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Activation of Hydrogen by Active Carbon with Adsorbed Alkali Metal

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H_2–D_2 exchange readily takes place on active carbon with adsorbed alkali metal at 0°C. The rate of exchange is first order in total pressure. Activation energy is lower on potassium–carbon (1–2 kcal/mol) than on sodium–carbon (2–7 kcal/mol). The catalytic activity runs parallel with the electron spin density of the catalyst as the alkali content is increased. Observed differences between sodium and potassium in the dependence of alkali content is ascribed to a loss of potassium into a graphite structure. The active site seems to be formed on the carbon surface by the adsorbed alkali atoms, while agglomeration of alkali atoms to form a metallic phase reduces the number of sites. The hydrogen adsorption seems to be dissociative.

INTRODUCTION

A novel catalyst system for the ammonia synthesis, alkali metal-promoted transition metals, has been found in this laboratory (*1*). A particularly high activity is obtained when the catalyst mixture is supported on active carbon. The role of active carbon has been interpreted as a medium of electron transfer from alkali to transition metal as well as a support of alkali metal (*2*). There is a critical concentration of alkali metal below which no catalytic activity for the ammonia synthesis is observed. In this respect the interaction between active carbon and alkali metal seems to call for an investigation. This has been done in terms of the hydrogen activation as well as the electron spin density, since it was known that graphite–alkali metal complexes are active in H_2–D_2 exchange (*3*, *4*). Meanwhile it was found that a characteristic ESR signal, which diminishes on adsorption of hydrogen is observed for the alkali metal-adsorbed carbon, while no signal for the carbon alone (*5*).

The present paper reports on the correlation among the H_2–D_2 exchange activity, the extent of H_2 adsorption, the electron spin density, and the concentration of alkali metal (Na and K) on carbon. H_2–D_2 exchange over carbon has been studied since the classical work of Bonhoeffer-Farkas on the *o*–*p* H_2 conversion (*6*). Although a sugar charcoal was claimed to be active for the H_2–D_2 exchange at 50°C (*7*), a later work failed to reproduce this activity (*8*). In the present case the coconut carbon used has no or, if any, very little activity for the H_2–D_2 exchange.

EXPERIMENTAL

Catalyst

The coconut carbon was obtained from Daiichi Tanso Co., 6–12 mesh grains were washed with pure water ten times to remove electrolytes. It was evacuated at 400°C for 2 hr and cooled to room temperature in vacuum. Metallic potassium was admitted onto the carbon in an atmosphere of dry nitrogen at room temperature and again heated up to 250°C in vacuum and to 400°C in helium to be adsorbed on carbon. To ensure distribution of alkali metal on carbon, helium gas (100 Torr) was circulated through the bed of carbon at 400°C for 5 hr. The catalyst thus prepared was later decomposed by water and analyzed for alkali concentration by titration with hydrochloric acid. During the adsorption of alkali metal, carbon grains were occasionally crashed into smaller grains.

The catalyst samples for ESR measurements were prepared similarly. Only one difference was shorter period of helium circulation, giving uneven distribution of alkali metal. Since only a small amount of sample was required for ESR measurement, samples of a range of alkali contents were obtained in one preparation. Those samples were respectively determined for alkali.

Procedure

The apparatus for the rate measurements was a conventional closed circulating system of about 200 ml. The rate measurements were made using a 1:1 mixture of H_2 and D_2. The isotopic analyses were made by gas chromatography using molecular sieve 5A column at liquid nitrogen temperature. The rate of H_2–D_2 exchange, R, was obtained by

$$\log(x_0 - x_e)/(x_t - x_e) = Rt/2.303n,$$

where x_0, x_t, and x_e are the mole fractions of HD at $t = 0$, t, and equilibrium, respectively, and n the total amount of hydrogen ($H_2 + D_2 +$ HD) in the system.

A Varian ESR spectrometer (model EPR 12) which 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 by comparing with a standard sample of DPPH.

RESULTS

H_2–D_2 Exchange Activity as a Function of Alkali Content

Determination of exchange rate was made with two series of catalysts: sodium and potassium on active carbon. Hereafter they are denoted as AC–Na and AC–K. The rates of exchange at 0°C and 200 Torr are shown in Fig. 1 as functions of alkali content. The activity of carbon without alkali was examined with a sample evacuated at 400°C for 2 hr. No HD was detected in 3 hr at 0°C and 200 Torr (H_2–D_2 = 1:1), whereas after 22 hr 5% HD was detected, corresponding to a rate of 0.0086 ml STP min^{-1} g^{-1} AC. The activity of carbon alone is negligibly small.

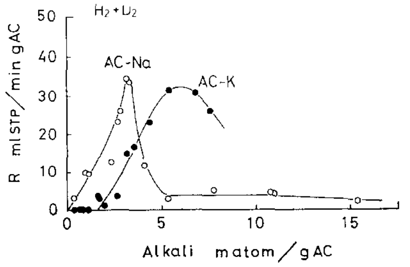

FIG. 1. Rate of exchange as function of alkali content at 0°C and 200 Torr.

The result in Fig. 1 discloses that the activity of AC–Na increases with Na content, passes through a sharp maximum at about 3.5 matom/g AC and decreases to a plateau value, while that of AC–K increases with K content higher than 1.5 matom/g AC and passes through a maximum at around 6 matom/g AC. There is a clear distinction between AC–Na and AC–K in their modes of activation. The ineffective part of alkali observed with AC–K does not appear on Ac–Na.

Since such ineffective potassium might be due to a reaction of potassium with oxygen compound involved in carbon, the carbon sample was pretreated with hydrogen at 400°C for 4 hr. In this treatment, 1.0 mmol of hydrogen was consumed per gram of carbon. Potassium was added on this treated carbon (2.0 matom/g AC). The activity of this sample (R = 0.82 ml STP min^{-1} g^{-1} AC) is in agreement with the value shown in Fig. 1. Accordingly, the ineffective part of potassium can not be explained in terms of the reaction with oxygen compound. Furthermore, the observed absence of ineffective part in AC–

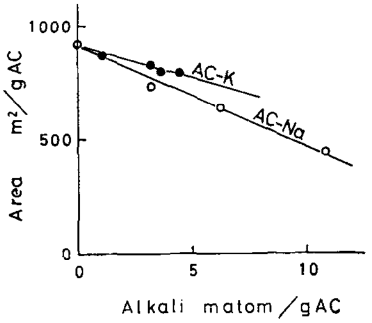

FIG. 2. Surface area of catalysts as function of alkali content.

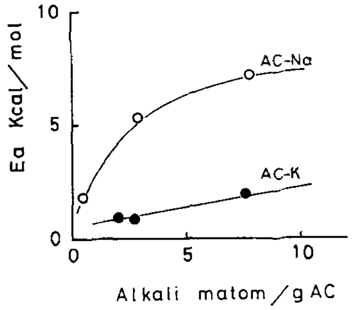

FIG. 4. Activation energy of exchange as function of alkali content.

Na system is consistent with this interpretation.

The BET area of catalysts as shown in Fig. 2 discloses that the surface area linearly decreases with alkali content in both series. There is no indication to be connected with the characteristic change in activity as shown in Fig. 1.

Kinetics of H_2–D_2 Exchange

The kinetics of H_2–D_2 exchange over an AC–K catalyst (2.7 matom/g AC) was determined at 0°C as a function of total pressure up to 200 Torr. As shown in Fig. 3, the exchange rate *R* is proportional to the total pressure. The temperature dependence of the exchange rate was determined in the range −78 to 60°C. The activation energies associated with the exchange rate are plotted against the alkali content in Fig. 4. The activation energy is much lower in AC–K than in AC–Na, while it increases with the alkali content in both systems. The value on AC–K is also much lower than that on graphite–K (6.3 kcal/mol) (*4*).

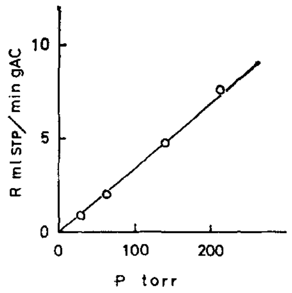

FIG. 3. Pressure dependence of the exchange rate at 0°C.

Chemisorption of Hydrogen and Carbon Monoxide

Chemisorption of hydrogen and carbon monoxide was examined with an AC–K catalyst (7.0 matom/g AC) at 0°C. The results are summarized in Fig. 5. A considerable amount of hydrogen is adsorbed, while the adsorbed hydrogen is mostly irreversible at 0°C and partly desorbs at 90°C as shown by the second adsorption after evacuation at 90°C for 15 min. The adsorption of carbon monoxide is more extensive than hydrogen [compare (3) with (2)] and it is irreversible too. Thus the catalyst adsorbed with carbon monoxide hardly adsorbs hydrogen (curve 4) and thus has no activity for the H_2–D_2 exchange.

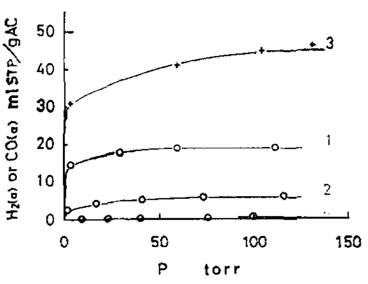

FIG. 5. Adsorption isotherms of H_2 and CO at 0°C on an AC–K catalyst. 1. First adsorption of H_2. 2. H_2 adsorption after evacuation at 92°C. 3. CO adsorption after evacuation at 92°C. 4. H_2 adsorption on CO-adsorbed surface.

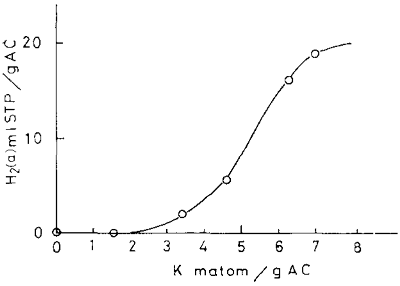

FIG. 6. Amount of hydrogen adsorption as function of potassium content at 0°C and 100 Torr.

Figure 6 shows the variation of hydrogen adsorption with potassium content in AC–K at 0°C and 100 Torr. It is obvious that the extent of adsorption runs parallel with the exchange rate. The ineffective part of potassium is again observed.

The Reaction of Prechemisorbed H_2 with Gas Phase D_2

Since the chemisorbed hydrogen seems to have a correlation with the exchange reaction as suggested by the abovementioned parallelism, the reaction of prechemisorbed H_2 with gas phase D_2 (3.2 Torr) was examined on an AC–K catalyst (3.4 matom/g AC) at 0°C. The result is illustrated in Fig. 7. Although the reaction of prechemisorbed H_2 is obvious, the reaction rate to form HD in the initial stage, 0.0086 ml STP min^{-1} g^{-1} AC is much less than the estimated value of $R = 0.24$ ml STP min^{-1} g^{-1} AC under the condition (based on the first-order kinetics). Hence the adsorbed hydrogen is not a major intermediate of exchange.

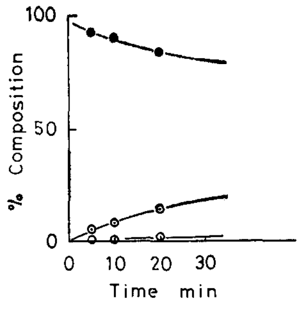

FIG. 7. Time course of reaction of preadsorbed hydrogen with gas phase deuterium.

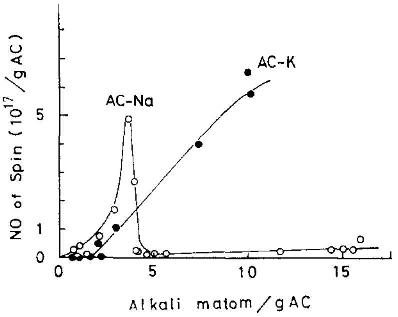

FIG. 8. Spin density of catalyst as function of alkali content.

Spin Density of Catalyst as Functions of Alkali Content

The alkali-added carbon gives an ESR band at $g = 2.004$ (Na) or $g = 2.007$ (K) which diminishes on introduction of hydrogen as previously reported (*5*). The spin density of catalysts as determined from the ESR spectra is plotted against alkali content in Fig. 8. The spin density increases with sodium content, passes through a sharp maximum at around 3.5 matom/g AC and decreases to a low plateau value, while it increases with potassium content above 1.5 matom/g AC. The variation with alkali content is strikingly parallel with that of catalytic activity shown in Fig. 1. The only difference is that the spin density does not level off at higher alkali content.

DISCUSSION

Active Site

It may be derived from the above experimental results that, when alkali content of the catalyst is varied, the exchange activity runs parallel with the adsorption capacity for hydrogen as well as with the spin density of the catalyst. Since the ESR band diminishes on introduction of hydrogen at room temperature and is restored by evacuation at higher temperature (*5*), it appears that the hydrogen adsorption takes place at the location of electron spin, causing the decrease in spin density by electron pairing. The abovementioned parallelism with the exchange activity further suggests that the active site is similar to the site of hydrogen adsorption in nature.

It is clear that the electron spins are formed by an interaction of alkali metal with the carbon surface. Considering the electronegativity difference between carbon and alkali metal, some electrons should be donated from alkali to carbon, resulting in adsorbed alkali ions. The observed spins are ascribable to those electrons accepted by carbon. Nonexistence of hyperfine splitting is consistent with this interpretation. Thus the active site seems to be located on the carbon surface near the alkali ion. The hydrogen adsorption may be understood as a dissociation of a hydrogen molecule to form two hydrogen atoms by the interaction with those unpaired electrons. In fact HD formation is predominant in the reaction of $D_2(g)$ with the adsorbed hydrogen.

Different Behaviors of AC–Na and AC–K

It is observed that both the exchange activity and the spin density depend on the alkali content in different manners. This difference should be explained on the ground of the above interpretation. It is now recalled that sodium metal hardly forms a lamellar graphite complex while potassium is readily accommodated in the graphite lattice (*9*). If the potassium atoms first enter into the graphite lattice instead of being adsorbed, the observed result is reasonably understood. Sodium can be adsorbed without forming the graphite complex. Although the active carbon is characterized by its amorphous structure, it is accepted that a graphite lattice still remains in active carbon. This was confirmed by X-ray diffraction on the sample carbon. Although the graphite–potassium compound is known to be active for the H_2–D_2 exchange, the activity also depends on the potassium content (*4*). It is likely that the activity of graphite compound is also due to the adsorbed alkali.

If the adsorbed potassium or sodium is responsible for the activation, the decrease in activity as well as in spin density of AC–Na in high sodium region seems to be caused by agglomeration of sodium atoms to form a metallic phase. The metallic phase of sodium would be less electron-donative than the isolated atoms, resulting in the decrease of electron spins. Although a similar feature is expected for potassium, the added potassium atoms are partly accommodated by the graphite lattice, and may have a higher mobility on the carbon surface, thus giving rise to the observed shift of optimum alkali content from sodium to potassium. The observed lack of parallelism in the high potassium content region seems to call for a further study. Since cesium is also known to form the graphite compound, AC–Cs is expected to behave similar to AC–K, which is not confirmed yet. The above interpretation in terms of agglomeration of sodium as well as relevance to the ammonia synthesis catalyst will be further investigated in a subsequent paper on the basis of ESR spectra.

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