The Number of Organic Radicals on a Decationated Y-Type Zeolite before, during, and after Irradiating with Ultraviolet Light or Heating

Hiroshi Kashiwagi
Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University,
Sugitani, Toyama 930-01

(Received March 18, 1991)

A decationated Y-type zeolite (HY) was adsorbed by a single organic compound from a heptane solution, and dried in vacuo. The numbers of the radicals in these binary systems before, during, and after irradiating with ultraviolet (UV) light or heating were followed by electron paramagnetic resonance spectroscopy and then compared. During UV irradiation, the number of radicals increased from the constant number of spins before illumination (C_1) to the second constant number of spins (C_2). After stopping the illumination, the C_2 decreased up to the third constant number of spins (C_3). The C_3 value was smaller than C_2, but was significantly greater than C_1. The enhancement of radicals induced by UV light, expressed quantitatively in terms of the C_3/C_1 ratio, was pronounced when either a weak donor or a weak acceptor was adsorbed on HY calcined at a low temperature. C_1 was proportional to the amount of adsorption up to the maximal amount of adsorption, whereas C_2 and C_3 were proportional only at a considerably decreased amount of adsorption. A similar tendency was observed when the binary systems were heated at 40 or 80 °C. A quantitative determination of the mechanically induced enhancement of radicals would prompt either an improvement in the reproducibility of physicochemical data or an elucidation of the solid acidity or basicity.

Organic radical formation on the surface of an aluminosilicate due to a charge-transfer interaction has frequently been studied.[1)] In order to find some new factors available for improving the reproducibility of the physicochemical data concerning relatively complicated systems, or for correlatively and comprehensively elucidating the solid acidity or basicity, we followed in a preceding paper the time course of the number of spins (NOS) in either a binary system comprising a decationated Y-type zeolite (HY) and a single organic compound or a ternary system comprising HY and two organic compounds after removing a solvent (heptane).[2)] The NOS values and their time courses were dependent on the calcination temperature of HY (T_{ca}) as well as the electron-donating or -accepting characteristics of the organic molecules. The NOS values of the binary system were reversible and linear up to the amount of adsorption,[2,3)] whereas those of the solvent-free ternary (HY–two organic) systems, which were irreversible and nonlinear to the amount of adsorption, were dependent on the order of adsorption.[2)]

The NOS values of the solvent-free ternary systems were suitable for quantitative consideration of this kind of irreversibility. However, vigorous stirring of the HY–organic binary system in heptane caused another qualitative irreversible dependence of NOS on the amount of adsorption. Furthermore, this kind of irreversibility was also induced in solvent-free binary systems either by ultraviolet (UV) irradiation or by heating.

The radical species produced at solid (Lewis) acid sites induced by photoillumination were identified based on analyses of the hyperfine structures of the electron paramagnetic resonance (EPR) spectra.[4)] In addition, the stoichiometric formation of complexes between the Lewis acids and the radicals induced by photoirradiation was confirmed.[4)]

In the present study, we followed by EPR spectroscopy the NOS values of the solvent-free HY–organic binary systems before, during, and after UV irradiation or before, during, and after the application of heat. The results obtained with binary systems comprising both HY calcined at 400 or 650 °C and perylene (PE, a strong donor), naphthalene (NA, a weak donor), tetracyanoethylene (TCNE, a strong acceptor), or 1,3-dinitrobenzene (DNB, a weak acceptor) were compared with one another. The NOS values obtained after illumination or heating were significantly greater than those obtained before the treatment. The enhancement of radicals was related to the T_{ca} and electron-donating or -accepting characteristics of the organic molecules. Furthermore, nonlinear dependence of the NOS values on the amount of adsorption was determined quantitatively. We thought that a quantitative consideration of the mechanically induced enhancement of radicals would prompt the finding of some new factors necessary either for improving the reproducibility of physicochemical data of relatively complicated systems or for elucidating the mechanically induced solid acidity or basicity.

Experimental

Materials. An HY was obtained by calcining an NH_4^+-exchanged Y-type zeolite (Si/Al=1.90) at 400 or 650 °C. The purification of PE, NA, TCNE, and DNB has been previously described.[2)]

Procedure. HY was brought into contact with a heptane solution (0.01—0.1 mol dm^{-3}) of PE, NA, TCNE, or DNB, dried under reduced pressure (ca. 3 Pa), and stored in an EPR cell in dry nitrogen at 25 °C until the first constant number of spins (C_1) was attained. This binary system, being stored in the EPR cell, was then irradiated with UV light or heated at 40 or 80 °C with occasional shaking until the second constant number of spins (C_2) was reached. After stopping either the illumination or heating, the sample was permitted to stand at 25 °C until the third constant number of spins (C_3) was attained. The EPR spectra were followed throughout all of these processes.

The heating temperature was adjusted by using a thermostat. A JEOL ES-05 H-type UV irradiation unit fitted with a 500-W mercury lamp was used for illumination.

Spectral Measurement. The EPR spectrometer, experimental conditions, and method for determinating both NOS and amount of adsorption have been described previously.[2] The experimental errors in NOS and the amount of organic molecules adsorbed on HY were less than 10%.[2]

Results and Discussion

Time Courses of NOS before, during, and after UV Irradiation or Heating. As described previously, a fairly well-resolved hyperfine structure was obtained in the EPR spectrum of the PE or NA cation radicals on solid acid sites or of the DNB anion radicals on solid base sites; the spectrum of the TCNE anion radicals, however, was unresolved.[3,5]

The time courses of the NOS before, during, and after UV irradiating or before, during, and after heating were examined using a solvent-free binary system comprising a maximal amount of adsorption (A_{max}) of PE, NA, TCNE, or DNB and HY calcined at 400 or 650 °C. As descrived previously,[2] the NOS for the binary system before illumination was initially small, gradually increased with the passage of time, and finally reached C_1.

The time courses of NOS during or after UV irradiation are demonstrated in Figs. 1 and 2, respectively.[6] As shown from Fig. 1, the NOS increases with the passage of time from C_1 to C_2 after the start of UV irradiation. As illustrated in Fig. 2, NOS is the greatest (C_2) immediately after stopping the illumination; it gradually decreases with the passage of time, finally reaching C_3. As described below, the NOS values and their time courses are dependent on T_{ca} and the electron-donating or -accepting characteristics of the organic molecules.

The time courses of the values of NOS obtained before, during, or after heating at 40 or 80 °C were analogous to

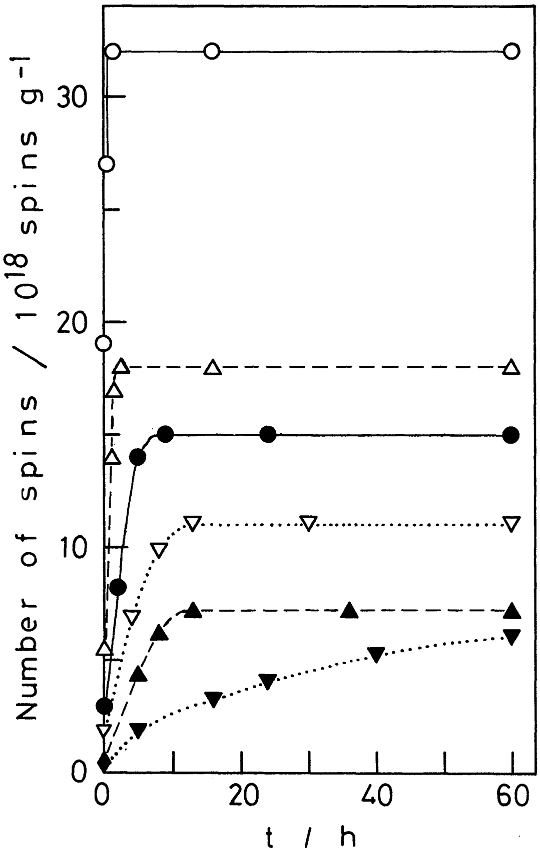

Fig. 1. Time course of the number of PE cation radicals on HY calcined at 650 (○) or 400 (●) °C, TCNE anion radicals on HY calcined at 650 (△) or 400 (▲) °C, or DNB anion radicals on HY calcined at 650 (▽) or 400 (▼) °C during UV irradiation. The amount of the organic molecules adsorbed on HY was A_{max}.

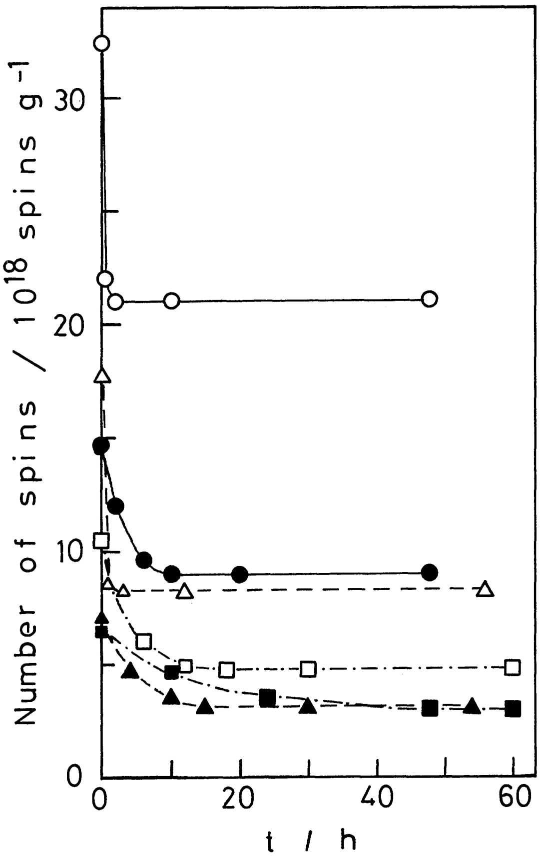

Fig. 2. Time course of the number of PE cation radicals on HY calcined at 650 (○) or 400 (●) °C, NA cation radicals on HY calcined at 650 (□) or 400 (■) °C, or TCNE anion radicals on HY calcined at 650 (△) or 400 (▲) °C after stopping illuminating. The amount of adsorption was A_{max}.

Table 1. Constant Number of Spins and the Time Required for Attaining the Constant upon UV Irradiation[a)]

Organic compound	T_{ca}	C_1	C_2	C_3	C_3/C_1	t_{C1}	t_{C2}	t_{C3}
	°C	10^{18} spins g^{-1}				h		
PE	650	19	32	21	1.1	1	1.5	2
	400	2.9	15	9.0	3.1	8	9	10
NA	650	4.4	11	5.8	1.3	8	9	10
	400	0.92	7.0	3.4	3.7	40	45	50
TCNE	650	5.5	18	8.3	1.5	2	2.5	3
	400	0.61	7.2	3.2	5.2	12	13	15
DNB	650	1.8	11	4.8	2.7	10	13	18
	400	0.22	6.5	2.7	12	120	130	140

a) The amount of adsorption on HY was A_{max}.

Table 2. Constant Number of Spins and the Time Required for Attaining the Constant upon Heating at 80 °C[a)]

Organic compound	T_{ca}	C_1	C_2	C_3	C_3/C_1	t_{C1}	t_{C2}	t_{C3}
	°C	10^{18} spins g^{-1}				h		
PE	650	19	28	19	1.0	1	1.5	2
	400	2.9	11	5.8	2.0	8	9	10
NA	650	4.4	9.8	4.8	1.1	8	10	11
	400	0.92	5.4	1.8	2.0	40	45	50
TCNE	650	5.5	13	6.5	1.2	2	2.5	3
	400	0.61	4.9	2.1	3.4	12	14	15
DNB	650	1.8	6.6	3.0	1.7	10	14	20
	400	0.22	2.5	1.1	5.0	120	135	150

a) The amount of adsorption on HY was A_{max}.

those obtained upon UV irradiation.

Enhancement of Radicals by Illuminating or by Heating. Table 1 summarizes the values of C_1, C_2, C_3, the time required for attaining the C_1 (t_{C1}), the time required for attaining C_2 (t_{C2}), and the time required for attaining C_3 (t_{C3}), as well as the ratio C_3 to C_1 (C_3/C_1) obtained upon UV irradiation of the HY–organic system at a given amount of adsorption (A_{max}). Tables 2 and 3 list the corresponding values obtained upon heating at 80 or 40 °C, respectively. Although not shown in Table 3, the values of t_{C1}, t_{C2}, and t_{C3} obtained by heating at 40 °C were close to those obtained by heating at 80 °C (Table 2).

In general, C_3 is significantly greater than C_1, indicating that an enhancement of the radicals is induced by either heating or photoillumination applied after HY is adsorbed by the organic molecules. The C_1, C_2, and C_3 are small, while the t_{C1}, t_{C2}, t_{C3}, and C_3/C_1 are large when either a weak donor (NA) or a weak acceptor (DNB) is adsorbed on HY calcined at a low temperature (400 °C).

Dependence of the C_2 and C_3 Values on the Amount of Adsorption. As described previously,[2)] the C_1 value of the solvent-free HY–organic binary system before photoillumination increased linearly with an increase in the amount of adsorption, finally reaching a maximum number of spins at the amount of adsorption of A_{max}. Independent of T_{ca}, the A_{max} value for PE, NA, TCNE, or DNB was determined to be 3.1, 6.2, 3.6, or 2.2×10^{20} molecules/g-HY, respectively.[2)] The maximum numbers of spins/g-HY, shown as the C_1 in Table 1, however, were significantly dependent on T_{ca}.

Table 3. Constant Number of Spins upon Heating at 40 °C[a)]

Organic compound	T_{ca}	C_1	C_2	C_3	C_3/C_1
	°C	10^{18} spins g^{-1}			
PE	650	19	21	19	1.0
	400	2.9	5.3	3.7	1.3
NA	650	4.4	5.9	4.5	1.0
	400	0.92	1.8	1.2	1.3
TCNE	650	5.5	7.0	5.7	1.0
	400	0.61	1.6	0.94	1.5
DNB	650	1.8	2.8	2.0	1.1
	400	0.22	0.75	0.40	1.8

a) The amount of adsorption was A_{max}.

The dependence of the C_2/C_1 or C_3/C_1 obatined upon photoillumination on the amount of adsorption/A_{max} (A) from 0.1 to 1.0 is demonstrated in Table 4 or 5, respectively. The C_2 and C_3 values at A=0 were, of course, nil. On the surface of HY calcined at 650 °C, as can be seen from Table 5, the C_3 value for PE, NA, TCNE, or DNB is identical with the corresponding C_1 value at an A value of less than 0.6, 0.3, 0.5, or 0.1, respectively. With a further increase in the A value, C_3 gradually becomes greater than the corresponding C_1. On the surface of HY calcined at 400 °C, C_3 becomes greater than C_1, even at a decreased A value (less than 0.1); it further increases with an increase in the A value.

Table 4. Dependence of the C_2/C_1 Ratio on the Amount of Adsorption upon UV Irradiation

Organic compound	T_{ca}	C_2/C_1 at $A^{a)}$=									
	°C	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
PE	650	1.6	1.6	1.6	1.6	1.6	1.6	1.7	1.7	1.7	1.7
	400	3.9	4.0	4.1	4.2	4.4	4.6	4.8	5.0	5.1	5.2
NA	650	2.0	2.0	2.1	2.1	2.2	2.2	2.3	2.3	2.4	2.5
	400	4.1	4.4	4.9	5.4	5.9	6.4	6.8	7.2	7.4	7.6
TCNE	650	3.0	3.0	3.0	3.0	3.1	3.1	3.2	3.2	3.3	3.3
	400	8.0	8.1	8.5	8.9	9.3	9.8	10	11	12	12
DNB	650	4.9	5.0	5.1	5.3	5.4	5.5	5.7	5.8	5.9	6.1
	400	12	13	14	15	17	19	21	24	28	30

a) The amount of adsorption/A_{max}.

Table 5. Dependence of the C_3/C_1 Ratio on the Amount of Adsorption upon UV Irradiation

Organic compound	T_{ca}	C_3/C_1 at $A^{a)}$=									
	°C	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
PE	650	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.1
	400	1.3	1.4	1.5	1.6	1.7	1.8	2.0	2.4	2.8	3.1
NA	650	1.0	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.3
	400	1.9	2.1	2.3	2.5	2.7	2.8	3.0	3.3	3.6	3.7
TCNE	650	1.0	1.0	1.0	1.0	1.0	1.1	1.3	1.5	1.5	1.5
	400	1.6	1.8	2.1	2.5	2.9	3.5	4.0	4.6	5.0	5.2
DNB	650	1.0	1.1	1.2	1.4	1.6	1.9	2.2	2.5	2.7	2.7
	400	2.8	3.2	3.8	4.6	5.4	6.8	8.1	9.9	11	12

a) The amount of adsorption/A_{max}.

In the vicinity of A=1.0, however, the slope of the increase curve of C_3 decreases. Therefore, different from the C_1, C_3 is proportional to the amount of adsorption only at a decreased amount of adsorption.

The C_2/C_1 depends on the amount of adsorption, similarly to C_3/C_1. It can be seen from Table 4 that the C_2 values are much greater than C_1 and C_3. However, C_2/C_1 is constant at a decreased A value. It increases with a further increase in the A value. Therefore, C_2 is linear with respect to the amount of adsorption for a small amount of adsorption. The range of the A values providing a linear dependence of C_2 on the amount of adsorption is somewhat wider than that of C_3. Moreover, the ratio of C_2/C_1 at A=0.1 to that at A=1.0 is much smaller than the corresponding ratio for C_3/C_1.

Both C_3/C_1 and the C_2/C_1 are great, while the range of A values providing the linear dependence of C_2 and C_3 on the amount of adsorption is small when a weak donor (NA) or a weak acceptor (DNB) is adsorbed on HY calcined at 400 °C. At an identical A value, the C_2/C_1 or C_3/C_1 obtained at T_{ca}=650 °C is remarkably smaller than that obtained at T_{ca}=400 °C. Although not shown in Tables 4 and 5, the t_{C2} and t_{C3} values increased very slightly with an increase in the amount of adsorption.

The values of C_2/C_1 or C_3/C_1 obtained upon heating (40 or 80 °C) depended on the amount of adsorption in a manner similar to those shown in Table 4 or 5, respectively.

The C_2 and C_3 Values Obtained upon Heating Twice at Different Temperatures. The solvent-free HY–organic binary system was at first heated at a low temperature (40 °C) until attaining C_2; heating was then stopped and left at 25 °C until attaining C_3. This binary system was again heated at a sufficiently high temperature (80 °C) until attaining another C_2; heating was then stopped and left at 25 °C until attaining another C_3. In this case, the C_2 and C_3 values obtained upon the second heating at 80 °C was little influenced by the first heating at 40 °C. On the contrary, when the binary system was treated at first at 80 °C and subsequently at 40 °C, the final C_3 was identical with that obtained without the second heating at 40 °C.

Heating with a Slow Raise in Temperature. The C_2 and C_3 values shown in Tables 2 and 3 were obtained by placing the HY–organic system, having been stored at 25 °C, directly into a thermostat of 40 or 80 °C. On the other hand, when the temperature of the binary system was slowly raised from 25 to 40 or 80 °C (less than 0.3 °C h^{-1}), the C_2 and C_3 values at an increased amount of adsorption became smaller than those shown in Tables 2 and 3. By way of heating with a slow temperature rise, the C_2 and C_3 obtained at a heating temperature of 40 °C became proportional to the amount of adsorption up to A=1.0. Although the range of the A values providing the linear dependence on the amount of adsorption increased, the C_2 and C_3 obtained by heating at 80 °C were still nonlinear to the amount of adsorption.

Comparison of the Results Obtained by Continuous and Discontinuous Photoirradiation. Although not shown in Table 1, the C_3 obtained at a decreased irradiation duration ($<t_{C2}$) was smaller than that shown in Table 1. The C_3 obtained by continuous irradiation was smaller than that obtained by discontinuous irradiation of the same total duration. For example, the C_3 for NA or DNB (A_{max}) on HY calcined at 400 °C induced by continuous irradiation for 20 h was 2.9 or 0.75×10^{18} spins/g-HY, respectively, while the corresponding value induced by 20-times irradiation for 1 h was 3.0 or 0.91×10^{18} spins/g-HY, respectively. This difference in the C_3 value was pronounced when NA or DNB was adsorbed on HY calcined at 400 °C. In general, the C_3 values and their nonlinear dependence on the amount of adsorption became pronounced in the case of discontinuous photoirradiation. Similarly, the C_3 induced by continuous heating was somewhat smaller than that induced by discontinuous heating of the same total duration.

As shown from Tables 1 and 2, t_{C1} is the smallest, while t_{C3} is greatest among the t_{C1}, t_{C2}, and t_{C3} values. Generally, the time required for attaining a constant number of spins increased with an increase in the number of operations (discontinuous heating or illumination).

Enhancement of Radicals Induced by General Mechanical Energy. General mechanical energy (e.g., shaking or compressing) applied after the adsorption of the organic molecules on HY qualitatively increased the C_2/C_1 and C_3/C_1 ratios and decreased the range of A values providing the linear dependence of the C_2 and C_3 values on the amount of adsorption.

Strong and Weak Acid or Base Sites. According to the preceding paper,[2] there coexist two kinds of active sites on the surface of HY: A strong active site is related to an induction of PE cations or TCNE anion radicals on HY calcined at 650 °C, whereas a weak active site is related to the formation of radicals from a weak donor (NA) or a weak acceptor (DNB) on HY calcined at a low temperature (400 °C). Since weak active sites may be related to a slow increase in the NOS values,[2] they may play some important roles in the mechanically induced enhancement of radicals, especially in a binary system comprising NA or DNB and HY calcined at 400 °C.

Improvement of the Reproducibility of Physicochemical Data of Relatively Complicated Systems. By using the physicochemical properties of complicated systems it is quite difficult to reproduce the same phenomena constantly. In the case of HY–organic systems, the NOS values of the binary systems were proportional,[2,3] while those of the ternary systems were not proportional to the amount of adsorption.[2] As described above, a similar nonlinearity (irreversibility) was induced by either heating or irradiating the HY–organic systems. A quantitative determination of the mechanically induced enhancement of radicals, and of the nonlinear dependence of NOS on both the amount of adsorption and the method of applying the mechanical energy, may be available for finding some new factors necessary for improving the reproducibility of physicochemical data of relatively complicated systems.

Radical Formation Induced by Mechanical Energy Applied after the Adsorption of Organic Molecules on HY. The results described above may also provide some new factors necessary for constructing a model of solid acid or base sites. The spin-generating sites on the surface of an aluminosilicate have been attributed to Lewis acid sites,[1,3] which are known to be produced from Brönsted acid sites at an elevated T_{ca} (over 500 °C).[1,3] However, radicals were induced by mechanical energy, such as UV light or heat, and applied after the adsorption of organic molecules on HY calcined at 400 °C. Extremely, the PE cations or TCNE anion radicals were induced by either heating or illuminating an NH_4^+-exchanged zeolite without any calcination which had been adsorbed by the organic molecules. A pronounced increase in the NOS obtained with a binary system comprising either a weak donor (NA) or a weak acceptor (DNB) and HY calcined at a low temperature (400 °C) as well as great t_{C1}, t_{C2}, and t_{C3} values might indicate some important roles of weak acid sites on the surface of HY.[2]

Conclusion

The NOS values of the HY–organic binary systems were proportional,[2,3] while those of the HY–two organic systems were only partly proportional to the amount of adsorption.[2] The nonlinearity of the NOS to the amount of adsorption was also induced by heating or irradiating the solvent-free binary systems. These findings may provide some new factors necessary for improving the reproducibility of physicochemical data.

Although the charge-transfer interaction, mechanochemistry, and properties of polymers appear in large and relatively complicated systems, they may disappear when a large, complicated system is divided into subsystems possessing appropriately equal sizes. In the present study we dealt quantitatively with the mechanically (UV light or heat) induced enhancement of radicals and the nonlinear dependence of NOS on the amount of adsorption, regarding not only the surface of HY, but also adsorbate molecules, the experimental conditions (e.g., temperatures and UV light), and the methods and processes of heating or illuminating as constituents of a large system. Such a correlative, comprehensive approach would prompt an elucidation of solid acidity or basicity. The other factors necessary for constructing a model of solid acidity or basicity will be described in a subsequent publication.

References

1) K. Tsutsumi and H. Takahashi, "Zeoraito," ed by N. Hara and H. Takahashi, Kodansha Scientific Publishers, Tokyo (1975), pp. 72—78, and references therein.

2) H. Kashiwagi, *Chem. Lett.*, **1990**, 1063; H. Kashiwagi, *Bull. Chem. Soc. Jpn.*, **64**, 423 (1991).

3) D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **86**, 749 (1964).

4) For example: B. M. Hoffman and T. B. Eames, *J. Am. Chem. Soc.*, **91**, 5168 (1969); P. H. Kasai and R. J. Bishop, Jr., "Zeolite Chemistry and Catalysis," ed by J. A. Rabo, ACS Monograph (1976), Vol. 171, p. 350.

5) B. D. Flockhart, L. McLoughlin, and R. C. Pink, *J. Catal.*, **25**, 305 (1972); K. Hirota, K. Kuwata, and Y. Akagi, *Bull. Chem. Soc. Jpn.*, **38**, 2209 (1965).

6) Even during irradiating with UV light or during heating at 80 °C, the shape and intensity of an EPR spectrum of the HY–organic system after attaining the C_2 was unchanged. After stopping illuminating or heating, the organic molecules adsorbed on HY were recovered unchanged by desorbing them with a large excess of the solvent. Since HY (Si/Al=1.9) was composed of relatively weak acid sites (Refs. 1 and 2), no further reaction of the ion radicals produced on HY occurred even during irradiating or heating.