A STUDY OF SUPPORTED TUNGSTEN CATALYSTS
FOR PROPYLENE DISPROPORTIONATION OBTAINED
FROM TETRAKIS(π-METHALLYL)-TUNGSTEN

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The influence of preparation and treatment conditions on the catalytic activ-
ity in propylene disproportionation has been studied on catalysts prepared by
interaction of W(π-C4H7)4 with SiO2. The influence of the prehydration tem-
perature of silica gel and the temperature of the treatment of the catalyst
with hydrogen has been found to be appreciable. Comparison between the ac-
tivity of the catalysts and the average oxidation state of tungsten ions suggests
that the oxidation state of tungsten ions in the active catalyst component is
+4.

INTRODUCTION

The activity of supported π-allyl complexes of tungsten in olefin dispro-
portionation was first reported in 1971 /1/. We have previously reported /2/ on the
high activity of the catalysts prepared by the interaction of π-allyl Mo and W
complexes with silica gel as compared with the activity of catalysts prepared by
conventional methods. Recently, the preparation of active disproportionation cat-
alysts has been reported using W(CH3)6 /3, 4/ and W(CH2C6H5)4 /5/.

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The present communication gives more detailed data about the influence of the treatment conditions of catalysts obtained in the reaction of tetrakis(\(\pi\)-methallyl)-tungsten with SiO\(_2\) on the oxidation state of tungsten ions and the catalytic activity.

**EXPERIMENTAL**

Tetrakis(\(\pi\)-methallyl) tungsten was synthesized by a Grignard reaction from WCl\(_6\) at about 20°C.

The catalysts were prepared by treating SiO\(_2\) (with a surface area of 300 m\(^2\)/g, calcined in vacuum at 600°C) with a solution of W(C\(_4\)H\(_7\))\(_4\) in pentane. All the procedures in the preparation of these catalysts were carried out under conditions preventing the catalyst from contact with air.

The "standard" catalyst was prepared by the impregnation of SiO\(_2\) with an aqueous solution of ammonium tungstate followed by calcination in air at 500°C.

The activity was measured in the kinetic region using a batch recirculation reactor. The activities were measured on the basis of the initial rates.

The amount of oxygen adsorbed on the reduced catalysts was measured in a pulse apparatus with chromatographic analysis.

**EXPERIMENTAL RESULTS**

a) Reduction and oxidation of the catalysts. The catalysts prepared by interacting W(\(\pi\)-C\(_4\)H\(_7\))\(_4\) with SiO\(_2\) were subjected to reduction, then their oxygen uptake was measured. For the catalysts reduced at -500°C, oxygen uptake attains its maximum value (O:W = 2) at 200°C and remains unchanged as the oxidation temperature is increased further (Fig. 1). The "standard" catalyst reduced at 500°C adsorbs practically no oxygen at temperatures below 200°C. Oxygen uptake at temperatures above 300°C appears to be due to the oxidation of tungsten ions in the particles of lower tungsten oxides at high temperatures.

Upon varying the reduction temperature of the W(\(\pi\)-C\(_4\)H\(_7\))\(_4\)/SiO\(_2\) catalyst, maximum oxygen uptake is observed in subsequent oxidation after reducing the catalyst at temperatures from 400 to 600°C (Fig. 2). The amount of adsorbed oxygen is independent of the tungsten content of the catalyst (between 2 and 8 wt. %).

The W(\(\pi\)-C\(_4\)H\(_7\))\(_4\)/SiO\(_2\) catalysts reduced at 500-600°C and then oxidized at 200°C are colorless (with a tungsten content of 1-8 %). The electronic spectra of these samples have no absorption bands at 14000-30000 cm\(^{-1}\), which indicates that there are no tungsten ions in an oxidation state lower than W(VI).