

XPS Characterization of Iron Fischer-Tropsch Catalysts

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INTRODUCTION

The carburization of iron catalysts during the Fischer-Tropsch synthesis has received considerable attention, with techniques such as Mössbauer spectroscopy, x-ray diffraction, and thermomagnetic analysis being used to identify the bulk iron phases which are formed (1-4). Based on a recent Mössbauer study of unsupported iron (4), it is fairly well established that the ϵ -Fe₂C and χ -Fe₅C₂ carbides form at normal synthesis temperatures (ca. 250°C), while substantial amounts of cementite (θ -Fe₃C) are formed at temperatures above 350°C. Studies of both supported (1,5) and unsupported (4,6) iron have shown that the synthesis activity of an initially reduced catalyst is low, and increases to a maximum as carburization proceeds. Earlier work done at the Bureau of Mines (7) also suggests that controlled pre-carburization of fused iron catalysts at lower temperatures may improve long-term activity maintenance during the synthesis.

Although recent carburization studies have typically involved CO conversion levels in the range of a few percent or less, it is clear from work done at the Bureau of Mines (7,8) that higher conversion levels lead to significant oxidation of iron catalysts to Fe₃O₄. The working catalyst can thus consist of a mixture of metallic, carbide, and oxide phases, the relative amounts depending on catalyst pretreatment, synthesis conditions, and time on stream. A result of this complex behavior is that no clear picture exists regarding the nature of the catalytically active surface, or its dependence on the conditions employed in the synthesis. Much of the early work involving surface techniques (XPS/AES) in the study of CO hydrogenation over iron was carried out using foils or single crystals as model catalyst surfaces (9-11). Efforts in these studies focused on characterization of the carbon adlayer which developed on the metal surfaces during exposure to synthesis conditions.

In this paper, we address the XPS characterization of iron phases which occur on the surfaces of Fischer-Tropsch catalysts. Results obtained for single-phase metal, oxide, and carbide samples are presented. Methods for estimating the extent of carbide formation during low conversion synthesis, and the extent of catalyst oxidation at high conversions are also illustrated.

EXPERIMENTAL

The XPS measurements were performed in an AEI ES200 ESCA spectrometer, equipped with a hemispherical electrostatic energy analyzer and aluminum-anode x-ray source. Electron binding energies were referenced to the Au(4f_{7/2}) line of a gold foil at 84.0 eV. Samples were introduced into the system through a small volume (30 cc), differentially pumped reaction cell, attached directly to the vacuum chamber. The samples were mounted on a copper stage which could be heated resistively to 500°C, with temperature measurement by a chromel-alumel thermocouple junction. While in the cell, samples could be exposed to static or flowing gases at pressures up to one