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Nature of Alkali Metal–Active Carbon Catalyst as Revealed by Electron Spin Resonance Spectra

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Active carbon adsorbed with sodium or potassium vapor gives an ESR band at $g =$ 2.004–5 which diminishes on introduction of hydrogen, and catalyzes the H_2–D_2 exchange reaction. The number of spins thus observed is closely correlated to the catalytic activity of the H_2–D_2 exchange. The observed spins may be classified into two types, A and B, according to their temperature dependence. The predominant species, Type A, is in conformity with Curie's Law, while Type B assumes conduction electron of semiconductor. The Type A spins are likely to be responsible for the catalysis of H_2–D_2 exchange through the reaction

$$2e^- + H_2 \rightleftharpoons 2H^-.$$

Although carbon monoxide increases the spin density, it behaves as a strong poison.

INTRODUCTION

A novel catalyst system for the ammonia synthesis, alkali-metal promoted transition metals on active carbon has been found in this laboratory (*1*). One of the roles of active carbon has been presumed to be to accept electrons from alkali metal and donate them to transition metal (*2*). On this view the electronic interaction between alkali metal and active carbon is worth further study. It was accordingly attempted to study the interaction by means of ESR. Thus a characteristic ESR signal, which diminished on adsorption of hydrogen, was found (*3*) and correlated to the H_2–D_2 exchange activity (*4*).

The present paper describes the nature of ESR signal to discuss the electronic state of alkali-promoted active carbon which seems to be related to the role of active carbon in the above-mentioned ammonia synthesis catalyst. Some ESR spectra of carbon have been reported, but those electron spins responsible for the spectra are reportedly unstable and disappear after high temperature heat treatment (*5*). The active carbon used in this study had been produced from coconut by high temperature reaction with steam so that no significant spectra were detected from the unpromoted active carbon. No such revealing spectra as observed in this study were found before on carbon.

EXPERIMENTAL METHODS

1. ESR Measurements

A "Varian" ESR spectrometer (Model EPR12) operated at a cavity resonance frequency of 9.1 GHz (*X* band) was used. The *X* band cavity was a TE102 mode type. Relative intensities were determined by graphical integration. The number of spins was determined relative to DPPH.

2. Catalysts

The coconut carbon obtained from Daiichi Tanso Co. was crushed into 20–40 mesh grains and washed thoroughly with pure water. About 2 g of the carbon sample was evacuated at 400°C for 2 hr and placed into a dry nitrogen atmosphere at room temperature, where a weighed amount of metallic potassium held in a capillary was admitted onto the carbon sample. The mixture was again heated up to 250°C in vacuum and to 400°C in helium to have potassium adsorbed on the carbon. Helium gas was then circulated through the carbon bed at 400°C for 2 hr, which was not long enough to distribute potassium through the bed. The samples (about 0.05 ml) for the ESR measurements were taken layer by layer from the unevenly distributed bed so that samples of a range of alkali contents were obtained in one preparation. Those samples were separately determined for alkali. All the transfer of alkali-added carbon was made in an atmosphere of dry nitrogen.

RESULTS

1. ESR Spectra of AC–K and AC–Na Catalysts

ESR spectra of the active carbon–potassium (AC–K) and –sodium (AC–Na) are shown in Fig. 1. Both spectra are assymmetric and rather broad (about 100 G) as usually observed for solid material. The *g* values of the spectra are 2.005 ± 0.002 for AC–K and 2.004 ± 0.002 for AC–Na. Since the active carbon without added alkali metal gave no such spectrum, it is clear that the electron spins as revealed by the ESR spectrum are caused by the addition of potassium or sodium.

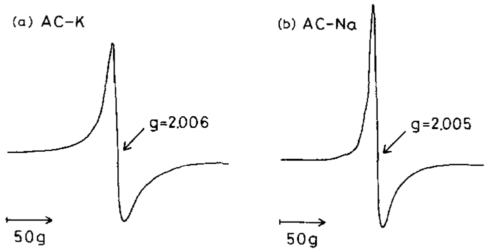

FIG. 1. ESR spectra of alkali-added active carbon at room temperature. (a) AC–K; (b) AC–Na.

As reported in the preceding paper (*4*), the spin densities of both AC–K and AC–Na as functions of alkali metal content were found to run parallel with the catalytic activities for the H_2–D_2 exchange. AC–Na exhibits a maximum at around 3.5 mmol Na/g AC, while AC–K is inactive and exhibits little spins at lower concentration than about 1.5 mmol K/g AC, above which both the activity and spin density increase with potassium content. The variation of spin density is illustrated later in Fig. 4.

2. Variation of the ESR Spectra with Temperature

The nature of unpaired electron as detected by the ESR was examined by its dependence on temperature. No detectable change was observed in *g* value of low temperature spectra. The ESR intensities obtained with two AC–K samples of different potassium contents (1.5 and 3.8 mmol/g AC) are shown in Fig. 2 as a function of reciprocal temperature in Kelvin. Since straight lines are obtained in Fig. 2 and the ESR intensity (*I*) may be assumed to be proportional to the magnetic susceptibility, this result demonstrates that the unpaired electron in AC–K obeys Curie's law.

Since the spin density of AC–Na varies in a different way from that of AC–K as

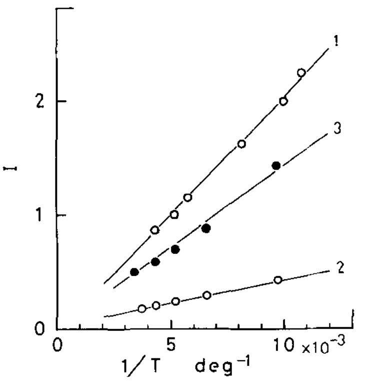

FIG. 2. Temperature dependence of ESR intensity. (1) AC–K (3.8 mmol/g AC); (2) AC–K (1.5 mmol/g AC); (3) AC–Na (3.9 mmol/g AC).

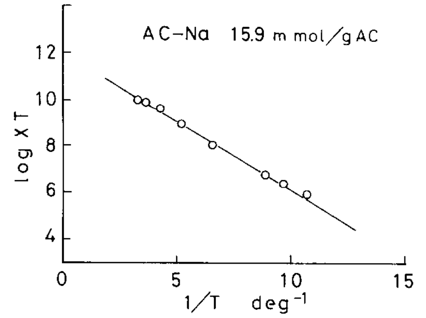

FIG. 3. Temperature dependence of ESR intensity of sodium-rich AC–Na (15.9 mmol/g AC).

the alkali content increases, giving a maximum at around 3.5 mmol Na/g AC, the temperature dependence of the ESR intensity was examined with two samples of AC–Na, one near the maximum (3.9 mmol Na/g AC) and the other far beyond the maximum (15.9 mmol Na/g AC). Although the ESR intensity for the former sample was found to obey Curie's law as shown in Fig. 2, this was not the case for the latter sample. The ESR intensity of the latter was in conformity with the relation,

$$x \propto [\exp(-A/T)]/T, \qquad (1)$$

which is known to be characteristic of the conduction electrons of semiconductor (*6*) (Fig. 3).

3. Variation of Line Width with Sodium Content

It is shown above that the characteristic variation of spin density with increase in sodium content of AC–Na is accompanied by the change in nature of ESR spectra as demonstrated by the different laws to which the spectra conform. This change is accompanied by a line width broadening. The variation of line width ΔH_{msl} with sodium content is illustrated in Fig. 4 together with the variation of spin density. The line width abruptly increases at around 4.5 mmol Na/g AC, where spin density decreases sharply, and passes through a maximum, while, in the case of AC–K, the line width stays at 13 ± 5 G independent of potassium content. The characteristic variation of ΔH_{msl} for AC–Na may be interpreted in terms of dipole-dipole interaction followed by exchange narrowing.

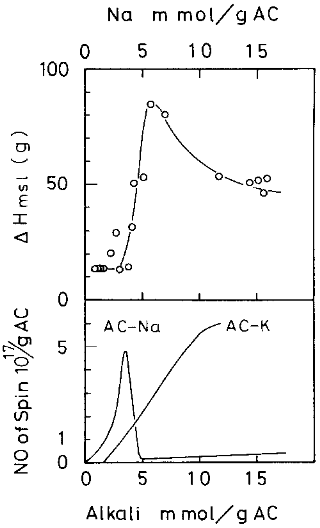

FIG. 4. Variations of line width and spin density with alkali content.

4. Different Behaviors of Sodium and Potassium in the Case of Ammonia Catalyst

The different behaviors of sodium and potassium in the promotion of active carbon has been ascribed to a preferential incorporation of potassium into graphite lattice which is admittedly difficult to take place in the case of sodium (*7*). In other words low content potassium is lost into graphite lattice instead of being adsorbed on the surface, whereas sodium is effectively used to form adsorbed atoms. If this interpretation is valid, a similar difference may appear in the promotion of ammonia synthesis over ruthenium–active carbon–alkali metal (Ru–AC–K or Na) catalysts.

In this respect, the effect of alkali content on the rate of ammonia synthesis over Ru–AC–Na and –K was examined with particular reference to lower contents. The results are illustrated in Fig. 5. It is clearly shown that the ineffective sodium is very

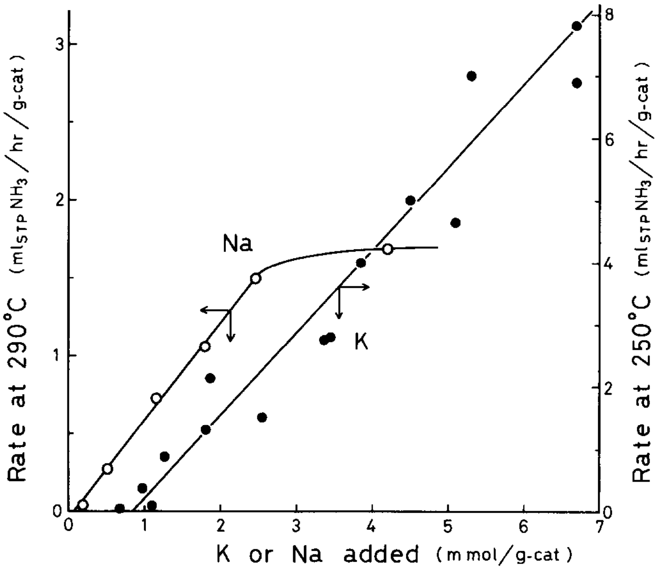

FIG. 5. Variation of ammonia synthesis rate over Ru–AC–K catalyst with alkali content ($N_2 + 3H_2 =$ 600 Torr).

small, if any, while about 1.0 mmol/g AC of ineffective potassium is observed. Thus the effect of alkali metal in Ru–AC–alkali system seems to be consistent with that in AC–alkali. However the effects of sodium content become dissimilar at higher content. Both the H_2–D_2 activity and spin density pass through a maximum, while the ammonia synthesis rate levels off. This difference are discussed below.

5. The Effects of Adsorption of Hydrogen and Carbon Monoxide on the ESR Spectra

As previously reported (*4*), the spin density of AC–alkali is closely correlated to the catalytic activity for the H_2–D_2 exchange which is poisoned by carbon monoxide. In this respect the effects of hydrogen and carbon monoxide adsorption on the spectra are of interest.

The change of spectra on introduction of hydrogen over an AC–K catalyst at room temperature is illustrated in Fig. 6. It is obvious that the spin density is decreased by hydrogen retaining *g* value. The decrease was over within 30 min. Evacuation of gas phase hydrogen gave no change at room temperature, whereas the initial spectra were restored after evacuation at 90°C for 2 min. It is to be noted that no other signal appeared on introduction of hydrogen. These results suggest that hydrogen is adsorbed by an interaction with the unpaired electrons. Indeed, separate experiments disclosed a consistent behavior that hydrogen is irreversibly adsorbed at 0°C while it is desorbable at 90°C (*3*). Thus it appears that the unpaired electrons are partially lost by a reaction with hydrogen, possibly forming adsorbed H^-.

On the other hand the effect of carbon monoxide adsorption is quite different as illustrated in Fig. 7. It is obvious that the spin density increases on introduction of carbon monoxide retaining *g* value. No

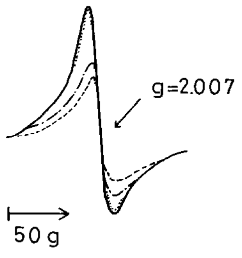

FIG. 6. Effect of hydrogen adsorption on the ESR spectra of AC–K (4.9 mmol/g AC). (—) 0 min, (-·) 5 min, (---) 30 min after introduction of H_2, (···) after evacuation at 100°C for 2 min.

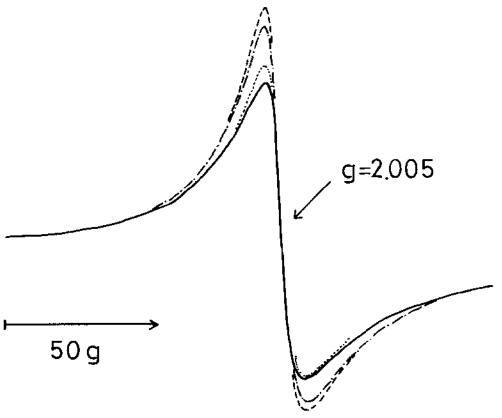

FIG. 7. Effect of carbon monoxide adsorption on the ESR spectra of AC–K (6.9 mmol/g AC). (—) Without CO, (–·) 10 min, (---) 30 min after introduction of CO, (···) after evacuation at 100°C for 2 min.

other signal was observed. Evacuation of gas phase caused a slow decrease at room temperature and further evacuation at 100°C for 2 min restored the initial spectra. Thus the adsorbed carbon monoxide seems to be responsible for the increase in spin density.

If those electron spins caused by carbon monoxide adsorption are identical, in nature, with those by alkali metal, the catalytic activity should be increased by carbon monoxide. But this was not borne out in the experimental results. As shown in Fig. 8 even a small amount of carbon monoxide gives a remarkable decrease in the catalytic activity. Carbon monoxide seems to occupy the active sites thus poisoning the catalyst but without decreasing the spin density and further creating new spins.

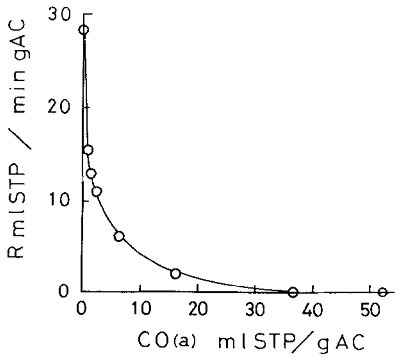

FIG. 8. Effect of carbon monoxide adsorption on the rate of H_2–D_2 exchange at 0°C on AC–K (4.5 mmol/g AC).

DISCUSSION

1. Nature of Electron Spins

The electron spins observed here may be classified into two types, A and B, according to their temperature dependence. Type A obeys Curie's law and Type B does not. Those spins of both AC–K and –Na in the region where the spin density increases with alkali content are likely to belong to Type A. Type B is that found in the high sodium content sample of AC–Na.

Since Type A obeys Curie's law, those spins must be isolated and localized. *g* values are different from those of sodium film (1.97) (*8*) and colloidal potassium (1.998) (*9*). They are likely to be formed by the adsorbed alkali atoms. This view is supported by the facts that such sharp ESR spectra are not known with graphite–potassium compound, and that the spectra are clearly observed even with sodium which is known to be hardly incorporated into graphite lattice. The ineffectiveness of low content potassium is reasonably understood on this view. It is reasonable that the adsorbed alkali atoms donate electrons to carbon resulting in those spins, because carbon is admittedly an electron acceptor. The spin density accordingly increases with the alkali content up to a certain value.

There is a difference between AC–K and AC–Na. When alkali increases, the spin density of AC–Na passes through a sharp maximum at around 3.5 mmol Na/g AC, while that of AC–K increases all the way to 10 mmol K/g AC until the active carbon is saturated with potassium at the temperature of pretreatment (400°C). This difference may be firstly due to the loss of potassium into the graphite lattice. Since the maximum values of spin density obtained in both systems are rather similar in spite of about three fold difference in the alkali contents, potassium is apparently less effective than sodium in forming spins. This lower effectiveness may be partly due to the loss into the graphite lattice, resulting in a relatively lower surface concentration of potassium. Thus if a much higher potassium content of AC–K was obtained, there could be a maximum.

If the lower effectiveness of potassium to form spins is fully ascribed to the loss into the graphite lattice, the difference in alkali contents to produce largest number of spins, i.e., about 12 mmol/g AC for AC–K and 3.5 mmol/g AC for AC–Na, should have been consumed to form the graphite–potassium compound. However since the most potassium-rich compound is known to be C_8K, the required amount of graphite lattice is too much for the active carbon. Thus there must be another unidentified reason to bring about the difference between sodium and potassium.

The next problem to be explained should be the decrease of spin density after the maximum. Since this decrease is accompanied by the line width broadening, the dipole–dipole interaction must be being intensified, demonstrating that the adsorbed sodium atoms are located closer. In such situation some extent of spin pairing would become possible. Thus the decrease of spin density seems to be due to the spin pairing caused by the increase in the number of adsorbed atoms. If this is the case, the catalytic activity for the H_2–D_2 exchange which runs parallel with the spin density must be ascribed to the unpaired electrons of Type A. Since it is known that the stability of diatomic molecule decreases in the order (*10*).

$$H_2 > Li_2 > Na_2 > K_2,$$

the spin pairing tendency of sodium would be larger than that of potassium. This difference in the spin pairing tendency would be the reason why AC–Na exhibits a maximum of spin density while AC–K does not.

In the high sodium content region where Type B spins are observed, the added sodium might be agglomerated forming a metallic phase. But the observed spectra cannot be ascribed to the conduction electrons of sodium metal, because the ESR intensity was temperature dependent (*11*). The temperature dependence suggests the Type B spins to be conduction electrons of semiconductor. The activation energy according to Eq. (1) is obtained from Fig. 3 to be 0.27 kcal/mol, which is reasonable as an energy gap between conduction band and donor level of active carbon.

2. *Nature of AC–Alkali as a Component of Ammonia Catalyst*

It has been shown that transition metals supported on active carbon are inactive for the ammonia synthesis, whereas pure transition metals are active, and that the transition metals supported on active carbon are strikingly activated by the addition of alkali metal. These findings have been interpreted in terms of electron accepting nature of active carbon (*2*). That is, when a transition metal is supported on active carbon, the electron concentration in the transition metal which is the activity determining factor is reduced by the electron transfer to the carbon, thus rendering the transition metal inactive. This inactive state is not only relieved but also activated by the addition of alkali metal.

The present study has been made as a part of examination of above interpretation. The appearance of electron spins on addition of alkali metal demonstrates that the electron concentration of active carbon is increased by the addition of alkali metals, as expected. It is to be noted that the different behaviors of sodium and potassium are similarly observed in two systems; Ru–AC–alkali as the ammonia synthesis catalyst and AC–alkali as the spin holder. That is, the low content potassium is commonly ineffective, while this is not the case for sodium. This seems to mean that the effective activation of transition metal supported on the active carbon is made only by the adsorbed alkali metal and not by the intercalated one. The surface electron concentration seems to be responsible for the catalytic activity.

In the case of ammonia catalyst, alkali atoms are adsorbed not only on the carbon surface but also on the transition metal surface. In fact unsupported transition metals are activated by the addition of alkali metals for the ammonia synthesis. Accordingly the rate of ammonia synthesis over Ru–AC–Na levels off, while the spin density of AC–Na decreases as the sodium content increases. Somewhat smaller amount of ineffective potassium in the case of Ru–AC–K would be due to the fact that potassium can be adsorbed directly on ruthenium surface as well as on the carbon surface.

3. Interactions with Hydrogen and Carbon Monoxide

It is clear from the experimental results that the adsorption of hydrogen on AC–Na or AC–K reduces the spin density. This may take place in two ways;

(a) $H_2 + 2e \rightarrow 2H^-$,
(b) $H_2 + 2(K^+ + e^-) \rightarrow 2KH$.

As previously reported (*4*), the amount of hydrogen adsorption increases with the potassium content of AC–K above 1.5 mmol/g AC and thus runs parallel with the spin density. This may be explained by either of (a) and (b). But it was also shown (*4*) that a large part of adsorbed hydrogen is irreversibly held on the surface at 0°C where the H_2–D_2 exchange rapidly takes place, and that the irreversible hydrogen is not the intermediate of H_2–D_2 exchange because the exchange rate of the preadsorbed H_2 with gas phase D_2 is much slower than the rate of H_2–D_2 exchange. In this respect, the strongly adsorbed and less active hydrogen is presumably held on potassium as KH through the reaction (b), and the H_2–D_2 exchange reaction seems to take place via the reaction (a).

On the other hand carbon monoxide increases the spins retaining *g* value, while the catalytic activity is drastically reduced by carbon monoxide. The increase in spin density suggests that a paramagnetic species is formed by reaction with carbon monoxide. There is a classical observation that carbon monoxide reacts with potassium to form $(KCO)_6$ (*12*). The reactions,

(c) $K_2 + 2CO \rightarrow 2KOC\cdot$,
(d) $(K^+ + e^-) + CO \rightarrow KOC\cdot$,

might be responsible for the increase of spin density (c) and the deactivation (d).

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