Catalytic Steam Gasification of Carbon
Summary of Work Supported by DOE Grant FG03-87ER13762
During the Period 7/15/87 - 9/26/90

Michel Boudart
Department of Chemical Engineering
Stanford University

DOE/ER/13762-T1

I. Tungsten Carbides as Catalytic Materials

Unsupported carbide powders with high specific surface area, namely α -WC ($35 \text{ m}^2\text{g}^{-1}$, hexagonal), β -WC_{0.61} ($100 \text{ m}^2\text{g}^{-1}$, cubic face centered) and β -WC_{0.5} ($15 \text{ m}^2\text{g}^{-1}$, hexagonal) have been prepared. The key element in this preparation is the successful removal of surface polymeric carbon by careful gasification to methane by means of dihydrogen. This preparation has been patented, US Patent #4,851,206.

These tungsten carbide powders have been used in catalytic reactions of oxidation of H₂ and hydrogenolysis of alkanes.

• **Oxidation Reactions**

Since many important industrial processes are based on catalytic oxidation reactions, it is interesting to investigate a simple case of an oxidation reaction, namely the oxidation of H₂ with either O₂ or N₂O. The reaction of H₂ and O₂ is interesting both from an application oriented and an academic point of view. Explosive H₂/O₂ mixtures might accidentally build up in closed systems, where both gases are handled, or after an uncontrolled chemical reaction, e.g., after an accident in a nuclear power plant. It is desirable to have a material that catalyzes the reaction of H₂ and O₂ to water in a controlled manner, meaning at a certain constant reaction rate, that allows for sufficient reaction energy dissipation, rather than through a free radical chain mechanism, that results in an explosion.

It has been found that rates per unit surface area are about as high on our WC powder as on a Pt/Al₂O₃ catalyst for the H₂-O₂ reaction.

• **Reactions of Alkanes**

It is known that tungsten carbide catalysts catalyze the hydrogenolysis reaction of various alkanes such as butane, hexane, and neopentane. After exposure to oxygen they also show some isomerization activity. The role of the oxygen was suggested to create oxycarbides on the surface that provide acidic sites on which a classical isomerization reaction via carbenium ions can occur. Since acidic isomerization sites and metal or metalcarbide sites or ensembles may be different, this mechanism is referred to as "dual function" mechanism, as, e.g., it is known for platinum on acidic alumina supports in the petrochemical reforming process. The other effect proposed is a more subtle one, namely that of a "spectator" oxygen that creates tungsten sites in high oxidation states on which

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED PH

MASTER

a carbene mechanism can take place as it is known for the metathesis reaction. A better understanding of these mechanisms is of great importance due to their potential impact on the mechanism of important fuel reactions.

II. Xe NMR as a Probe of Adsorption and Reaction in Porous Catalysts

Diffusion of H_2 and O_2 into the pores of pellets made from $Pt/\gamma-Al_2O_3$ powders, chemisorption of H_2 and O_2 on the bare Pt surface, and the reaction of H_2 or O_2 with O or H respectively prechemisorbed on Pt, have been studied by ^{129}Xe NMR. Information on the distribution of chemisorbed species along the pores has been obtained by observing one or two NMR peaks and recording their chemical shift. In this manner, competition between diffusion and reaction can be followed by ^{129}Xe NMR under reaction conditions.

III. Catalysis in Model Supported Catalysts

This phase of the work has been started and is now being pursued as described in the Termination Proposal submitted to BES-DOE.

PUBLICATIONS

"Molybdenum Carbide Catalysts I. Synthesis of Unsupported Powders", J.S. Lee, S.T. Oyama, and M. Boudart, J. Catal. 106, 125 (1987).

"Molybdenum Carbide Catalysts II. Topotactic Synthesis of Unsupported Powders", J.S. Lee, L. Volpe, F.H. Ribeiro, and M. Boudart, J. Catal. 112, 44 (1988).

"Molybdenum Carbide Catalysts 3. Turnover Rates for the Hydrogenolysis of n-Butane", J. S. Lee, S. Locatelli, S. T. Oyama, and M. Boudart, J. Catal. 125, 157 (1990).

"Interstitial Compounds of Molybdenum and Tungsten as Potential Catalytic Materials", Michel Boudart and S. Ted Oyama, Proceedings, 12th Iberoamerican Symposium on Catalysis, Rio de Janeiro, Brazil (July-August 1990), Vol. 2, Instituto Brasileiro de Petróleo, Rio de Janeiro, Brazil, 1990.

"Titration by H_2 and O_2 of Bare or Covered Pt Surfaces Followed by ^{129}Xe NMR", G. P. Valença and M. Boudart, J. Catal., in press.

SUBMITTED FOR PUBLICATION

"Reactivity of Tungsten Carbides I. Catalytic and Temperature-Programmed Reactions of Methanol", J.S. Lee and M. Boudart, submitted to Catalysis Letters.

ARTICLES IN PREPARATION

"The Reaction Between H_2 and O_2 on Tungsten Carbide Catalysts", G.J. Guskey and M. Boudart.

"Preparation and Surface Composition of Tungsten Carbide Powders with High Specific Surface Area", M. Boudart, R. A. Dalla Betta, G. J. Guskey and F. H. Ribeiro.

"Reactions of Neopentane and 3.3 Dimethylpentane on Tungsten Carbides. The Effect of Surface Oxygen on Reaction Pathways", F. H. Ribeiro, Ralph A. Dalla Betta, Michel Boudart, Joseph Baumgartner, and Enrique Iglesia.

"Reactions of n-Hexane over βW_2C and WC: The Effect of Surface Oxygen", F. H. Ribeiro, Ralph A. Dalla Betta, Michel Boudart, and Enrique Iglesia.

"Isotopic Tracer and Deuterium Exchange Studies on WC", F. H. Ribeiro, Michel Boudart, Enrique Iglesia, and Joseph Baumgartner.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**