

# A MONTE CARLO APPROACH TO DESCRIBE THE REDUCTION PROFILES OF BIDIMENSIONAL MoO<sub>x</sub> STRUCTURES GROWN ON AN ALUMINA SUSTRATE

M. C. ABELLO<sup>1\*</sup>, A. P. VELASCO<sup>2</sup>, O. A. FERRETTI<sup>3</sup> and J. L. G. FIERRO<sup>4</sup>

1 INTEQUI, Instituto de Investigaciones en Tecnología Química (UNSL- CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina, e-mail: [cabello@unsl.edu.ar](mailto:cabello@unsl.edu.ar)

2 Departamento de Física, Facultad de Ciencias Físico Matemáticas y Naturales (UNSL), Ejército de los Andes 950, 5700 San Luis, Argentina

3 CINDECA, Centro de Investigación y Desarrollo en Ciencias Aplicadas. Dr. Jorge Ronco (UNLP -CONICET) y Departamento de Ingeniería Química. (UNLP), 47 N° 257, 1900 La Plata, Argentina

4 Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, E-28049-Madrid, Spain

**Abstract**--The reducibility of molybdenum oxide supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was studied by temperature programmed reduction (TPR). Interpretation of the reduction profiles was successfully achieved by applying the Monte Carlo method and taking into account the presence of different molybdenum species on the support surface. Seven reactions were assumed to take place along the reduction process. The first hydrogen consumption peak was assigned to the reduction of Mo<sup>6+</sup> ions present as well-dispersed polymeric species into Mo<sup>+5</sup>, while the second one accounts for the reduction not of the Mo<sup>5+</sup> ions generated in the first reduction into Mo<sup>+4</sup> but also for the reduction of monomeric Mo<sup>6+</sup> species.

**Keywords**— Mo catalysts; Monte Carlo method, Temperature programmed reduction.

## I. INTRODUCTION

The interaction of molybdenum oxides on the alumina surface and their reduction processes have been extensively investigated as documented in many literature reports (Massoth, 1978; Wang and Hall, 1982; Lewis and Kydd, 1992; Wang *et al.*, 1999; Kim *et al.*, 1992; Lopez Cordero *et al.*, 1991; Del Arco *et al.*, 1993; Spevack and McIntyre, 1993; Hu *et al.*, 1995; Suarez *et al.*, 1985; Rajagopal *et al.*, 1994, 1995; Okamoto *et al.*, 1998(a, b); Abello *et al.*, 2001; Thomas *et al.*, 1982). As a general rule, alumina-supported molybdenum oxide catalysts consist of a monolayer of molybdenum oxide built up on the alumina surface. At a high molybdenum oxide content, this simple structure becomes much more complex since a tridimensional MoO<sub>3</sub> and an aluminum molybdate phase also coexist with the monolayer structure.

Although there are several methodologies to investigate catalyst reducibility, temperature programmed reduction remains prominent. TPR profiles of MoO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst containing variable amounts of molybdenum oxide have been previously reported (Lopez Cordero *et al.*, 1991; Rajagopal *et al.*, 1994; Abello *et al.*, 2001; Damyanova *et al.*, 2002). From these studies, good agreement in the number of peaks, reduction temperatures, final oxidation state of

molybdenum and H<sub>2</sub> consumption can be derived from different TPR operating conditions. In addition to these parameters, the coordination of Mo<sup>6+</sup> with O<sup>2-</sup> ions in tetrahedral and/or octahedral coordination and the development of a tridimensional MoO<sub>3</sub> phase are often used to assign the peaks of TPR profiles. However, a detailed examination of all these studies reveals some discrepancies and, in several instances, controversial interpretations. Many authors have assigned the first peak to reduction of weakly bound octahedrally coordinated Mo<sup>6+</sup> species to the alumina surface into Mo<sup>+4</sup> (Lopez Cordero *et al.*, 1991; Rajagopal *et al.*, 1994). In opposition to this interpretation, others have associated the first reduction peak to the reduction of Mo<sup>6+</sup> to Mo<sup>+5</sup> (Abello *et al.*, 2001). The peak placed at high temperature of reduction has usually been attributed to the deep reduction of all molybdenum species, including highly dispersed tetrahedral species, strongly bound to the support. Accordingly to the above, this study was undertaken with the aim of obtaining a better understanding of the experimental temperature programmed reduction profiles of alumina supported molybdenum oxide by applying a Monte Carlo model. In particular, the focus of the discussion is based on the reduction features of the different surface MoO<sub>x</sub> species.

## II. EXPERIMENTAL

### A. Sample preparation

A commercial alumina calcined at 600 °C for 3 h was used as support. This support was impregnated with an excess of an aqueous heptamolybdate (AHM, Baker reagent grade) solution. The concentration of solution was 0.005 M (pH = 5.6) and the volume of solution was chosen in order to obtain a 13 wt% MoO<sub>3</sub> in the final catalyst called 13Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The excess water was removed under reduced pressure in a rotary evaporator at 60 °C, and then the impregnate was dried at 100 °C overnight. Finally, it was calcined in air at atmospheric pressure according to the following procedure: the temperature was raised linearly for 2.5 h up to 450 °C, kept constant at 450 °C for 3 h, raised linearly up to 600 °C and then maintained for 5 h at 600 °C.