EVIDENCE BY ELECTRICAL CONDUCTIVITY FOR AN EXCESS OF BISMUTH AS $\text{Bi}^+$ INTERSTITIALS AT THE SURFACE OF GAMMA PHASE $\text{Bi}_2\text{MoO}_6$. CONSEQUENCE FOR SELECTIVITY IN PROPENE CATALYTIC OXIDATION

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Bismuth molybdate in the alpha phase $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ behaves as an intrinsic semiconductor, whereas the gamma phase ($\text{Bi}_2\text{MoO}_6$) appears as an n-type semiconductor, whose conduction electrons originate from the formation of $\text{Bi}^+$ interstitials in the excess $\text{Bi}_2\text{O}_3$ layer, present at the surface. The elimination of the excess of $\text{Bi}_2\text{O}_3$ could account for the synergic effect observed in the mild catalytic oxidation of propene.

Молибдат висмута в α-фазе $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ ведет себя как внутренний полупроводник, в то время как γ-фаза, $\text{Bi}_2\text{MoO}_6$ представляет собой полупроводник n-типа, чьи электроны проводимости происходят от образования интерстициальных $\text{Bi}^+$ в избыточном $\text{Bi}_2\text{O}_3$ слое, присутствующем на поверхности. Удаление избыточка $\text{Bi}_2\text{O}_3$ обязано синергичному эффекту, наблюдаемому в мягким каталитическом окислении пропена.

INTRODUCTION

Bismuth molybdates are well-known catalysts for (amm)oxidation of olefins [1-3]. A synergic effect was observed between alpha and gamma phases in propene mild oxidation [4]. An optimum selectivity in acrolein formation of ca. 94 % was found for

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a composition ranging between 10 and 60 mol % of alpha phase, the catalysts being prepared by different methods [5]. Bismuth molybdate in the gamma phase often exhibits an excess of super-

ficial bismuth [4-6], which could have an important effect on catalytic properties.

In the present paper, it is attempted to evidence by electrical conductivity measurements the nature of bismuth excess and to propose an explanation for the difference in catalytic properties of bismuth molybdates.

EXPERIMENTAL

Catalysts. The gamma phase (Bi₂MoO₆) was prepared according to Batist's method [6] by reaction of ammonium heptamolybdate with bismuthyl nitrate. The solid was then dried for 24 h at 110°C and calcined at 480°C for 24 h. The alpha phase Bi₂Mo₃O₁₂ was also prepared by coprecipitation but with molyb-
dic acid [6]. The excess of molybdenum was removed by washing with concentrated ammonia. After drying at 110°C for 2 h, the solid was calcined at 480°C for 12 h.

The gamma phase exhibits a surface excess of bismuth, as determined by ESCA [4,5]. Surface and bulk Bi/Mo ratios were found equal to 2.6 and 2.03, respectively.

Electric conductivity. The electric conductivity was measured in a static cell specially designed for studying the solid-gas electronic interactions at the surface of powdered oxides [7]. The solids were outgassed at room temperature, then put in contact with 160 Torr of pure oxygen and sub-

sequently heated to 300°C.

RESULTS

Temperature and partial pressure of oxygen were varied in domains close to those used in catalysis: 240 < T < 300 Torr and 10 < P₂O₂ < 400 Torr (1 Torr = 133.3 Pa).

Influence of temperature. The electrical conductivity of both phases were found to vary exponentially with temperature as evidenced by the Arrhenius plots of Fig. 1. The alpha phase.