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Oxidation of Coals in Liquid Phases. IX. Kinetics of the Base-Catalyzed Oxidation of Acetate Ion by Oxygen at Elevated Temperatures

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The kinetics of the oxidation of the acetate ion by oxygen have been studied to clarify the mechanism of the formation of oxalate from coal in concentrated alkaline solutions at elevated temperatures. The rate for the oxidation in a nickel reactor in the presence of 3 g of iron powder was expressed as $-\mathrm{d}m_{\mathrm{Ac}}/\mathrm{d}t=k'\ m_{\mathrm{Ac}}m_{\mathrm{OH}}{}^2P_{\mathrm{O_2}}$, where k' is the apparent rate constant, m_{Ac} is the molality of acetate ion, m_{OH} is molality of the hydroxide ion, and $P_{\mathrm{O_2}}$ is the partial pressure of oxygen. This result indicates that the oxidation of the acetate ion proceeds according to a base-catalyzed mechanism. The activation energy was 160 kJ mol^{-1}. In addition, the rate of oxidation was affected by the coexistence of the metal powder and the oxidation activity in the order Cu > Ni > Co > Mn ≒ Fe > Cr. The catalytic effect of metal oxides on the rate is discussed.

Oxalate ion is formed with a 30—50% yield of carbon in the oxidation of coal by oxygen in concentrated NaOH solutions at 498—523 K.[1,2] The yield of oxalate ion increases with increasing concentration of NaOH. Essentially, the oxidation of coal may take place via a base-catalyzed oxidation mechanism, since similar yields of oxalate have been obtained in the oxidation of various model compounds such as phenols and carboxylates including acetate.[3]

In spite of the importance of this reaction mechanism for increasing the yield of oxalate from coal, the mechanism of the oxidation of carbonaceous materials under alkaline conditions has not been investigated kinetically in detail. In the present work, kinetic studies have been carried out to clarify the mechanism of the formation of oxalate and to improve the yield of oxalate from coal using acetate ion as the simplest model compound. This is one of the important intermediates in the oxidation of coal in alkaline solutions.

Experimental

A beaker made of nickel or carbon steel was set in a 1 dm^3 SUS 316 autoclave; the stirrer and sampling tube were of the same material as the beaker. Water (550 g), sodium acetate (0.08 mol kg^{-1} H_2O), NaOH, and Na_2CO_3, and metal powder (under 100 mesh), were put into the autoclave, and the amount of Na_2CO_3 was adjusted to coincide with the ionic strength of a 5 molal NaOH solution. The NaOH and Na_2CO_3 concentrations (molal) were 2, 0.253; 3, 0.171; and 4, 0.083; respectively. After replacement of air with N_2 three times, the autoclave was heated to a temperature 20 K below the reaction temperature. The sample solution was withdrawn immediately after oxygen was introduced during stirring at 500—800 rpm (reaction time of 0). The temperature rapidly rose on pressurization of oxygen, reaching the final reaction temperature in 15 min. A sample solution (8—15 cm^3) was then withdrawn at 30-min intervals. The volume of each sample was calculated from its weight and the density of the solution corresponding to the same NaOH concentration. The concentrations of acetate and oxalate ions were determined by ion chromatography after sodium/hydrogen ion exchange.

Results and Discussion

Oxalate and carbonate ions are formed by the oxidation of acetate ion in the reaction, and the ratio of oxalate to carbonate has been found to vary extensively with the reactor materials. We have not succeeded in finding any corrosion-resistant material under such corrosive conditions and have been obliged to use stainless steels or nickel as the reactor material. Even these metals were corroded considerably to form metal oxides during the reaction time under the present conditions, and the resulting metal oxides affected the rate of the oxidation and the selectivity. The selectivity of the oxalate ion was highest in the presence of iron powder using the nickel beaker.[4]

Catalytic Effect of Various Metals Contained in Stainless Steels. The following preliminary experiments have been carried out to elucidate the significance of adding iron powder.

Activity of Metals: The first order plots of the concentration of acetate ion in the reaction with 3 g of various metal powders in the nickel beaker are shown in Fig. 1. The rate of oxidation of the acetate ion was approximately proportional to the acetate ion concentration and nearly the same in the presence of Cr, Mn, and Fe, all of which have standard electrode potentials lower than that of Ni. On the other hand, the rate of oxidation was accelerated slightly in the presence of Ni the standard electrode potential of which is higher than those of Cr, Mn, and Fe. The first order plots shifted gradually upward with reaction time as was observed in the absence of Ni. Cobalt only slightly affected the rate of oxidation. Copper, the standard electrode potential of which is higher than that of Ni, promoted the reaction remarkably. These results indicate that Cr, Mn, and Fe inhibit the effect of nickel on the reaction rate which was used as the reactor material whereas Cu promotes the reaction. This is an interesting phenomenon suggesting the promotion of the oxidation of coal by the addition of copper oxide.

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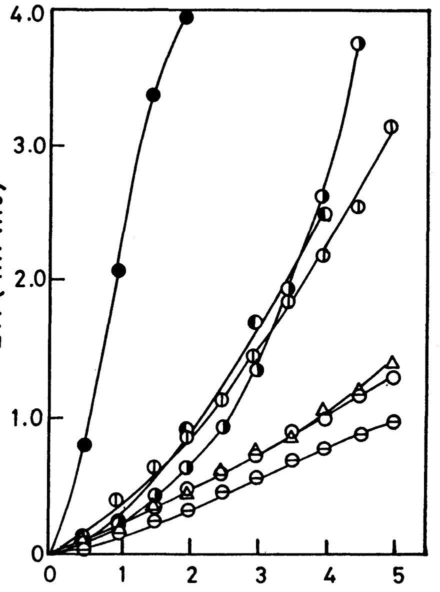

Fig. 1. Effect of metal powders on the rate of oxidation of acetate ion in a Ni reactor at 523 K, 5 mol NaOH/kg H_2O, and P_{O_2} 5 MPa.
● Cu, ◑: Ni, ⦶: Co, O: Fe, ⊖: Cr, △: Mn, ◐: none.

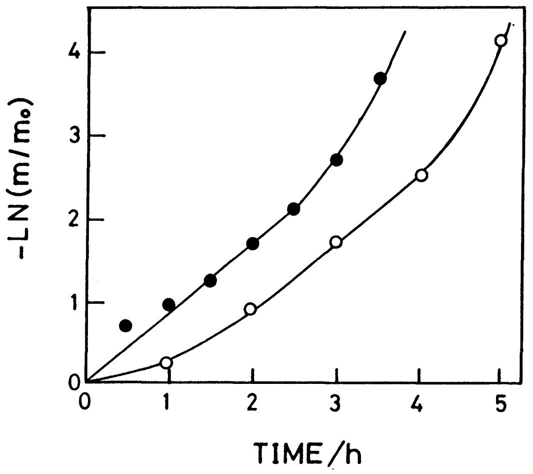

Fig. 2. First order plots of concentration of acetate ion in a Fe and a Ni reactors at 523 K and P_{O_2}5 MPa.
●: Fe, O: Ni.

This effect has been confirmed for the oxidation of lignite.[5]

Effect of Reactor Material: Figure 2 demonstrates the first order plots of concentration of acetate ion in nickel and carbon steel reactors without metal powder. The initial rate of oxidation in the steel reactor was obviously greater than that in the nickel reactor. The reason is that in the case of the steel reactor the temperature of the solution rose rapidly up to 540 K, 17 K higher than the reaction temperature of 523 K due to the heat of extreme oxidation of the steel, and it took 30 min until the temperature decreased to 523 K. After the temperature rise had settled, the rate of oxidation in the steel reactor approached that in the nickel reactor and the two became approximately equal between 1.5 and 3 h. A large amount of Fe_2O_3, haematite, was produced by corrosion of the steel.

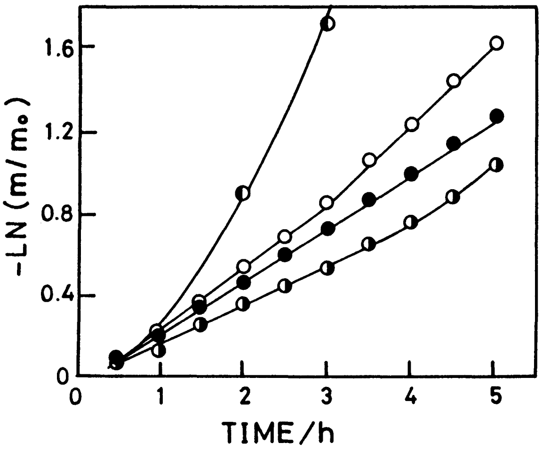

Fig. 3. Effect of Fe powder and Fe_2O_3 on the rate of oxidation in a Ni reactor at 523 K and P_{O_2} 5 MPa.
◑: Fe 1 g, ●: Fe 3 g, O: Fe_2O_3 4.3 g, ◐: none .

Effect of the Amount of Iron Powder on the Reaction in the Nickel Reactor: Figure 3 shows the effects of the amount of iron powder and reagent haematite on the rate of oxidation. Only 1g of iron powder retarded the oxidation of acetate ion in the nickel reactor, but the rate of oxidation was slightly increased in the presence of 3 g of iron powder. This indicates that 1 g of iron powder is enough to control the activity of the nickel reactor. On the other hand, excessive Fe_2O_3 formed by the oxidation of an additional 3 g of iron powder begins to promote the oxidation of the acetate ion. The fact that the rate of oxidation in the steel reactor was approximately equal to that in the nickel reactor under the steady state, supports the hypothesis that Fe_2O_3 promotes the oxidation as oxides of nickel. Namely, the role of iron powder in the nickel reactor seems to change from that of depressor to that of catalyst when increasing amounts of iron powder are added.

The rate of the oxidation of acetate ion with the addition of haematite corresponding to 3 g of iron powder was apparently greater than that with the addition of 3 g of iron powder. This result also supports the hypothesis that excessive Fe_2O_3 accelerates oxidation, since in this case, a large amount of haematite is present from the beginning of the oxidation. This is different from the case of the oxidation with iron powder where Fe_2O_3 is produced gradually with increase in the reaction time. In addition, the first order plot shifted gradually upward compared to that of the iron powder. Thus, iron powder is required to maintain the linearity of the first order plot. With an addition of 1 g of iron powder, however, the first order plot shifted upward during the course of the reaction as shown in Fig. 3. This shows that the oxidation of acetate ion had begun to be accelerated due to complete consumption of the metallic iron. Consequently, 3 g of iron powder is necessary to maintain the linearity of the first order plot at least for 6 h. Under such reaction conditions, the effects of various parameters on the rate of oxidation of the acetate ion can easily be observed. It is especially important to elucidate the dependency of the rate of the oxidation of the acetate ion on the hydroxide ion concentration to confirm if the oxidation of acetate ion proceeds by a base-catalyzed mechanism. Thus, the kinetic study was just carried out in the presence of 3 g of iron powder in the nickel reactor.

The Rate Equation of the Oxidation of Acetate Ion with 3 g of Iron Powder. The effects of NaOH concentration, partial pressure of oxygen, and temperature have been measured; this system is written below as Ni(Fe).

Effect of NaOH Concentration: Figure 4 shows the first order plots of the concentration of the acetate ion with varying NaOH concentration. It shows that the reaction is first order with respect to acetate ion. The reason why the first order plots do not pass through the origin is that the initial temperature was lower than the reaction temperature in the steady state. The hydroxide ion concentration was calculated using the pK_b (1.07 at 523 K[6]) and an extended Debye-Hückel equation as set forth below since NaOH does not dissociate completely at elevated temperatures.

The following reactions can be assumed at t=0:

$$\mathrm{NaOH} \overset{K_b}{\rightleftharpoons} \mathrm{Na^+} + \mathrm{OH^-} \tag{1}$$

$$\mathrm{NaAc} \longrightarrow \mathrm{Na^+} + \mathrm{Ac^-} \tag{2}$$

$$\mathrm{Na_2CO_3} \longrightarrow 2\mathrm{Na^+} + \mathrm{CO_3^{2-}} \tag{3}$$

$$K_b = a_{Na}a_{OH}/a_{NaOH} \tag{4}$$

a: activity of the corresponding species

The dissociation constant of NaOH, K_b, can be expressed by the molalities of the sodium ion, m_{Na}, the acetate ion, m_{Ac}, the carbonate ion, m_c, the total NaOH, m_o, the undissociated NaOH, m_{NaOH}, and the hydroxide ion, m_{OH}, the degree of dissociation of NaOH, α, and the activity coefficient for monovalent ion, γ, respectively.

$$K_b = \gamma^2 m_{Na} m_{OH}/m_{NaOH} \tag{5}$$

$$= \gamma^2\alpha\,(m_{Ac}+\alpha m_o+2m_c)/(1-\alpha) \tag{5'}$$

The ionic strength, I, is given by Eq. 6. Activity coefficients

$$I = m_{Ac} + \alpha m_o + 2m_c \tag{6}$$

are expressed by Eq. 7 in the measurement of the solubility of $CaSO_4$ up to 623 K and 5 molal NaCl solutions.[7]

$$\log\gamma = -Z_i^2 S I^{1/2}/(1+A_k I^{1/2}) \tag{7}$$

Z_i: charge of ion i, S: limiting slope of the Debye-Hückel Eq. (0.9785 at 523 K),[8] A_k: 1.74 at 523 K.[7]

The hydroxide ion concentration (αm_o) was obtained by calculating the degree of dissociation in each condition using Eqs. 5'—7.

The relationship between the apparent rate constant and calculated hydroxide ion concentration is shown in Fig. 5. The rate of oxidation of the acetate ion was approximately proportional to the second order in hydroxide ion concentration.

Effect of Partial Pressure of Oxygen: Figure 6 shows the effect of the partial pressure of oxygen on the apparent rate of oxidation. The rate of oxidation was proportional to the partial pressure of oxygen.

Effect of Temperature: The activation energy of the oxidation obtained from the Arrhenius plot of the

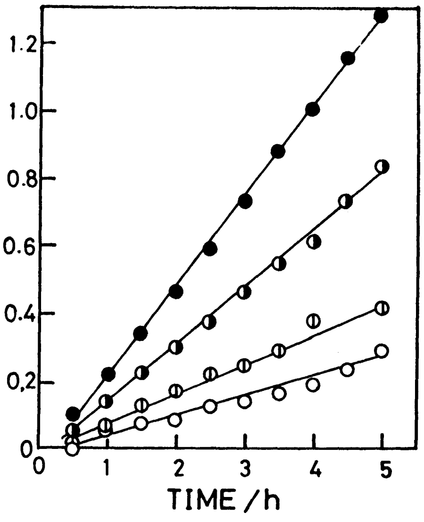

Fig. 4. Effect of NaOH concentration on the rate of oxidation in Ni(Fe) at 523 K and P_{O_2} 5 MPa. NaOH concn (mol kg^{-1} H_2O) ○: 2.00, ⦶: 3.00, ◑: 4.00, ●: 5.00.

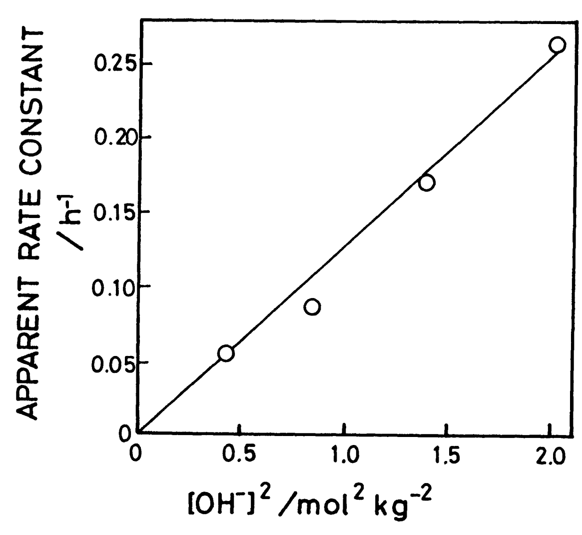

Fig. 5. Relationship between the apparent rate constant and hydroxide ion concentration in Ni(Fe) at 523 K and P_{O_2} 5 MPa.

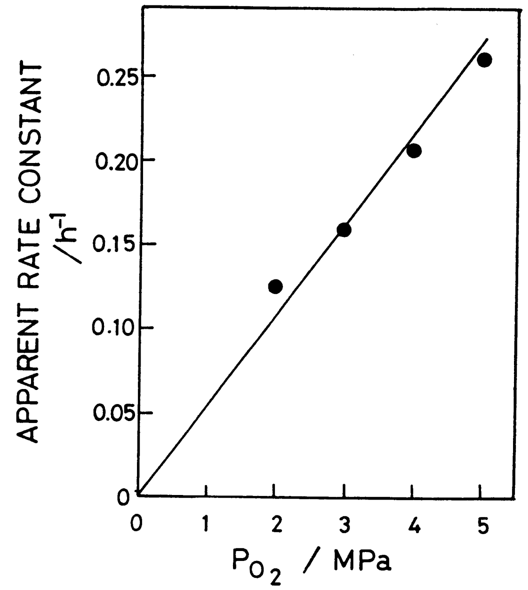

Fig. 6. Effect of partial pressure of oxygen on the rate of oxidation in Ni(Fe) at 523 K and 5 mol kg^{-1} H_2O.

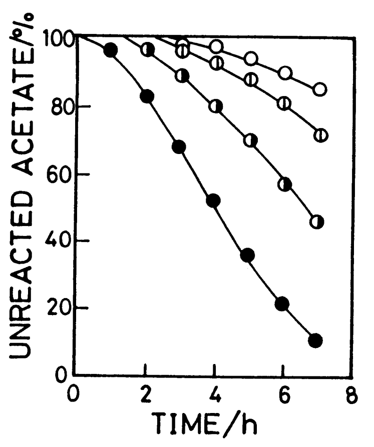

Fig. 7. Effect of NaOH concentration on the rate of oxidation in Ni(R) at 503 K and P_{O_2} 5 M Pa. NaOH concn (mol kg^{-1} H_2O) ○: 2.00, ⦶: 3.00, ◑: 4.00, ● 5.00.

apparent rate constants at 503, 513, and 523 K was 160 kJ mol^{-1}. This value clearly shows that the rate-determining step is a chemical reaction process.

Rate Equation of the Oxidation: Finally from the above results, the rate of the oxidation of the acetate ion in the presence of 3 g of iron powder in the nickel reactor can be expressed by Eq. 8.

$$-\mathrm{d}m_{\mathrm{Ac}}/\mathrm{d}t = k' m_{\mathrm{Ac}} m_{\mathrm{OH}}^{2} P_{\mathrm{O_2}} \qquad (8)$$

k': the apparent rate constant, m_{Ac}: molality of the acetate ion, the m_{OH}: molality of the hydroxide ion, $P_{\mathrm{O_2}}$: partial pressure of oxygen.

Oxidation of Acetate Ion without Iron Powder. This system is written as Ni(R) below.

Effect of NaOH Concentration: The first order relationship was not obtained at 523 K, since the rate of the oxidation increased exponentially with the reaction time in the beginning. This tendency is more evident at 503 K as is shown in Fig. 7. This may indicate that some oxide of nickel is involved in the rate-determining step of the reaction and that its amount increases exponentially with the reaction time, since the acetate ion concentration changes slightly in the beginning.

Effect of Partial Pressure of Oxygen: In this case, the effect appeared only in the beginning, and the rate of the oxidation became constant independent of the pressure of oxygen as is shown in Fig. 8. This may indicate that the amount of the oxide of nickel formed is little affected by the partial pressure of the oxygen.

Effect of Initial Concentration of Sodium Acetate: In the case of Ni(Fe), naturally, the initial concentration did not affect the rate of oxidation as it was first order with respect to the acetate ion concentration. However, the rate of oxidation of the acetate ion in Ni(R) at 503 K became constant after 2 h and was proportional to the initial concentration of the acetate ion as is shown in Fig. 9.

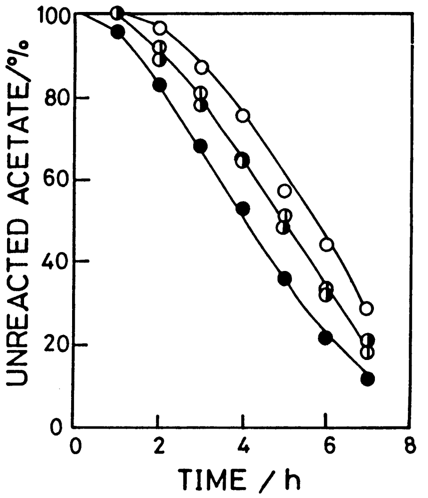

Fig. 8. Effect of partial pressure of oxygen on the rate of oxidation in Ni(R) at 503 K and 5 mol NaOH/kg H_2O. P_{O_2}(MPa) ○: 2.0, ⦶: 3.0, ◑: 4.0, ●: 5.0.

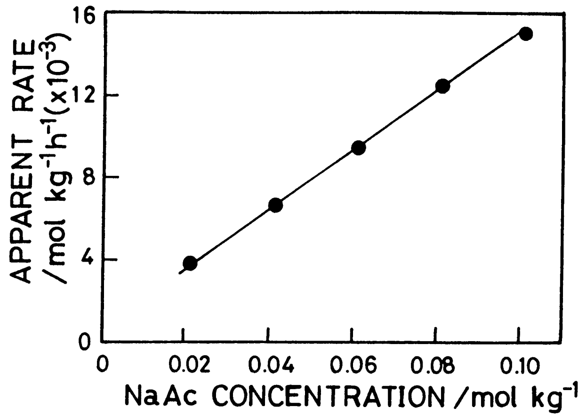

Fig. 9. Effect of initial concentration of acetate ion on the apparent rate constant in Ni(R) at 503 K and P_{O_2} 5 MPa.

The difference in the cases of Ni(Fe) and Ni(R) is discussed in the following mechanism.

Mechanism of the Oxidation of Acetate Ion. Base and Metal Oxide-Catalyzed Oxidation Mechanism: It is thought that this oxidation reaction involves a base-catalyzed oxidation mechanism[9)] as follows:

$$XCH_3 + OH^- \overset{K}{\rightleftharpoons} XCH_2^- + H_2O \ (X{=}COO^-) \qquad (9)$$

$$XCH_2^- + O_2 \xrightarrow[(MeO)]{k} XCH_2\cdot + O_2^{\cdot -} \qquad (10)$$

$$XCH_2\cdot + O_2 \longrightarrow XCH_2OO\cdot \qquad (11)$$

$$XCH_2OO\cdot + XCH_2^- \longrightarrow XCH_2OO^- + XCH_2\cdot \qquad (12)$$

$$XCH_2OO\cdot + O_2^{\cdot -} \longrightarrow XCH_2OO^- + O_2 \qquad (13)$$

K: equilibrium constant, k: rate constant, MeO: metal oxide

The peroxoanion formed from the oxidation of the carbanion, XCH_2OO^- , is easily oxidized further to oxalate ion.

In Ni(Fe), acetate and hydroxide ions increase the concentration of the carbanion, which is a reactant in the rate-determining step, according to the first order dependence of its formation on the concentrations of acetate and hydroxide ions, as shown by Eq. 9. We may assume Henry's law for the solubility of oxygen in the solutions at constant NaOH concentration and temperature. Thus, the concentration of oxygen should be proportional to its partial pressure. In this case, however, the reaction mechanism seems to be a base-catalyzed oxidation reaction involving the iron oxide catalyst as shown in Eq. 10. There are two results supporting this. Firstly, the rate of the oxidation is proportional to the second order in the concentration of hydroxide ion. This seems to indicate that the rate of formation of a catalyst, the iron oxide, is proportional to the concentration of the hydroxide ion. Although such measurements have not been carried out in the present work or found in the literature, in the anodic oxidation of iron in a 1 mol kg^{-1} LiOH solution at 473 K, oxoanions of iron are formed by the reaction of iron and hydroxide ion.[10)] Secondly, the rate of oxidation increased with increasing amount of iron powder as shown in Fig. 3. This means that the soluble species of iron can not be the major oxidizing species, since the solubilities of iron oxides in alkaline solutions are very low[11)] and the reaction solutions should be saturated with iron ion even with the addition of 1 g of iron powder. Consequently, the oxidation of acetate ion in Ni(Fe) proceeds on the surface of the iron oxide due to a base-catalyzed and iron oxide-catalyzed oxidation mechanism as shown in Eq. 10.

The mechanism in Ni(R) should be similar to that in the above-mentioned case. A distinct difference is that the rate of reaction in Ni(R) increased exponentially with the reaction time in the initial stage; it then became constant as is shown in Figs. 7 and 8. The rate of reaction is proportional with respect to the initial acetate ion concentration as is shown in Fig. 9. These results may be boldly explained as follows. The amount of nickel oxide formed by corrosion of the reactor material increases exponentially with the reaction time. By analogy with the mechanism of the oxidation of acetate ion in Ni(Fe), the rate in Ni(R) should also be proportional to the products of the concentration of the carbanion and amount of nickel oxide. If the concentration of the carbanion decreases exponentially with the reaction time and both rates compensate each other, the rate of oxidation of the acetate ion becomes constant and is approximately proportional to the initial concentration of acetate ion.

Figure 10 shows the effect of the amount of nickel powder on the oxidation of acetate ion in Ni(R) at 503 K. The rate of the oxidation increases with increasing amounts of nickel. Clearly, these results support the hypothesis that the nickel oxide formed by the corrosion acts as a catalyst since nickel powder is easily oxidized under the reaction conditions. It seems that the hydroxide ion concentration accelerates mainly the formation of the catalyst compared to the amount of nickel powder or partial pressure of oxygen.

The Valency of Nickel in the Oxides Formed in Ni(R): When the Ni(R) run has finished, a greenish white precipitate and a small amount of a black substance are suspended in the solution. Two peaks were observed in the ESCA spectra of the precipitate at 857.8 and 856.4 eV for Ni $2p_{3/2}$ which may correspond to 856.2 and 855.2 eV for reagent Ni_2O_3, respectively. This indicates that Ni^{3+} is contained in the precipitates. There are many types of oxide of nickel having excess oxygen.[12)] Only NiO, however, was identified in the precipitates by XRD. According to the

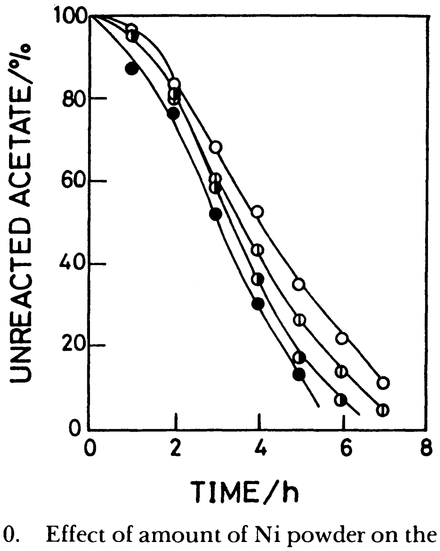

Fig. 10. Effect of amount of Ni powder on the oxidation in Ni(R) at 503 K and P_{O_2} 5 MPa. Amount of Ni(g) ○: 0, ⦶: 2, ◑: 4, ●: 6.

potential-pH diagram of a Ni-water system at 523 K,[13-16] even Ni_2O_3 can be formed under the reaction conditions, at a calculated pH of 10.8 (2 mol kg^{-1}) $-$11.2 (5 mol kg^{-1}) and P_{O_2} 5 MPa. However, in Ni(R), Ni^{3+} probably is not the catalyst but the reactant which directly oxidizes the carbanion, since the partial pressure of oxygen only slightly affected the rate of oxidation as is shown in Fig. 8, in contrast to the case for Ni(Fe) shown in Fig. 6.

Retardation Mechanism of the Oxidation in Ni(Fe): This mechanism can be reasonably explained by the action of metals or Fe_2O_3 added on Ni^{3+} formed by the corrosion of the nickel reactor. There are two factors which cause this phenomenon. One is an electrochemical effect and the other is a mechanical effect.

The former occurs when a metal whose electrode potential is lower than that of nickel is present in the solution as is shown in Fig. 1. According to the mechanism of oxidation in Ni(R), this effect brings about protection of the formation of Ni^{3+} because of the cathodic polarization of the nickel surface covered by iron powder in alkaline solutions or the reduction of Ni^{3+} by iron powder and FeO as shown in Eqs. 14 and 15.

$$2Ni^{3+} + Fe + 6OH^- \longrightarrow 2NiO + FeO + 3H_2O \quad (14)$$

$$2Ni^{3+} + 2FeO + 6OH^- \longrightarrow 2NiO + Fe_2O_3 + 3H_2O \quad (15)$$

The retardation seems to take place without adherence of oxides since it was recognized in Ni(Cr) in which soluble chromate was formed instead of Cr_2O_3. The sole suspension of haematite in the oxidation with the carbon steel reactor does not seem to retard the rate as shown in Fig. 3. In the case of Ni(Fe_2O_3), however, retardation was also observed. This may be caused by the nickel surface being covered with haematite since the electrochemical effect can not take place in this case. Actually, haematite adhered tightly to every part of the nickel reactor in contact with the solution and could not be removed easily by brushing. Consequently, haematite adhering to the nickel surface inhibits the formation of Ni^{3+} by preventing the nickel surface from coming in contact with the solution. Haematite, however, seems not to control the formation of Ni^{3+} completely as it can not reduce Ni^{3+} like iron does. Thus, Ni^{3+}, which forms gradually, accelerates the rate of oxidation.

Copper accelerated the oxidation and this mechanism should be further studied.

Conclusion

In the kinetics of the oxidation of acetate ion by oxygen in strong alkaline solutions at elevated temperatures, the following results have been obtained. In the case of Ni(Fe), the first order plots of acetate ion concentration remain approximately linear while metallic iron remains in the solution. This is realized by the inhibition of the formation of Ni^{3+} by the metallic iron. The rate equation of the oxidation in Ni(Fe) can be expressed as follows: $-\mathrm{d}m_{\mathrm{Ac}}/\mathrm{d}t=k' m_{\mathrm{Ac}} m_{\mathrm{OH}}{}^2 P_{O_2}$ where k' is the apparent rate constant. This equation shows quantitatively that the oxidation of acetate ion in alkaline solutions proceeds by a base-catalyzed mechanism. The activation energy is 160 kJ mol^{-1}. In the case of Ni(R), the Ni^{3+} species formed by the oxidation of the nickel reactor was thought to be the reactant which oxidizes the carbanion and increases with the reaction time. In the presence of metal powder, the rate of oxidation in a nickel reactor is in the following order: Cu>Ni>Co>Mn≒Fe>Cr. The effect of metals on the oxidation is also discussed.

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