

CARBOCHLORINATION OF MOLYBDENUM TRIOXIDE: KINETIC TREATMENT

M. W. OJEDA¹, J. B. RIVAROLA¹ and O. D. QUIROGA²

¹*Instituto de Investigaciones en Tecnología Química (Universidad Nacional de San Luis-CONICET)
C.C. 290, 5700 San Luis, Argentina
e-mail: mojeda@unsl.edu.ar*

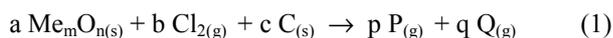
²*Instituto de Investigaciones para la Industria Química (Universidad Nacional de Salta -CONICET)
Buenos Aires 177, 4400 Salta, Argentina
email: oquiroya@unsa.edu.ar*

Abstract — The kinetics of MoO₃ 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 Cl₂ concentrations. The following global reaction was obtained by identification of the reaction products: $2 \text{MoO}_{3(s)} + 2 \text{Cl}_{2(g)} + \text{C}_{(s)} \rightarrow 2 \text{MoO}_2\text{Cl}_{2(g)} + \text{CO}_{2(g)}$. 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:



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 Ta₂O₅ carbochlorination at low temperatures, González *et al.* (1998) established the presence of O₂ 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 MoO₃ 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 MoO₃ 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;