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Time Courses of the Numbers of Ion Radicals Produced in a Ternary System of a Decationated Y-Type Zeolite and Two Organic Compounds

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The number of ion radicals formed from a single organic compound or two organic compounds adsorbed on a zeolite was time-dependent. Cation radicals from a stronger electron donor adsorbed in advance were replaced by those from a weaker donor. The coexistence of donor and acceptor molecules increased the spin-generating sites of both cation and anion radicals.

The majority of electron paramagnetic resonance (EPR) spectroscopic investigations on the charge-transfer interaction between aluminosilicates and organic compounds, producing cation or anion radicals on solid acid or base sites, respectively, were carried out at adsorption equilibrium.[1)] However, it sometimes took 2 d or more for an aluminosilicate-containing system to attain an equilibrium,[2)] suggesting the practical significance of the presence of non-equilibrium states. We have observed EPR spectroscopically the development or decay of an equilibrium state of the number of spins induced in a binary system of glycolic acid and silica-alumina.[3)] Recently, we observed the time courses of the number of spins/g (NOS) with a ternary system of a decationated Y-type zeolite (HY) and two organic compounds. Then, the main object of this report is to describe the effects of the presence of the second organic compound on the time courses of NOS of the first organic compound.

An HY was obtained by calcining an NH_4^+-exchanged Y-type zeolite (Si/Al = 1.90) at 400 or 650 °C. At first, HY was brought in contact with an n-heptane solution (0.01 mol dm^{-3}) of perylene (PE), naphthalene (NA), tetracyanoethylene (TCNE), or 1,3-dinitrobenzene (DNB), and dried under reduced pressure. A fairly well-resolved hyperfine structure was obtained in the EPR spectrum of PE or NA cation radical or of DNB anion radical produced on HY, whereas the spectrum of TCNE anion radical was unresolved. The NOS value, expressed as spins per gram of dry HY, was determined with

Table 1. Values of g, A_{max}, MNS, and t_{eq} for the binary system containing HY and A_{max} of PE, NA, TCNE, or DNB

Organic compound	T_{ca} / °C	g	A_{max} 10^{20} molecules/g	MNS 10^{18} spins/g	t_{eq} / h
PE	650	2.0026	3.1	19	1
	400	2.0026	3.1	2.9	8
NA	650	2.0024	6.2	4.4	8
	400	2.0024	6.2	0.92	40
TCNE	650	2.0027	3.6	5.5	2
	400	2.0027	3.6	0.61	12
DNB	650	2.0041	2.2	1.8	10
	400	2.0041	2.2	0.22	120

benzene solutions of 1,1-diphenyl-2-picrylhydrazyl as standards. The NOS value obtained with this binary system increased with an increase in the amount of organic molecules adsorbed,[4)] reaching finally the maximal number of spins/g-HY (MNS) at the maximal amount of organic molecules adsorbed (A_{max}). The A_{max} value was practically defined by the minimal number of organic molecules for providing MNS per gram of HY. Experimental errors in the values of NOS and A_{max} were less than 10%. The values of MNS, A_{max}, and the time required to attain an adsorption equilibrium (t_{eq}) as well as g values are listed in Table 1. Table 1 shows that the t_{eq} value is not so small especially when HY was calcined at 400 °C. The NOS value was small initially, increasing gradually, and reaching finally an MNS. A_{max} was independent of the calcination temperature of HY (T_{ca}).

In general, NOS of each ion radical produced in a ternary system of HY and two organic compounds could be obtained independently due to an EPR spectrum of the ternary system to be almost the superposition of the spectra of the corresponding binary systems and to the separation of one or more spectral bands for every ion radical. HY was in contact with a given volume of 0.01 mol dm^{-3} of n-heptane solution of PE (containing therein 0.1 times the A_{max} of PE), dried in vacuo, impregnated again with a given volume of 0.01 mol dm^{-3} of n-heptane solution of NA (containing the A_{max} of NA), dried again under reduced pressure; then NOS was finally measured. A decrease in NOS of PE cation radicals and an increase in NOS of NA cation radicals with time up to their respective equilibrium states are demonstrated in Fig. 1. The value of equilibrium NOS (NOS_{eq}) of the ternary system increases, while the corresponding t_{eq} value decreases with an increase in T_{ca}. The NOS_{eq} value of NA cation radicals shown in Fig. 1 is smaller than MNS shown in Table 1, but is greater than the value calculated by assuming NOS being dependent linearly on the amount of the organic com-

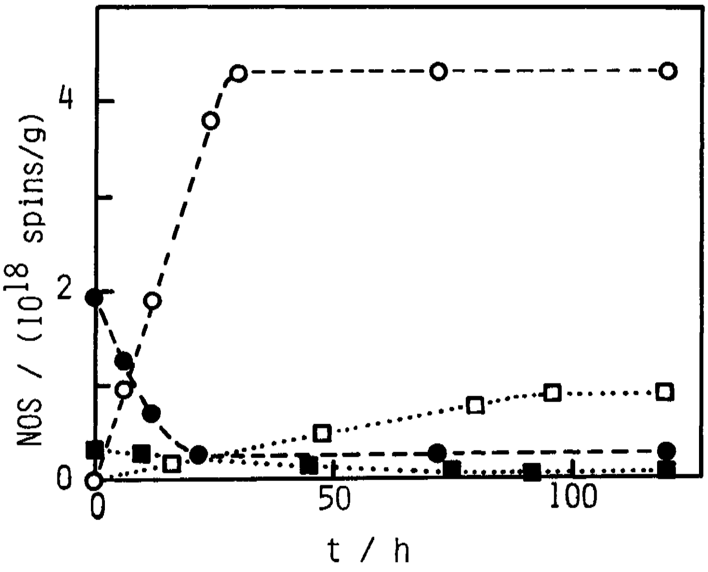

Fig. 1. Time courses of NOS for PE (●) and NA (○) at T_{ca} = 650 °C, and PE (■) and NA (□) at T_{ca} = 400 °C.

pound adsorbed,4) and the amount of adsorbate molecules being 1/11 times the A_{max} for PE or 10/11 times the A_{max} for NA (0.84 or 4.0 x 10^{18} spins/g, respectively, at T_{ca} = 400 or 650 °C). The NOS_{eq} value of PE cation radicals shown in Fig. 1 is considerably greater than the value calculated in a similar manner (0.26 or 1.7 x 10^{17} spins/g, respectively, at T_{ca} = 400 or 650 °C). Thus, the presence of NA influences NOS for PE, or vice versa. Similar results were obtained with a ternary system being treated in the order of HY-NA-PE, HY-TCNE-DNB, or HY-DNB-TCNE. Different from an acid or base in a solution, even cation radicals from a stronger electron donor adsorbed in advance were mostly replaced by those from a weaker donor, reaching eventually a new equilibrium. Similarly, anion radicals from a stronger acceptor were replaced by those from a weaker acceptor.

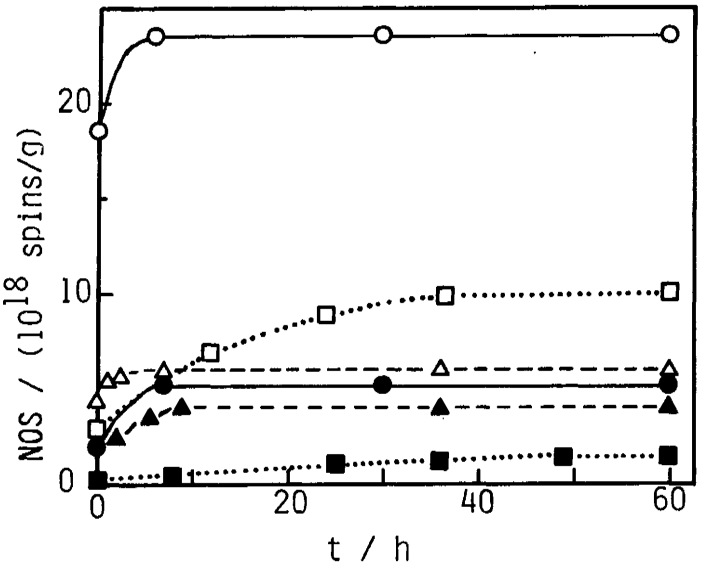

Fig. 2. Time courses of NOS for DNB (●) and PE (○) at T_{ca} = 650 °C, DNB (▲) and NA (△) at T_{ca} = 650 °C, and DNB (■) and PE (□) at T_{ca} = 400 °C.

On the other hand, HY was in contact with a given volume of 0.01 mol dm^{-3} of n-heptane solution of DNB (containing 0.1 times the A_{max} of DNB), dried under reduced pressure, impregnated again with a given volume of 0.01 mol dm^{-3} of n-heptane solution of PE (containing therein the A_{max} of PE), and finally dried again in vacuo. Fig. 2 illustrates the time courses of NOS of DNB anion radicals and of PE or NA cation radicals. As can be seen from Fig. 2, the NOS values both of DNB anion radicals and of PE or

NA cation radicals increase with the passage of time up to their respective equilibrium states. The values of NOS_{eq} of both ion radicals are much greater than those expected from MNS of the corresponding binary systems. The ratio of NOS_{eq} to MNS was pronounced when a weaker donor, weaker acceptor, or HY calcined at 400 °C was employed. The t_{eq} value of this ternary system for PE cation radicals was greater, while that for DNB anion radicals was smaller than t_{eq} of the corresponding binary system. A similar time course of NOS was observed when HY was at first in contact with PE or NA, subsequently with TCNE or DNB. Very little spin formation in a mixture of PE and DNB without HY suggests the generation of radicals only on active sites of HY. In the case of a ternary system of HY, DNB, and PE at a constant DNB content (A_{max}), NOS of DNB anion radicals increased with an increase in PE content from 0 (1.8×10^{18} spins/g) to 0.15 times the A_{max} (4.8×10^{18} spins/g), and became constant at a further increased PE content. Whereas, NOS for PE (0, 8.2, or 21×10^{18} spins/g, respectively, at a PE content of 0, 0.15, or 1.0 times the A_{max}) increased during the constant NOS for DNB. The observation of superimposed spectra of ion radicals from DNB and PE presumably indicates the presence of no interaction between ion radicals on HY. Then, the formation of cation and anion radicals occurs at different sites, and an increase in the number of solid base sites gives rise to an increase in that of coexisting acid sites.

Surface-physicochemical properties at non-equilibrium states have not been paid much attention. However, a great t_{eq} value obtained with the ternary system of HY and two organic compounds suggests the importance of non-equilibrium states when an aluminosilicate is used, for example, as a practical catalyst. A quantitative consideration of enhanced radical formation with the coexistence of two organic compounds would prompt the improvement in controlling the physicochemical properties of complicated zeolite-organic systems reproducibly. Further, we think that the structures of spin-generating sites of an aluminosilicate should be reconsidered by taking into account the NOS values at non-equilibrium states.

References

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