X-RAY PHOTOELECTRON STUDY OF THE INTERACTION OF H₂ AND H₂+O₂ MIXTURES ON THE Pt/MoO₃ MODEL CATALYST

A. V. Kalinkin, A. V. Pashis, and V. I. Bukhtiyarov

The effects of H₂ and H₂ + O₂ gas mixtures of varying composition on the state of the surface of the Pt/MoO₃ model catalyst prepared by vacuum deposition of platinum on oxidized molybdenum foil were investigated by X-ray photoelectron spectroscopy (XPS) at room temperature and a pressure of 5-150 Torr. For samples with a large Pt/Mo ratio, the XP spectrum of large platinum particles showed that the effect of hydrogen-containing mixtures on the catalyst was accompanied by the reduction of molybdenum oxide. This effect results from the activation of molecular hydrogen due to the dissociation on platinum particles and subsequent spill-over of hydrogen atoms on the support. The effect was not observed at low platinum contents in the model catalyst (i.e., for small Pt particles). It is assumed for the catalyst that the loss of its hydrogen-activating ability is a consequence of the formation of platinum hydride. Possible participation of platinum hydride as intermediate in hydrogen oxidation to H₂O₂ is discussed.

Keywords: Pt/MoO₃ catalyst, hydrogen, H₂ + O₂ gas mixtures, X-ray photoelectron spectroscopy.

INTRODUCTION

As is well known, platinum metals are the most effective catalysts of profound oxidation of hydrogen [1],

\[ 2H_2 + O_2 = 2H_2O. \]  \hspace{1cm} (1)

T. A. Pospelova et al. found another reaction route, which gave hydrogen peroxide and was realized when a mixture of hydrogen and oxygen was bubbled through an aqueous solution of hydrochloric acid containing palladium colloid [2],

\[ H_2 + O_2 = 2H_2O_2. \]  \hspace{1cm} (2)

In the last decade, there was growth of interest in this reaction in view of its potential application in industry as an alternative of the existing hydroquinone method for the production of hydrogen peroxide [3]. The authors investigated the effects of the catalyst composition [4-6], partial pressure of reagents [7, 8], pH of the solution [8-11], the acid and solvent effects [3, 4, 10, 11], and the contribution from the “parasitic reactions” of H₂O₂ decomposition and hydrogenation [5, 6, 12-14] on the activity, selectivity, and extent of reaction (2). Nevertheless, the nature of the active center responsible for the synthesis of hydrogen peroxide and the reaction mechanism are currently problems open to discussion. In this work we investigated, using X-ray photoelectron spectroscopy (XPS), the effects of hydrogen and H₂ + O₂ mixtures on the state of the surface of the Pt/MoO₃ model catalyst under the conditions close to optimum for the formation of H₂O₂. The choice of the sample was dictated by two factors. First, this catalyst showed high activity both in the H₂O₂ formation reaction and in the conjugated
oxidation reaction of benzene with a \( H_2 + O_2 \) mixture, for which hydrogen peroxide was regarded as an intermediate [15-17]. Second, the Pt/MoO\(_3\) system is capable of being reduced to \( H_2 \), forming molybdenum bronze and can be regarded as a test object for establishing the role of the states of hydrogen on the catalyst surface in this reaction.

**EXPERIMENTAL**

All work was carried out on a VG ESCA-3 X-ray photoelectron spectrometer (AlK\(_a\) radiation). The spectrometer was preliminarily calibrated against the positions of the gold and copper metal lines, \( Au4f_{7/2} = 84.0 \) eV and \( Cu2p_{3/2} = 932.6 \) eV. Molybdenum foil 30 \( \mu \) thick was used as a support fixed on a special holder. The holder was designed in such a way that the sample could be heated in vacuum and various gases by passing an electric current through the foil. The temperature was measured with a chromel-alumel thermocouple spot-welded to the reverse side of the sample. The molybdenum oxide film was prepared by oxidation of molybdenum foil in oxygen at \( P = 10 \) Torr and \( 300^\circ C \) for 100 min, which provided full screening of metal lines with the oxide in the XP spectrum. The catalyst was prepared by thermal deposition of platinum on an oxide film at room temperature of the support. The amount of deposited platinum was estimated from the intensity ratio of the Pt4f/Mo3d lines. The catalyst was treated in various gas mixtures directly in the chamber for spectrometer preparation at room temperature. The samples were transferred to the analyzer chamber for reproducing the XP spectra after various treatments while keeping them out of contact with the atmosphere.

**EXPERIMENTAL DATA**

To investigate the role of the support in reaction (2) we studied the effect of hydrogen and \( H_2 + O_2 \) mixtures on pure molybdenum oxide film at gas phase pressures of 5-150 Torr and exposure times from 10 min to 20 h. XPS did not reveal any changes in the spectral region of Mo3d, which indicated that the reaction medium did not interact with the MoO\(_3\) surface. An excellent result was obtained when the sample was exposed to atomic hydrogen. Atomization of \( H_2 \) was carried out on an incandescent tungsten wire at \( \sim 2000^\circ C \) and \( 10^{-6} \) Torr. Figure 1 presents the changes observed in the region of Mo3d as functions of the time of exposure to atomic hydrogen. As can be seen from the figure, at small exposure times, the reduction of oxide is accompanied by the formation of the Mo(V) state with a binding energy \( E_{\text{bnd}}(\text{Mo3d}_{5/2}) = 230.8 \) eV. At larger exposure times, additional peaks appear, which are characterized by \( E_{\text{bnd}} = 229.8 \) eV corresponding to the Mo(IV) state. After saturation, the Mo(IV) state dominates in the spectrum in accordance with the formula of molybdenum bronze, \( H_{1.6}\text{MoO}_3 \) [18].

*Fig. 1.* Changes in the Mo3d spectral region for the MoO\(_3\) film in the course of hydrogen atomization on tungsten wire at \( P_{H_2} = 10^{-6} \) Torr for (1) 1 min, (2) 3 min, (3) 10 min, (4) 30 min, (5) 100 min, and (6) 300 min; (7) starting MoO\(_3\); (a) original spectra and (b) difference spectra.