0.1 mol dm^{-3}) of the second adsorbate (a given amount (0—$A_{\max}$) of adsorption), drying again in vacuo, and storing in an EPR cell in dry nitrogen at 25 °C.

Spectral Measurement. The EPR spectrometer, experimental conditions, the method of the independent determination of the numbers of spins of coexisting two-radical species, and the measurement of the amount of adsorption were described previously.[1] An EPR spectrum was obtained at a microwave power of 0.2 mW, a modulation amplitude of 3.2×10^{-3} mT, and a time constant of 0.1 s. The experimental errors in the CNS and the amount of organic molecules adsorbed on HY were less than 10%.[1]

Results

Characteristics of EPR Spectra of the Ternary Systems. As described previously, a fairly well-resolved hyperfine structure was observed in the EPR spectrum of the PE or NA cations or the DNB anion radicals on HY, whereas the spectrum of the TCNE anion radicals was unresolved.[2,3] An EPR spectrum of a ternary system comprising HY and two organic compounds was almost the superposition of the spectra of two binary (HY-organic) systems. This suggested both the occurrence of no interaction between coexisting two-radical species on HY and the generation of individual ion radicals at different sites.[1]

Dependence of the CNS Values on the Adsorption Order. Ternary System Comprising HY, a Donor, and an Acceptor: Figure 1 shows the dependence of the numbers of coexisting cations and anion radicals on the order of adsorption with a ternary system comprising HY, DNB (a weak acceptor), and either NA (a weak donor) or PE (a strong donor) at a given composition. An EPR spectrum of an HY-free binary mixture comprising either DNB and PE or DNB and NA was different (unresolved single peak at g=2.0024) from that of the ternary system under consideration and was adequately weak (CNS<1.0×10^{16} spins/g). Therefore, the radical formation shown in Fig. 1 must be induced in the presence of HY. Point **a** in Fig. 1 corresponds to the maximal number of radicals obtained with a binary system comprising HY and A_{max} of DNB (○), NA (●), or PE (■) in the absence of the second adsorbate. Points **b**—**f** suggest an increase in the number of radicals with increasing amount of the second adsorbate. Thus, the coexistence of donors and acceptor molecules on HY enhances both the cations and anion radicals.

When donors (A_{max}) and acceptor molecules (A_{max}) were adsorbed simultaneously on HY from a heptane solution and dried in vacuo, the numbers of coexisting DNB anions and NA cation radicals were determined to be 3.5 and 5.0×10^{18} spins/g, respectively; those of the DNB anions and PE cation radicals were found to be 4.8 and 21×10^{18} spins/g, respectively. These values were different from those shown at points **f** in Fig. 1. Then, the CNS value of a donor or the acceptor adsorbed on HY was the smallest when the donor and acceptor were adsorbed simultaneously, and was the greatest when employed as the second adsorbate. Thus, the CNS values of the ternary system possessing the same composition depend on the order of adsorption. A similar adsorption-order dependence was observed with a ternary system comprising HY, TCNE (a strong acceptor), and either NA or PE, or with ternary systems possessing various compositions.

In the case of the order of adsorption of HY–DNB–NA, the CNS of DNB at a constant DNB content (A_{max}) increases linearly with an increase in the CNS of NA. Similarly, a linear relationship is obtained with a ternary system prepared in the order of HY–NA–DNB or HY–PE–DNB. Analogous to the previous results,[4] however, the number of DNB anion radicals formed in a ternary system adsorbed in the HY–DNB–PE order increases with an increase in the number of PE cation radicals along the same straight line as that obtained with the ternary system arranged in the HY–DNB–NA order. It passes over the maximal number of NA cation radicals, reaching finally a plateau. Whereas, the CNS of the PE cation radicals increases up to a PE content of A_{max}, even during the constant number of coexisting DNB anion radicals. Although not shown in Fig. 1, the CNS value of TCNE anion radicals in a ternary system adsorbed in the order of HY–PE or NA (A_{max})–TCNE (0—A_{max}) increased along the same straight line as that obtained with a ternary system prepared in the HY–PE or NA (A_{max})–DNB (0–A_{max}) order. Eventually, the numbers of coexisting cations and anion radicals were independent of, while their maximal numbers of spins were dependent on, the spin-generating abilities of the donors and acceptor molecules. The increment of CNS, defined by the CNS at point **f** divided by that at point **a**, is great when a weak donor (NA) or a weak acceptor (DNB) is employed.

Ternary System Comprising HY and Two Donors: Figure 2 depicts plots of the CNS values of coexisting PE and NA cation radicals adsorbed on the surface of HY. Since the amount of radicals generated in an HY-free binary mixture comprising PE and NA is small (less than 1×10^{14} spins/g), the CNS values under consideration must be induced in the presence of HY. A plot of the CNS values shown in Fig. 2 lies to the upper part of an

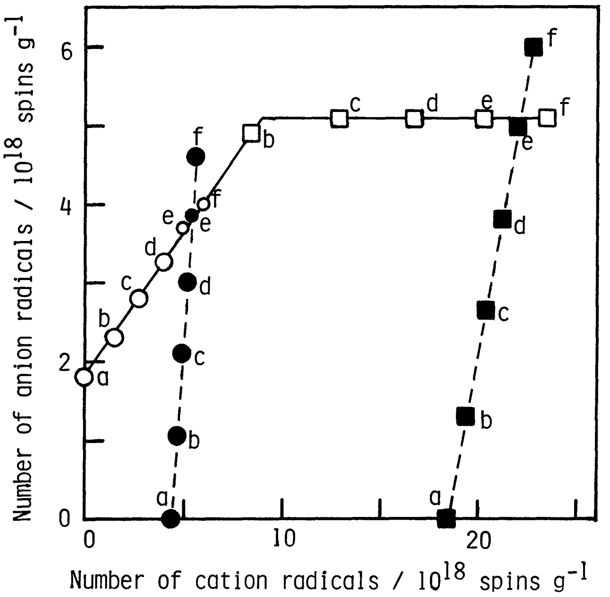

Fig. 1. Dependence of the numbers of either NA or PE cations (abscissa) and DNB anion radicals (ordinate) on the order of adsorption. The order of adsorption, ○: HY–DNB–NA; □: HY–DNB–PE; ●: HY–NA–DNB; ■: HY–PE–DNB. The content of the first-adsorbed organic compound is A_{max}. The content of the second-adsorbed organic compound is 0.0 (**a**), 0.20 (**b**), 0.40 (**c**), 0.60 (**d**), 0.80 (**e**), or 1.0 (**f**) times A_{max}.

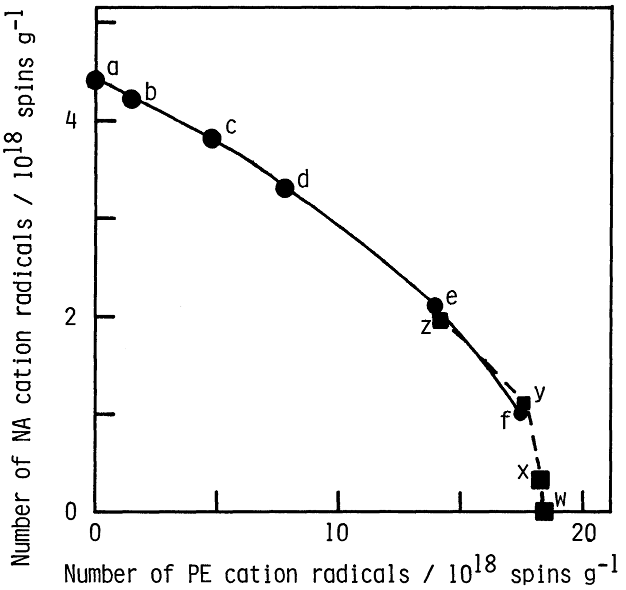

Fig. 2. Dependence of the numbers of PE (abscissa) and NA (ordinate) cation radicals on the adsorption order. The adsorption order and composition, ●: HY–NA (A_{max})–PE (0.0 (**a**), 0.10 (**b**), 0.30 (**c**), 0.50 (**d**), 1.0 (**e**), or 2.0 (**f**) times A_{max}); ■: HY–PE (A_{max})–NA (0.0 (**w**), 0.50 (**x**), 1.0 (**y**), or 2.0 (**z**) times A_{max}).

imaginary straight line connecting points **a** and **w**. This suggests that the coexistence of NA and PE on HY causes an increase in the number of both NA and PE cation radicals. A similar tendency was observed with the coexisting DNB and TCNE anion radicals on HY.

When NA ($A_{\max}$) and PE ($A_{\max}$) were adsorbed simultaneously on HY from a heptane solution and dried in vacuo, the CNS values of NA and PE were 0.95 and 14×10^{18} spins/g, respectively. The CNS value of each donor is smallest when simultaneously adsorbed on HY to another donor, and is the greatest when adopted as the first adsorbate. The increment of the CNS value of NA as the first adsorbate, defined by the ratio of the CNS at the point **e** to that at the point **a** in Fig. 2, is greater than the corresponding value of PE (the CNS value at the point **y** divided by that at the point **w**). A similar tendency was observed with coexisting DNB and TCNE anion radicals on HY, and with ternary systems possessing various compositions. Thus, the CNS values of the ternary (HY–two donor or HY–two acceptor) system possessing the same composition depend on the adsorption order.

The Enhancement of Radicals and Adsorption-Order Dependence Observed with Other Aluminosilicates. In a similar manner as above, the enhancement of ion radicals and the dependence of the CNS values on the order of adsorption were observed with other HY type zeolites (Si/Al=1.65, 2.20, 2.40, 2.65, 4.8, and 5.6), decationated mordenites (Si/Al=10, 15, and 20), Na^+-, K^+-, Mg^{2+}-, Ca^{2+}-, Sr^{2+}- and Ce^{4+}- exchanged Y-type zeolites, silica–alumina (Si/Al=2.2 and 5.3), and γ-alumina. An HY possessing a small Si/Al ratio (e.g., Si/Al=1.90) was found to be suitable for quantitative examination of the adsorption-order dependence. That is to say, no reaction of ion radicals occurred on the HY (Si/Al=1.90) surface in the atmosphere of nitrogen at 25 °C, while the reactivity of ion radicals produced on a decationated zeolite increased with an increase in the Si/Al ratio, and became considerable at Si/Al=10 or more.[1] In addition, the CNS values of both cations and anion radicals induced on HY possessing a small Si/Al ratio (1.90) were sufficiently great for our purposes.

Discussion

Thermodynamically, physicochemical data of a simple system obtained at equilibrium are independent of the adopted processes. We have previously described the reversible and linear dependence of the CNS value of an HY–organic binary system on the amount of adsorption.[1] As described above, the complication of the system (HY–two organic system) arose from an enhancement of the coexisting two organic ion radicals adsorbed on HY, nonlinear and irreversible dependence of the CNS values on the amounts of adsorption, and the dependence of the CNS values on the adsorption order. These results might reflect some roles of the non-equilibrium states of relatively complicated systems. Therefore, an independent, quantitative determination of the CNS values would be available for finding some new factors necessary either for improving the reproducibility of physicochemical data of relatively complicated systems or for elucidating solid actidity or basicity on the HY surface.[1] Other factors responsible for the reproducibility or the solid acid–base property will be described in a subsequent publication.

The nonlinear dependence of the CNS values on the amount of adsorption and the adsorption-order dependence may arise from the variation in surface energy as a result of chemical modification (pretreatment)[5] and of mechanochemical transformation of surface properties.[6] Though qualitatively, the occurrence of this nonlinear dependence may result from the heat of adsorption or the heat of spin formation. This heat may be effectively removed from the surface of HY to solvent molecules during contact with solutions, but may cause a local augmentation in surface energy or a local variation in the surface property in a solvent-free system.[5,6]

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