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Kinetic mechanism of reactions of carbon tetrachloride with TT-niobium oxide and niobium phosphate

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Abstract

The rate of reaction of CCl_4 with lattice oxygen atoms of the TT-phase niobium oxide (TT-Nb_2O_5) at 453 K was limited by the diffusion of CCl_4 through the layer of a solid reaction product, $NbOCl_3$, formed around the outer surface of niobium oxide. This contrasts to the reaction occurring on the amorphous niobium phosphate in which an inner niobium phosphate participates in the reaction leading to the complete oxidation of CCl_4 to CO_2. For the reaction of CCl_4 on TT-Nb_2O_5 at temperatures above 573 K, the chemical reaction occurring on the surface of the niobium oxide controls the decomposition rate due to the disappearance of the layer of $NbOCl_3$ by its sublimation.

Keywords: Carbon tetrachloride; Niobium oxide

1. Introduction

The process of the decomposition of chrolofluorocarbons (CFCs) into harmless compounds should be developed to reduce the global environmental pollution. Many investigations concerning CFC decomposition in the presence of water and/or molecular oxygen [1–5] as well as the reductive dechlorination of CFC with molecular hydrogen [6–8] have been reported. Although it has been proposed that the cleavage of the C–Cl bond is an important step in the whole CFC decomposition [1,4], little information for the requirements of the surface properties of solids or catalysts for C–Cl bond cleavage has been presented. In our previous paper [9], niobium oxide of TT-phase (TT-Nb_2O_5) oxidized CCl_4 into CO_2 very selectively (without formation of phosgene, $COCl_2$) among metal oxides tested, such as TiO_2, Al_2O_3, ZrO_2, SiO_2–Al_2O_3 and amorphous Nb_2O_5, in the absence of water and oxygen. Since oxygen was excluded from the reaction system, the decomposition of CCl_4 on TT-Nb_2O_5 can be regarded as the oxidation of CCl_4 by lattice oxygen atoms of the TT-Nb_2O_5 occurring at the gas–solid interface, similar to the reduction process of metal oxide into metal by hydrogen molecule [10]. In the reduction process of metal oxide by H_2, two kinetic mechanism, diffusion-controlled and chemical reaction-controlled, are well demonstrated [10]. In our previous paper [11], it was suggested that the reaction of TT-Nb_2O_5 was controlled by the diffusion of CCl_4 through the layer of the solid reaction product formed around the outer surface of the oxide. However, further studies are necessary to verify the suggestion.

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In this paper, the kinetic mechanism of the reaction between TT-Nb_2O_5 and CCl_4 is briefly reviewed and compared to that of niobium phosphate, from the point of view of the reduction of the metal oxide by CCl_4.

2. Experimental

The TT-Nb_2O_5 was prepared by calcination of niobic acid ($Nb_2O_5 \cdot nH_2O$, No. AD-350 supplied by Companhia Brasileira de Metalurgia e Mineralo (CBMM)) at 1023 K. The TT-Nb_2O_5 was evidenced by its X-ray diffraction pattern. The niobium phosphate (Nb:P = 2.2:1 atomic ratio, P_2O_5 = 15.9 wt.-%) was also supplied by CBMM. The phase of the niobium phosphate calcined at 873 K was found to be amorphous.

The reaction of metal oxide (0.2 g) with CCl_4 was carried out under the atmospheric pressure in a tubular flow reactor made of quartz with an inner diameter of 12.5 mm. The following typical condition was applied to the reaction: CCl_4 4.5 kPa, He 96.8 kPa, total flow rate 2.4 l/h, $W/F = 0.083$ g h l^{-1}. Usually, the metal oxide powder of 10–20 mesh was used after crushing the powder disk formed under 200 kg/cm^2 pressure. The CCl_4 was supplied to the reaction by passing a helium carrier through CCl_4 saturators and a column of $MgSO_4$ powder to dry the gas mixture. The outlet gas mixture of CCl_4, CO_2 and $COCl_2$ from the reactor was analyzed by on-line gas chromatography in a Gasukuropack-54 column. The outlet gas was passed through a K_2CO_3 aqueous solution (0.5 M), and trapped chlorides were quantified by $AgNO_3$ and $Na_2S_2O_3$ titration. In the absence of metal oxide in the quartz reactor, CCl_4 decomposition did not occur under the present experimental conditions.

The degree of the reduction of the metal oxide, α, was defined as the ratio of the number of O atoms in the reaction products to that in the metal oxide at the initial stage. The selectivity to CO_2 and conversion of CCl_4 were calculated by the equations described earlier [4].

The BET specific surface area of the metal oxide was determined by nitrogen adsorption at 77 K.

In order to evaluate the distribution of the chlorine along the depth from the surface in the metal oxide after the reaction with CCl_4, the energy dispersed X-ray spectroscopic (EDS) measurements were conducted on the EDAX PV9900I (Philips Co., Ltd.).

3. Results and Discussion

The reaction products in vapor phase were CO_2 and $COCl_2$. No CO was detected during the reaction at any reaction temperature and at any process time. Typical results of the change with increasing process time in the CCl_4 conversion (left axis) and the CO_2 selectivity (right axis) on TT-Nb_2O_5 at 453 K and 673 K are shown in Fig. 1. At any reaction temperature,

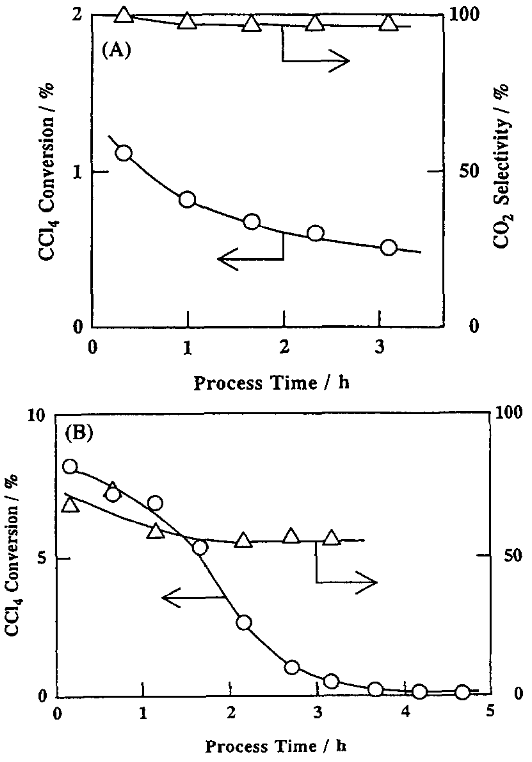

Fig. 1. The time course of CCl_4 conversion (left axis) and CO_2 selectivity (right axis) on TT-Nb_2O_5 at (A) 453 K and (B) 673 K.

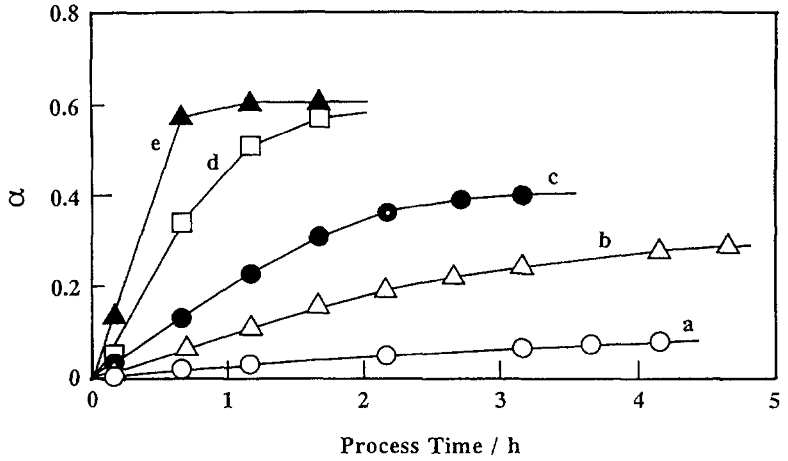

Fig. 2. The changes in α (degree of reduction of TT-Nb_2O_5) as a function of time at (a) 573, (b) 623, (c) 673, (d) 723 and (e) 773 K.

the CCl_4 conversion gradually decreased as the process time increased. As reported previously [9], TT-Nb_2O_5 exhibited a higher activity than any other metal oxide tested: Al_2O_3, SiO_2–Al_2O_3, TiO_2 and V_2O_5. The selectivity to CO_2 on TT-Nb_2O_5 was higher than that obtained on amorphous Nb_2O_5. The specific activity (per surface area) for CO_2 formation of TT-Nb_2O_5 (BET specific surface area, 50 m^2 g^{-1}) is four times greater than that of the amorphous Nb_2O_5 (120 m^2 g^{-1}). The carbon balance on the TT-Nb_2O_5 at the process time of 3 h at 453 K was ca. 95%, indicating that carbon compounds did not remain on the surface during the reaction.

At reaction temperatures higher than 673 K, the CCl_4 conversion decreased to almost zero and the reactant TT-Nb_2O_5 disappeared after several h, indicating a complete reaction of TT-Nb_2O_5 with CCl_4. Since O_2 was not supplied as a reactant, the CCl_4 was oxidized into CO_2 or $COCl_2$ only by lattice oxygen atoms of the TT-Nb_2O_5. Thus, the reaction between TT-Nb_2O_5 and CCl_4 can be regarded as the oxidation of CCl_4 by TT-Nb_2O_5.

Fig. 2 shows the change in α (degree of reduction of TT-Nb_2O_5) as a function of the process time at various reaction temperatures (573–773 K). At higher reaction temperatures (723 and 773 K), the value of α becomes a constant value of 0.6 for longer process time. The α value of 0.6 means that 60% of the oxygen atoms of the TT-Nb_2O_5 was removed by the reaction with CCl_4. After the reaction at 723 K and 773 K, the TT-Nb_2O_5 did not remain on the reactor bed; a white powder product with a yellowish cast was deposited at the outlet of the reactor. The powder was dissolved in deionized water without exposure to air and the amount of Cl^- ion in the solution (pH < 7) was determined by titration using Mohr's method. The ratio of the amount of Cl^- in the solution to the amount of niobium in the powders obtained from the reaction with CCl_4 at 723 K were 2.98. This ratio corresponds to the Cl/Nb ratio of the compound, $NbOCl_3$, whose color was white. The yellowish cast in the product powder may be due to the presence of a small amount of $NbCl_5$, whose color is yellow.

The following two reactions can explain the experimental results:

$$Nb_2O_5 + 2CCl_4 \rightarrow 2NbOCl_3 + CO_2 + COCl_2 \quad (1)$$

$$2Nb_2O_5 + 3CCl_4 \rightarrow 4NbOCl_3 + 3CO_2 \quad (2)$$

Eq. 2 is obtained by taking into account the further reaction of $COCl_2$ with Nb_2O_5. When both of the reactions occur in the present reaction system, the value of oxygen fraction at the completion of the reactions is 0.6, well corresponding to the experimental results shown in Fig. 2.

In order to estimate a precise reaction rate, the CCl_4 conversion and CO_2 selectivity were compared at the same α value. Fig. 3 shows the changes in the reaction rate and CO_2 selectivity as a function of the reaction temperature at constant α of 0.2. The total reaction rate, or the sum of the formation rates of CO_2 and $COCl_2$, increased as the reaction temperature increased. The increase in the $COCl_2$ formation rate is not remarkable, while that in the CO_2 formation rate is remarkable. A plot of the logarithm of the (total) reaction rate to a reciprocal of the reaction temperature at a constant α of 0.2 reveals that the apparent activation energies for CO_2 and $COCl_2$ formations were 96.6 kJ mol^{-1} and 54.2 kJ mol^{-1}, respectively. These values were almost unchanged at various values of α: 0.1 or 0.3. A low activation energy for the rate of $COCl_2$ formation may be due to the fact that $COCl_2$ is an intermediate in the reaction to give a complete oxidation product, CO_2.

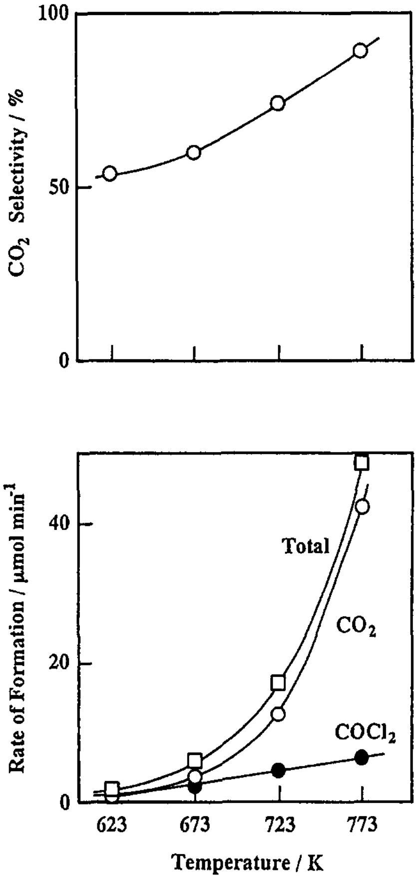

Fig. 3. The changes in the reaction rate and CO_2 selectivity for the reaction of CCl_4 and TT-Nb_2O_5 as a function of the reaction temperature at a constant α of 0.2.

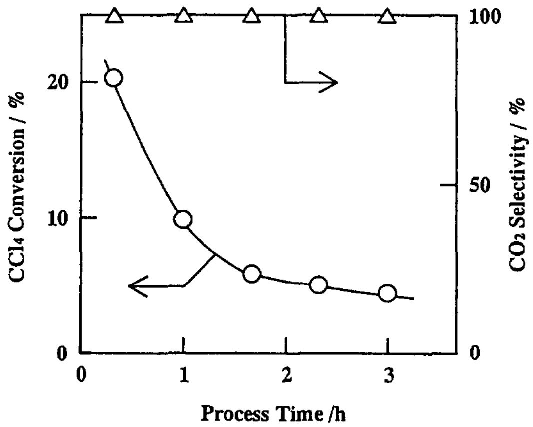

Fig. 4. The time course of CCl_4 conversion (left axis) and CO_2 selectivity (right axis) on niobium phosphate at 673 K.

The decomposition of CCl_4 is found to occur on the niobium phosphate (BET specific surface area, 130 m^2 g^{-1}). Fig. 4 shows a typical reaction result of the change with increasing process time in the CCl_4 conversion and CO_2 selectivity on the niobium phosphate at 673 K. As observed on TT-Nb_2O_5, the CCl_4 conversion decreased as the process time increased. However, the CO_2 selectivity on the niobium phosphate was very high (100%) in contrast to the reaction on TT-Nb_2O_5 at 673 K (Fig. 1B). The change in α as a function of the process time at various reaction temperatures is shown in Fig. 5. At a constant α of 0.10, the dependencies of CCl_4 conversion and CO_2 selectivity on the reaction temperature (Fig. 6) are different from those obtained for TT-Nb_2O_5, especially for the CO_2 selectivity.

Generally, the reduction of metal oxide, assuming a contacting sphere model, is expressed as

$$\frac{k_p}{r_0 d_0}(C_0 - C_{eq})t$$
$$= \left[1 - (1-\alpha)^{1/3}\right] + \frac{r_0 k_p}{k_d}$$

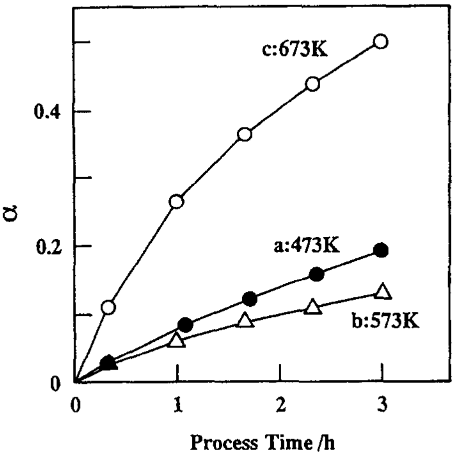

Fig. 5. The changes in α (degree of reduction of niobium phosphate) as a function of time at (a) 473, (b) 573 and (c) 673 K.

$$\times\left[\frac{1}{2}-\frac{\alpha}{3}-(1-\alpha)^{2/3}\right] \qquad (3)$$

where α is the degree of reduction, r_0 is the radius of metal oxide at the initiation, C_0 is the concentration of reducing reagent at r_0, C_{eq} is the equilibrium concentration of reducing reagent, d_0 is the density at r_0, k_p is the rate constant of the reaction and k_d is the diffusion coefficient of reducing reagent [10]. This is the integrated rate equation giving the degree of reduction, α, as a function of time t.

If $k_p \ll k_d$ or $k_p/k_d = 0$, then

$$\frac{k_p}{r_0 d_0}(C_0 - C_{eq})t = \left[1-(1-\alpha)^{1/3}\right] \qquad (4)$$

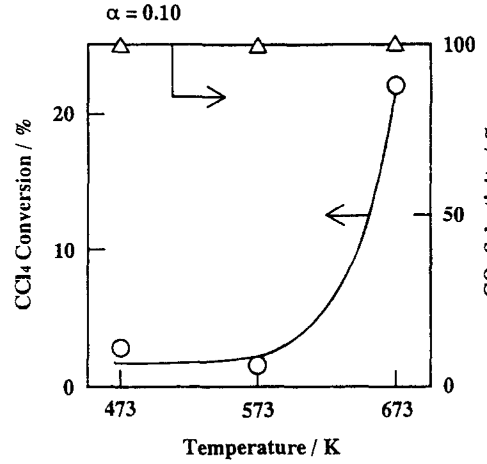

Fig. 6. The changes in the reaction rate and CO_2 selectivity for the reaction of CCl_4 and niobium phosphate as a function of the reaction temperature at a constant α of 0.1.

If $k_p \gg k_d$ or $k_d/k_p = 0$, then

$$\frac{k_p}{r_0 d_0}(C_0 - C_{eq})t = \frac{r_0 k_p}{k_d}\left[\frac{1}{2}-\frac{\alpha}{3}-(1-\alpha)^{2/3}\right] \qquad (5)$$

A linear correlation holds between $[1-(1-\alpha)^{1/3}]$ and t for the chemical reaction control at the metal oxide/reduced phase interface. If the overall reaction rate is limited by the diffusion of reducing reagent (CCl_4, in this case) through the reaction product layer, a plot of $[1/2-\alpha/3$

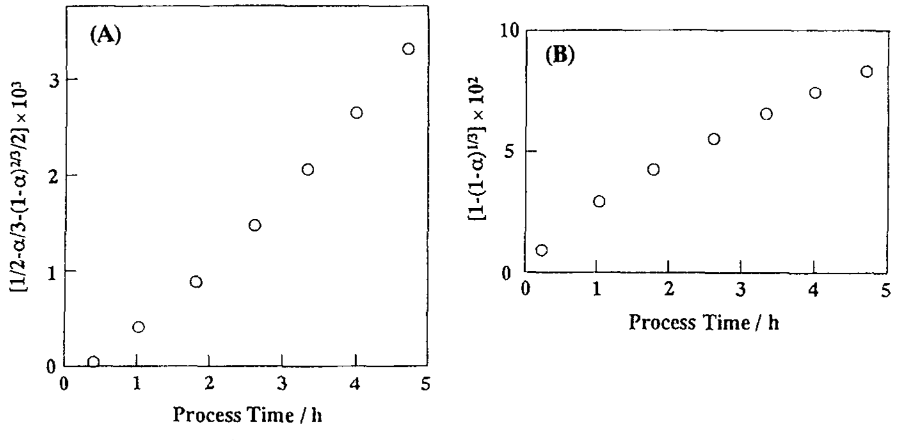

Fig. 7. Plot of (A) $[1/2-\alpha/3-(1-\alpha)^{2/3}/2]$ and (B) $[1-(1-\alpha)^{1/3}]$ versus time for the reaction of TT-Nb_2O_5 with CCl_4 at 453 K.

$-(1-\alpha)^{2/3}/2]$ against t may become a straight line.

Fig. 7A shows a plot of $[1/2-\alpha/3-(1-\alpha)^{2/3}/2]$ against the process time, t, for the reaction at 453 K on TT-Nb_2O_5. A plot of $[1-(1-\alpha)^{1/3}]$ against t for the same reaction is shown in Fig. 7B. As can be seen, the plot in Fig. 7A fits a straight line rather than that in Fig. 7B, suggesting that the diffusion control mechanism is dominant for the reaction at 453 K on TT-Nb_2O_5. Fig. 8 shows both plots for the reaction at 473 K on niobium phosphate. The plot in Fig. 8A fits a straight line in contrast to that in Fig. 8B. This suggests that the whole reaction occurring on niobium phosphate at 473 K is controlled by the chemical reaction between CCl_4 and niobium phosphate.

To ensure these suggestions, the following experiment was performed. The CCl_4 reaction was carried out on the pelletized TT-Nb_2O_5 and niobium phosphate with various amount. If the inner metal oxide in the pellet of the metal oxide participates in the reaction with CCl_4, the reaction rate per g is independent on the amount or the size of the pellet. Fig. 9 shows the relationship between the rate of CO_2 formation per g or per apparent outer area and the amount of pelletized TT-Nb_2O_5, and of niobium phosphate at 453 K after the process time of 1 h. As clearly shown, the rate per apparent outer area of the pellet of TT-Nb_2O_5 was constant for different sizes of pellets, whereas the rate per g of the pellet was not. This indicates that the inner niobium oxide in the pellet of TT-Nb_2O_5 did not equally participate in the reaction with CCl_4 and the oxide at the surface of the pellet mostly reacts with CCl_4. It is stressed that the reaction of the TT-Nb_2O_5 with CCl_4 at 453 K was controlled by the diffusion of the CCl_4 through the outer layer of the oxide pellet and the inner niobium oxide did not encounter the reactant CCl_4. The EDS profile of the pellet after the reaction with CCl_4 at 453 K ($\alpha = 0.012$ at 5 h) revealed that the Cl element was detected only near the outer surface of the oxide pellet. On the other hand, for niobium phosphate, the rate per g of pellet is independent on the amount of the pellet. This result suggests that the inner niobium phosphate *equally* participates in the reaction with CCl_4. The EDS showed that the distribution of the Cl element is flat and not dependent on the distance from the surface of the pellet of niobium phosphate. The reaction may occur on the surface of the pri-

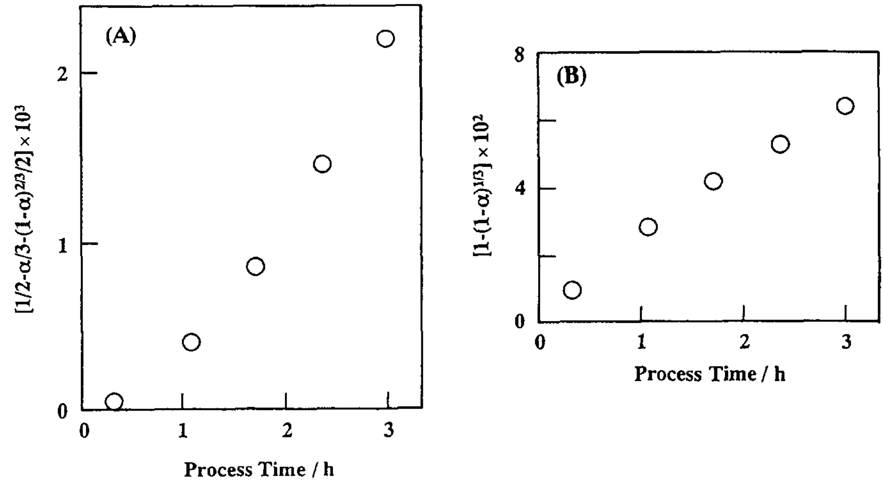

Fig. 8. Plots of (A) $[1/2-\alpha/3-(1-\alpha)^{2/3}/2]$ and (B) $[1-(1-\alpha)^{1/3}]$ versus time for the reaction of niobium phosphate with CCl_4 at 473 K.

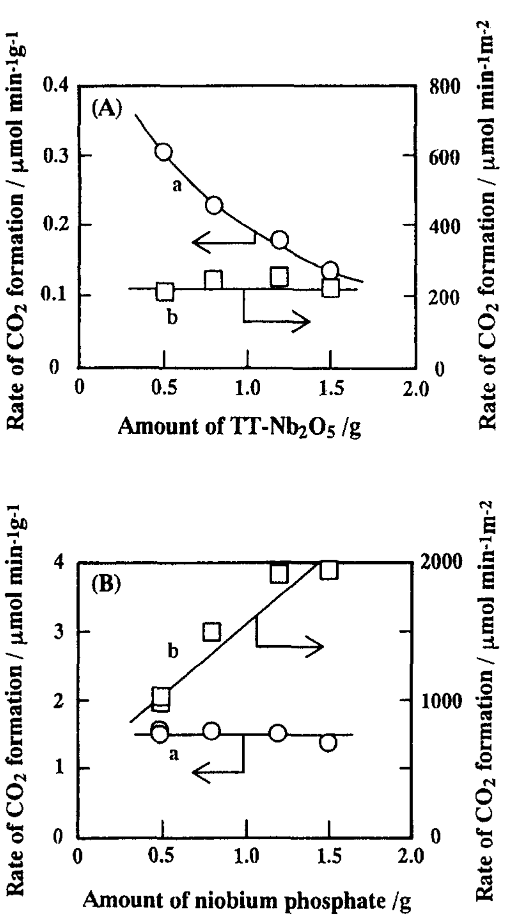

Fig. 9. Relationship between the rate of CO_2 formation (a, per g and b, per apparent area) and the amount of pelletized (A) TT-Nb_2O_5 and (B) niobium phosphate at 453 K.

mary particles constructing the pellet, and, therefore, the Cl distribution is apparently uniform throughout the pellet.

4. Conclusions

The reaction of TT-Nb_2O_5 with CCl_4 at 453 K was controlled by the diffusion of CCl_4 through the layer of a reaction product, $NbOCl_3$, formed around the outer surface of the Nb_2O_5. For the reaction at temperatures above 573 K, the chemical reaction occurring on the surface of the Nb_2O_5 controls the total reaction rate, due to the disappearance of the layer of $NbOCl_3$ by its sublimation. For niobium phosphate, the inner niobium phosphate participates in the reaction with CCl_4. Therefore, the reaction was controlled by the chemical reaction between niobium phosphate and CCl_4, leading the complete oxidation of CCl_4 into CO_2. At the present time, the reason for the participation of the inner niobium phosphate in the reaction is not well understood. Further investigation of the role of phosphate and chloride ions in the reaction of the niobium phosphate is necessary.

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