Journal of Thermal Analysis, Vol. 39 (1993) 75-86

EFFECT OF ALKALI ADDITIVES ON THE KINETICS OF $WO_3 + CCl_4$ REACTION

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(Received January 30, 1992)

The chlorination kinetics of alkali-added (K and Li) tungsten trioxide were studied by thermogravimetry, using gaseous CCl_4 as chlorinating agent. The reactivity of the modified samples was compared to the results on the chlorination of pure WO_3. Similar apparent activation energies were found for the pure and alkali-added samples. However, potassium additive resulted in a strong decrease of the initial reaction rate, while surface lithium has no influence on it.

During the chlorination a continuous decrease of the linear reaction rate was observed for both samples, which was explained by retarding effects of surface by-products and alkali additives. For describing the isothermal TG curves an appropriate kinetic model, based on the monotonously increasing inhibition of these species was assumed. The curve calculated with this model fits well to the experimental results.

Keywords: chlorination, kinetics, $WO_3 + CCl_4$ reaction

Introduction

Chlorination reactions of metal oxides belong to the special chapter of heterogeneous reaction kinetics where the rate depends on several factors characterizing the solid phase, as actual surface structure and phase composition, surface contaminations and additives, etc. Thus various surface additives or even impurities may have a great influence on the reaction rate [1, 2].

Beside of their theoretical importance volatile tungsten halides have also an important role in producing and purifying metallic tungsten [3–5]. However, relatively few data have been published on the chlorination reactions of tungsten oxides [6, 7].

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In our previous work [8] kinetic studies were made on the reactions of WO_3 with $COCl_2$ and CCl_4. A continuous decrease of the linear reaction rate was observed during chlorinating by CCl_4, which was explained by surface deposition of the non-removable by-products. The present paper deals with the effects of alkali additives on the kinetics of chlorination by CCl_4. An appropriate kinetic model is proposed for interpretation of the conversion *vs.* time curves, which involves the retarding effects of non-removable by-products as well as the surface enrichment of alkali additives.

Experimental

The chlorination reactions were carried out in a fused silica reactor coupled with a Mettler semimicro recording balance [9]. Tungsten trioxide of analytical grade (Reanal, $s^\circ = 4.6\ m^2 \cdot g^{-1}$) was used as sample WO_3. Samples modified with lithium and potassium (WO_3-Li(s) and WO_3-K(s), $s^\circ = 4.6$ and $4.1\ m^2 \cdot g^{-1}$ resp.) were prepared by impregnation of sample WO_3 by alkali acetate solution, followed by calcination. This treatment resulted in 0.22% Li_2O and 0.36% K_2O content in the samples, respectively.

The chlorinating agent was reagent grade CCl_4, which was introduced from a bubbler. Nitrogen of 4N purity, dried in the usual manner, was used as carrier gas. Before chlorination the samples were preheated in situ at 770 K for 30 minutes in an O_2-N_2 gas mixture. During the measurements the conditions of a differential type flow reactor were maintained, as a large inlet of active gas was used.

The specific surface area of the initial samples was determined by the usual BET method. The chemical composition of the surface of sample WO_3 before and after the chlorination process was studied also by XPS.

Results and discussion

Thermodynamic aspects

Thermochemical calculations on the $WO_3 + CCl_4$ system [8] had shown that the formation of $WOCl_4(g)$ from $WO_3(s)$ is highly favoured, while processes producing solid by-products and oxygen-deficient W-oxides are also allowed. Some additional data on thermodynamically possible side reactions are given in Table 1. The temperature dependence of the equilibrium constants was calculated using the data published in JANAF Tables [10]. The main chlorination process is described by reaction 1. Some of the possible side processes (reactions 2a-2c) result in the formation of solid carbon and oxygen-deficient surface. The chlorination of lower oxides of tungsten (reactions 3a-3c) are thermodynamically

Table 1 Equilibrum constants for reactions (1–4)

	Reactions*	$\log K_p$				
		600 K	700 K	800 K	900 K	1000 K
1	$WO_3+CCl_4=WOCl_4+CO_2$	12.983	12.549	12.201	11.916	11.672
2.a	$25WO_3+CCl_4=25WO_{2.96}+0.5C+0.5CO_2+2Cl_2$	2.845	4.000	4.843	5.523	6.000
2.b	$10WO_3+CCl_4=10WO_{2.9}+0.5C+0.5CO_2+2Cl_2$	0.270	1.785	2.913	3.783	4.460
2.c	$3.6WO_3+CCl_4=3.6WO_{2.72}+0.5C+0.5CO_2+2Cl_2$	0.878	2.314	3.368	4.180	4.814
3.a	$WO_{2.96}+CCl_4=WOCl_4+0.98CO_2+0.02C$	12.828	12.394	12.046	11.761	11.518
3.b	$WO_{2.9}+CCl_4=WOCl_4+0.95CO_2+0.05C$	12.583	12.383	12.008	11.702	11.442
3.c	$WO_{2.72}+CCl_4=WOCl_4+0.86CO_2+0.14C$	12.448	11.935	11.532	11.204	10.929
4	$CCl_4=C+2Cl_2$	–1.032	0.122	0.978	1.638	2.160

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

highly favoured. Beside of volatile $WOCl_4(g)$ solid C(s) is also formed in these reactions. Moreover, the thermal decomposition of $CCl_4(g)$ to chlorine and solid C(s) (process 4) becomes thermodynamically favoured above 600 K.

Kinetic results

The reactivity of samples WO_3 and WO_3-K(s) was tested by anisothermal thermogravimetric measurements. Figure 1 shows the mass loss *vs.* temperature curves measured in flowing CCl_4/N_2 at p_1 = 10.1 kPa. The volatilization of $WOCl_4(g)$ starts at higher temperatures and the slope of the TG curve is much lower for the potassium-added sample that for the pure WO_3. Similar inhibiting effect of K was observed previously [11] during the chlorination of titania by CCl_4. The retardation of the reaction was explained by the donor feature of K-additive: as potassium resulted in a decrease of the acceptor character of the surface. Therefore the probability of the polarization and dissociation of the chlorinating agent is decreased, while the dissociation of CCl_4 on the neighbouring potassium ions is supposed to be unfavoured because of steric hindrance.

The kinetics of the reaction were studied in detail 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 shown in Fig. 2, while the apparent activation energies calculated from the slope of the Arrhenius curves are given in Table 2.

Table 2 Apparent activation energies for the chlorination of pure and alkali-added tungsten trioxide

Sample	E / kJ·mol^{-1}
WO_3	100 (540–700 K)
WO_3-Li(s)	99 (570–670 K)
WO_3-K(s)	89 (570–750 K)

Similar E_a values (89–100 kJ·mol^{-1}) were found for the three samples. There was no measurable change in the initial reaction rate in the case of lithium-added tungsten oxide, however, potassium resulted in a strong decrease of the initial rate.

The effect of alkali additives during the chlorination was studied by isothermal measurements. Figure 3 shows a selected set of the TG curves with the same initial reaction rate. (Chlorination temperature: 640 K for pure WO_3 and WO_3-Li(s), 700 K for WO_3-K(s), respectively.) A continuous declination of the α-t curves was observed at alkali-added samples compared to the chlorination of pure WO_3. The decrease of the reactivity is particularly clear on sample WO_3-K(s).

A monotonous decrease of the linear reaction rate (–dr/dt) was also detected previously [8] during the chlorination of pure WO_3 by CCl_4, which was explained by the surface deposition of non-removable by-products. According to the results of the thermochemical calculations, the deposition of solid carbon together with the formation and volatilization of lower oxides of tungsten are favoured or allowed processes.

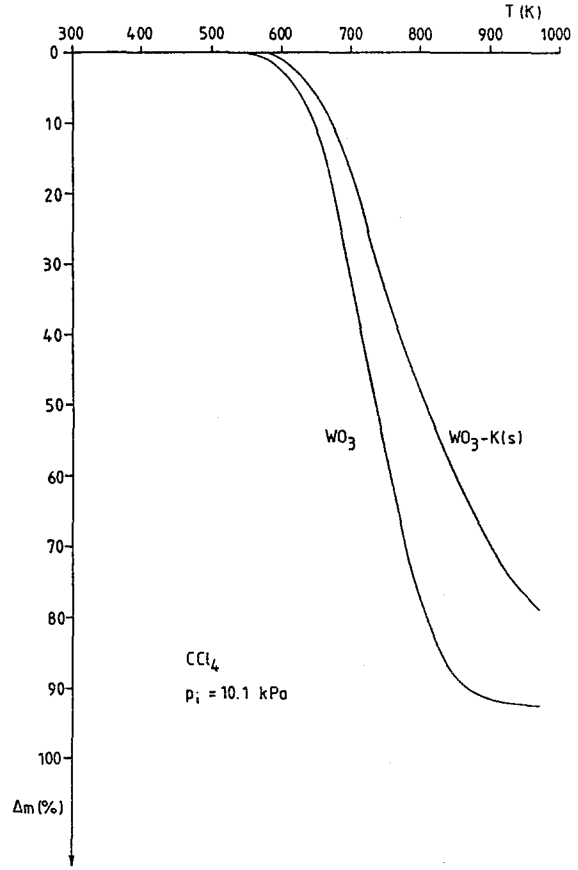

Fig. 1 Mass loss *vs*. temperature curves for the chlorination of pure and potassium added tungsten trioxide by CCl_4. Heating rate: 10 deg·min^{-1}

To obtain more information on the surface composition, the chlorinated tungsten oxide ($\alpha = 80\%$) was analyzed by XPS method. Neither WC nor any other impurities were detected on the surface. Nevertheless, a slight shift of the 0 1s line (0.2 eV) was observed towards the lower values, and the C-content of the surface is increased significantly.

Considering the results of ESCA measurements and thermochemical calculations, we think that the decrease of the linear reaction rate is due to the formation of non-removable C-deposit. The proposed kinetic model [8] based on this assumption was suitable for describing the isothermal TG curves. However, as it is also indicated by the different character of the kinetic curves shown in Fig. 3, that model is not applicable for the reactions of samples WO_3-K(s) and WO_3-Li(s).

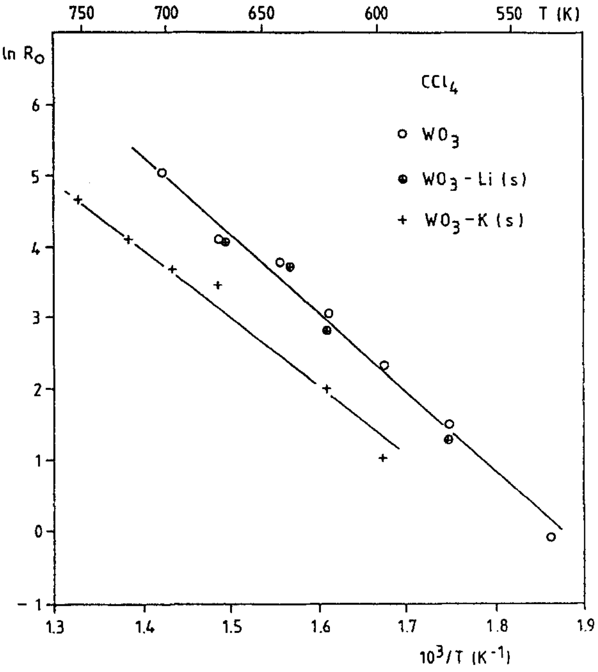

Fig. 2 Arrhenius representation of the initial reaction rates

Therefore we suppose that the continuous decrease of the linear reaction rate is cause not only by the formation of non-removing by-products, but by alkali additives as well. According to this assumption the proposed model involves the monotonously increasing inhibition by solid by-products and the surface enrichment of alkali additives during shrinking of the particles. In the following kinetic approach we used the model suggested for the $WO_3 + CCl_4$ reaction [8] as well as the kinetic model developed earlier for the chlorination of titania containing phosphorous impurities [12].

Kinetic model

The proposed kinetic model is based on the following assumptions.

(i) The particles are closely spherical and of uniform size, $^{\circ}R \equiv 1$ (in arbitrary units). The conversion can be obtained from the particle radii as $\alpha = 1-r^3$.

(ii) Similar to the case of WO_3 a side reaction producing non-removable surface products (C-deposits) is taking place parallel to the volatilization. The surface coverage by the non-volatile products can be described as:

$$\frac{d\,\theta_c}{d\,t} = k_1 \cdot (1 - \theta_c) \tag{1}$$

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

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

(iii) It is also supposed that the volatilization rate through the surface deposit (θ_c) is negligible compared to the chlorination of the pure WO_3 surface.

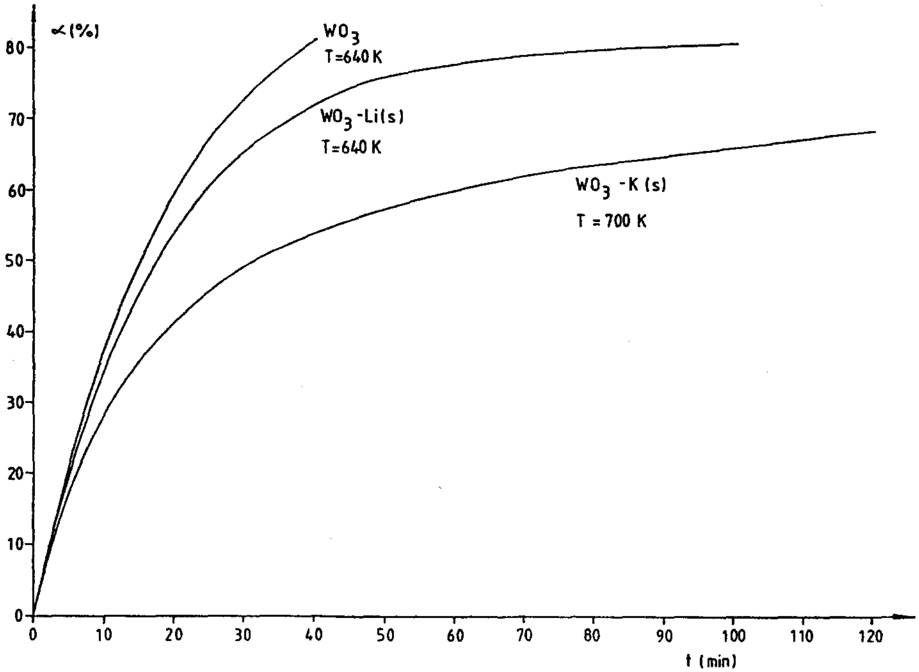

Fig. 3 Conversion *vs.* time curves. T = 640 K for sample WO_3 and WO_3-Li(s); T = 700 K for sample WO_3-K(s)

(iv) The surface alkali additives behave as retardant of the chlorination by CCl_4. During the reaction the coverage by alkali is increasing due to the volatilization of WO_3 matrix. The surface enrichment of alkali additives can be expressed as:

$$\theta_a = \frac{{}^{o}R^2}{r^2} \cdot {}^{o}\theta_a \tag{3}$$

where θ_a is the fraction of the surface covered by K or Li, ${}^{o}\theta_a$ refers to the initial coverage.

(v) The fraction of the surface available for direct chlorination is $(1-\theta_a)\cdot(1-\theta_c)$. At θ_a=1 or above the rate of this process is zero.

(vi) Parallel to the direct chlorination, a diffusion controlled process, i.e. chlorination through the alkali additives takes place. Below the monolayer coverage the linear rate of this reaction is proportional to $\theta_a \cdot (1-\theta_c)$. At $\theta_a \geq 1$ the rate of the diffusion processes through the alkali layers will be inverse to θ_a, i.e. the linear reaction rate is proportional to $(1-\theta_c)/\theta_a$.

Thus, depending on the value of θ_a, the following equations are proposed for describing the linear reaction rate.

$\theta_a < 1$ (Below the monolayer coverage)

$$-\frac{\mathrm{d}r}{\mathrm{d}t} = k_2(1-\theta_a)\cdot(1-\theta_c) + k_3\,\theta_a\cdot(1-\theta_c) \tag{4}$$

where k_2 and k_3 are the apparent rate constants of the direct chlorination and that of the volatilization through the alkali layers, respectively.

Rearrangement of Eq. (4) gives:

$$-\frac{\mathrm{d}r}{\mathrm{d}t} = k_2\left[1-\left(1-\frac{k_3}{k_2}\right)\cdot\theta_a\right]\cdot\left(1-\theta_c\right) \tag{5}$$

For particles of unit radius (${}^{o}R \equiv 1$) Eq. (3) gives:

$$\theta_a = \frac{{}^{o}\theta_a}{r^2} \tag{6}$$

From Eqs (2), (5) and (6):

$$-\frac{\mathrm{d}r}{\mathrm{d}t} = k_2\left[1-\frac{{}^{o}\theta_a\cdot\left(1-\frac{k_3}{k_2}\right)}{r^2}\right]\cdot e^{-k_1 t} \tag{7}$$

which becomes after rearrangement:

$$-\frac{r^2\,\mathrm{d}r}{r^2-a} = k_2\cdot e^{-k_1 t}\,\mathrm{d}t \tag{8}$$

where $a \equiv {}^{o}\theta_a\cdot(1-k_3/k_2)$

By integrating of Eq. (8). from $r = {}^{o}R \equiv 1$ to r and $t = t_o$ to t we obtain:

$$1-r+\frac{\sqrt{a}}{2}\ln\frac{1-\sqrt{a}}{1+\sqrt{a}}+\frac{\sqrt{a}}{2}\ln\frac{r+\sqrt{a}}{r-\sqrt{a}}=\frac{k_2}{k_1}\cdot\left[1-e^{-k_1 t}\right] \tag{9}$$

The initial reaction rate (v_o) can be expressed from Eq. (7) using the values of $r = {}^{o}R \equiv 1$ at $t=t_o$:

$$v_o=3\cdot\left[-\frac{\mathrm{d}r}{\mathrm{d}t}\right]_{t=0}=3\cdot k_2\cdot\left[1-{}^{o}\theta_a\cdot\left(1-\frac{k_3}{k_2}\right)\right]=3\cdot k_2\cdot\left(1-{}^{o}\theta_a\right)+3\cdot k_3\cdot{}^{o}\theta_a \tag{10}$$

Thus the rate constant of the direct chlorination (k_2) is given as:

$$k_2=\frac{\frac{v_o}{3}-k_3\cdot{}^{o}\theta_a}{1-{}^{o}\theta_a} \tag{11}$$

Equation (8) is valid up to $\theta_a = 1$. According to Eq. (3) the monolayer coverage of K or Li can be characterized by a particle radii $r^* = \sqrt{{}^{o}\theta_a}$. The time required to achieve the monolayer coverage (t^*) can be calculated from Eq. (9), using the value of $r = r^* = \sqrt{{}^{o}\theta_a}$.

$\theta_a > 1$ (Above the monolayer coverage)

After the monolayer coverage has been reached the rate is controlled by the diffusion through the layers of alkali additives.

$$-\frac{\mathrm{d}r}{\mathrm{d}t}=k_3\cdot\frac{(1-\theta_c)}{\theta_a}=k_3\cdot\frac{r^2}{{}^{o}\theta_a}\cdot e^{-k_1 t} \tag{12}$$

Rearrangement of Eq. (12) gives:

$$-\frac{\mathrm{d}r}{r^2}=\frac{k_3}{{}^{o}\theta_a}\cdot e^{-k_1 t}\,\mathrm{d}t \tag{13}$$

Integrating from $r = r^* \equiv \sqrt{{}^{o}\theta_a}$ to r and from $t = t^*$ to t we obtain:

$$\frac{1}{r}-\frac{1}{\sqrt{{}^{o}\theta_a}}=\frac{k_3}{k_1\cdot{}^{o}\theta_a}\left[e^{-k_1 t}-e^{-k_1 t^*}\right] \tag{14}$$

Now ${}^{o}\theta_a$ and the ratio of the rate constants (k_3/k_2, k_2/k_1) should be regarded as interpolation variables. Thus the conversion *vs.* time curves can be calculated using the *r vs. t* functions given by Eqs (9) and (14) below and above the monolayer coverage, respectively.

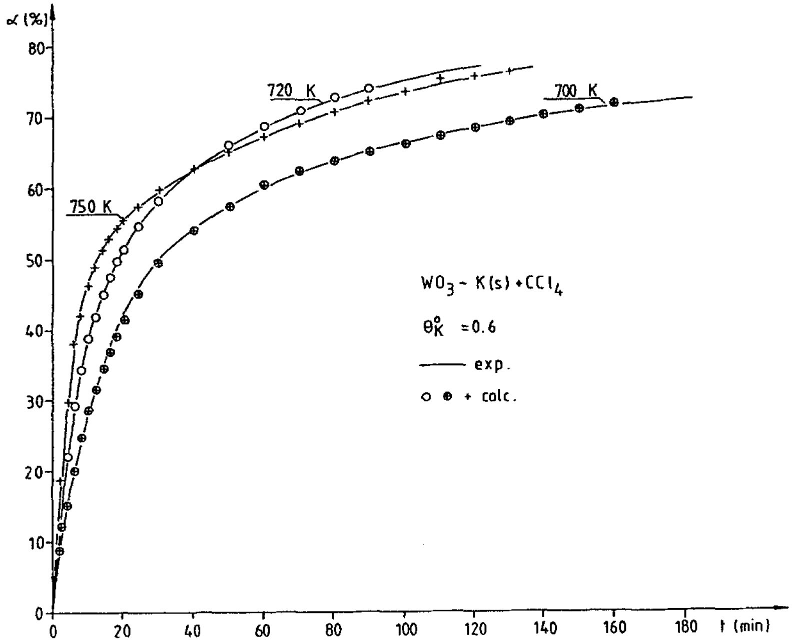

Fig. 4 Calculated and observed conversion *vs.* time curves for the chlorination of WO_3-K(s) by CCl_4

Figure 4 shows the measured conversion *vs.* time data for sample WO_3-K(s) and the calculated curves using an appropriate value of the initial K-coverage of $^{o}\theta_K = 0.6$. The suitable k_3/k_2 and k_2/k_1 values were varying between 0.03–0.11 and 3–12, resp. As can be seen, a fairly good correspondence of the measured and calculated curves was obtained.

Figure 5 shows the fitting of the measured data and the calculated curve for sample WO_3-Li(s). During the calculation an initial Li-coverage of $^{o}\theta_{Li} = 0.35$ was used and the suitable ratios of k_3/k_2 and k_2/k_1 were between .,01–0.03 and 30–40, respectively. In this case also a satisfactory agreement of the observed and the calculated data was obtained.

As the results show the proposed kinetic model is applicable to describe the retarding effects of both solid by-products and alkali additives during the chlorination of surface modified tungsten oxide by CCl_4.

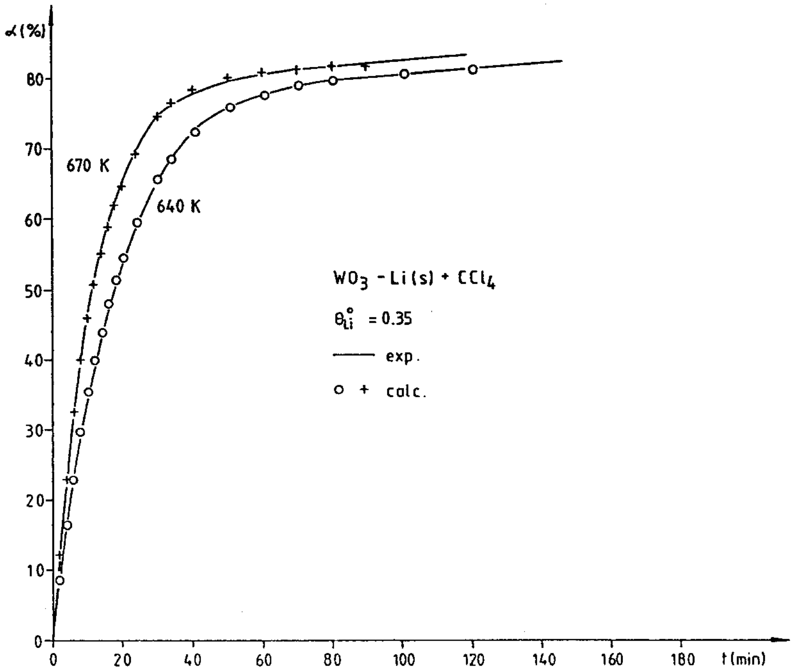

Fig. 5 Calculated and observed conversion *vs.* time curves for the chlorination of WO_3-Li(s) by CCl_4

Conclusions

Apparent activation energies of 89–100 kJ·mol^{-1} were obtained for the chlorination of pure and alkali-added tungsten oxide by CCl_4. Potassium additive resulted in a strong decrease of the initial reaction rate, while surface lithium had no influence on it.

During the chlorination a continuous decrease of the linear reaction rate ($-dr/dt$) was observed for both samples. This is caused by the retarding effect of carbon deposits and that of surface alkali. The surface concentration of these species is increasing during the reaction resulting in a monotonously increasing inhibition. The proposed kinetic model, based on these assumptions, was applicable to describe the time dependence of the isothermal TG curves up to high conversions.

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Zusammenfassung — Mittels Thermogravimetrie wurde die Chlorierungskinetik von alkaliversetztem (K und Li) Wolframtrioxid untersucht, wobei CCl_4 als Chlorierungsreagens fungierte. Die Reaktivität der modifizierten Proben wurden mit der von reinem WO_3 verglichen. Für die reinen und für die alkaliversetzten Proben wurden ähnliche scheinbare Aktivierungsenergien gefunden. Der Zusatz von Kalium verursacht jedoch eine starke Abnahme der ursprünglichen Reaktionsgeschwindigkeit, während oberflächiges Lithium keinen Effekt zeigt.

Während der Chlorierung wurde eine ständige Senkung der linearen Reaktionsgeschwindigkeit für beide Proben festgestellt, was mit Rückhalteeffekten von oberflächigen Nebenprodukten und Alkalizusätzen erklärt wird. Zur Beschreibung der isothermen TG-Kurven wurde ein entsprechendes kinetisches Modell angenommen, welches auf einer monoton steigenden Inhibition dieser Proben basiert. Die auf der Grundlage dieses Modelles berechnete Kurve stimmt recht gut mit den experimentellen Ergebnissen überein.