TG STUDY ON THE CHLORINATION OF MoO$_2$ BY CCl$_4$

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Abstract

Molybdenum-dioxide samples were produced by reduction of MoO$_3$ in flowing H$_2$. The chlorination kinetics of the pure crystalline MoO$_2$ and samples containing a mixture of Mo-oxides were studied by thermogravimetry, using gaseous CCl$_4$ as chlorinating agent. The initial samples and the chlorinated residues were investigated by XRD and BET methods, as well.

The pure molybdenum-dioxide sample was remarkably less reactive than the partially reduced non-stoichiometric molybdenum-oxides or MoO$_3$. The characteristic sigmoid shape of the TG curves were explained by the difference in the reactivity of molybdenum-oxides and by the change of the specific surface area during chlorination.

The observed reaction order of $n=0.5$ suggests a fast, reversible dissociative adsorption of CCl$_4$ before the volatilization step. For samples of low specific surface area activation energies of 123 and 97 kJ·mol^{-1} were obtained, and the kinetic curves could be well fitted by an Avrami–Erofeev equation. For sample of much higher specific surface area a diffusion controlled reaction ($E_a=52$ kJ·mol^{-1}) was supposed, and the kinetic model of contracting spheres could be applied.

Keywords: chlorination of MoO$_2$, kinetics, TG

Introduction

In gas–solid heterogeneous reactions the rate depends on several factors characterizing the solid sample. The role of phase composition and morphological structure may be significant during the gasification of oxides of altering valence.

Chlorination behaviour of MoO$_3$ were studied in some recent publications [1–3]. However, a relatively few data are available concerning the reaction of molybdenum-oxides of lower valence state [4–5].

In our previous work [6] kinetic studies were made on the reactions of MoO$_3$ with gaseous CCl$_4$. The aim of the present paper is to establish the reactivity

sequence of the molybdenum-oxides of lower valence as well as to give a detailed kinetic investigation on the volatilization of pure crystalline MoO_2 by gaseous CCl_4.

Experimental

TG measurements were carried out in a specially constructed reactor attached to a Mettler semimicro recording balance.

Powder-like molybdenum-dioxide samples were prepared from MoO_3 (analytical grade, REANAL, $s^\circ = 3.5$ $m^2 \cdot g^{-1}$ by reduction with flowing hydrogen at 770 K. The crystalline structure of the samples were determined by XRD, and the specific surface areas were measured by the usual BET method. The chemical and physical characteristics of the samples are given in Table 1. As shown by electron microscopy samples A and B consisted of well developed thin plates.
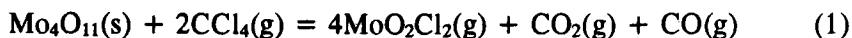
Table 1 The chemical and physical characteristics of the samples

Sample	s° / $m^2 \cdot g^{-1}$	Structure
A	0.6	pure, crystalline MoO_2
B	0.8	80–85% MoO_2 + Mo_4O_{11}, MoO_3, $Mo_{17}O_{47}$
C	15	80–85% MoO_2 + Mo_4O_{11}, MoO_3, $Mo_{17}O_{47}$

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 inert carrier gas.

Results and discussion

The kinetics of the reaction were studied by isothermal TG measurements. Figs 1/a, b and c show the conversion (relative mass loss) vs. time curves in the temperature range of 560–800 K. As can be seen, no mass gain was observed relating to formation of solid reaction products even in the beginning part of the chlorination process. During the chlorination of pure MoO_2 (sample A) the conversion vs. time curves are sigmoid shaped, while in the cases of samples B and C the reaction starts with a fast mass loss due to chlorination of the non-stoichiometric partially reduced oxides and of MoO_3:
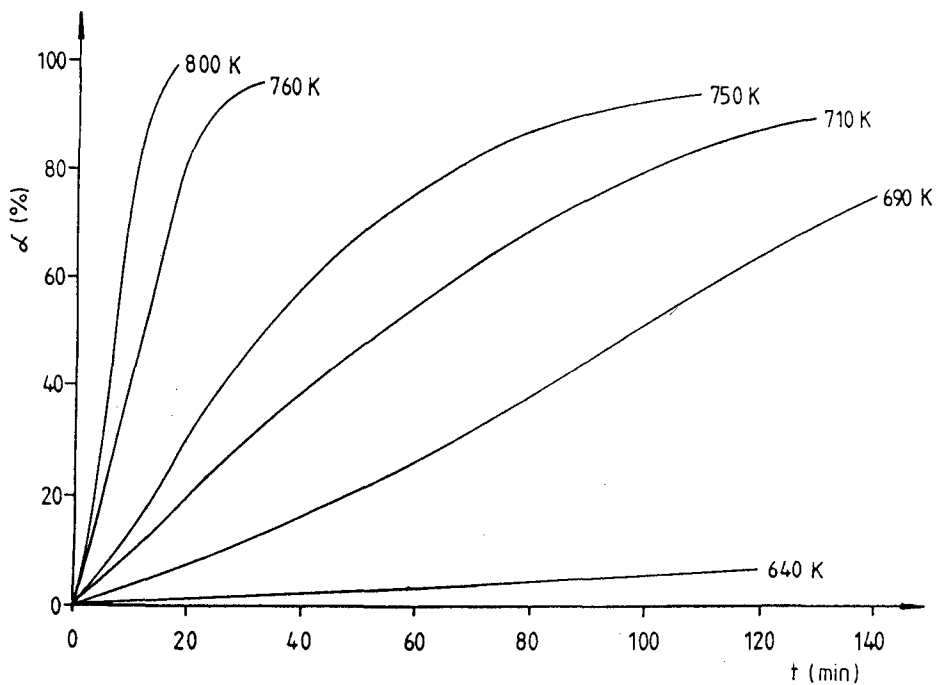
$$Mo_4O_{11}(s) + 2CCl_4(g) = 4MoO_2Cl_2(g) + CO_2(g) + CO(g) \qquad (1)$$

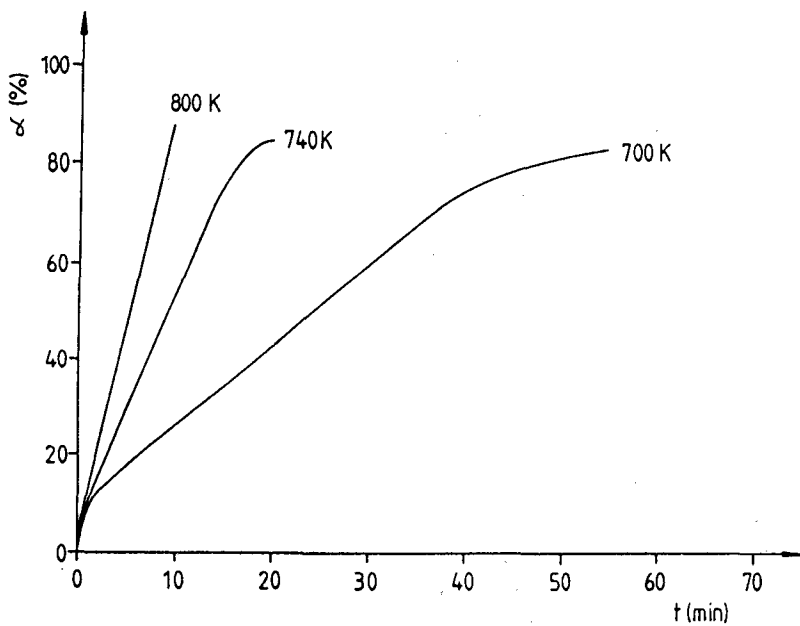$$MoO_3(s) + 1/2CCl_4(g) = MoO_2Cl_2(g) + 1/2CO_2(g) \qquad (2)$$

Fig. 1/a Conversion *vs.* time curves for sample A

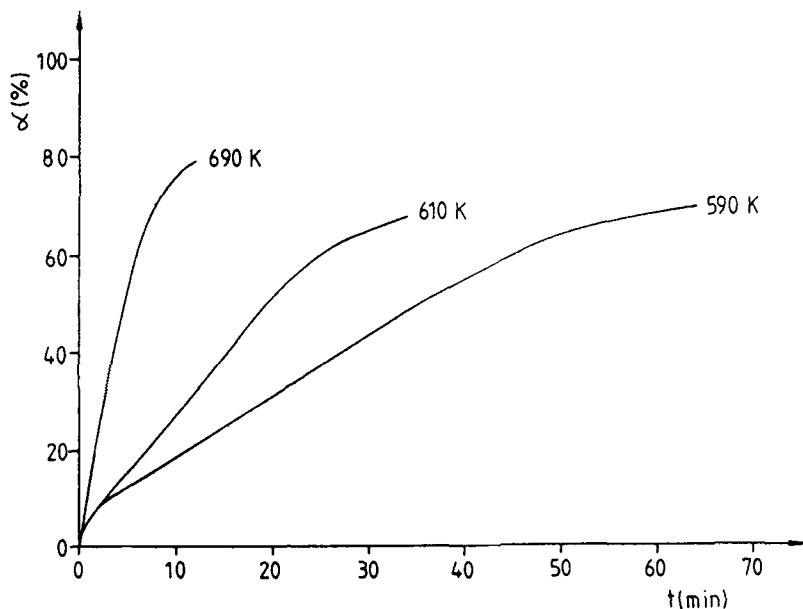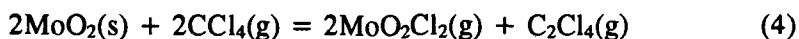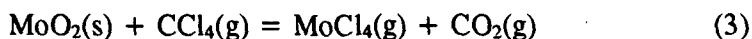Fig. 1/b Conversion *vs.* time curves for sample B

Fig. 1/c Conversion *vs.* time curves for sample C

In the second stage of the reaction the less reactive MoO_2 reacts with CCl_4 producing volatile molybdenum-chloride or oxychloride:

$$MoO_2(s) + CCl_4(g) = MoCl_4(g) + CO_2(g) \qquad (3)$$

$$2MoO_2(s) + 2CCl_4(g) = 2MoO_2Cl_2(g) + C_2Cl_4(g) \qquad (4)$$

In accordance with this expectation only crystalline MoO_2 was detected by XRD in the chlorinated residue ($\alpha = 45\%$) for both the pure MoO_2 (sample A) and samples containing originally other molybdenum-oxides, as well.

The conversion (α) *vs.* time data were fitted to several models based on Eq. 5:

$$-\frac{d\alpha}{dt} = kf(\alpha) \qquad (5)$$

which is commonly used in the gas–solid reaction kinetics. Table 2 shows the kinetic equations which proved to be the most satisfactory one for describing the isothermal TG curves. The plots of the integral forms of the corresponding rate equations are represented in Figs 2/a, b and c.

As can be seen, for samples of low specific surface area (samples A and B) the best fit was obtained with an Avrami–Erofeev type equation. As during the
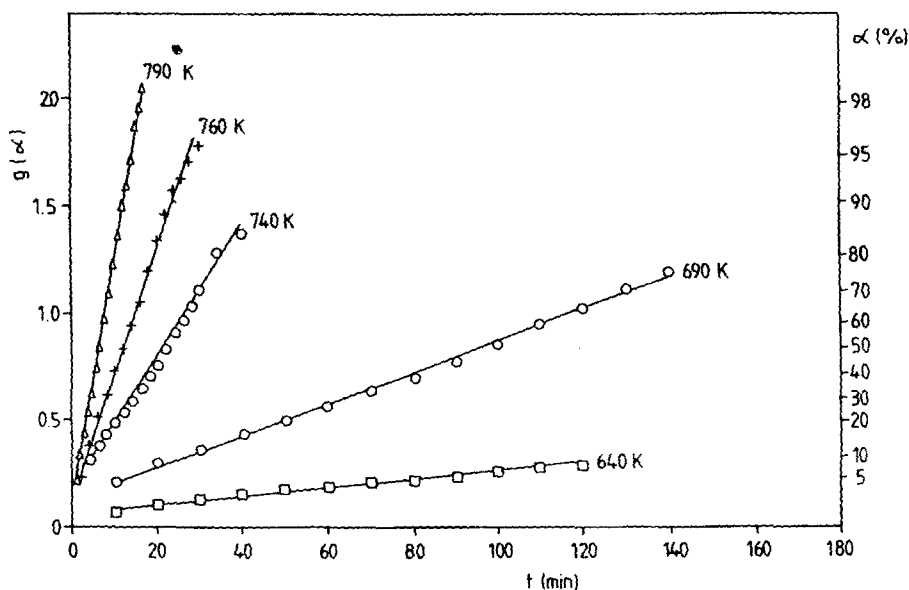
Fig. 2/a $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$ *vs. t* curves for sample A
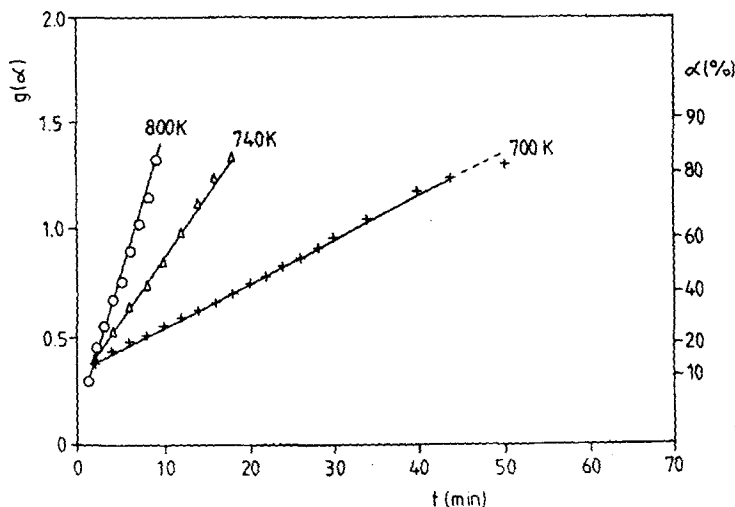

Fig. 2/b $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$ *vs. t* curves for sample B

chlorination solid reaction product is not forming, nucleation and growth can not be taken into consideration. Therefore this model is a formal description of the kinetic data. We assume that the sigmoid shape of the conversion *vs.* time curves can be explained by an increase in the specific surface area during the chlorination. This expectation was supported by the results of BET measure-

ments, as after a conversion of $\alpha = 45\%$ the residue of sample A had remarkably higher specific surface area (3.3 $m^2 \cdot g^{-1}$) than originally.
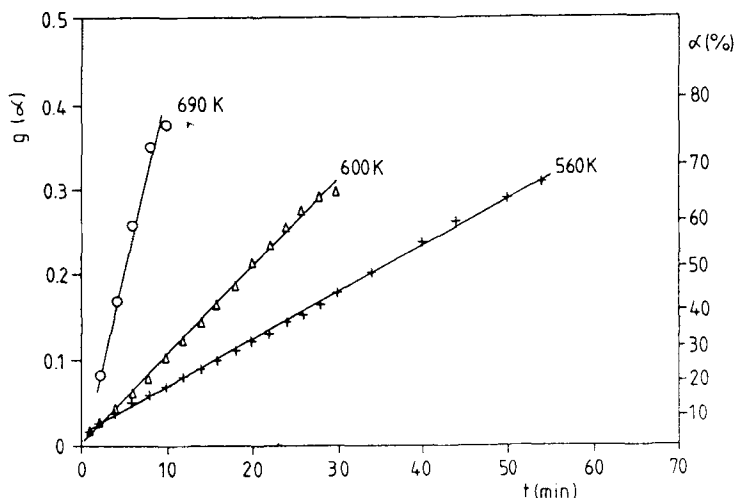

Fig. 2/c $g(\alpha) = [1 - (1 - \alpha)]^{1/3}$ vs. t curves for sample C

As it is seen in Fig. 2/c, in the case of sample C of high specific surface area, the model of contracting spheres proved to be the most satisfactory one for describing the kinetic data.

Figure 3 shows the Arrhenius representation of the rate constants. The apparent activation energies are given in Table 2. As can be seen the values are very close for samples of low specific surface area (97 and 123 kJ·mol^{-1} for sample A and B, respectively). For these samples the chemical reactions are supposed to determine the rate. The much lower activation energy obtained for sample C of significantly higher surface area can be explained by pore-diffusion control.

The partial pressure dependence of the reaction rate was studied in the range of 2–12 kPa CCl$_4$. The reaction order was calculated from the logarithmic representation of the rate constants. According to the data a formal order of $n = 0.5$ was found for sample A. As a consequence, linear k vs. $p^{1/2}$ plot was obtained

Table 2 Kinetic equations and apparent activation energies

Sample	T / K	Model	$f(\alpha)$	$E / kJ \cdot mol^{-1}$
A	640–790	Avrami–Erofeev	$(1 - \alpha)[- \ln (1 - \alpha)]^{1/2}$	123
B	700–800	Avrami–Erofeev	$(1 - \alpha)[- \ln (1 - \alpha)]^{1/2}$	97
C	560–690	Contracting spheres	$(1 - \alpha)^{-1/3}$	52

as shown in Fig. 4. The observed reaction order suggests a fast reversible dissociative adsorption of the active gas before the volatilization step.
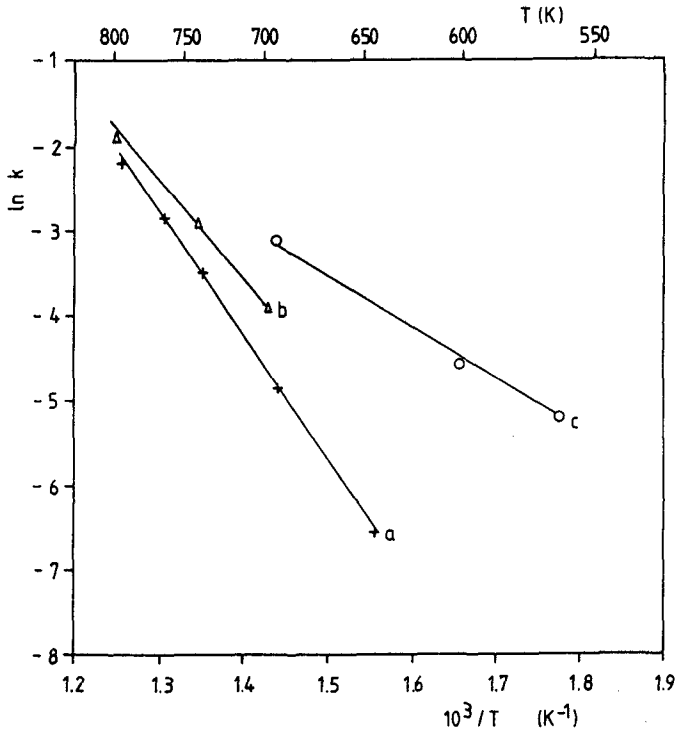

Fig. 3 The Arrhenius representation of the rate constants; a sample A; b sample B; c sample C
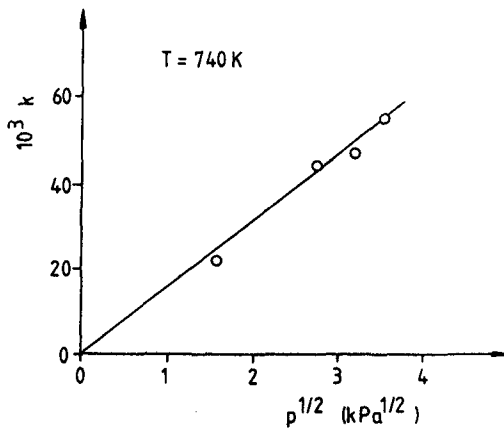

Fig. 4 Rate constants (k) vs. $p^{-1/2}$ function for chlorination of sample A by CCl_4; $T = 740$ K

Conclusions

In the chlorination by CCl_4, MoO_2 is remarkably less reactive than MoO_3 or the partially reduced, non-stoichiometric molybdenum-oxides.

Apparent activation energies of 123 and 97 $kJ \cdot mol^{-1}$ were obtained for the pure crystalline MoO_2 and for the sample containing other molybdenum-oxides, as well. The remarkably lower activation energy (52 $kJ \cdot mol^{-1}$) found for the sample of significantly higher specific surface area is attributed to the effects of the pore diffusion processes.

On the basis of the partial pressure dependence the dissociative adsorption of CCl_4 is supposed to precede the volatilization process.

The sigmoid shape of conversion *vs.* time curves can be explained by an increase in the specific surface area during the volatilization.

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References

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Zusammenfassung — Durch Reduktion von MoO_3 in dynamischer Wasserstoffatmosphäre wurden Molybdändioxidproben dargestellt. Mittels TG wurde unter Anwendung des gasförmigen Chlorierungsmittels CCl_4 die Chlorierungskinetik von reinem kristallinen MoO_2 und von Mo-oxidhaltigen Proben untersucht. Die Ausgangsproben und die chlorierten Reaktionsprodukte wurden mittels XRD und BET untersucht.

Die reine Molybdändioxidprobe war wesentlich weniger reaktionsfreudig als teilweise reduzierte nichtstöchiometrische Molybdänoxide oder MoO_3. Die charakteristische S-förmige Gestalt der TG-Kurve wurde mit Hilfe des Unterschiedes der Reaktionsfreudigkeit der Molybdänoxide und die Änderung der spezifischen Oberfläche während der Chlorierung erklärt.

Die beobachtete Reaktionsordnung $n = 0.5$ weist auf eine schnelle, reversible dissoziative Adsorption von CCl_4 vor dem Verdampfungsschritt hin. Für Proben mit geringer spezifischer Oberfläche erhielt man Aktivierungsenergien von 123 und 97 kJ/mol, die kinetischen Kurven konnten mit Hilfe der Avrami-Erofeev-Gleichung gut nachvollzogen werden. Für Proben mit wesentlich größerer spezifischer Oberfläche wird eine diffusionskontrollierte Reaktion ($E_a = 52$ kJ/mol) angenommen und das kinetische Modell kontraktierender Kugeln konnte angewendet werden.