TG STUDY OF THE CHLORINATION OF WO3 BY COCl2 AND CCl4

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The chlorination kinetics of tungsten trioxide was studied by thermogravimetry, using $COCl_2$ and gaseous CCl_4 as chlorinating agents. Thermochemical calculations were made on the main chlorination reactions and also on some assumed side reactions. On the basis of the kinetic results CCl_4 proved to be more reactive than $COCl_2$. For both gases apparent activation energies of about 100 $kJ.mol^{-1}$ and reaction orders of 0.5 were obtained in the temperature ranges where the reaction was controlled by chemical processes.

During the chlorination by $COCl_2$ the conversion *vs.* time data could be described by the contracting sphere model. When chlorinating by CCl_4 a continuous decrease of the linear reaction rate was observed. Thus, for describing the isothermal TG curves a kinetic model, based on the retarding effect of non-removable surface side products, was assumed. With this model a fairly good correspondence of the measured and calculated kinetic curves was obtained.

In those cases when a metal forms a volatile chloride or oxichloride, chlorination is a useful tool both for processing of low-grade ores and purifying metals. Among other substances, pure tungsten may be produced from volatile tungsten halides by thermal decomposition or chemical reduction [1-3]. In spite of the great technical importance of this relatively few data have been published on the chlorination reactions of tungsten oxides [4-5].

Our aim was to give a comparative kinetic study of the reactions of WO_3 with $COCl_2$ and gaseous CCl_4.

Experimental

TG measurements were carried out in a special reactor attached to a Mettler semimicro recording balance [6]. Tungsten trioxide of analytical

grade (Reanal, $s^o = 4.6 \, m^2 g^{-1}$) was used. The chlorinating agents were phosgene of 3N purity and reagent grade CCl_4, which was introduced from a bubbler. N_2 of 4N purity, dried in the usual manner, was used as carrier gas. Before the chlorination, the samples were pretreated in situ at 770 K for 30 minutes in an O_2-N_2 mixture. During the measurements the conditions of a differential type flow reactor were maintained, as a large excess of inlet active gases was used.

The specific surface area of the initial samples and the chlorinated residues were determined by the usual BET method.

Results and discussion

Thermodynamic aspects

Thermochemical calculations for the main reactions and for some assumed side reactions were made for the temperature range 600-1000 K, using the data published int he Janaf tables [7] and in ref. [8]. The temperature dependence of the equilibrium constants for reactions (1-13) are given in Table 1. The chlorination reactions, resulting in volatile W-oxichlorides, are highly favoured. As the data shows, WO_3 is of high thermodynamic stability under inert conditions (reactions 5-7): the equilibrium pressure of O_2, calculated from the given log K_p values, is in the range of 10^{-13} or even lower. In the presence of chlorinating agents, however, the formation of oxygen-deficient W-oxides becomes favoured (Eqs 8-9). The probable products are $WO_{2.72}$, chlorine and carbon-dioxide. Naturally, analogous reactions leading to $WO_{2.90}$ or $WO_{2.96}$ are also allowed. During the reduction of WO_3 the formation of solid C or WC are also processes of thermochemical probability (Eqs 10-13).

Kinetic results

Figure 1 shows the mass loss *vs.* temperature curves measured at a linear heating rate of 10 deg.min^{-1}. As can be seen, the formation and volatilization of W-oxichlorides became measurable above 560 K for CCl_4 and 600 K for $COCl_2$, i. e. CCl_4 is more reactive than $COCl_2$.

The temperature dependence of the reaction rate was studied by isothermal TG measurements. The initial reaction rate was determined in the steady-state region as the slope of the mass loss *vs.* time curves related to unit mass. The Arrhenius representation of the initial reaction rates is

Tabla 1 Equilibrium constants for reactions (1-13)*

	Reactions	log K_p		
		600 K	800 K	1000 K
1	$WO_3 + 2\ COCl_2 = WOCl_4 + 2\ CO_2$	15.030	13.215	12.080
2	$WO_3 + COCl_2 = WO_2Cl_2 + CO_2$	10.930	10.766	10.620
3	$WO_3 + CCl_4 = WOCl_4 + CO_2$	12.983	12.201	11.672
4	$WO_3 + 1/2\ CCl_4 = WO_2Cl_2 + 1/2\ CO_2$	9.907	10.259	10.416
5	$7.143\ WO_3 = 7.143\ WO_{2.72} + O_2$	-30.358	-21.050	-15.371
6	$20\ WO_3 = 20\ WO_{2.90} + O_2$	-31.800	-21.960	-16.080
7	$50\ WO_3 = 50\ WO_{2.96} + O_2$	-26.650	-18.100	-13.000
8	$3.571\ WO_3 + COCl_2 = 3.571\ WO_{2.72} + Cl_2 + CO_2$	2.417	3.386	3.939
9	$7.143\ WO_3 + CCl_4 = 7.143\ WO_{2.72} + 2\ Cl_2 + CO_2$	2.787	5.758	7.469
10	$1.786\ WO_3 + COCl_2 = 1.786\ WO_{2.72} + Cl_2 + 0.75\ CO_2 + 0.25\ C$	1.463	2.191	2.611
11	$3.571\ WO_3 + CCl_4 = 3.571\ WO_{2.72} + 2\ Cl_2 + 0.5\ CO_2 + 0.5\ C$	0.879	3.368	4.814
12	$1.886\ WO_3 + COCl_2 = 1.786\ WO_{2.72} + Cl_2 + 0.9\ CO_2 + 0.1\ WC$	0.984	2.165	2.894
13	$3.771\ WO_3 + CCl_4 = 3.571\ WO_{2.72} + 2\ Cl_2 + 0.8\ CO_2 + 0.2\ WC$	-0.732	2.802	4.863

* WO_x, WC and C (graphite) are solids, ad all the remaining reaction components are gases

shown in Fig. 2 and the calculated activation energies are given in Table 2. Practically the same E values were obtained for the two chlorination reactions. It can also be seen that the intial rates by CCl_4 are higher than those of by $COCl_2$.
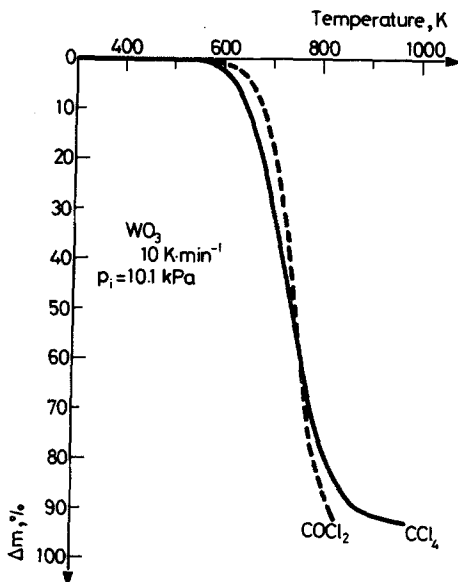

Fig. 1 Mass loss *vs.* temperature curves for the reactions of $WO_3 + COCl_2$ and $WO_3 + CCl_4$. Heating rate: 10 K/min

Table 2 Apparent activation energies and reaction orders for the chlorination of WO_3

	E (kJ/mol)	n
$WO_3 + COCl_2$	94	0.5
	(530-720 K)	(600-650 K)
$WO_3 + CCl_4$	100	0.5
	(530-700 K)	(620-670 K)

The pressure dependence of the reaction was studied in the range of 10-50 kPa for $COCl_2$ and 1-12 kPa for CCl_4, respectively. The formal orders calculated from the logarithmic representation of the initial rates are given in Table 2. According to the kinetic results a half order was found for both chlorinating agents. As a consequence, linear R_0 *vs.* $p^{1/2}$ plots were obtained (Figs 3 and 4), giving evidence of the fast, reversible, dissociative adsorption of the active gases.
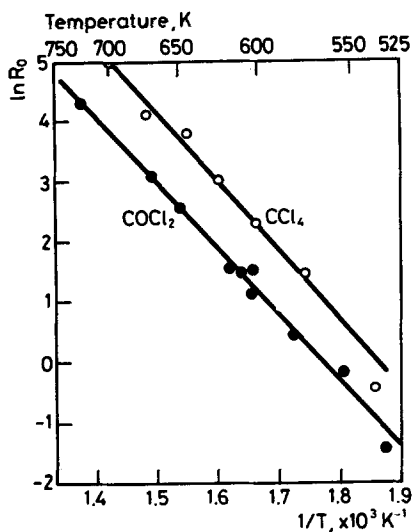
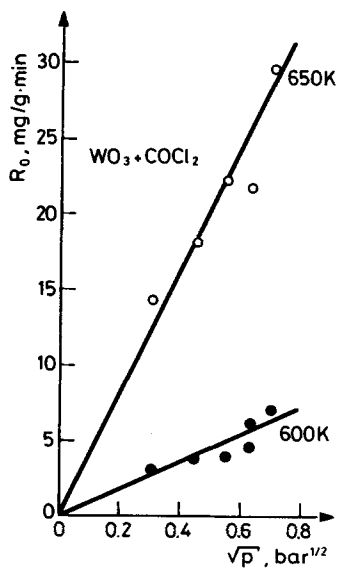Fig. 2 Temperature dependence of the initial reaction rates

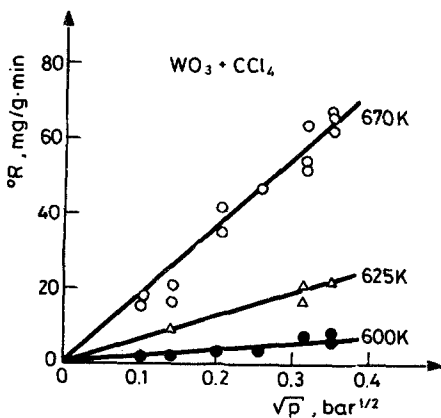Fig. 3 R_o vs. $p^{1/2}$ functions for clorination by $COCl_2$

Fig. 4 R_0 vs. $p^{1/2}$ functions for clorination by CCl_4
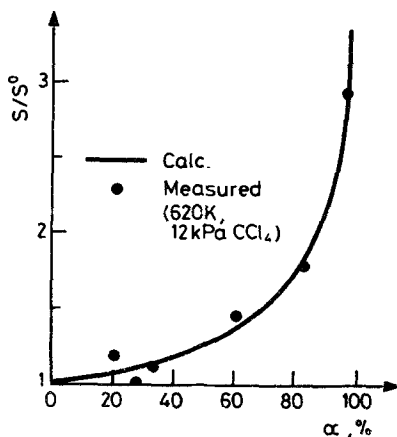

Fig. 5 Change of the specific surface area during the chlorination by CCl_4: measured data, $T = 670$ K; calculated curve, using the model of contracting spheres

As is known, the specific surface area generally increases monotonously during the gasification reactions of solid samples of low initial surface area. Figure 5 shows the change of the specific surface area of WO_3 during the chlorination by CCl_4. This figure also represents the curve calculated for the case of the gasification of spherical particles of uniform size. As can be seen, a fairly good correspondence of the measured and calculated data was observed, thus the "contracting sphere model" can be expected to be valid in the whole conversion range.

Therefore, $g(\alpha)$-time functions were calculated, using the model of contracting spheres, where $g(\alpha)$ is the linearized form of the respective rate equation. The $g(\alpha)$-t representations are shown in Figs 6 and 7 for the two chlorinating agents. As can be seen, the model of contracting spheres can be used for the reaction of $WO_3 + COCl_2$, however, it is not valid for the chlorination by CCl_4.
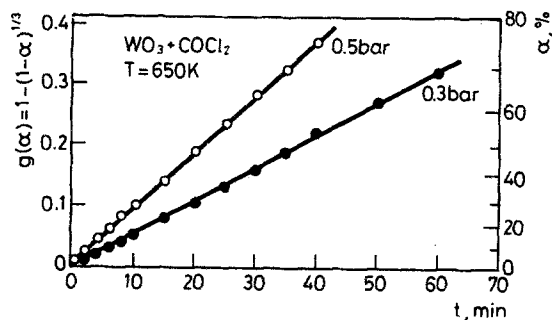
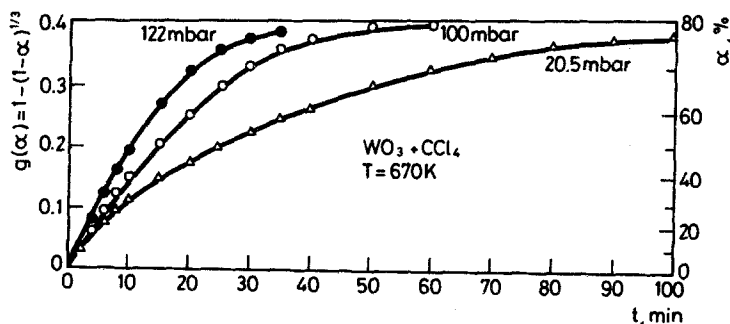Fig. 6 $g(\alpha)$ vs. time curves for the chlorination by $COCl_2$

Fig. 7 $g(\alpha)$ vs. time curves for the chlorination by CCl_4

In all probability, the declination of the $g(\alpha)$-time curves is caused by the loss of reactivity of the solid sample. During the chlorination of WO_3 by CCl_4 the continuous decrease of the linear reaction rate can be caused by the formation of a non-removable product layer on the surface. Our thermodynamic calculations have shown that parallel to the chlorination the partial reduction of the surface is also allowed. This can result in an oxygen-deficient surface and C or WC deposits. (It has to be mentioned

here that from the point of view of reaction kinetics, CCl_4 is much more in-clined to form solid carbon than $COCl_2$ does, as the binding energy of the $C = O$ bond is much higher than that of the C-Cl bonds.) Therefore, during the chlorination by CCl_4 the following model is proposed to describe the ob-served declination of the conversion *vs.* time curves:

The partial reduction of the solid phase goes together with surface deposition of non-removable side products (C or WC). In the first approach it can be supposed that the volatilization rate through the covered surface is negligible compared to that of the pure WO_3 surface. The surface coverage by the non-volatile products can be described as:

$$\frac{d\Theta}{dt} = k_1(1-\Theta) \tag{1}$$

where k_1 is the apparent rate constant of the reduction process, involving also the terms of pressure and temperature dependence. By integrating Eq. (1) we have:

$$\theta = 1 - e^{-k_1 t}. \tag{2}$$

Because of the retarding effect of these surface contaminants, the decrease of the linear reaction rate perpendicular to the surface can be ex-pressed as:

$$\frac{dr}{dt} = k_2(1-\Theta) \tag{3}$$

where k_2 is the apparent rate constant of the chlorination process and r stands for the particle radii. The r *vs.* t functions can be obtained by in-tegrating Eq. (3):

$$r = 1-(k_2/k_1)(1-e^{-k_1 t}) \tag{4}$$

For the calculation of the conversion values we can suppose that the mass of the non-volatile surface species is negligible compared to that of the whole particles. Thus the conversion *vs.* time functions for spherical par-ticles can be expressed as:

$$\alpha = 1-[1-(k_2/k_1)(1-e^{-k_1 t})]^3 \tag{5}$$

Now the two rate constants k_1 and k_2 (for the reduction and chlorination processes, respectively) should be regarded as interpolation variables.

Figure 8 shows the conversion vs. time data measured at 670 K and the calculated curves using the proposed kinetic model. As can be seen, a fairly good correspondence of the measured and calculated curves was obtained, suggesting that the proposed kinetic model is applicable to describe the retarding effect of the non-removable surface side products.
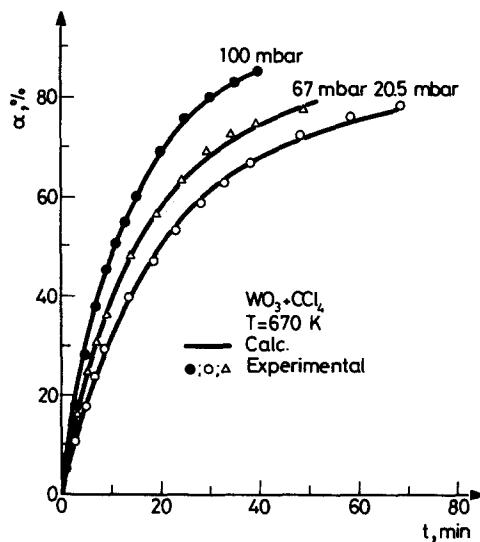

Fig. 8 Calculated and observed conversion vs. time curves for the chlorination of WO3 by CCl4

Conclusions

During the chlorination of tungsten trioxide CCl4, proved to be more reactive than COCl2. Kinetic data obtained in the chemically controlled region have revealed the same activation energies (≈ 100 kJ.mol^{-1}) and half order pressure dependence for the two chlorinating agents.

The chlorination by COCl2 occurs according to the contracting sphere model, characterized by a linear rate of $dr/dt = $ constant. When chlorinating by CCl4, the reactivity of the solid phase decreases continuously. This monotonous decrease can be explained by surface reduction processes which occur parallel to the volatilization and result in an oxygen-deficient

surface and deposits of solid C or WC. The surface enrichment of these impurities causes a continuous loss of the linear reaction rate. In the proposed kinetic model the retarding effect of the non-removable surface species is assumed. This allows a proper fitting of the conversion versus time curves up to high conversions.

References

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Zusammenfassung — Mittels Thermogravimetrie wurde die Kinetik der Chlorierung von Wolframtrioxid mit $COCl_2$ bzw. gasförmigem CCl_4 untersucht. Für die Hauptchlorierungsreaktionen und einige angenommene Nebenreaktionen wurden thermochemische Berechnungen getätigt. Ausgehend von den kinetischen Ergebnissen erwies sich CCl_4 als reaktionsfreudiger als $COCl_2$. In dem Temperaturbereich, in dem die Reaktion durch chemische Prozesse kontrolliert wird, erhielt man eine scheinbare Aktivierungsenergie von etwa 100 $kJmol^{-1}$ und eine Reaktionsordnung von 0.5.

Bei der Chlorierung mit $COCl_2$ können die Konversion/Zeit Daten mit dem Contractingsphere Modell beschrieben werden. Bei der Chlorierung mit CCl_4 kann eine ständige Abnahme der linearen Reaktionsgeschwindigkeit beobachtet werden. Somit wurde für die Beschreibung der isothermen TG-Kurven ein kinetisches Modell angenommen, welches auf dem Rückhalteeffekt von unabspaltbaren Nebenprodukten an der Oberfläche beruht. Mit diesem Modell konnte eine gute Übereinstimmung zwischen experimentellen und rechnerischen kinetischen Kurven erzielt werden.