Time Courses of the Numbers of Spins from a Single or Two Organic Compounds on a Decationated Y-Type Zeolite

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The time courses of the number of organic radicals produced on the surface of a decationated Y-type zeolite (HY) were followed with electron paramagnetic resonance spectroscopy after the removal of heptane (a solvent). Regardless of the presence of the heptane, the relationship between the amount of adsorption and the number of spins for a binary system of HY and a single organic compound was linear and reversible, suggesting the significance of the presence of an adsorption equilibrium. On the surface of HY, there are two kinds of active sites possessing different times required for attaining constant numbers of spins. Cation radicals from a strong donor (perylene) adsorbed in advance on HY were gradually replaced by those from a weak donor (naphthalene), while a small number of cation radicals from naphthalene adsorbed in advance on HY remained after contact with a sufficiently large quantity of perylene. The coexistence of both donor and acceptor molecules on HY increased the number of both cations and anion radicals, which were significantly dependent on the order of adsorption.

The charge-transfer interaction, resulting in the formation of either cation radicals on solid acid sites or anion radicals on solid base sites on the surfaces of zeolites, was frequently studied using electron paramagnetic resonance (EPR) spectroscopy up to the early 1970's.[1-4] The majority of EPR spectroscopic investigations on the charge-transfer interaction between zeolites and organic compounds were carried out at adsorption equilibrium.[1] These results have been applied, for example, to an evaluation of the activity of zeolites as solid acid or base catalysts and to the construction of a model of active sites.[1]

In general, the content of an organic compound adopted in a mechanistic study of a contact reaction is usually much smaller than that employed in a practical catalytic synthesis. Provided that the spectroscopic studies were carried out with multicomponent systems comprising an aluminosilicate and relatively large quantities of adsorbate molecules, it was observed that some new phenomena occurred only in a complicated system, but disappeared in a simple system. These results might be applicable, for example, to a quantitative evaluation of the activity of practical catalysts.

The time courses of the number of spins induced in a binary system comprising silica-alumina and a large quantity (10%) of glycolic acid after the removal of a solvent were considered quantitatively from both pharmaceutical and mechanochemical points of view.[5] In this case, the number of spins (NOS) was initially small, gradually increased, attained a constant number of spins (CNS), and then decreased from CNS during the final stage.[5] The values of CNS and the duration of CNS (a measure of the oxidation rate or polymerization of glycolic acid) were dependent on the calcination temperature of silica-alumina, on the mechanical energy (shaking or compressing) applied during or after mixing, on the conditions for storing the mixed systems (temperature, atmosphere, or humidity), and on the time interval between mixing and ultraviolet irradiation.[5]

From the viewpoint of surface or catalytic chemistry, we attempted to follow by EPR spectroscopy the time courses of the number of radicals produced from a single or two organic compounds (0.1—10 times the maximal amount of adsorbate molecules/g-HY (A_{max})) adsorbed on the surface of a decationated Y-type zeolite (HY). Since the formation of radicals on HY is attributable to a charge-transfer interaction,[1] the behaviors of radicals from perylene (PE) as a strong donor (ionization potential=6.90 eV),[6] naphthalene (NA) as a weak donor (ionization potential=8.13 eV),[6] tetracyanoethylene (TCNE) as a strong acceptor (electron affinity=2.3 eV),[7] or 1,3-dinitrobenzene (DNB) as a weak acceptor (electron affinity $<$0.7 eV) on HY were compared.

A long time was required for a Hammett indicator adsorbed on an aluminosilicate to attain equilibrium.[8] In the case of HY, the time courses of NOS have not been paid much attention. However, it took a long time for the NOS of an HY-organic system to attain a constant value, suggesting the significance of the presence of nonequilibrium states when HY is applied, for example, to practical contact reactions.

Regardless of the presence of a solvent, the dependence of NOS on the amount of adsorption was found to be linear and reversible in the case of a binary system of HY and a single organic compound, suggesting the significance of adsorption equilibrium. Qualitatively, however, rapid heating or vigorous stirring of this HY-organic system in contact with heptane resulted in an irreversible dependence of NOS on the amount of adsorption. However, the NOS values of ternary systems comprising HY and two organic compounds after the removal of the solvent were suitable for quantitative considerations on this irreversibility. Eventually, cation radicals from a strong donor (PE) adsorbed in advance were gradually replaced by

those from a weak donor (NA), while cation radicals from NA adsorbed in advance remained even after subsequent contact with PE. Further, the coexistence of donor and acceptor molecules on HY increased the number of both the cation and anion radicals, which were considerably dependent on the order of adsorption. Thus, the NOS values of binary (HY-organic) systems behave like being in equilibrium, while those of some ternary (HY-two organic) systems were dependent on the adsorption processes.

The main object of this report is to describe the time courses of NOS with zeolite-organic systems after removing the solvent and to try to search for some new factors necessary for considering NOS of slightly complicated systems, both quantitatively and reproducibly. The obtained results may be available, at least, for improving the reproducibility of some physicochemical data of slightly complicated systems. They may be expected in the future to provide a technique for supplying an HY possessing constant and the desired efficiency or a model of active sites.

Experimental

Materials. An HY was obtained by calcining an NH_4^+-exchanged Y-type zeolite (Si/Al=4.8) at 400 or 650 °C. PE or DNB was recrystallized from toluene or 1/1 (v/v) ethanol/water, respectively. NA and TCNE were purified by sublimation. Freshly distilled heptane was used as a solvent.

Procedure. A binary system of HY and a single organic compound was obtained by impregnating HY with a given volume of a heptane solution (0.1 mol dm^{-3}) of PE, NA, TCNE, or DNB (containing the A_{max} of the organic compound), followed by drying under reduced pressure (ca. 300Pa).

A ternary system of HY and two electron donors or HY and two electron acceptors was obtained by impregnating HY with a given volume of a heptane solution (0.01 mol dm^{-3}) of the first organic compound (containing therein 0.1 times the A_{max} of the organic compound), followed by drying under reduced pressure, soaking again with a given volume of a heptane solution (0.1 mol dm^{-3}) of the second organic compound (containing therein 10 times the A_{max} of the organic compound), and drying again in vacuo. A ternary system arranged in the order HY-TCNE or DNB (A_{max})-PE or NA (A_{max}) or HY-PE or NA (A_{max})-TCNE or DNB (A_{max}) was prepared similarly.

Determination of the Number of Molecules Adsorbed on HY from Heptane Solutions. The number of organic molecules adsorbed when HY (20—50 mg) was brought in contact with a heptane solution (1.0×10^{-4}—3.0×10^{-1} mol dm^{-3}) of an organic compound for a given time of contact (0—72 h) at 25 °C was determined spectrophotometrically.

EPR Measurement. The EPR spectra of the binary and ternary systems were obtained in dry nitrogen at 25 °C with a JEOL JES-FE3X type spectrometer (X band, 100 kHz modulation) at a microwave power of 0.2 mW and a modulation amplitude of 3.2×10^{-3} mT. The NOS values, expressed as spins per gram of dry HY, were estimated by a comparison with standard carbon samples which had previously been calibrated with solutions of 2,2-diphenyl-1-picrylhydrazyl in benzene.[3] The experimental errors in NOS and the amount of organic molecules adsorbed/g-HY were less than 10%.

Results and Discussion

EPR Spectra of Radicals on HY. A fairly well-resolved hyperfine structure was obtained in the EPR spectrum of the PE or NA cation radical or of the DNB anion radical, whereas the spectrum of the TCNE anion radical was unresolved. The EPR spectra of PE, NA, TCNE, and DNB adsorbed on HY were analogous to those reported by Stamires and Turkevich,[2] Flockhart et al.,[3] Hirota et al.,[4] and so on.

An EPR spectrum of a ternary system of HY and two organic compounds was almost the superposition of the spectra of two binary (HY-organic) systems. In addition, one or more band(s) was observed separately from the spectrum of each ion radical. Therefore, the NOS values of two radical species on HY could be determined independently.

Adsorption Equilibrium for Binary Systems during Contact with Heptane Solutions. The adsorption isotherm of PE or TCNE from heptane solutions at 25 °C is shown in Fig. 1. In the low-concentration region of the isotherm, the amount of adsorption is proportional to the number of PE or TCNE molecules in contact with HY, decreasing its increase, and

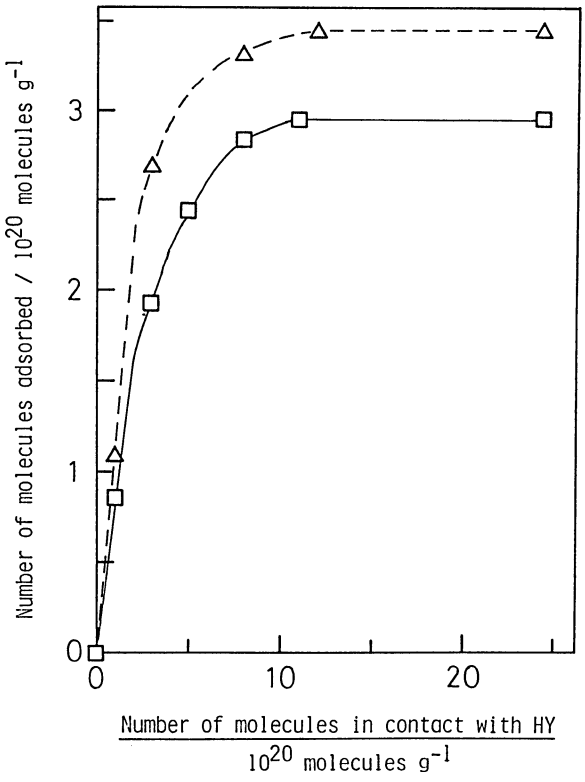

Fig. 1. Room temperature isotherm of PE (□) or TCNE (△) adsorption from heptane solutions on HY calcined at 650 °C.

finally reaching a plateau. Similar results were obtained for the adsorption of NA or DNB.

Figure 2 shows the dependence of the amount of adsorption on the contact time from immediately after bringing HY into contact with heptane solutions (0.1 mol dm^{-3}). During the initial stage, the amount of molecules adsorbed increased linearly with the contact time, decreasing its increase, and finally reaching a plateau. Similar results were confirmed at a PE or TCNE concentration from 0.001 to 0.3 mol dm^{-3} or with the adsorption of NA or DNB. Independent of the calcination temperature of HY (T_{ca}), the time required for reaching the plateau for PE, NA, TCNE, or DNB was ca. 45, 60, 50, or 50 h, respectively.

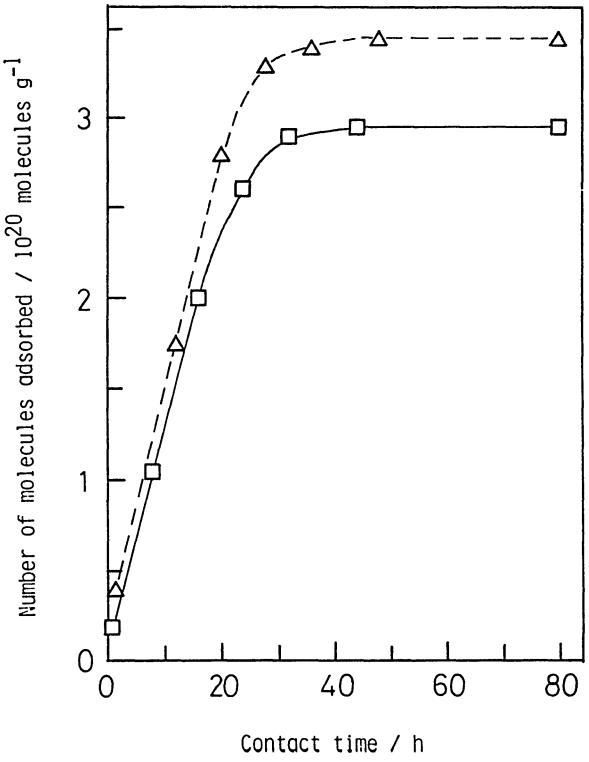

Fig. 2. Time courses of the numbers of PE (□) or TCNE (△) molecules adsorbed on HY calcined at 650 °C from heptane solutions (0.1 mol dm^{-3}) at 25 °C.

Figure 3 illustrates the increase of NOS obtained at the plateau with the adsorption of PE or TCNE from heptane. In agreement with the results of Stamires and Turkevich,[2] NOS increases linearly with an increase in the amount of adsorption, finally reaching the maximal number of spins (g-HY)$^{-1}$ (MNS) at the amount of adsorption of A_{max}. Similar results were obtained with the adsorption of NA or DNB on HY.

The values of A_{max} and MNS as well as g are summarized in Table 1. As shown from Table 1, A_{max} and g are independent of T_{ca}, while MNS is significantly dependent on T_{ca}.

It can be seen from Fig. 3 that the ratio of NOS to the amount of adsorption is independent of the concentrations of the solutions. This suggests the absence of specific parts of HY surfaces advantageous either for the adsorption or for radical formation. That is, both adsorption and radical formation occur

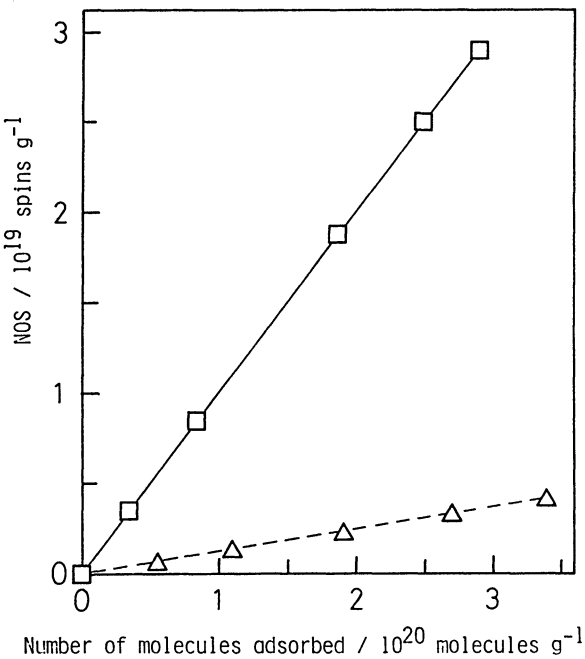

Fig. 3. Increase in NOS with adsorption of PE (□) or TCNE (△) from heptane solutions on HY calcined at 650 °C.

Table 1. Values of g, A_{max}, and MNS for PE, NA, TCNE, or DNB Adsorbed on the Surface of HY

Organic compound	T_{ca} / °C	g	A_{max} / 10^{20} molecules g^{-1}	MNS / 10^{18} spins g^{-1}
PE	650	2.0026	2.9	29
	400	2.0026	2.9	4.1
NA	650	2.0024	6.0	5.4
	400	2.0024	6.0	1.1
TCNE	650	2.0027	3.4	4.2
	400	2.0027	3.4	0.85
DNB	650	2.0041	2.1	2.9
	400	2.0041	2.1	0.26

uniformly on the surface of HY.

When PE or TCNE was desorbed with a large excess of heptane, NOS decreased with a decrease in the number of molecules adsorbed along the same straight line shown in Fig. 3. This reversible relation between NOS and the amount of adsorption may indicate the significance of the presence of an equilibrium upon the adsorption of PE or TCNE on HY from heptane solutions. Though qualitatively, this linear and reversible relationship disappeared when the HY-organic systems were stirred vigorously or heated rapidly during contact with heptane.

Time Courses of NOS for Binary (HY-Organic) Systems Free from Heptane. Figure 4 depicts the time courses of NOS for PE, NA, TCNE, or DNB on HY from immediately after the removal of heptane. NOS is initially small, increases with the passage of time, and finally reached a constant number of spins. CNS increased with an increase in the amount of organic molecules in contact with HY up to A_{max} along the same straight line shown in Fig. 3. The values of CNS were almost identical with those of MNS given in Table 1.

The EPR spectra of these binary systems were unchanged after attaining CNS. A considerable amount of adsorbate molecules were recovered unchanged by desorbing them with a large excess of heptane. CNS decreased with a decrease in the number of adsorbate molecules along the same straight line shown in Fig. 3. This linear and reversible dependence of CNS on the amount of adsorption may support the importance of adsorption equilibrium, even in a heptane-free binary system. Since HY is composed of abundant but relatively weak active sites,[1] radicals produced on HY can possibly remain unchanged for a long time.

The time required for attaining CNS (t_{CNS}) for the HY-organic system in contact with heptane was 45—60 h. The t_{CNS} for a heptane-free system, however, ranges from 1 h (PE on HY calcined at 650 °C) to 140 h (DNB on HY calcined at 400 °C). The rapid diffusion of PE or TCNE molecules may be due to the heat of radical formation on the surface of HY, which might be effectively removed by solvent molecules. CNS increases, while t_{CNS} decreases when a weak donor (NA), weak acceptor (DNB), or HY calcined at a low temperature (400 °C) was employed.

Table 2 shows the dependence of t_{CNS} on the amount of adsorption from 0.1 to 1.0 times A_{max}. The t_{CNS} value for PE or TCNE is independent of the amount of adsorption over the entire region examined. Whereas, the value of t_{CNS} for NA or DNB is near to that for PE or TCNE, respectively, at an adequately decreased amount of adsorption, it increases stepwise, and then remains unchanged at a further increased amount of adsorption. This suggests the coexistence of both an active site possessing a large t_{CNS} and one having a small t_{CNS} on the HY surface. The former may correspond to a weak active site, because a weak donor or acceptor is related to its occurrence.

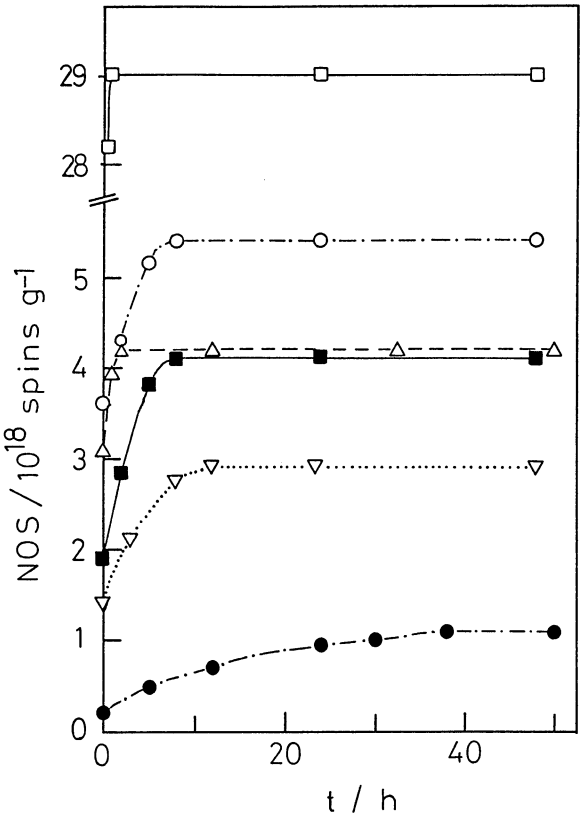

Fig. 4. Time course of the number of PE cation radicals on HY calcined at 650 (□) or 400 (■) °C, of NA cation radicals on HY calcined at 650 (○) or 400 (●) °C, or of TCNE (△) or DNB (▽) anion radicals on HY calcined at 650 °C from immediately after drying HY having been impregnated with a heptane solution (containing A_{max} of the organic compound) under reduced pressure.

Table 2. Dependence of t_{CNS} on the Amount of Adsorption

Organic compound	T_{ca} / °C	t_{CNS}/h				
		A[a]=0.1	A=0.2	A=0.3	A=0.5	A=1.0
PE	650	1	1	1	1	1
	400	8	8	8	8	8
NA	650	1	1	8	8	8
	400	10	10	40	40	40
TCNE	650	2	2	2	2	2
	400	12	12	12	12	12
DNB	650	2	10	10	10	10
	400	12	120	120	120	120

a) Amount of organic molecules adsorbed divided by A_{max}.

Time Courses of NOS for Two Electron Donors Coexisting on HY. Figure 5 demonstrates a decrease in the number of PE cation radicals and an increase in that of NA cation radicals up to their CNS values, when HY was first adsorbed by PE (0.1 times A_{max}) and

then by NA (10 times A_{max}). The CNS value of the NA cation radicals is almost identical with MNS (shown in Table 1), while that of the PE cation radicals is considerably small.

If a base is gradually added to an aqueous solution containing several acids, the base reacts preferentially with one particular acid possessing the strongest acidity until it is exhausted; it then reacts with another acid having the second strongest acidity. In the case of two donors on HY, however, even cation radicals from a strong electron donor (PE) adsorbed in advance were mostly replaced by those from a weak donor (NA), eventually reaching a new equilibrium. The coexistence of two cation radicals, however, were also qualitatively observed when HY was impregnated with a heptane solution containing both PE and NA.

The t_{CNS} value of PE or NA for this ternary system is considerably greater than that obtained with the corresponding binary system (Fig. 4). CNS for each cation radical increases, while t_{CNS} decreases with an increase in T_{ca}.

A decrease in the number of NA cation radicals and an increase in that of PE cation radicals up to their CNS was obtained with a ternary system adsorbed in the order HY (T_{ca}=650 or 400 °C)-NA (0.1 times A_{max})-PE (10 times A_{max}). Table 3 summarizes CNS and t_{CNS} for two coexisting radical species for this order of adsorption. The CNS value for PE is identical with MNS (Table 1), while a small amount of NA cation radicals remains on HY, even during the final stage.

Different from an acid or base dissolved in a solution, a significant amount of radicals from a weak donor (NA) adsorbed in advance remained at a stationary state attained after subsequent contact with a sufficient quantity of a strong donor (PE).

The t_{CNS} value for NA or PE for this ternary system is much greater than that for the binary system (Fig. 4). CNS increases, while t_{CNS} decreases with an increase in T_{ca}.

Time Courses of NOS for Two Electron Acceptors Coexisting on HY. Figure 6 depicts one curve showing the decrease in the number of TCNE anion radicals and another the increase in the number of DNB anion radicals with a ternary system adsorbed in the HY-TCNE (0.1 times A_{max})-DNB (10 times A_{max})

Table 3. Values of CNS and t_{CNS} for Each Cation Radical[a)]

T_{ca} / °C	Cation radical	CNS / 10^{18} spins g^{-1}	t_{CNS} / h
650	NA	0.06	30
	PE	29	22
400	NA	0.014	95
	PE	4.1	120

a) Order of adsorption: HY (calcined at 650 or 400 °C)-NA (0.1 times the A_{max})-PE (10 times the A_{max}).

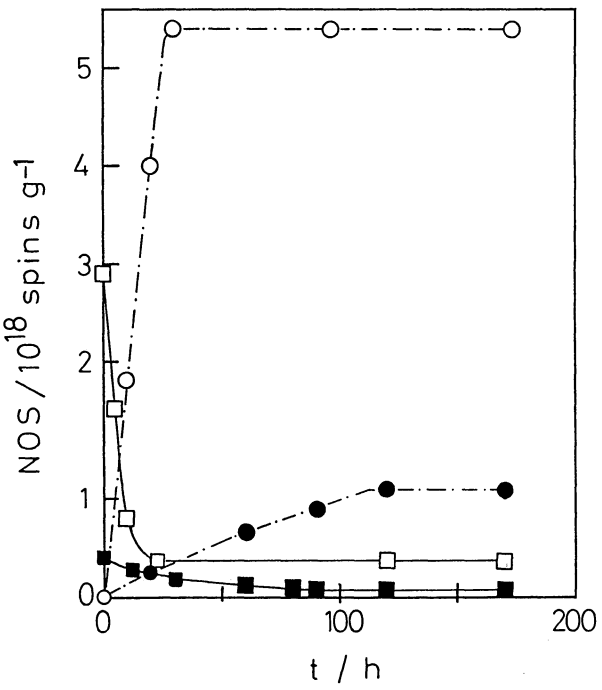

Fig. 5. Time courses of the numbers of PE (□) and NA (○) cation radicals on HY calcined at 650 °C and of PE (■) and NA (●) cation radicals on HY calcined at 400 °C. Order of adsorption: HY-PE (0.1 times the A_{max})-NA (10 times the A_{max}).

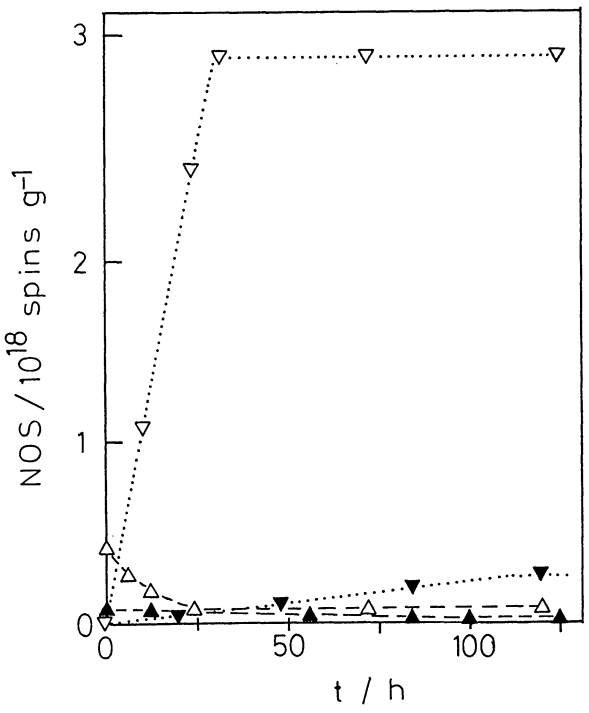

Fig. 6. Time courses of the numbers of TCNE (△) and DNB (▽) anion radicals on HY calcined at 650 °C and of TCNE (▲) and DNB (▼) anion radicals on HY calcined at 400 °C. Order of adsorption: HY-TCNE (0.1 times the A_{max})-DNB (10 times the A_{max}).

Table 4. Values of CNS and t_{CNS} for Each Anion Radical[a)]

T_{ca} °C	Anion radical	CNS 10^{18} spins g^{-1}	t_{CNS} h
650	DNB	0.040	32
	TCNE	4.2	24
400	DNB	0.012	120
	TCNE	0.85	100

a) Order of adsorption: HY (calcined at 650 or 400 °C)-DNB (0.1 times the A_{max})-TCNE (10 times the A_{max}).

Table 5. Values of CNS and t_{CNS} for Coexisting Cation and Anion Radicals on HY[a)]

Order of adsorption	Ion radical	CNS 10^{18} spins g^{-1}	t_{CNS} h
HY-PE-DNB	PE	31.5	6
	DNB	8.0	6
HY-NA-DNB	NA	7.9	10
	DNB	6.4	10

a) Order of adsorption: HY (calcined at 650 °C)-PE or NA (A_{max})-DNB (A_{max}).

order. Table 4 lists the CNS and t_{CNS} of coexisting DNB and TCNE anion radicals in the case of the order of adsorption of HY (T_{ca}=650 or 400 °C)-DNB (0.1 times A_{max})-TCNE (10 times A_{max}). In these cases, anion radicals from a strong acceptor (TCNE) adsorbed in advance were replaced by those from a weak acceptor (DNB), while anion radicals from DNB adsorbed in advance remained even after subsequent contact with a sufficiently large quantity of TCNE.

Time Courses of NOS for Both Donor and Acceptor Molecules Coexisting on HY. Figure 7 shows the time courses of the number of both DNB anions and either PE or NA cation radicals with a ternary system adsorbed in the order HY-DNB-PE or NA. The number of both anions and cation radicals increase with the passage of time up to their CNS. The values of CNS for both anions and cation radicals are much greater than those of MNS shown in Table 1. The ratio of CNS (Fig. 7) to MNS (Table 1) was significant when a weak donor (NA), weak acceptor (DNB), or HY calcined at 400 °C was employed. For example, the ratios for coexisting DNB (A_{max}) and NA (A_{max}) on HY calcined at 400 °C were 3.7 and 4.6, respectively, while those for coexisting DNB (A_{max}) and PE (A_{max}) on HY calcined at 650 °C were 2.4 or 1.1, respectively. Apparently, an increase in the number of solid base sites gives rise to an increase in the number of coexisting solid acid sites, or vice versa.

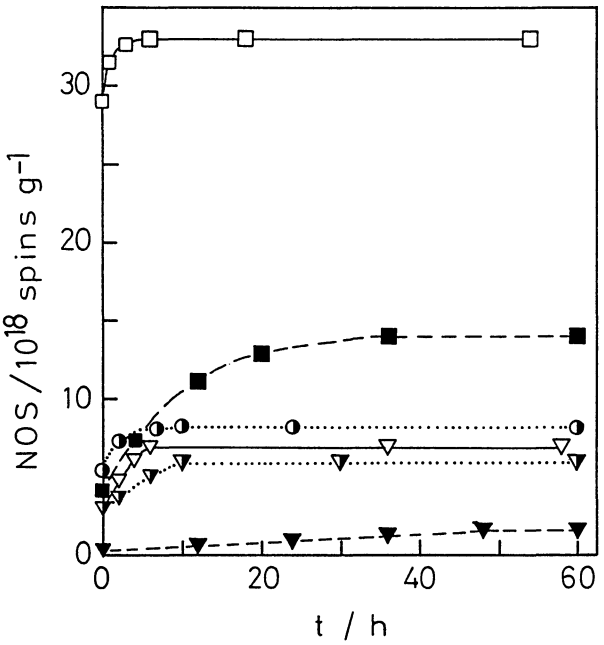

Fig. 7. Time courses of NOS for DNB (▽) and PE (□) on HY calcined at 650 °C, for DNB (◥) and NA (◑) on HY calcined at 650 °C, and for DNB (▼) and PE (●) on HY calcined at 400 °C. Order of adsorption: HY-DNB (A_{max})-PE or NA (A_{max}).

Comparing the time courses of NOS shown in Fig. 7 with those shown in Fig. 4, t_{CNS} for PE or NA in the ternary system increases, while the corresponding t_{CNS} for DNB decreases remarkably. In the neighborhood of CNS, NOS increases rather steeply in the case of DNB, while it increases slowly in the case of coexisting PE or NA. A similar tendency was observed with a ternary system adsorbed in the order HY-TCNE (A_{max})-PE or NA (A_{max}).

Similar time courses of NOS were obtained with a ternary system adsorbed in the order HY (T_{ca}=650 °C)-PE or NA (A_{max})-DNB (A_{max}). Table 5 summarizes CNS and t_{CNS} for two coexisting radical species for this adsorption order.

Dependence of CNS on the Order of Adsorption. In general, a physicochemical property obtained at an equilibrium is independent of the process for reaching equilibrium. Actually, the relationship between CNS and the amount of adsorption for a binary (HY-organic) system was linear and reversible, supporting the importance of equilibrium. As can be seen from Fig. 7 and Table 5, however, the CNS values of a ternary system comprising HY (T_{ca}=650 °C), DNB (A_{max}), and either PE or NA (A_{max}) are significantly dependent on the order of adsorption. On the other hand, the CNS values of this ternary system in contact with heptane were dependent only on the concentrations of two organic compounds, but independent of the order of adsorption.

The dependence on the adsorption order was pronounced for solvent-free systems. The results described above may be applicable to practical catalytic reactions in the solid or gaseous phase. Although it was difficult to observe quantitatively, it occurred in complicated solutions.

The NOS value of a binary system comprising glycolic acid and silica-alumina without a solvent depended on the method of applying mechanical energy (shaking or compressing) or on the time interval between mixing and ultraviolet irradiation.[5] Chemical modifications of the surface energy[9] and mechanochemical transformation of the surface structure or surface property[10] have already been investigated. Then, the dependence of NOS on the order of adsorption may result from either the heat of adsorption or the heat of radical formations.[5] Though this heat may be effectively removed from the surface of HY to the solvent molecules, it may cause a local augmentation in surface energy or a local variation in the surface property in the absence of a solvent.[5,9,10] Other causes of the dependences on the adsorption order will be presented in a subsequent publication.

Interaction between Cation and Anion Radicals Coexisting on HY. Very little radical formation in a mixture of PE and DNB without HY suggests the formation of radicals only on HY. In the case of a ternary system adsorbed in the HY-DNB-PE order at a constant DNB content (A_{max}), CNS for the DNB anion radical increased with an increase in the PE content from 0 (2.9×10^{18} spins/g) to 0.23 times the A_{max} (6.9×10^{18} spins/g), and became unchanged at a further increased PE content. However, CNS for PE (0, 11, or 33×10^{18} spins/g, respectively, at a PE content of 0, 0.23, or 1.0 times the A_{max}) increased, even in the region where CNS for DNB was independent of the PE content. In addition, an observation of the superimposed spectra of the DNB anion and the PE cation radicals suggests little interaction between the anion and cation radicals on HY. Therefore, the formation of anions and cation radicals may occur at different sites.

Practical Application. Probably the most important factor necessary for a quantitative, reproducible consideration concerning the physicochemical properties of slightly complicated systems may be t_{CNS}. A great t_{CNS} usually obtained with an HY-organic system suggests a significant role of nonequilibrium states when HY is used as a practical catalyst. As shown in Fig. 4, the t_{CNS} of PE or TCNE is much smaller than that of NA or DNB. Then, the difference in the spin-generating ability between PE and NA or between TCNE and DNB determined soon after adsorption may be considerably greater than the corresponding difference obtained at equilibrium.

The second factor may be the order of adsorption. Thermodynamically, a physicochemical property obtained at equilibrium is independent of the process to reach equilibrium. Regardless of the presence of heptane, the dependence of CNS of a binary (HY-organic) system on the amount of adsorption was linear and reversible, suggesting the significance of equilibrium. The CNS values of the ternary systems of HY and two organic compounds in contact with heptane was independent of (while those of the ternary system without heptane were dependent on) the adsorption order. The dependence became pronounced when the number of components or the amount of adsorption increased.

The cation radicals formed from two donors or anion radicals from two acceptors on HY exhibited peculiar acid-base characteristics. Further, the CNS of a donor was enhanced by the coexistence of an acceptor. At least, a quantitative consideration of this enhanced radical formation would prompt an improvement in controlling the reproducibility of some physicochemical properties (e. g., the activities of HY as a practical catalyst) of complicated zeolite-organic systems. In the future, a technique for forcing HY to exhibit a constant, desired efficiency might be obtained.

A few results which are probably available for constructing a model of active sites were obtained. As shown in Table 2, there coexist two kinds of active sites on the surface of HY. These exhibit different t_{CNS}. An active site having a small t_{CNS} may correspond to a strong active site, since the PE cation or the TCNE anion radicals on HY calcined at 650 °C is concerned. An active site possessing a large t_{CNS}, however, may correspond to a weak active site, since a weak donor (NA) or acceptor (DNB) on HY calcined at 400 °C is concerned for its occurrence. The latter may play a role in enhanced radical formation in the presence of both a donor and an acceptor or in the dependence on the adsorption order.

Spin-generating sites of HY have been attributed to Lewis acid or base sites, which are known to be produced from Brönsted acid or base sites at a T_{ca} greater than 500 °C.[1,2] However, radicals were produced on HY calcined at 400 °C, especially when HY was in contact with both donor and acceptor molecules. Apparently, an increase in the number of anion radical-generating sites gives rise to an increase in the number of coexisting cation radical-generating sites, or vice versa. Other results necessary for constructing a model of active sites will be described in a subsequent publication.

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