CARBOCHLORINATION OF MOLYBDENUM TRIOXIDE: KINETIC TREATMENT

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Abstract — **The kinetics of MoO_3 chlorination in the presence of carbon is analyzed. The experimental data were obtained in a fixed-bed isothermal reactor, operated at atmospheric pressure between 543 and 603 K, and at different feed flows and Cl_2 concentrations. The following global reaction was obtained by identification of the reaction products: $2 MoO_{3(s)} + 2 Cl_{2(g)} + C_{(s)} \rightarrow 2 MoO_2Cl_{2(g)} + CO_{2(g)}$. On the basis of the analysis of experimental data, thermodynamic results and observations by other authors, three basic stages are distinguished: 1) *Formation of the chlorinating agent*; 2) *Chlorination of molybdenum trioxide*; 3) *Carbon oxidation*. This mechanism allows to explain the greater reactivity of carbochlorination reactions at low temperatures as compared to direct chlorination. A detailed scheme is proposed for the kinetic treatment, which reveals that 22 stages are involved in this complex reaction. The experimental data were processed with different kinetic models, and it was found that the "nucleation and growth" model, conveniently adapted to non catalyzed heterogeneous reactions is the one that better matches the experimental data.**

Keywords — **Carbochlorination, Molybdenum Trioxide, Kinetic Treatment.**

I. INTRODUCTION

The chlorination of metal oxides in the presence of carbon (carbochlorination) has attracted the interest of numerous researchers, since this reaction allows to recover metals of commercial interest at temperatures lower than those required by direct chlorination. The carbochlorination of metal oxides is a complex fluid-solid reaction:

$$a \, Me_mO_{n(s)} + b \, Cl_{2(g)} + c \, C_{(s)} \rightarrow p \, P_{(g)} + q \, Q_{(g)} \qquad (1)$$
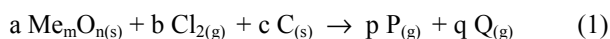
where a, b, c, p and q are stoichiometric coefficients, Me represents a metal and subscripts (s) and (g) indicate the aggregation state of the reagents and reaction products.

It has been observed that in these reactions, the presence of carbon has a two-fold effect on the chlorination rate. On the one hand, it thermodynamically favors the formation of the metal oxichlorides, as confirmed by Nagata (1987). On the other hand, numerous authors have reported that carbon exerts a catalytic effect on chlorination reactions (Bernard *et al*., 1974; Barin and Schuler, 1980; Bicerolu and Gauvin, 1980; Pasquevich and Amorebieta, 1992). The mechanisms that have been proposed for the carbochlorination of metal oxides are not clear or conclusive enough, and important discrepancies exist between the numerous investigations carried out on this issue, even between those studies using the same system. So far, neither detailed nor generalized models for this type of reactions have been described in the literature. It must be noted, however, that most authors agree on the fact that the reaction should occur through the formation of gaseous intermediates, such as phosgene (Stefanyuk and Morozov, 1965; Barin and Schuler, 1980); oxichlorides (Dunn, 1979); and atomic chlorine (Barin and Schuler, 1980; Pasquevich *and* Amorebieta, 1992). Even though none of these species have been detected during carbochlorination reactions, it can be inferred from the studies of Amorebieta and Colussi (1985) that the most likely intermediate is atomic chlorine. It should also be pointed out that the chlorine reactions on a carbon surface depend on its surface reactivity (Chen and Back, 1979; Papirer *et al*., 1995; González *et al*., 1999). In a study of amorphous Ta_2O_5 carbochlorination at low temperatures, González *et al*. (1998) established the presence of O_2 in the reaction zone. In this work, we will experimentally study the effects of reaction temperature and time, flow and feed composition on the rate of MoO_3 carbochlorination, with the purpose of contributing experimental information and proposing a methodology for the kinetic treatment of complex fluid-solid reactions.

II. EXPERIMENTAL

Experimental equipment. Figure 1 shows a schematic representation of the experimental system employed for the chlorination and carbochlorination of MoO_3 where: **DCM**, represents the drying, control and measuring device, respectively; **EO** is the electric oven; **S** is the solid reagent sample holder; **R** is the reactor; **T** is the thermocouple; **CT** is the collecting tube; **DT** is the digital thermometer; **WT** stands for the washing traps;

and **O** the outlet. The system was operated as follows: approximately 1×10^{-4} kg of the sample to be chlorinated was placed on the sample holder **S** and N_2 was passed until the working temperature was reached; at that point the N_2 flow was stopped and the chlorinating agent was circulated at a preset flow, which was interrupted when the programmed reaction time had finished; N_2 was circulated again at room temperature for 1800 s in order to remove the remaining chlorinating agent and cool the reactor.
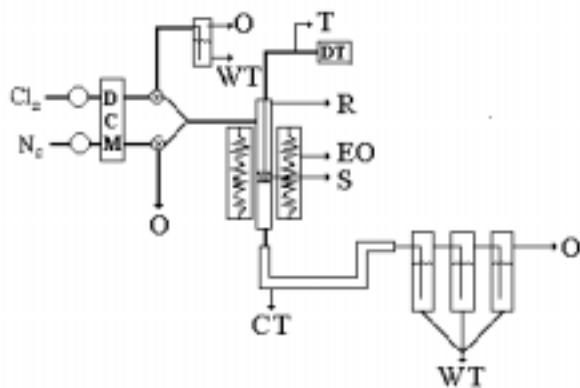
Figure 1. Flow sheet of the experimental system.

Gaseous reagents: The gaseous reagents used were: (a) Commercial Cl_2 (Indupa, $\geq$ 98%); (b) N_2 (A.G.A., $\geq$ 99.99%), used both as diluent and carrier gas.

Solid reagents: The solid reagents used were: (a) Powder MoO_3 (Analar BDH, $\geq$ 99,99%, surface area 0.4×10^3 m^2/kg). (b) Amorphous powder carbon (carbon black type, Cabot Corporation, surface area 11.1×10^3 m^2/kg).

The reagent solid samples used in the carbochlorination experiments were mixtures of MoO_3 and carbon particles (previously selected by particle size and dried in stove for 120 minutes at 110°C), obtained a 3/1 C/MoO_3 molar ratio and 60 minutes of mixing times. These preparation conditions were studied in a previous work (Ojeda *et al.*, 2002).

The characterization of starting material and residues by SEM was performed on a Philips model 515 microscopy. This device can analyze the sample fluorescent X rays, using an EDAX energy dispersive detector (EDXS)

III. EXPERIMENTAL RESULTS
The degree of transformation was defined as: **X** = $(m_o - m) / m_o$, where m_o is the initial mass of MoO_3 and m is the mass of unreacted MoO_3.

MoO_3 direct chlorination assays. MoO_3 direct chlorination was studied between 573 and 873 K, at 0.33×10^{-6} m^3/s feed flow and X measurements at 1800 and 3600 s. The results obtained showed that this reaction only starts at 803 K, and is significant at 873 K.

Carbochlorination assays. *Effect of reaction temperature and time*: the effect of temperature on the reaction rate was studied in the 523-603 K temperature range and at reaction times varying between 300 and 7200 s, with a feed flow of 0.25×10^{-6} m^3/s of pure Cl_2. The results obtained indicate that the reaction starts at a temperature close to 543 K, and that conversion increases with higher temperatures and reaction times.

Effect of the feed rate: the effect of the feed rate on the reaction rate was studied with pure Cl_2 at 573 K, within the $0.00\text{-}0.67\times10^{-6}$ m^3/s range. The results obtained show that the X values slightly decrease with increasing flows. This can be explained taking into account that the reaction goes through the formation of gaseous intermediates. This phenomenon has also been reported by other authors (Scheiman *et al.*, 1962; Smith, 1977; Ruiz *et al.*, 1994; Bidaye *et al.*,1999).
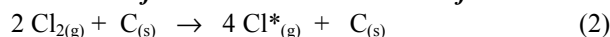
Effect of the feed composition: the effect of the feed composition was studied within the range between 0.5 and 1 of chlorine molar fraction at two reaction temperatures (573 and 583 K) and two flow levels (0.25×10^{-6} and 0.33×10^{-6} m^3/s). The conversion of MoO_3 was observed to slightly increase when the chlorine concentration in the feed is higher.
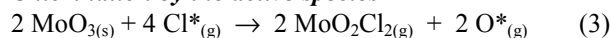
IV. KINETIC TREATMENT
The following procedure was used for the kinetic treatment of the MoO_3 carbochlorination data: 1°) formulation of a kinetic mechanism, considering the elementary reaction stages; 2°) schematic presentation and analysis of the stages involved in a complex fluid-solid reaction; 3°) selection and development of kinetic models; 4°) analysis of the experimental results obtained by the selected models; 5°) discrimination of the selected models.

Kinetic mechanism. The following was taken into account for the formulation of a kinetic mechanism: a) the results obtained by the thermodynamic equilibrium calculations performed on a set of probable chlorination and carbochlorination reactions; b) studies by other researchers suggesting that the chlorine atom is the most likely intermediate; c) chemical analyses performed at different levels of the studied factors revealed that MoO_2Cl_2 and CO_2 are the only reaction products. The following kinetic mechanism for MoO_3 carbochlorination is thus proposed:
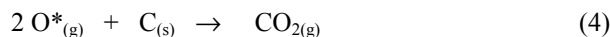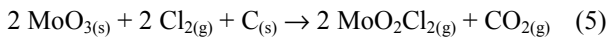
Activation of Chlorine on the carbon surface:
$$2\,Cl_{2(g)} + C_{(s)} \rightarrow 4\,Cl^*_{(g)} + C_{(s)} \qquad (2)$$

Chlorination by the active species
$$2\,MoO_{3(s)} + 4\,Cl^*_{(g)} \rightarrow 2\,MoO_2Cl_{2(g)} + 2\,O^*_{(g)} \qquad (3)$$

Carbon oxidation:
$$2\,O^*_{(g)} + C_{(s)} \rightarrow CO_{2(g)} \qquad (4)$$

Global reaction:

$$2 \, MoO_{3(s)} + 2 \, Cl_{2(g)} + C_{(s)} \rightarrow 2 \, MoO_2Cl_{2(g)} + CO_{2(g)} \quad (5)$$

Involved stages. On the basis of the proposed reaction mechanism - Eqs.(2) to (4) - the scheme shown in Fig. 2 was designed. It can be seen that 22 stages are involved in the carbochlorination of MoO_3. Some of these are serially combined while others occur in parallel. Stages (1), (7), (15), (16) and (22) correspond to the mass transport by convection of reagents and/or products; stages (2), (6), (8), (13), (14), (17) and (21) correspond to the diffusion of the reagents and/or intermediates and/or products through the film surrounding the solids; stages (3), (5), (9), (11), (12), (18) and (20) correspond to the diffusion of the reagents and/or gaseous intermediates and/or products through the pores, and stages (4), (10) and (19) summarize the stages of formation of the reaction interface, adsorption of the reagents and/or gaseous intermediates, chemical reaction on the surface and desorption of the gaseous intermediates and/or reaction products. It must also be noted that stage (4) corresponds to the activation Cl_2 on the carbon surface to form $Cl^*_{(g)}$ -Eqn. (2)-, which, in order to reach the surface of MoO_3 has to overcome the resistance offered by stages (5) to (9), and, particularly in stage (7) it is likely to be transported by convention by the gas current circulating in the reactor. The chlorination of MoO_3 by the active species, Eqn. (3), is represented by stage (10), in which the reaction products $MoO_2Cl_{2(g)}$ and $O^*_{(g)}$ are formed. $MoO_2Cl_{2(g)}$ that has to overcome the resistance offered by stages (12), (14) and (16) in order to leave the reaction zone. The intermediate $O^*_{(g)}$, which, in order to reach the carbon surface, has to overcome the resistance offered by stages (11), (13), (15), (17) and (18). Stage (19) represents the reaction of carbon oxidation, given by Eqn. (4). The scheme presented in Fig. 2 is among the simplest that can be proposed for a carbochlorination reaction. It does not explicitly include reactions of the $2 \, Cl^*_{(g)} \rightarrow Cl_{2(g)}$ type, which have a high probability of occurrence. This was due to the facts that 1°) including such reactions would make the analysis of this system more complex without contributing relevant information; and 2°) these reactions can be included when formulating each of the stages in which the intermediate $Cl^*_{(g)}$ is involved. The proposed scheme provides a global view of the complexity of the kinetic treatment of carbochlorination reactions and also allows to prevent the effect of certain factors upon the reaction rate.

Kinetic models. The development of theoretical kinetic models for the scheme presented in Fig. 2, considering different hypothesis, is a practically impossible task. However, if it is taken into account that the observed reaction rate is controlled by the rate of the slowest stage, it becomes possible to correlate the experimental data with the models developed for the kinetic treatment of simple gas-solid reactions. This criterion was adopted for the kinetic treatment of the MoO_3 carbochlorination

experimental data, bearing in mind that the reaction mechanisms may vary under the different working conditions.
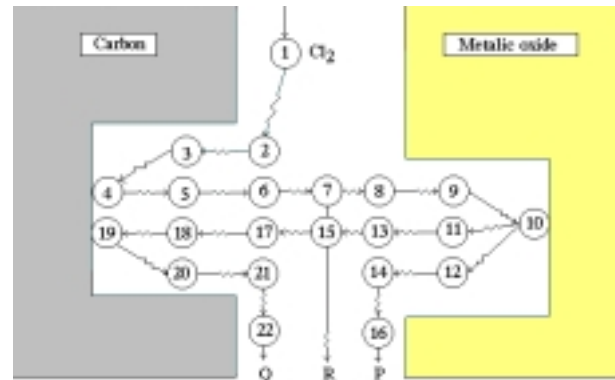
Figure 2. Steps in metallic oxide carbochlorination

Kinetic treatment results. The experimental data of MoO_3 carbochlorination were treated by 25 different models. Six models based on "nucleation and growth" theory, showed an acceptable match with the experimental data. After performing the corresponding model discrimination, the following was selected as the most probable:

$$X = b_1 \left\{ 1 - (1 + b_2 \, t) \exp (-b_2 \, t) \right\} \quad (6)$$

where $b_1 = \sigma_g \, \Omega° \, N_{s°} \, b \, m_B \, r_s / k_{N1}$ and $b_2 = k_{N1}$; being t: reaction time; σ_g: nucleus form coefficient; $\Omega°$: initial interface surface; $N_{s°}$: number of active sites per unit of initial interface; b: stoichiometric coefficient of solid reagent B; m_B: molecular weight of solid reagent B; r_s : reaction rate per surface; k_{N1}: kinetic coefficient of the rate of active site appearance for the case of order 1. Eqn. (6), according to Quiroga *et al.* (1994), corresponds to a "*nucleation and growth*" type model with sequential appearance rate of spontaneous active sites, due to the presence of a chemical species with a nucleus growth factor p=1 (monodimensional growth) and a nucleation order n=1. The correlation results are shown in Fig. 3, and the estimates of the kinetic and statistical parameters are presented in Table 1.

The activation energy values associated to coefficients b_1 and b_2 are E_1=175,890 J/mol and E_2=159,734 J/mol, respectively. The reaction rate was observed to vary exponentially with the volumetric flow in a magnitude of -0.19.

In order to corroborate the validity of this model, scanning electron microscopy (SEM) micrographs of MoO_3 particles before and after chlorination are presented and described. Figure 4 shows micrographs of MoO_3 particles mixed with unattacked carbon.

It must be noted that MoO_3 exhibits perfect cleavage according to $\{100\}$, matching the properties of molybdite (Fleischer, 1964). Figure 5 corresponds to micrographs of different samples of the reagent solid chlorinated under different conditions. It can be observed that

the chemical attack has taken place on the edges of the cleavage planes, correspond ing to the crystallographic planes containing the [b] [c] axes. This effect is more marked under more aggressive chlorination conditions, in which the corrosion of the plane edges and the distance between them has significantly increased, as compared to unchlrorinated or slightly attacked samples.

Table 1. Carbochlorination of MoO_3
Parameter estimation
Model: $X = b_1 [1 - (1 + b_2 t) \exp (-b_2 t)]$

Run Nº	T (K)	F_v x 10^6 (m³/s)	b_1	b_2 x 10^4 (s⁻¹)	E(%)
1	543	0.25	0.265	2.482	0.90
2	553	0.25	1.415	1.087	1.26
3	563	0.25	8.856	0.738	0.94
4	573	0.25	1.041	6.528	2.43
5	583	0.25	0.971	10.615	1.21
6	603	0.25	0.977	39.033	1.31
7	573	0.17	1.014	7.472	0.62
8	573	0.25	1.028	6.507	1.92
9	573	0.33	0.944	7.402	1.15
10	573	0.50	0.873	6.852	1.2
11	573	0.67	0.844	6.568	0.61

Furthermore, the attack takes place without close contact between the MoO_3 particles and carbon, which matches reports by other authors (Barin and Schuler, 1980; Pasquevich *et al.*, 1992). From these micrographs it can be concluded that the MoO_3 particles undergo an intense chemical attack during chlorination, characterized by specifically proceeding on the edges of the cleavage planes, advancing unidirectionally. This totally matches the kinetic model proposed by this carbochlorination reaction.
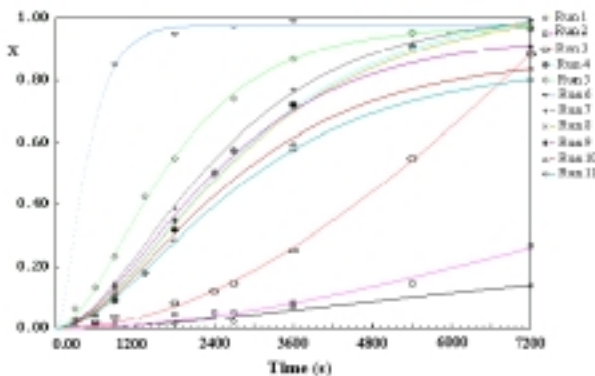
Figure 3. Experimental data correlation by Model: $X = b_1 [1 - (1 + b_2 t) \exp (-b_2 t)]$, under the operation conditions described in Table 1, for a chlorine molar fraction of 1.

V. CONCLUSIONS

Direct chlorination showed that the reaction starts at 803 K and is significant at 873 K; while carbochlorination is initiated at 543 K and conversion increases with temperature and reaction time. Increasing feed flows were found to decrease the conversion of MoO_3 and increasing Cl_2 concentrations were found to increase the reaction rate slightly.

A kinetic mechanism was proposed, given by Eqs. (2) to (4), on the basis of the thermodynamic equilibrium calculation of a set of probable chlorination and carbochlorination reactions, previous studies suggesting that the chlorine atom is the most probable intermediate, and chemical analyses which indicated that MoO_2Cl_2 and CO_2 are the only reaction products.

A scheme was designed representing the stages of transport, adsorption, reaction and desorption involved in the reaction, matching the kinetic mechanism pro posed. This scheme allowed to see that 22 stages are involved in the reaction, from which it could be inferred that: 1º) the reaction mechanisms may change under different working conditions; 2º) the observed reaction rate is controlled by the rate of the slowest stage; 3º) the experimental data can be treated by models developed for simple gas-solid reactions.

The experimental data of MoO_3 carbochlorination were treated by 25 different kinetic models. After model discrimination, the most probable one was of the "nucleation and growth" type with sequential appearance rate of spontaneous active sites.

The validity of the proposed kinetic model is justified by SEM micrographs of MoO_3 particles which show that the chemical attack takes place on preferential sites located on the edges of the crystallographic planes containing the [b] [c] axes, with a unidirectional advance of the reaction front.
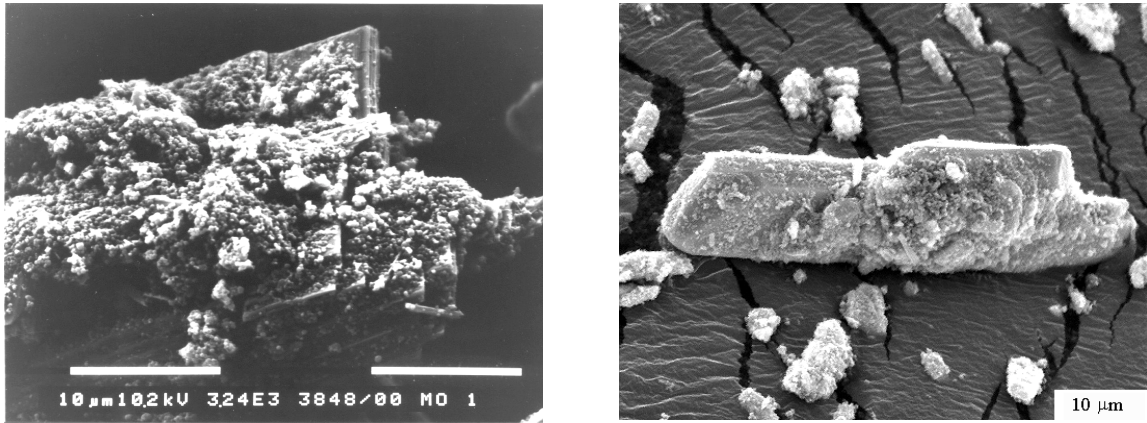
Figure 4. Micrographs of MoO₃ particles mixed with carbon, non-chlorinated.
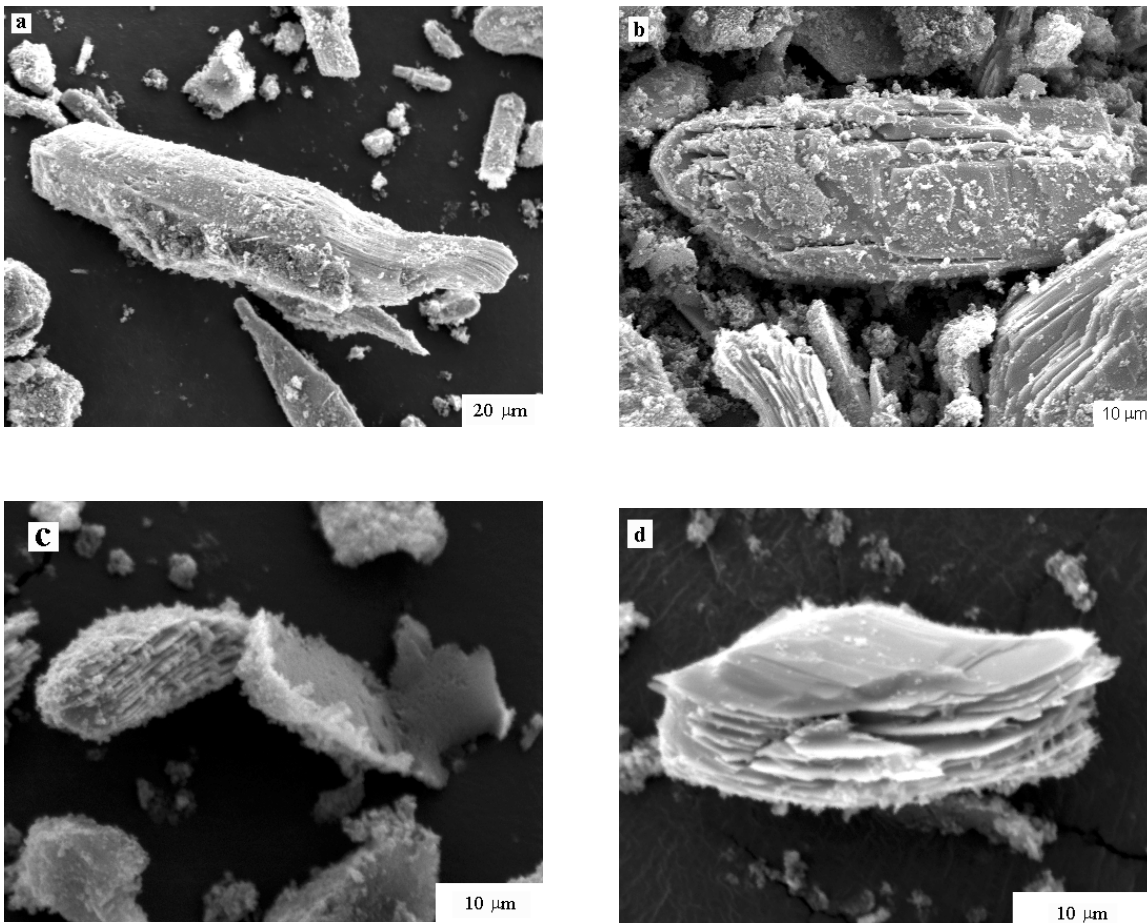

Figure 5. Micrographs of MoO₃ particles mixed with carbon, chlorinated at 573 K and with different reaction times (a) 900 s; (b) 1800 s; (c) 2700 s; (d) 3600 s.

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