ELSEVIER

Catalysis Today 23 (1995) 251–267

CATALYSIS TODAY

Physical characterization of molybdenum oxycarbide catalyst; TEM, XRD and XPS

Pascale Delporte [a], Frédéric Meunier [a], Cuong Pham-Huu [a], Philippe Vennegues [b], Marc J. Ledoux [a,*], Jean Guille [c]

[a] *Laboratoire de Chimie des Matériaux Catalytiques, EHICS-ULP, 1 rue Blaise Pascal, 67000 Strasbourg, France*
[b] *CRHEA, Parc de Sophia Antipolis, Rue Bernard Gregory, 06570 Valbonne, France*
[c] *GEMME, IPCMS, EHICS-ULP, UMR46 CNRS, 23 rue du Loess, 67037 Strasbourg, France*

Abstract

Controlled reduction of MoO_3 can produce different phases of catalytic interest. One of these phases has been considered as being an oxycarbide of molybdenum. Various techniques mainly TEM but also XRD and others have been extensively used to understand the mechanism of formation and the structure of this oxycarbide. Its structure is reminiscent of the MoO_3 structure as shown by XRD, but reconstructed by shear planes and the introduction of carbon atoms to fill oxygen vacancies, both blocking the formation of MoO_2 the normal product of the slow reduction of MoO_3. The HRTEM pictures showed a 'chevron-like' arrangement and the electronic microdiffraction a square lattice reminiscent of the (0*k*0) planes of MoO_3.

1. Introduction

Since the first experimental results obtained by Boudart and Levy [1], several other publications [2,3] have illustrated the ability of metallic carbides to catalyze many chemical reactions. A large volume of literature [4–6] emphasizes the importance of the synthetic methods used to obtain products with high specific surface areas. Recently, both the work of Iglesia and coworkers [7–10] and that of our own group [11,12], have brought to light a new problem, linked to the activation process of the carbidic phases, the role of an oxidizing treatment (by air or oxygen) on the activity and the selectivity of these new catalysts.

The introduction of small quantities of oxygen on the 'clean' surface of tungsten carbide has, following Iglesia and coworkers [7], deeply modified the selectivity of this carbide for the isomerization reaction of saturated hydrocarbons, at the expense of the cracking reactions. An extensive study by CO and NH_3 chemisorption and by the use of many different reactive molecules [7–9] has led these authors to propose a reaction mechanism of the conventional bifunctional type, with dehydrogenation–hydrogenation steps on sites with a metallic character and steps of isomerization on sites of acidic type. However it should be stressed that in spite of the large amount of work carried out by this group, very few physical characterizations of the materials (other than chemisorption and BET) confirm the chemical results; in addition no reaction under flow allowing the evolution of the surface to be followed has been published. Finally, without it being explicitly expressed, this team seems to favor a surface of

* Corresponding author.

0920-5861/95/$09.50
SSDI 0920-5861 0920-5861(94)00166-9