KINETIC STUDIES ON CARBON TETRACHLORIDE - NIOBIUM PENTOXIDE REACTION

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ABSTRACT

Niobium pentachloride used for producing niobium metal, is generally prepared by the chlorination of Nb_2O_5 by gaseous Cl_2 in presence of a reducing agent like carbon. Gaseous Carbon tetrachloride has been found to be a more effective chlorinating agent for some refractory metal oxides like TiO_2 and ZrO_2. In this investigation, chlorination of Nb_2O_5 with carbon tetrachloride vapour in mixture with nitrogen, has been carried out in a temperature range of 793 to 853K where the CCl_4 is decomposed in situ to elemental carbon and chlorine. The amount of Nb_2O_5 chlorinated was found to be directly proportional to the period of chlorination. Studies on the chlorination of Nb_2O_5 have also been carried out at 833K and p_{CCl_4} of 0.6 atm. using four different particle size varying from -65 to -400 mesh. It has been observed that the fraction of Nb_2O_5 chlorinated increased with decrease in particle size due to increase in the surface area. In the temperature range of 793 to 853K, an activation energy of 115 kJ/mole at p_{CCl_4} of 0.2 atm and a lower value of 57 kJ/mole at p_{CCl_4} of 0.6 atm, have been obtained. At the chlorination temperature of 833K, it has been possible to chlorinate about 95 pct. of Nb_2O_5 in about 75 minutes by using only 10 pct. of CCl_4 in N_2 (p_{CCl_4} = 0.1 atm). The same extent of chlorination can be achieved at the same temperature only in 18 to 20 minutes by using p_{CCl_4} of 0.6 atm. By using very low p_{CCl_4} for producing niobium chloride from its oxides, the environmental problems can be minimised considerably.

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INTRODUCTION

Gaseous chlorine has been a very effective reagent for opening up most of the refractory metal ores as well as for chlorinating their oxides. The pure oxides of titanium, zirconium, hafnium, niobium and tantalum are chlorinated by chlorine in presence of a reducing agent like carbon to produce their respective chlorides[1-6] which in turn are reduced by a metal like magnesium or by gaseous hydrogen. The chlorination reactions are generally carried out around 900^0 to 1000^0C requiring special equipments.

In view of high temperature and greater energy consumption in this process, the possibility of using carbon tetrachloride was examined by Jena, Gameiro and Brocchi[7] in a study on the kinetics of chlorination of briquetted anatase by carbon tetrachloride. At a low temperature of 673K, it was possible to chlorinate 90 pct. of anatase in 60 minutes. In another investigation by Jena, Brocchi and Villela[8], low temperature chlorination of ZrO_2 by gaseous carbon tetrachloride was carried out resulting in high chlorination of the oxide. In a typical run, complete chlorination of ZrO_2 by CCl_4 could be achieved at 800K only in 15 minutes. Though thermodynamically at lower temperatures carbon and chlorine chlorination seems to be more feasible than that by CCl_4 (Table 1), but in practice reverse has been observed[9]. This may be due to the fact that in the former case two solids (C and TiO_2) react with a gas where as in the other case only solid TiO_2 reacts with gaseous CCl_4. However, at somewhat higher temperature (beyond 800K), the ΔG^0 value for CCl_4 chlorination tends to be more negative than the C and Cl_2 chlorination. Beyond 800K, CCl_4 decomposes in to very reactive elemental carbon and chlorine which is evident from ΔG^0 values[10] for CCl_4 as given in Table 2. In the above mentioned studies on chlorination of ZrO_2[8], the rate of chlorination was found to be much higher above 800K. This might be due to the reaction of the oxide with the active elemental carbon and chlorine, produced due to the decomposition of the carbon tetrachloride in-situ.

In view of this, an investigation on the chlorination of niobium pentoxide in the temperature range of 793 to 853K with carbon tetrachloride vapour at different partial pressures, has been undertaken to examine the extent of this low temperature chlorination.

EXPERIMENTAL

Weighed amount of niobium pentoxide powder (each time 1g) of 99.9 pct. purity, was taken in an alumina boat and was placed in a horizontally placed silica tube. The silica tube was heated to the desired temperature by an electric resistance tube furnace. The temperature of the furnace was controlled within ± 2°C. The silica tube was provided with facilities for the inlet of the reacting gas and outlet for product gases. Liquid carbon tetrachloride used, was chemically pure grade. The CCl_4 vapour of the desired pressure was prepared by bubling pure and dry nitrogen (from the cylinder) at a suitable rate (measured by a flow meter) through pure CCl_4 liquid, kept in a glass flask which was heated by a water bath at the desired temperature[7]. The system is shown in Fig. 1. The gaseous mixture of CCl_4 and N_2 was passed into the reaction tube after positioning the alumina boat containing the weighed amount of Nb_2O_5 in the uniform temperature zone. The product gases during chlorination were released through an exhaust tap after passing through a saturated solution of sodium hydroxide. After conducting the chlorination for a desired time, the boat was taken out of the system, cooled in a desiccator and weighed. In this way the chlorination experiments were carried out for desired periods at different experimental conditions.

RESULTS AND DISCUSSION

Initially chlorination of niobium pentoxide by carbon tetrachloride at a partial pressure of 0.6 atm. was carried out at 833K using four different particle sizes of the oxide varying from -60 to -400 mesh (BSS). The results are given in Table 3. It was found that by decreasing the particle size of the oxide, the rate of chlorination was increased due to increase in surface area. For example, by using a particle size of the oxide between -65 +100 mesh, the extent of chlorination was 38 percent in 12 minutes, whereas during the same period the chlorination was 69.3 pct. by using a particle size of -400 mesh. In subsequent experiments, a particle size of -400 mesh of Nb_2O_5 was used.

At 833K, the effect of partial pressures of CCl_4 in N_2 was investigated by varying P_{CCl_4} from 0.1 to 0.6 atm. The results are summarised in Fig. 2. It is found that in all cases, the amount of Nb_2O_5 reacted is proportional to the time of chlorination. Further, the amount of chlorination increased sharply with increase in the partial pressure of CCl_4. For example, 95 pct. of Nb_2O_5

could be chlorinated during a period of 75 minutes and 18 minutes by using CCl_4 of 0.1 atm. and 0.6 atm. respectively, as shown in Table 4.

The effect of temperature in the range of 793 to 853K on the chlorination of the niobium pentoxide by carbon tetrachloride vapour having a partial pressure of 0.6 atm in mixture with nitrogen, was carried out. This temperature range was selected for these experiments as thermodynamically the carbon tetrachloride is mostly decomposed to active elemental carbon and chlorine. In this temperature range, the amount of niobium pentoxide chlorinated was found to be directly proportional to the time of chlorination as observed in earlier experiments. The results are summarised in the Fig. 3. The amount of niobium oxide chorinated per unit time was found to be increasing steadily with temperature. By applying Arrhenius equation and plotting ln v against $\frac{1}{T}$ (K^0) X 10^3 (Fig. 4), the activation energy of the chlorination process was calculated and found to be 57 kJ/mole.

The effect of temperature in the same range by using a lower partial pressure of carbon tetrachloride $\left(p_{CCl_4} = 0.2\,\text{atm} \right)$ was also investigated. The amounts of $Nb_2O_5(g)$ chlorinated at different times (min) and temperatures are given in Fig. 5. In this case, the chlorination rate of the oxide also increased with increase in temperature but the temperature coefficient was found to be significantly greater than those obtained at the higher partial pressure of carbon tetrachoride $\left(p_{CCl_4} = 0.6\,\text{atm} \right)$. By plotting ln v against $\frac{1}{T} \times 10^3$ as shown in Fig. 6, the activation energy of the chlorination of Nb_2O_5 is found to be 115 kJ/mole. This value is nearly double of that obtained by using CCl_4 at a partial pressure of 0.6 atm.

These two very different activation energy values clearly suggest that the chlorination of Nb_2O_5 by carbon tetrachloride vapour at high and low partial pressure follow two different reaction mechanisms. In this regard, the rate values calculated from the results obtained from the experiments on the effect of partial pressure of carbon tetracloride on the chlorination of Nb_2O_5 (Fig. 2), were examined. At lower partial pressure, the rate of chlorination is found to be proportional to the square root of p_{CCl_4} where as at the higher pressure range, it is observed to be directly proportional to p_{CCl_4}. This also supports the suggestion regarding occurrence of two separate mechanisms at two different p_{CCl_4} ranges, used in this investigation. In another work of the authors[11], the details of these mechanisms have been discussed in the light of Langmuir's

Adsorption Isotherm[12], particularly in view of the dependence of the kinetics of chlorination on the particle size of the Nb_2O_5 used (Table 3).

Though at the chlorination temperature of 833K, most of the CCl_4 present in the reacting gas mixture might be dissociated to elemental carbon and chlorine, yet at higher p_{CCl_4}, the gaseous products would contain some unreacted chlorine bearing gases. Therefore, to clean the outgoing gases, more alkali would be needed for scrubbing. In view of this, it may be environmentally safe to use CCl_4 having a partial pressure of 0.1 or 0.2 atm. in mixture with N_2, where the exit gas can be made nearly free of chlorine bearing gases. Further, with this low p_{CCl_4}, the chlorination of Nb_2O_5 is comparatively quite fast even at a low temperature of 833K.

CONCLUSIONS

1. In the temperature range of 793 to 853K, the rate of chlorination of Nb_2O_5 by CCl_4 vapour, has been found to be very fast because of the decomposition of the latter in to active elemental carbon and chlorine.

2. With decrease in particle size of Nb_2O_5 powder and increase of the partial pressure of CCl_4, the rate of chlorination of the oxide increases.

3. The rate of chlorination of the Nb_2O_5 is found to increase with increase of temperature. However, a high activation energy value (115 kJ/mole) at low p_{CCl_4} and a low activation energy value (57 kJ/mole) at high pressure have been observed, suggesting the occurrence of two different mechanisms of the chlorination.

4. Because of the near complete chlorination of Nb_2O_5 powder even at a low partial pressure of 0.1 atm at a temperature of 833K, the process seems to be attractive from commercial as well as environmental points of view.

5. Because of the promising results, it is worth while to make pilot scale studies of this process in order to obtain the optimum experimental conditions for large scale chlorination of Nb_2O_5.

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TABLE 1

Comparison of Standard free energy values of the following two reactions: at different temperatures

(1) $TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2$

(2) $TiO_2 + CCl_4 = TiCl_4 + CO_2$
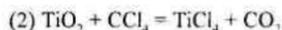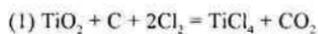
Temp K	$-\Delta G^0_1$ (kJ/mole)	$-\Delta G^0_2$ (kJ.mole^{-1})
500	243.89	204.53
600	249.75	228.19
800	261.48	262.73
900	267.34	281.99

TABLE 2

Standard Free energy change (ΔG^0) of CCl_4 at different temperatures (TK)

Temp K	$\Delta G^0_{CCl_4}$ (kJ.mole^{-1})
298	-68.25
400	-53.38
500	-39.36
600	-21.56
700	-12.35
800	+1.88
900	+14.65
1000	+24.49
1500	+93.37

TABLE 3

Effect of particle size of Nb_2O_5 on its chlorination with CCl_4 ($p_{CCl_4} = 0.6$ atm), at 833K for a chlorination time of 12 minutes

Particle size (mesh) of Nb_2O_5	Fraction of Nb_2O_5 chlorinated
-65 +100	0.381
-150 +200	0.398
-270 +325	0.610
-400	0.693

TABLE 4

Relationship of partial pressure of CCl_4 (p_{CCl_4}) and time of chlorination to achieve 95 pct. of chlorination of Nb_2O_5 at 833K

p_{CCl_4}(atm)	Time (min)
0.1	75
0.2	54
0.4	29
0.6	18

1. Water bath
2. Insulating material
3. Constant temperature water bath
4. Thermometer
5. Flask containing CCl_4
6. Gas preassure control system
7. Chromel-alumel thermocouple
8. N_2 inlet
9. Outlet of CCl_4 and N_2 mixture to chlorinating reactor
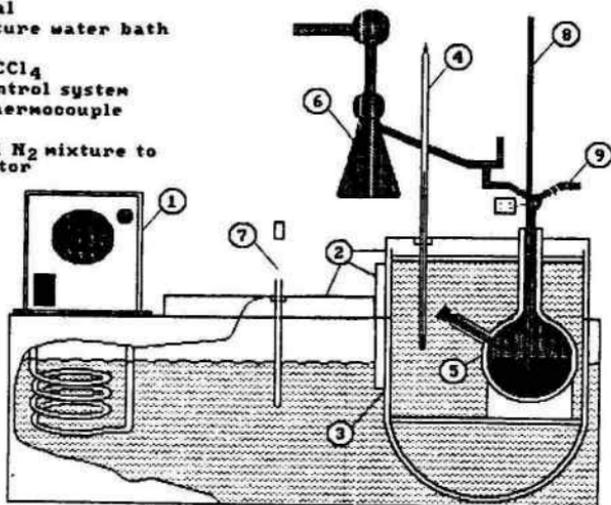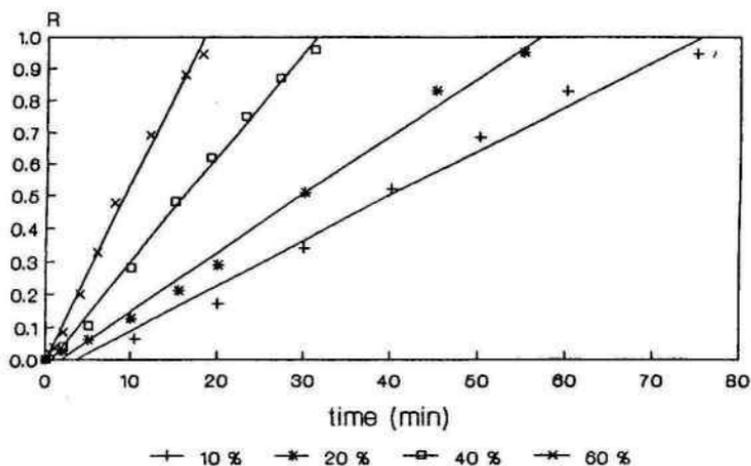
Fig.1. CCl_4 - N_2 gas mixture preparation set up

Fig.2. Effect of the partial pressure
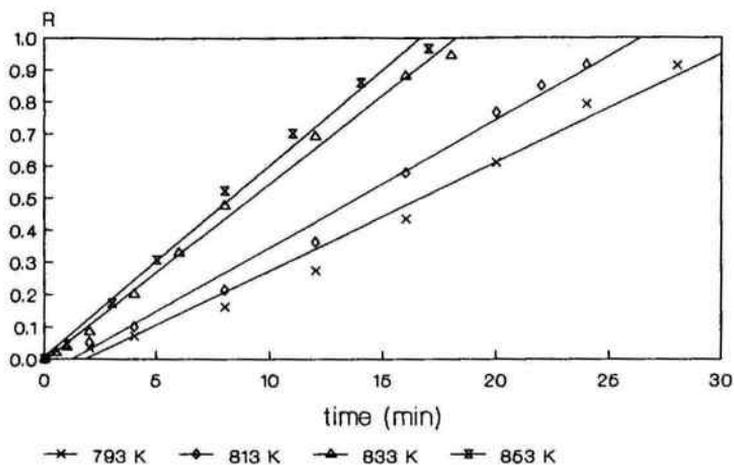of CCl4 on the fraction of Nb2O5
chlorinated at different times at 833K.

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Fig.3. Effect of temperature(793 - 853K)
on the fraction of Nb2O5 chlorinated at
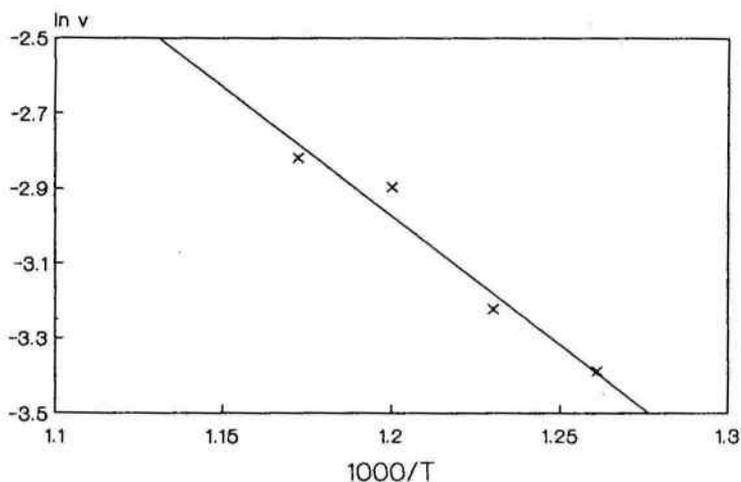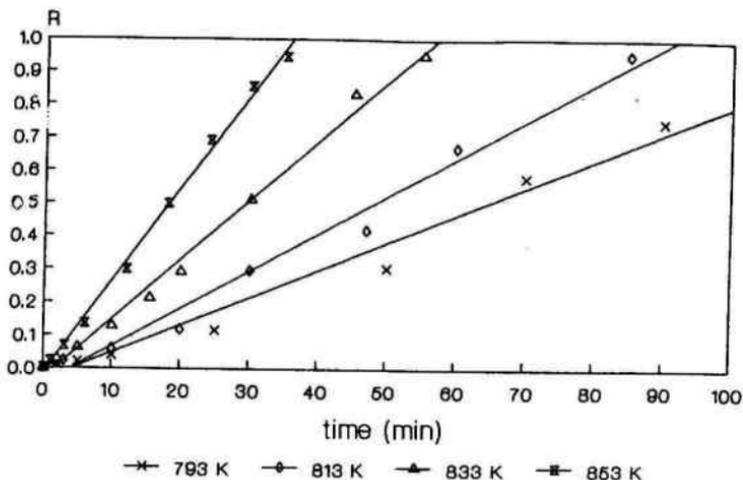different times using CCl4 at 0.6 atm.

Fig.4. ln v vs. 1/T (using pCCl4=0.6atm
in the temperature range of 793 to 853K)

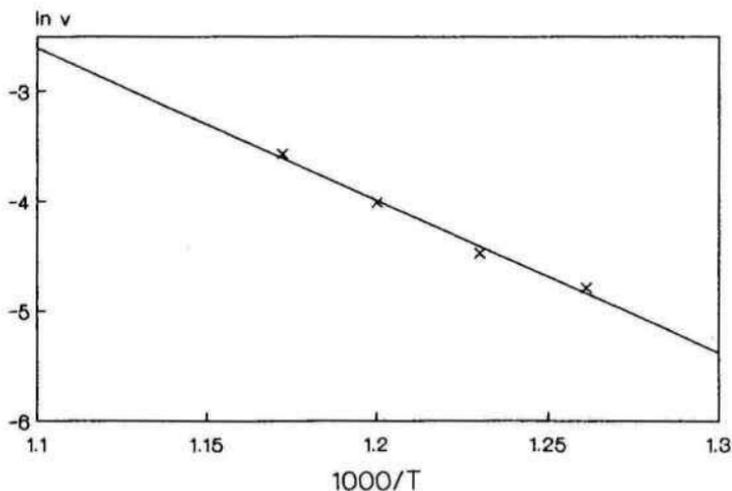Fig.5. Effect of temperature (793-853K) on the fraction of Nb2O5 chlorinated at different times using CCl4 at 0.2 atm.

$-\!\!\times\!\!-$ 793 K $-\!\!\diamond\!\!-$ 813 K $-\!\!\blacktriangle\!\!-$ 833 K $-\!\!\blacksquare\!\!-$ 853 K

Fig.6. ln v vs. 1/T (using pCCl4=0.2atm in the temperature range of 793 to 853K)