HYPERION CATALYSIS INTERNATIONAL

38 SMITH PLACE
CAMBRIDGE, MASSACHUSETTS 02138
PHONE: (617) 354-9678
FAX: (617) 354-9691

NEW NANOSCALE CATALYSTS BASED ON MOLYBDENUM AND TUNGSTEN CARBIDES AND OXYCARBIDES

(FINAL REPORT)

Award No: DE-FC02-98CH10933
Principal Investigator: David Moy (retired)
Project period: 01/1999-10/2001
Project amount: \$997,500

Author: Jun Ma
Contributors: Robert Hoch¹, Jim Leacock¹, Jun Ma¹, Jason Willey¹,
Asif Chishti¹; Fabio Ribeiro², Jun Yang²,
Geoffrey Johnson²; Dean Matson³; Charles Bolthrunis⁴,
Waheed Mukudam⁴, Chungming Chi⁴

1. Hyperion Catalysis International, Inc
2. Worcester Polytechnic Institute
3. Pacific Northwest National Laboratory
4. Washington Group International

NEW NANOSCALE CATALYSTS BASED ON MOLYBDENUM AND TUNGSTEN CARBIDES AND OXYCARBIDES

TABLE OF CONTENTS

1. Cover page	
2. Executive summary.....	2
3. Introduction.....	6
4. Cumulative project milestone information.....	12
5. Budget.....	19
6. Technical report.....	20
7. Commercialization report.....	73
8. Appendix	

Section 2 Executive Summary

Transition metal carbides such as Mo and W carbides reportedly have similar activities to noble metals in a variety of reaction, but these carbides have to be of nanoscale dimensions to possess sufficient active surface. The award research program aims to develop such a catalytic material. Such Pt group mimics have acquired the colloquial name “Poor man’s platinum”.

Our approach to nanoscale poor man’s platinum involves the use of carbon nanotubes as a template and/or support for Mo or W carbide. The commercial production of carbon nanotubes and their conversion into useful catalyst support structures represents a pre-existing Hyperion technology. In particular, much use was made of extruded, rigidized assemblages of nanotubes (extrudate), which we can produce with controlled porosity.

In this DOE funded project, we seek to demonstrate:

1. the use of carbon nanotube extrudate to support and stabilize catalytic metal carbide nanoparticles for use in fixed bed or trickle bed applications,
2. use of novel methods to synthesize catalytic metal carbide nanorod aggregates from these extrudates with retention of extrudate form,
3. application of these carbides to commercially interesting systems; three reactions of industrial significance were proposed: ethyl benzene dehydrogenation, nC_4^+ isomerization and diesel HDS.

First, subsequent to the submission of our proposal, but prior to the beginning of the project, we discovered an innovative technique of Mo carbide synthesis. Although similar to what we initially proposed, the new method is more favorable regarding the ease of quality control and mass production. The preparation followed a stepwise solid-state reaction path that both allowed the dispersion of Mo precursors onto the nanotube support and reduced the oxide component into carbide with nanometer dimensions. This solid phase synthesis was employed throughout the project.

Major accomplishments under the program include:

1. We succeeded in synthesizing a series of nanoscale Mo carbide catalysts using the new method after the DOE program started. The carbide could be made either as nanoparticles supported uniformly on the surface of carbon nanotubes, or as freestanding nanorods. In both cases, the structure of porous assemblages of carbon nanotubes was retained. Furthermore, parallel experiments were carried out with other carbonaceous materials such as activated carbon and graphite as carbon source for comparison purposes. It was found that carbon nanotubes exhibit superior capabilities in controlling and stabilizing the small carbide particles by their templating effect.
2. Detailed characterization studies have revealed the mechanism of carbide formation, elucidated bulk and surface properties, and given us control of particle size. The Mo precursor was found to undergo a two-step reaction in order to form a carbide phase. During the two steps, a spontaneous dispersion took place when the MoO_3 precursor was reduced into MoO_2 by carbon, and the intermediate MoO_2 species further transformed into Mo carbide upon calcining at higher temperatures. The as-made Mo carbide sample exhibited strong oxygen chemisorption upon exposure to air without treatment after synthesis. This property could cause excessive oxidation that would eventually drive the carbide phase back to Mo oxides. In order to protect the Mo carbide catalyst, a post-synthesis passivation was applied to all samples where a diluted oxygen stream (2% O_2/Ar) was passed through the sample and created a thin oxide layer. This surface layer was later detected by XPS and can be easily removed by a hydrogen activation treatment.
3. We have applied the Mo carbide catalysts in all three proposed reactions, namely butane isomerization, ethyl benzene dehydrogenation and hydrodesulfurization. During reaction evaluations, particularly in C_4 isomerization where a direct comparison to Pt could be made, it was found that our carbide catalysts did simulate the properties of Pt metals. However,

without proper treatment or modification, these catalysts exhibited much lower activity than noble metals. In addition, our Mo carbide catalysts also showed some novel properties that have not been seen from Pt metals:

- The hydrogenation activity is milder, in another word; hydrogenation over the nanoscale Mo carbide catalysts can be more selective. This property could be applied to many specific systems in both chemical, refinery and pharmaceutical industries where selective hydrogenation is desired over complete hydrogenation.
 - Our Mo carbide catalysts exhibited very strong sulfur resistance. During HDS reaction, even when the reaction proceeded into the steady state, part of the surface still maintained the carbide feature, and S/Mo atomic ratios were always lower than the stoichiometric value, 2.0, as in Mo_2S . Although no comparison has been made between Pt metals and Mo carbides regarding sulfur resistance in the current research, it is believed that our Mo carbide catalysts could find more useful applications to replace noble metals that are sensitive to sulfur poisoning.
4. Selected Mo carbide catalysts were sent to Washington Group International for evaluation in HDS of authentic diesel fuel. The engineering scale liquid phase reaction of hydrodesulfurization of diesel showed modest activity consistent with results from lab scale vapor phase HDS of thiophene. Although current commercial catalysts outperform these samples, the Mo carbides showed little hydrogenation activity, a property desired in hydrotreating gasoline, where the unsaturated $\text{C}=\text{C}$ bonds should not be attacked.

During the program period, we have also encountered some problems that hindered progress:

1. We were unable to make nanoscale W carbide of the same caliber as Mo carbide using the solid-state synthesis method. This was considered to be due to the high melting point and low vapor pressure of W oxide precursors. More volatile tungsten precursor such as $W(CO)_6$ might be promising. Generally, the W carbide we made had lower activities than Mo carbide; this was at least partially due to the dimensions of W carbide particles being much bigger. It is hard to conclude at this point whether W carbide exhibits better or worse catalytic performance than Mo carbide. Further research is needed in order to prepare true nanoscale W carbide and apply them in various reactions.
2. Mo and W carbides were found to be very susceptible to oxidation by steam, thus ruling out their use in steam ballasted reactions such as ethyl benzene dehydrogenation.

In conclusion, we have succeeded in making nanoscale Mo carbide catalyst that resembles Pt metals. Although the catalysts didn't exhibit commercial activities in the proposed test reactions, many applications remain as attractive future directions for these catalysts due to their novel characteristics.

Section 3 Introduction

Transition metal carbides have attracted a great deal of interest since Boudart and Levy raised the “poor man’s platinum” hypothesis based on their noble metal-like properties [1]. Normally, the early transition metals are more reactive towards decomposition of unsaturated hydrocarbons than their counterparts at the right side of the periodic table [2,3]. These activities often lead to cleavage of carbon-carbon bonds that are not desired in many industrial applications. The noble metals, on the other hand, behave in a somewhat less active manner as compared to early transition metals. These metals can hydrogenate unsaturated hydrocarbons with carbon-carbon bond remaining intact. After conversion into carbide, some early transition metals exhibit striking analogies between carbide activities and those of Group VIII metals like Pt and Ru in such reactions as dehydrogenation, isomerization and hydrogenolysis as summarized in several early studies [4-6]. The presence of interstitial carbon favorably changes the catalytic properties of these metals by alloying them to a non-metal element, leading to binary alloys [7].

To date, attempts to develop commercial applications with bulk metal carbides have been unsuccessful, however, the catalytic behavior of nanometer-sized carbide particles are reported to be sufficiently different from the bulk materials that new research in this area is warranted [8].

The synthesis of metal carbides has been traditionally carried out by reacting metal or metal oxide with carbon or carbon containing gases [9,10]. For direct carburization of MoO_3 with carbon or methane, the solid-vapor reaction is topotactic and generally, results in large particles that typically possess very poor catalytic activities. The present work was focused on preparation of nanoscale transition metal carbide, namely Mo and W carbides, using the proprietary **FIBRIL**TM nanotube as catalyst support or template.

FIBRIL nanotubes, a special material composed of parallel layers of trigonal carbon but in the form of a series of concentric tubes disposed about the longitudinal axis of the fibrils, were invented by Hyperion Catalysis International in 1983 [11]. Also known as

graphite fibrils or carbon fibrils, these highly graphitic carbon nanotubes have the morphology similar to those made by Iijima using arc-discharge method in 1991 [12]. But unlike buckytubes, Hyperion nanotubes are produced as aggregates uncontaminated with amorphous carbon or other graphitic non-tube structures. In further contrast to arc-grown tubes, the graphite fibrils are grown by a fully scaleable petrochemical type process. The surface area of these nanotubes is $\sim 250\text{-}300\text{ m}^2/\text{g}$ measured using BET method. This area is consistent with calculated geometric surface area and the density of nanotubes (ca. $1.9\text{-}2.0\text{ g/cm}^3$), taking into account the hollow core ($\sim 3\text{ nm}$), confirming that the measured surface area is wholly exterior geometric surface. In addition, the micropore (pore size $< 2\text{ nm}$) volume and area of these nanotubes are less than 0.01 cc/g and $1\text{ m}^2/\text{g}$ respectively. As compared to the total pore volume ($1\text{-}1.5\text{ cc/g}$) and surface area, the contribution by micropore is negligible. Carbon nanotubes can be oxidized to yield high concentration of surface oxygenated groups such as hydroxyl, carbonyl, carboxyl, anhydride, etc [13,14]. The functionalized nanotubes are more readily individualized by shear than “as-made” bundles and are highly dispersible in polar solvents. This functionality provides control of surface hydrophilicity or hydrophobicity and access to a wide range of anchoring sites for deposition or nucleation of catalyst precursors or for catalyst impregnation using standard ion exchange techniques. In addition, fibrils can be formed into extrudates either by cross-linking surface functional groups or by addition of polymeric binder. The fibril extrudates thus form the basis for a new class of catalyst support material comprising many unique properties as described above.

Prior to this program, conversion of carbon nanotubes to the corresponding Si carbide using a gaseous Si precursor had already been demonstrated [15,16]. We initially proposed to follow the analogous technique to make Mo and W carbides. However in work done after the proposal was written, but before the DOE project began, it was discovered that, due to the facile condensation of Mo oxides, a heavy coating of oxides generated on the surface of fibrils at a much faster rate than the desired reaction. This stops any subsequent reaction and disrupts stoichiometries. In order to gain more control of carburization, we developed a new technique in which Mo oxide precursor was

predispersed into a fibril network and followed with a stepwise sequential calcination. With this approach, we were able to prepare Mo carbides with nanometer scale in two different morphologies, nanoparticle and nanorod. When the funded project started, we used exclusively this solid phase synthesis instead of the gas phase approach described in our proposal. During the project period, we were however, unable to make W carbide with similar quality to Mo carbide. This was possibly due to the difficulty in dispersing W precursor over fibril surface. Thus the ease of making Mo carbide and ready scale-up to make large quantities led us to focus on developing potential applications with nanoscale Mo carbide catalysts.

Three reactions were selected as potential applications of Hyperion nanoscale Mo and W carbide catalysts. These applications are based on the available literature reports where early transition metal (Mo, W) carbides could resemble the catalytic properties of some noble metal catalysts [1, 4-7].

Butane isomerization is an important industrial reaction to make isobutane, a feedstock to produce reformulated gasoline. As the amounts produced from catalytic fluid cracking are not sufficient to meet requirements, processes have been developed to hydroisomerize normal butane to form isobutene. The reaction is usually carried out in gas phase under elevated pressure over a bi-functional catalyst [17-19]. The role of metals such as Pt, Ni, etc. is assumed to be dominant in activation of hydrogen which leads to hydrogenation or dehydrogenation steps. Mo and W carbides have been reportedly to have similar activities to noble metals such as Pt and Ru [20]. Thus, they might exhibit very low catalytic activity in the hydrocarbon skeleton isomerization, while hydrogenolysis or cracking reactions were favored. Ribeiro and co-workers reported that clean tungsten carbide surfaces gave uncontrolled hydrogenolysis of n-alkanes [21]. After a surface modification with oxygen at high temperatures, good skeletal isomerization activity was observed. Isomerization proceeded through dehydrogenation, similar to the pathway over Pt, but Pt/SiO₂ resulted in high dehydrocyclization. WC can also catalyze isomerization of neopentane, a reaction only observed on Pt metals before. Ledoux and co-workers [22] have studied similar reactions over Mo₂C activated in air at 350°C. Comparison to a Pt/zeolite catalyst showed a higher selectivity for isomerization

than obtainable with the Pt catalyst. In addition, the carbide catalyst showed resistance to sulfur and nitrogen catalyst poisoning. The improved activity was attributed to the formation of a thin layer of Mo oxycarbide on the carbide surface. The substitution of oxygen atoms into the carbide structure and the metal vacancies stabilized the adsorbed intermediate species. Thompson and his co-workers have also reported that the electronic environment of the transition metal carbide has the dominant effect in activation of hydrocarbons [23]. During the current program, we have performed the oxygen treatment as proposed in the original program. As-made Mo and W carbide was treated with air, O₂ and N₂O under different conditions, where the target product, oxycarbide, would form as reported by Ledoux. However, our catalyst behaved somewhat differently from Ledoux's catalysts. Instead of partial oxidation, our catalyst can easily undergo complete oxidation to form MoO₃. This is also the same situation happened to Lee and co-workers when they tried to prepare these so-called oxycarbides [24]. It is generally accepted that the surface properties of Mo and W carbides differ significantly when made with different methods. Therefore it is not surprising that our catalyst behaved quite differently from those made by Ledoux, which were prepared at very high temperatures, 1300~1500°C, and possessed low surface areas. The Hyperion-type Mo carbide exhibits very high dispersion and surface area. Therefore, these small carbide particles (3~5 nm) will be extremely sensitive towards oxygen treatment. The highly exothermic reaction between Mo carbide and oxygen makes the degree of oxidation very difficult to control. Alternatives can be visualized, but they are outside the scope of the current program.

Dehydrogenation of ethylbenzene to styrene monomer is another application selected in the current program. Styrene is one of the most important substances as raw materials for polymers. The reaction converting ethylbenzene to styrene is commercially catalyzed by an iron-based catalyst and is slightly endothermic. Heat is supplied from steam which is fed into the reactor with ethylbenzene. Furthermore, steam can also dilute the ethylbenzene to increase equilibrium conversion and suppress coke deposition on catalyst surface via thermal or catalytic cracking. Mo and W carbide exhibited modest conversion and selectivity when using steam as diluent. However, the oxidation of Mo

carbide and fibrils support caused irreversible deactivation. Even the catalysts having smaller particle sizes appeared to have stronger oxidation resistance, the deactivation still persisted. It was reported that CO₂ could play the same role as steam [25,26]. Moreover, CO₂ could remove H₂, one of the reaction products, from the reaction system by forming CO and H₂O. This could increase the equilibrium yield of styrene or attain the same yield at reduced reaction temperature. Comparison of the present commercial process using steam versus a new process using CO₂ indicated that the energies required for steam and CO₂ process were estimated to be 1.5×10^9 cal/t-styrene and 6.3×10^8 cal/t-styrene, respectively. Thus, the dehydrogenation of EB in the presence of CO₂ is also assumed to be an energy-saving process. According to these judgments, we carried out the reaction with CO₂. The Mo carbide structure did retain during the reaction, however, the catalytic performance only showed marginal improvement.

Hydrodesulfurization is the process of treating the petroleum distillates with hydrogen to remove sulfur from hydrocarbon molecules as hydrogen sulfide. The process is currently carried out over alumina or silica supported Co-Mo or Ni-Mo catalysts at elevated pressure and temperature. The sulfur level is typically reduced to 2000~3000 ppm in a conventional HDS process. Current US and some European countries require the sulfur level below 200 ppm and more severe regulation is expected to lower sulfur level to 50 ppm by 2005 and 10 ppm by 2008. The increasing importance of HDS in petroleum processing in order to produce clean-burning fuels has led to a surge of research on the chemistry and engineering of HDS. As documented in several reviews, early studies have centered on the study of model compound such as thiophene and evaluation of catalyst performance in such system [27-30].

Since the pioneering work by Stevens and Edmonds [31], a great deal of research has been devoted to developing carbon-supported catalysts for hydrotreating petroleum including HDS, HDN, and HDO processes. Although much work has demonstrated that carbon supported catalyst may have potential advantages over the current HDS catalysts, the alumina supported Co-Mo and Ni-Mo still remain as the state-of-art catalysts for hydrotreating process. The introduction of novel carbon materials as support medium could eventually alter this scenario, as improved chemical and physical features become

available to deal with the steric hindrance of alkyl substituents to which the sulfur atom is bound.

In the current program, most effort was spent on HDS investigation as the carbide catalysts exhibited a lot of promising properties. According to the research work done by Bussell and co-workers [32,33], alumina supported Mo carbide exhibited better activities than supported Mo nitride and Mo sulfide using thiophene as the test molecule. XRD analyses of fresh and spent catalysts showed that the surface of the Mo catalysts became sulfided under reaction condition, but the bulk structure of carbide and nitride particles were retained. These results indicated the potential that unsupported Mo carbide and nitride catalysts have for replacing the current catalysts supported on alumina. During our investigation, Mo carbide catalysts were seen to have similar behavior as described by Bussell but with much better activities. The initial activity in thiophene desulfurization was close to equilibrium conversion, however, a fast deactivation was observed possibly due to coking problem. At the steady state, our best catalyst had a 45% conversion; the highest among the available data reported in the literature. Additional modification to eliminate the deactivation during early reaction stage is warranted. Although outside the current scope, this modification remains as an attractive future direction to develop a new generation of HDS catalyst with open porosities and high surface area residing only in meso- and macropores.

Section 4 Cumulative Project Milestone Information

Project Kickoff

Scheduled: 03/98

Completed: 01/99

Our proposal and the Project schedule contained therein arbitrarily assumed a 03/98 project start date. Eventually, DOE forwarded a contract with a 09/30/98 date, but negotiating final details among Hyperion, its subcontractors and DOE took until mid-January. The kickoff meeting was held on January 13, 1999.

It is important when considering timing of milestones to remember whether one is looking at the proposed schedule (03/98 start) or the 10/98 start used in all quarterly reports to be consistent with DOE accounting paperwork. **The schedule dates in the section that follows those in the original proposal.**

Task 1: Synthesis & Characterization

Scheduled: 03/98-08/99

Completed: 08/00

Before the project started, a few experiments were attempted to synthesize Mo carbide via gas-solid interaction at elevated temperatures. It was shown from these experiments that facile condensation of Mo oxides or suboxides would take place during the gas-solid reaction and interrupted stoichiometry. No carbide formed via this method. In order to solve the problem, we developed a novel method, namely solid-state reaction to make Mo carbide and the method turned out to be quite successful. The advantage could be two-folds: easy synthetic procedure and ready control of product stoichiometry and catalyst loading. After the project formally started in January 1999, we used exclusively this method to make nanoscale Mo carbide catalysts and followed by detailed characterization work. By August 2000, we generally accomplished the synthesis and characterization task, and we have gained comprehensive understanding about the physical and chemical properties of Mo and W carbide nanoparticle and nanorod catalysts. In addition, in order to coordinate isomerization reaction screening, some Mo

carbide catalysts were subject to oxygen treatment in-situ or ex-situ, however, this treatment was insufficient to drive the catalytic activity of butane isomerization up. Although the detection of the so-called oxycarbide presents a significant challenge to our current analytical methods, we believed that this species existed in the interstitial spaces of the surface carbide structures.

Task 2: Characterization via XRD & chemisorption

Scheduled: 04/98-07/99

Completed: 09/00

This task provides information on the physical state of the candidate catalysts which will be used to infer catalytic effectiveness. These work were done by both Hyperion and Worcester Polytechnic Institute. WPI has conducted a series of experiments looking into chemisorption properties of Mo and W carbides. However, initial attempt appeared to be unsuccessful possibly due to carbon overcoats on the surface of carbide. After a hydrogen treatment, restarted chemisorption capability was found especially with oxygen. The crystalline phases were determined using XRD by Hyperion. This technique was also applied to provide particle size information besides transmission electron microscopy.

Task 3: Select catalysts for reaction screening

Scheduled: 05/98-08/99

Completed: 09/00

We selected a series of Mo and W carbide catalysts for reaction screening. These catalysts included fibril-supported nanoparticles (low loading), nanorods (high loading or stoichiometric) and oxygen treated oxycarbides.

Task 4: Characterization via EM, etc.

Scheduled: 05/98-08/99

Completed: 09/00

Characterization using advanced instruments such as transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scan electron microscopy (SEM), and X-ray diffraction (XRD) were carried out by Hyperion and Battelle Pacific Northwest National Lab. Some work was overlapped but very consistent with each other. Work done by PNNL also provided some detailed information on chemical composition of individual particles seen under the microscope using AES and revealed the possible cause of poor dispersion of tungsten carbide.

Task 5: Screen over test reactions

Scheduled: 05/98-09/99

Completed: 10/00

Both Hyperion and WPI participated in this work in their individual micro-reactor systems. The butane isomerization work was mostly carried out in Hyperion. Effects studied included: temperature (300-500°C), loading, various oxygen treatment conditions, H₂ to butane ratio (1-16), pressure (1-7 psig) and WHSV (1-10). The best performance obtained with Mo and W carbide after oxygen treatment gave approximate 4% isobutene, which is similar to that from untreated Pt/Al₂O₃ catalyst. Further treatment to improve the catalytic activity is available but outside the program scope. The attempt with this reaction ceased on 06/30/00.

The ethyl benzene dehydrogenation work was performed by WPI. Ethylbenzene was introduced to a reactor by a syringe pump and blended with either steam or CO₂. The reaction condition was chosen similar to that in actual industrial process. Generally, catalysts with lower carbide loading and smaller particle sizes tended to have better catalytic performance, lifetime and stability than those with higher loadings. The conversion varied from 20% to 40% with selectivity to styrene of 85~95%. The catalyst deactivation was attributed to possible carbon deposition and oxidation of carbides phases. Using CO₂ to replace steam as diluent can greatly enhance the stability of carbide phase but still couldn't prevent the deactivation from carbon deposition. Due to lack of promising results for industrial adoption, this work ceased on 05/30/00.

After wrapping up the ethyl benzene work, WPI started investigating HDS performance using Mo and W carbide as catalysts. The reaction undertaken was vapor phase HDS of thiophene. Reaction temperature was selected at 400°C. Best performance was found with Mo carbide loading of 24~40%. A >40% conversion was obtained which was among the highest value as reported in the literature. The catalyst exhibited a sharp deactivation during the first 30 minutes of reaction, possibly due to the carbon deposition. Methods of solving this problem is available but outside the current research scope. However, even with this drawback, the steady-state activity still seemed to be quite promising.

Task 6: Identify target performance

Scheduled: 03/98-04/98

Completed: 10/98

The best current commercial catalyst performance for the three industrial reactions was determined. Target for the new commercial catalyst for each reaction as well as corresponding condition was set for evaluation.

Task 7 Adjust catalyst synthesis and selectivity

Scheduled: 08/98-11/99

Completed: 12/00

Due to unsatisfied catalytic performance by Mo and W carbide in butane isomerization and ethyl benzene dehydrogenation, the adjustment of catalyst synthesis was focused on improving the HDS activity. Parameter screened included catalyst precursor, synthetic conditions, as well as catalyst pretreatment. Optimum formulation and pretreatment condition have been obtained.

Task 8 Select systems for process screen

Scheduled: 11/99

Completed: 12/00

Based on the steady state HDS activity, we selected a few catalysts for test in bench scale reactor in Washington Group.

Task 9 Kilogram level synthesis

Scheduled: 11/99-01/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001. Although this task wasn't fulfilled, the scale-up technique for producing kilogram level catalyst is available with our current manufacturing capability.

Task 10 Process screening

Scheduled: 11/99-03/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001. The nanoscale Mo carbide catalysts exhibited some modest activity in diesel HDS but are not judged commercially. However, WGI found some interesting phenomenon with our nanoscale Mo carbide catalysts. These catalysts exhibited very low hydrogenation properties which is highly desired in naphtha (gasoline), where unsaturated C=C bond is preferred. Another benefit is the reduced consumption of hydrogen in the process.

Task 11 Select system for lifetime and pilot plant test

Scheduled: 03/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001.

Task 12 Life and pilot testing

Scheduled: 03/00-08/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001.

Task 13 Process Design and economic evaluation

Scheduled: 07/00-11/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001. Because no products or processes are currently available based upon the work of this project, there has been no commercialization activity. However, Hyperion believes that the market opportunity for the reactions originally targeted has not significantly changed. We believe that the chance of a molybdenum carbide family catalyst finding use in ethyl benzene dehydrogenation is minimal. Both butane isomerization and diesel HDS remain viable targets for the technology, but will not be achieved with the catalysts in their present form. The kinds of modification required to address these targets are beyond the scope of work originally proposed to DOE. These kinds of catalyst modifications are the subject of our continuing internally funded work.

Task 14 Project status review

Scheduled: 04/98-11/00

Completed: 07/01

Project reports were submitted at end of each quarter. Annual review was also held on 11/18/99 and 11/02/00.

Task 15 Final tech and econ assess

Scheduled: 11/00-12/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001.

Project complete

Scheduled: 12/00

Completed: N/A

Not completed due to receiving the stop work order on 10/02/2001.

**New Nanoscale Catalysts
based on Mo and W
Carbides and Oxycarbides**

**Hyperion Catalysis International
Nanoscale Catalysts
Plan and Progress as of Thu 7/25/02**

Critical

Baseline Milestone

Rolled Up Split

Critical Split

Milestone

Rolled Up Task Progress

Critical Progress

Summary Progress

Rolled Up Baseline

Task

Summary

Rolled Up Baseline Milestone

Split

Rolled Up Critical

Rolled Up Milestone

Task Progress

Rolled Up Critical Split

External Tasks

Baseline

Rolled Up Critical Progress

Project Summary

Baseline Split

Rolled Up Task

Section 5 Budget Narrative

Work on this project was suspended based on a stop work order received on October 2, 2001. At that time the project was within its overall budget, but, however subject to a revised billing, in excess of the funds obligated to that time. Inasmuch as the technical objectives all also seemed at that time to be in need of recalibration, the stop work order was accepted without dispute. The following table shows the total costs through October 2 as finally accumulated and compares them with the original budget.

Table 5.1 Budget and actual cost breakdown

Object Class Categories	Budget					Actual Costs
	Applicant's Share	3rd Party Share	Total Cost Share	DOE Share	Total Cost	
a. Personnel	20.0	31.5	51.5	120.0	171.5	157.3
b. Fringe Benefits	6.4	10.0	16.4	38.4	54.8	50.3
c. Travel	1.2	1.9	3.1	7.1	10.2	2.8
d. Equipment						
e. Supplies	4.2	6.6	10.8	25.2	36.0	14.2
f. Contractual	103.7	163.5	267.2	623.5	890.7	418.7
g. Construction						
h. Other						
I. Total Direct Costs	135.5	213.5	349.0	814.2	1,163.2	643.3
j. Indirect Charges	63.1	99.6	162.7	183.3	346.0	164.0
k. Totals	198.6	313.1	511.7	997.5	1,509.2	807.3

Section 6 Technical Report

The award program was designed to develop a new class of catalysts that can mimic noble metals in a variety of reactions. The research work included catalyst synthesis, activation, characterization, reaction evaluation, catalyst production scale-up, and bench scale testing under industrial conditions. Detailed results and discussion are presented in the following section.

6.1 Summary of Research Work

Synthesis and Characterization of Mo carbide nanorods and nanoparticles:

The stoichiometric reaction that we wanted to perform is the following:

Initially, it was proposed to synthesize nanoscale Mo carbides by using fibrils as a reactant under conditions where their nanoscale dimensions might exert a templating, or shape memory effect. Thus the resultant materials we desire are highly porous assemblages of Mo carbide nanorods, 10-50 nm in diameter, or Mo/W carbide nanoparticles distributed on fibril nanotubes.

Before the DOE funded project began, we attempted to carry out this reaction under conditions where shape memory in the products is possible. This results from the stepwise reaction of gaseous molecules with a solid surface where transport or diffusion of the product was restricted, i.e., at temperatures far below the melting or boiling points. The only mobile components were the reactant oxide, and the product CO. In this case, carbon with the fibril morphology was expected to yield polycrystalline carbide nanorods with similar dimensions.

Porcelain boat experiment in which molybdenum trioxide (MoO_3) was vaporized at 600-1000°C through a bed of fibrils, either in powder or extrudate form, were completed and characterized by X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). In this set-up, there was no

independent control of vaporization of oxide, which occurred at the same temperature as the reaction of fibrils and oxide. XPS analyses indicated surface composition comprising graphitic carbon and oxides/suboxides of molybdenum. No clear indication of the formation of carbidic compounds of Mo was seen. SEM analyses showed the formation of extensive coatings on the surface of the extrudates, while the interior of the extrudates appeared to be unreacted fibrils. The coatings consisted of large ($>1\text{ }\mu\text{m}$) cubic crystallites that were probably oxides and suboxides of Mo (MoO_{3-x}). SEM analyses of products derived from fibril powders as starting material showed the similar types of large particles interspersed among fibril bundles. No apparent change in individual fibril could be detected. XRD analyses showed the presence of only graphitic carbon and Mo-oxides. No carbidic phases of Mo were observed. These analyses confirmed the earlier analyses by XPS and SEM.

During the next series of experiments, a reactor system was devised using a 1" quartz tube mounted vertically in a Lindberg tube furnace. Fibril extrudates or powder were placed in the maximum hot zone of the furnace, and MoO_3 or MoO_2 was vaporized from a quartz bulb with exit holes for vapor escape which had been glass-blown onto the end of a thermocouple tube. Judiciously locating the bulb at the proper distance from the hot zone allows for vaporization at any given temperatures (lower than the reaction temperature). The vapors were then swept into the reaction zone by inert gas. As in the porcelain boat experiments, the products consisted mainly of extrudates or powder aggregates coated with grey, scaly particles. XPS could only identify Mo-oxides/suboxides. SEM established that particle sizes ranged from *supra*- μm to $<100\text{ nm}$. In some cases, coated fibril bundles resembled nodules, 50-200 nm. Polycrystalline carbide nanorods, which were the aim of the experiment, however, were not observed. XRD analyses verified that the major products from these experiments were remaining fibril extrudate or powders coated with a layer of Mo-suboxides. Particle sizes were in the range of several micrometers. In several samples, at temperatures where MoO_3 vapor concentrations were low ($\sim 10^{-4}$ mole fraction), the hexagonal phase of Mo_2C was observed. However, the quantities were not deemed sufficient for practical catalytic consideration. We suspect that the principal impediment to preparing clean carbide

products by this method is the facile deposition of Mo-suboxide. Under any practical conditions, this deposition occurs at a much faster rate than the desired reaction, resulting in a heavy coating of oxides on the surface of fibrils. This stops any subsequent reaction and disrupts stoichiometries. Carrying out the reaction at higher temperatures ($>1050^{\circ}\text{C}$) to speed up the reaction is impractical from a process and materials of construction point of view.

Fig 6.1 Thermogravimetric analysis (TGA) pattern of making Mo carbide. (A) C/Mo=3.5, $(\text{NH}_4)_2\text{MoO}_4$ as precursor; (B) C/Mo=5, MoO_3 as precursor.

At this stage, we shifted emphasis from synthesizing carbide nanorods to preparing Mo carbide catalysts supported on carbon Fibrils. This was accomplished by impregnating nanoparticles of MoO_3 (or other Mo precursor) onto the surface of fibrils, and using the carbon to reduce the Mo to the carbide. Variables explored included calcination temperatures, initial C:Mo atomic ratios, and Mo precursors. During the investigation, we adopted an innovative method developed prior to the DOE program to make Mo carbide via a temperature-programmed solid-state reaction. A typical run is demonstrated in a thermogravimetric analysis as shown in Figure 6.1. Tracking of the

reaction by TGA showed the reaction between MoO_3 and C proceeds in a sequential manner, reduction of MoO_3 by carbon to MoO_2 at $\sim 450\text{-}550^\circ\text{C}$, followed by further reduction to Mo_2C at $\sim 675\text{-}725^\circ\text{C}$.

When the DOE funded project began, we used exclusively the solid phase synthesis described above to prepare Mo carbide catalysts with various loadings. Table 6.1 summarizes results from various experiments using the stepwise solid-state synthesis method. The data list the reaction temperatures, the Mo precursors, the initial C:Mo atomic ratios (3.5 is the stoichiometric ratio), the crystalline phases and average crystallite sizes obtained. The successful runs showed carbide without free oxide phases. Crystallite sizes were consistent with individual fibril dimension (average diameter 7-8 nm). SEM analyses verified the particle size ranges that were estimated by the XRD data. As demonstrated in these results, we succeeded in synthesizing the two morphologies of Mo_2C proposed for this program, namely, 1), unsupported carbide nanorods; and 2), carbide nanoparticles supported on fibril nanotubes. Two crystalline forms of Mo_2C , *hcp* and *fcc*, were also observed, but the hexagonal close packed (*hcp*) dominated in most samples. The stoichiometry was attained with well-distributed reactants at a C:Mo atom ratio=3.5. Higher ratios signified excess carbon (fibrils). Runs 223-23-1 and 1327-103-3A, gave the clearest evidence for the formation of freestanding Mo_2C nanorods and/or nanoparticles. These were obtained by reacting stoichiometric or near stoichiometric mixtures of MoO_3 and fibrils, either as powder or as extrudates. Product identification and morphologies were obtained by XRD (Figure 6.2), SEM (Figure 6.3), HRTEM (Figure 6.4) and XPS (Figure 6.5). In 223-23-1, with $\sim 15\%$ excess of carbon, the major product was identified by XRD as the hexagonal phase of Mo_2C . MoO_2 and graphitic carbon were seen as minor components. SEM showed the presence of both nanorods (diameter of 10-15 nm and length over 100 nm) and nanoparticles (~ 20 nm). More evidence for formation of Mo_2C nanorods and nanoparticles was obtained in Run 1327-103-3A, which resulted by reaction of a stoichiometric mixture of MoO_3 and fibril powder. Accurate dimensions of the nanorods were obtainable from HRTEM, which showed them to have diameters similar to fibrils (~ 7 nm); the particles ranged

Table 6.1 XRD Results of Making Mo Carbide From Impregnated Samples

Sample	C/Mo atom ratio	<i>hcp</i> -Mo ₂ C (hexagonal)	<i>fcc</i> -Mo ₂ C (cubic)	MoO ₂	Carbide Morphology
MoC	N/A	>100 nm			Particle
1327-103-3A MoO ₃ /800°C	3.5	35 nm			Nanorod/nano- particle
1327-115-3 MoO ₃ /800°C	3.5	26 nm			Nanorod
223-23-1 Mo(acac) ₂ /600°C	4	15~20 nm		Minor Component	Nanorod/nano- particle
236-12-2 MoO ₃ /1000°C	10	36~38 nm			Nanorod/nano- particle
223-34-2 Mo(acac) ₂ /800°C	20	15~20 nm	~15 nm		Nanoparticle
223-34-4 MoO ₃ /1000°C	20	20 nm			Nanoparticle
236-12-4 MoO ₃ /600°C	20	18 nm			Nanoparticle
236-12-3 MoO ₃ /600°C	30	8~10 nm	8~10 nm		Nanoparticle
223-31-4 MoO ₃ /800°C	35		5~8 nm		Nanoparticle
223-34-1 Mo(acac) ₂ /800°C	35	10~15 nm			Nanoparticle
223-33-1A MoO ₃ /800°C	40		5~8 nm		Nanoparticle
1501-50-2 MoO ₃ /800°C	50	5~10 nm			Nanoparticle
236-12-6 MoO ₃ /1000°C	50	20~25 nm	5~8 nm		Nanoparticle

Table 6.2 Surface Mo composition analyses of various Mo carbide samples from XPS analyses

C/Mo	Mo ₂ C	MoO ₂	MoO ₃
2	35.7	22.9	41.4
3.6	48.6	10.7	40.7
5	49.5	11.1	39.4
10	61.4	10.4	28.2
20	59.7	13.0	27.3
35	60.2	14.6	25.2

from ~7-25 nm. XPS provided some extra surface information of these Mo carbide samples (Table 6.2). Carbide Mo phase was detected on all test samples. Mo oxides/suboxides were also found on these samples and their quantities varied with changes in the initial C/Mo atomic ratios. The oxide phases were expected to form during passivation procedure, where a diluted oxygen in Ar was passed through the sample in order to create a protection oxide layer. XPS studies from Pacific Northwest National Lab have confirmed this assumption (See attached reports in Appendix section). The carbide Mo and C species were found to be dominant on the surface after the samples were etched with Ar ionic beam to remove the oxide layer.

The reaction from the stoichiometric mixture was studied in more detail to learn the course of the reaction. SEM and XRD analyses after calcination at 600°C showed a complete redistribution of oxide precursor from the very large, *supra*- μm particles of MoO_3 initially present to ~20-50 nm particles of MoO_{3-x} , well-dispersed amongst individual fibrils. This redistribution probably occurred through vaporization. Spreading of MoO_3 is known on metal oxides, such as alumina [34], but has not been observed on carbon. Further calcination to 800°C converted the MoO_{3-x} mixture to Mo_2C nanorods and nanoparticles, with additional reduction in particle size to 7-25 nm. Essentially, all traces of MoO_2 have disappeared and the only pattern discernible is that of Mo_2C . Even though redistribution of MoO_3 probably takes place through vaporization, both chemical transformations ($\text{MoO}_3 \rightarrow \text{MoO}_2$ and $\text{MoO}_2 \rightarrow \text{Mo}_2\text{C}$ by reduction by carbon) are believed to occur through solid-solid reactions.

Fig 6.2 X-ray diffraction patterns of Mo carbides. Empty diamond symbols denote γ - Mo_2C ; filled triangles denote β - Mo_2C ; filled square denotes graphite.

Fig 6.3 Scan electron micrographs of a Mo oxides and fibrils mixtures heated at 600°C (MoO_{3-x}) and 800°C (Mo_2C).

(A) Free-standing *hcp*- Mo_2C nanorods/nanoparticles from Run 1327-103-3A.

(B) Supported Mo_2C prepared from Run 223-12-6 (C/Mo=20)

Fig 6.4 HRTEM images of nanoscale Mo carbide samples.

Fig 6.5 XPS spectra of Mo3d and C1s regions of 1327-103-3A (C/Mo=3.5) before and after synthesis.

In a further investigation, this method was tested with different type of carbonaceous materials, namely activated carbon and SP1 graphite powder as shown in Figure 6.6. The synthesis with activated carbon followed the same procedure as described above, while a higher temperature was required with graphite in order to completely convert all oxide phases into carbidic form. Post synthesis XRD analyses were shown in Table 6.3, and carbon fibrils exhibited clear advantage when compared to other carbonaceous forms in making Mo carbides with the smallest particle sizes and the highest chemical purity.

Table 6.3 XRD analyses of catalyst composition after preparation (C/Mo=20)

Substrate	Final Temperature (°C)	Mo Phase		
		Mo ₂ C	MoO ₂	Mo
Fibril	800	8 nm		
Activated carbon	800	30 nm	80 nm	60 nm
Graphite	900	>100 nm

Fig 6.6 Temperature programmed reaction patterns (TGA) of MoO₃ with different carbonaceous materials.

In summary, we have accomplished proposed tasks in making nanoscale Mo carbide using fibril nanotubes as support and/or template. The method we adopted is innovatively developed prior to kickoff of the DOE program and different from the proposed approach. Furthermore, from a fundamental point of view, we have clarified the mechanism of forming such nanoscale Mo carbides, which could extend to other systems to make novel materials.

Particle size Control

Our primary objective is to prepare metal carbide with nanoscale dimensions. It has been demonstrated that Mo carbide could be prepared using fibril nanotubes as catalyst template and support. The mechanism involved a spontaneous distribution of Mo oxides in order to achieve true nanoscale dispersion of carbide particles. In order to gain better control of the growth of Mo carbide particles, we examined the effects of Mo loading as well as the possibility of catalyst re-dispersion.

Fig 6.7 Effect of preparation methods and Mo loading on the particle sizes of Mo carbides Method (1) is physical mixing and method (2) is impregnation.

The Mo precursor, primarily Mo oxides, was introduced into the fibrils using either physical mixing or incipient wetness impregnation. The samples were then subjected to the calcinations as described in the previous section, and the particle size of products was

measured using XRD. As shown in Figure 6.7, the particle size of Mo carbide decreased monotonically with the decrease of Mo loading. Application of impregnation method generally yielded smaller particles, and the smallest particles were less than 5 nm when the Mo loading is lower than 15%.

The catalyst redispersion was carried out by re-oxidizing formed Mo carbide from previous experiments and re-calcining it under the same condition to form Mo carbide. Therefore instead of starting with micrometer scale Mo oxide precursor, the new sample consisted of Mo precursor already in the nanometer range. Further calcinations could drive the particle size even smaller based on the spontaneous spreading of Mo oxide on fibril surface. A Mo carbide sample with 65% metal loading underwent the redispersion procedure and the final particle size was found to decrease from original 42 nm down to 30 nm.

Activation of Mo carbide catalysts:

Samples (1327-103-3A) based on the stoichiometric Co/Mo atom ratio (3.5/1) were sent to Worcester Polytechnic Institute for chemisorption measurement. Initial results indicate unexpectedly low H₂ chemisorption. While H₂ chemisorption does not correlate with catalytic dehydrogenation or isomerization activity, this observation is unusual for pure Mo₂C. As reported by Lee and co-workers, pure Mo₂C made by methane carburization exhibited good H₂ chemisorption property, although the number of sites was still half of that obtained through CO chemisorption [35]. One possible reason is the presence of carbon coating over carbide surface. In order to remove this carbon coating and activate the catalyst, a post-synthesis hydrogen treatment was applied to the Mo carbide sample. The treatment condition was selected at which the fibrils would not react with hydrogen.

Methane was found evolving from the catalyst as the temperature increased (Figure 6.8), an indicative of removal of carbon coating. As shown in Table 6.4, H₂ and CO did not chemisorb on the sample initially, but oxygen did. After the hydrogen treatment at 600°C for a period of 80~120 minutes, the carbide regain their chemisorption capability.

The CO adsorption was slightly improved while the oxygen adsorption was substantially enhanced. Hydrogen chemisorption, however, was still not observed.

Fig 6.8 Methane evolution from Mo carbide sample during hydrogen treatment at 600°C.

Table 6.4 Chemisorption measurement of selected Mo carbide samples

Sample	C/Mo	H ₂ treatment	Gas uptake (μmol/g)			BET (m ² /g)
			H ₂	CO	O ₂	
242-1-3	50	N/A	0	0	35.2	255
		120 min	0	2.4	52.6	260
242-69-5A-He	50	N/A	0	0	65.0	318
236-16-3A	50	N/A	0	0	8.3	276
		120 min	0	2.1	28.5	282
236-12-6	50	N/A	0	0	0	258
242-12-3	30	N/A	0	0	0	274
242-23-1A-He	5	N/A	0	0	44.8	77
		80 min	0	0	75.4	71
208-7-1	Fibril	N/A	0	0	0	396

The analysis of surface sites via chemisorption remains as a fundamental problem for many researchers. The ambiguous data from chemisorption was attributed to the poisoning by carbon and/or oxygen which are both very difficult to remove completely from the surface once contaminated [33].

Synthesis of W carbide:

Due to our success in making Mo carbide using solid-state reaction technique, we employed the same method to synthesize W carbide by reaction of WO_3 or oxide precursors with as-made fibrils. Reaction temperature required for complete reaction was 1000°C . Two carbides can form according to the following stoichiometries:

The most reliable method to insure even distribution of the tungsten precursor on fibrils was by incipient wetness impregnation of ammonium paratungstate $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$, abbreviated as A. Tung] or phosphotungstaic acid (PTA, $\text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot x\text{H}_2\text{O}$) onto fibrils using a mortar and pestle to knead the mix. As shown in Table 6.5, two tungsten precursors were converted into a mixture of W_2C and WC upon calcining at 1000°C . Only the two carbides are observed in the XRD patterns (Figure 6.9), except for those samples with excess C (Expts. 3,4,6 and 7). No observable oxide remained after calcination.

Fig 6.9 X-ray diffraction pattern of W carbide made from fibrils. Empty diamond symbols denote W_2C ; filled triangles denote WC.

Table 6.5 Summary of Tungsten Carbide Preparations

Experiment	C/W	Components	XRD
1. 242-72-3A	2:1	A. Tung and plain CC	W and WO ₂
2. 242-70-3A	3.5:1	PTA and plain CC	WC and W ₂ C
3. 242-70-3B	10:1	PTA and plain CC	WC and W ₂ C, Carbon
4. 242-70-3C	20:1	PTA and plain CC	WC and W ₂ C, Carbon
5. 242-72-3B	3.5:1	A. Tung and plain CC	WC, W ₂ C and possibly W
6. 242-72-3C	10:1	A. Tung and plain CC	WC and W ₂ C, Carbon
7. 242-72-3D	20:1	A. Tung and plain CC	WC and W ₂ C, Carbon

Calcination of a sample containing excess W (Expt.1, C:W=2:1) reacted all the carbon in the sample to extinction. Only W metal and WO₂ were observed in XRD, according to the following stoichiometry:

WC and/or W₂C are probably produced initially but then undergo further reaction with excess WO₂. In any event, the observation on metallic W serves as a marker for poor distribution of tungsten precursor, since this will result in areas of non-stoichiometry. This was seen in attempts to produce the carbides by physically mixing stoichiometric amounts (C:W=3.5 atom ratio) of WO₃ and fibrils (Experiment not included in Table 6.5). These generally produced mixtures of carbides, metallic W, WO₂ and carbon (XRD analyses). These latter experiments also show that WO₃ will not redistribute on conversion to WO₂, either by vaporization or surface migration, as was observed with the corresponding molybdenum carbide preparations from the physical mixtures. Thus, morphology of the tungsten carbides may well differ from the corresponding Mo carbides.

Fig 6.10 SEM images of W carbide made from (a) A. Tung and (b) PTA.

PNNL has done some detailed characterization work on W carbide samples and was able to identify the nanorod/needle structures as $W_{(2-x)}C$ by the positions of the W bands in Auger Electron Spectroscopy (AES). The bulk chemical composition, 242-72-3B, could not be determined since this is a surface characterization method only. In the regions of the nanorods, the surface atom ratios showed an excess of C. The C and W bands seen in the amorphous areas were best attributed to non-stoichiometric WO_{3-x} interspersed with unreacted carbon nanotubes. Neither the W nor C bands were consistent with the carbides. By visual account, the tungsten suboxides observed in these regions exceeded the amounts accountable to the W oxides in excess of stoichiometry. The best description of this sample is a mixture of free-standing WC/ W_2C nanorods interspersed with appreciable regions containing partially reacted tungsten suboxides (WO_{3-x}) and unreacted carbon nanotubes. The W precursors and C in these regions never reacted to form carbides. 242-72-3C and 242-72-3D: These preparations used C:W atom ratios of 10:1 and 20:1, respectively, and were designed to make nanoparticles of carbides supported on carbon nanotubes. They were prepared by the same method as the previous sample, except that the amounts of ammonium tungstate in the impregnation solution were adjusted to reach the proper C:W atom ratios. SEM and TEM analyses at Hyperion of these samples showed a great deal of inhomogeneity in their make-ups as described previously (Figure 6.10). Rather than 2-10 nm nanoparticles of carbides supported on individual nanotube strands as we obtained with the corresponding Mo_2C preps, the analyses showed large aggregates of carbon nanotubes interspersed between >100 nm particles presumed to be either carbides or suboxides of W. AES confirmed the

make-up of these samples. The results were similar to the previous sample, i.e., the nanorod/needle structures were consistent with carbide constitution and the amorphous regions were consistent with unreacted carbon nanotubes and WO_{3-x} . These analyses confirmed the general inhomogeneities of the products from these preparations. Rather than forming uniform nanorods of carbides in high conversions with the stoichiometric preps, only partial conversions occurred. Generally, conversions were estimated at ~50%, judging from the SEM analyses. Large regions of unreacted carbon and WO_{3-x} were clearly visible by microscopy and confirmed by AES. The same general picture emerged for those preps designed to make nanoparticles of carbides supported on individual nanotubes. In these, only carbide nanorods or large particles of carbide/suboxide interspersed between nanotubes were obtained. There was very little evidence for carbide nanoparticles supported on individual nanotubes. The corresponding preparations with Mo precursors yielded uniform nanorods in high yields from stoichiometric mixes or 2-8 nm nanoparticles supported on individual nanotubes when excess carbon was charged. The difference in the materials obtained from W precursors undoubtedly was due to the difference in volatility between MoO_3 and WO_3 . The former, MoO_3 is sublimeable at $T > 450^\circ\text{C}$. Thus, even μ -sized particles of MoO_3 present at low temperature are able to redistribute and spread over the nanotube surfaces during reaction at higher temperature under controlled conditions so that the stoichiometric reaction can be realized. In the case of WO_3 , this compound is essentially nonvolatile $< 1000^\circ\text{C}$, so no spreading of WO_3 can occur. This restricts the reaction between the suboxide and C because the mass transport process does not exist, and the reactions are limited to the stoichiometries of localized regions. Thus, the over-all stoichiometry according to the chemical equation is never reached, and the result is the formation of interspersed particles determined by the localized stoichiometries.

Since we had achieved great success in preparing nanoscale Mo carbide, in order to keep up with scheduled tasks, we shifted our focus to development of practical applications of Mo carbide catalysts. Synthesis of nanoscale W carbide was postponed.

Catalytic activity evaluation:

Butane isomerization:

Mo and W carbides were reportedly having noble metal-like behavior during hydrocarbon isomerizations. Earlier work by Boudart and co-workers, and by Ledoux and co-workers [21,22] on Mo₂C catalysts determined that pure carbides were very active for hydrogenolysis, and that unless the catalysts were activated using a rather severe oxidation treatment at temperatures up to ~400°C in air, hydrogenolysis was the only reaction observed. Isomerization of paraffins was seen only after this oxidation treatment that tended to create anion vacancies to serve as acidic sites.

Maximum theoretical conversions (equilibrium) for butane to convert to isobutane at the temperatures for this study (300-385°C) are ~50%.

The reaction evaluation was mainly carried out at Hyperion Catalysis. The reaction condition was selected as H₂:butane = 4-16, 250-400°C, WHSV~1-10. It has been found that without oxygen treatment the Mo carbide generally acts as cracking catalyst with very low isomer selectivity. Contacting stored catalysts without further oxidation showed only ~0.5% isomerization at ~360°C and steady increase in hydrogenolysis at >380°C. When a hydrogen treatment was applied to stored catalysts at 400-700°C, <1% butane conversion was observed at 390°C. Furthermore, contacting freshly prepared Mo₂C catalysts (not passivated or oxidized) with butane showed only mild hydrogenolysis (cracking) at temperatures from ~280°-400°C at the conditions probed. Only traces of isomerization were seen.

Oxidation treatments which ranged from 220°C for 30 minutes to 400°C for 14 hours in 3% O₂/argon were designed to deposit from ~5% to ~90% of the theoretical oxygen to the carbide (oxycarbide). Separate TGA experiments which recorded weight gain with time and temperature on contact with 3% O₂/argon dictated the conditions of the activation treatment. Initial experiment for the 1327-103-3A catalyst for butane

isomerization have given 2-4% conversions with selectivity to isobutane around 90-95% at 360-380°C after activation with 3% O₂/Ar or in air at 400°C. More experiments followed this manner and were summarized in Table 6.6 for molybdenum carbide (Runs 1-17) and tungsten carbide (Runs 18-22). The experiments looked primarily at the variations in the activation procedure with either full air or 3% O₂ in argon at temperatures between 220°-450°C. These treatments were not successful in raising yields of isobutane above ~5% with selectivities >90%.

Table 6.6 Summary of butane isomerization on Mo and W carbide catalysts

Catalyst (C:Mo/ Precursor)	Test#	H ₂ :C ₄ H ₁₀ /WHSV	Temp (°C)	Activation	Yield
1327-103-3A (3.5:1/MoO ₃)	1	16:1 / 5	365	o activation	0.45%
	2	16:1 / 5	390	r: 10°C/min to 500°C, 2°C to 00°C 2: 0.5 h at 700°C	0.35%
	3	16:1 / 5	380	% O ₂ /Ar: 14 hours at 350°C	4.4%
	4	16:1 / 2.5	360	ir: 14 hours at 350°C	0.85%
		4:1 / 1			3.65%
242-48-3 (3.5:1/A. moly)	5	6:1 / 2	380	2: 0.5 hours at 700°C % O ₂ /Ar: 1 hour at 400°C	2.3%
	6	6:1 / 2	379	2: 0.5 hours at 700°C % O ₂ /Ar: 14 hours at 400°C	2.1%
1327-103-3B (10:1/ MoO ₃)	7	6:1 / 2	405	2: 0.5 hours at 700°C % O ₂ /Ar: 14 hours at 350°C	2.1%
242-59-1 (3.6:1/MoO ₃)	8	6:1 / 2	380	n-situ preparation and no ctivation.	0.2%
	9	6:1 / 2	380	% O ₂ /Ar: 14 hours at 400°C	2.2%
242-49-3 (3.5:1/MoO ₃)	10	6:1 / 2	380	ir: 2 hours at 450°C	3.0%
242-59-3-2 (3.6:1/MoO ₃)	11	6:1 / 2 (1 psi)	385	ir: 30 minutes at 220°C	1.1%
	12	6:1 / 2 (1 psi)	385	ir: 1 hour at 220°C	0.75%

	13	6:1 / 2 (3 psi)	385	% O ₂ /Ar: 1 hour at 220°C	1.2%
	14	6:1 / 10 (6 psi)	363	% O ₂ /Ar: 1 hour at 230°C un for 24 hours % O ₂ /Ar: overnight at 230°C un for 3 hours % O ₂ /Ar: overnight at 300°C	1.25%
242-59-3-3 (3.6:1/MoO ₃)	15	6:1 / 2 (1 psi)	363	ir: 14 hours at 240°C	1.25%
	16	6:1 / 2 (1 psi)	363	ir: 14 hours at 280°C	1.15%
	17	6:1 / 2 (1 psi)	360	% O ₂ /Ar: 15 minutes at 230°C ir: 1.5 hours at 420°C	0.25%
236-15-2 (12:1/PTA)	18	6:1 / 2	360~400	% O ₂ /Ar: 14 hours at 400°C	-
242-72-3A (3.5:1/ATung)	19	6:1 / 2 (9 psi)	409	% O ₂ /Ar: 14 hours at 400°C	0.7%
242-72-3B (10:1/ATung)	20	6:1 / 2 (3 psi)	362	% O ₂ /Ar: 14 hours at 400°C	0.35%
	21	6:1 / 2 (1 psi)	385	% O ₂ /Ar: 20 hours at 300°C	0.45%
	22	6:1 / 2 (1 psi)	385	% O ₂ /Ar: 1 hour at 450°C	0.45%

Since very little cracking occurred, it is assumed that the inactivity of the catalysts were due to insufficient acidity. Treatment with air at T>350°C has been reported in the literature to activate these catalysts for hexane isomerization [22]. Presumably, the oxidation increases the acidity of the carbides by formation of the oxycarbides that facilitates the skeletal isomerization of the adsorbed intermediate (olefin). This increased acidity is sufficient to isomerize normal paraffins to single-branched, secondary paraffin structures. However, the failed attempts to isomerize butane to isobutane at even moderate rates, and the very sluggish response to these catalysts to oxidation suggested that the increased acidities were not sufficient to accelerate the isomerization of primary to tertiary structures.

While the yields obtained from some of the above experiments for butane isomerization were very modest, selectivities were very high. Problem still existed as the persistence of low activity of treated Mo carbide under current conditions. This

phenomenon can be seen as that oxidizing stored catalysts (no hydrogen treatment) at 220-450°C gave only very low conversions (generally <1%) at ~360°C. Increasing temperature led to increased cracking. Subsequent analyses of the catalysts after oxidation showed essentially complete conversion of Mo₂C to MoO₃ at the oxidation conditions. No Mo₂C phase was observable by XRD after oxidation.

Although these are very modest results, comparison with results from commercial Pt catalysts is interesting. Pt/SiO₂ or Pt/Al₂O₃, the catalysts that Mo₂C is trying to emulate give butane conversions of only 1-2% and 2-4%, respectively. The catalyst surface acidity or the electronic property of active sites was considered to be a very critical factor in this reaction. The monofunctional, non-acidic catalysts give only very modest yields, comparable to our Mo₂C catalyst. It is only after the Pt catalysts are made bi-functional, e.g., by partially chloriding the Al₂O₃ to greatly increase the acidity of the catalyst [36,37], or supporting Pt on an acidic support that Pt catalysts give near equilibrium (~50-60%) conversions to isobutane [38-41]. Therefore, increasing acidity of Mo₂C catalysts, perhaps by deeper O₂ activation or by some other activation procedure may well give conversions more in line with commercial Pt bi-functional catalysts. The change is attributed to the formation of bi-functional active sites similar to those on Pt/acidic support, where patches of carbides were responsible for the dehydrogenation-hydrogenation of the alkane, while acidic oxides were responsible for the protonation and isomerization. Metal carbides with strong charge transfer from metal towards non-metal atom have been demonstrated to have excellent activities in dehydrogenation and hydrogenolysis. Therefore, the modification of the electronic property of active species so as to improve their acidity is the key to further modify nanoscale Mo and W carbide and enhance their catalytic activity in hydrocarbon skeleton isomerization. Thus based on these judgments, the study on this application was halted. Further development of catalyst modifications would be outside the scope of the current program.

Ethyl benzene dehydrogenation:

The reaction evaluation was mainly performed by our sub-contractor, Worcester Polytechnic Institute. The catalytic properties of supported Mo₂C samples for dehydrogenation of ethyl benzene (EB) were studied in the presence of either steam or CO₂. The samples employed have various initial C/Mo ratio and were prepared under different conditions. The reaction was carried out in a plug flow reactor packed with 0.2g of sample. The gaseous reactants were fed through mass flow controllers and the liquid reactants were introduced by passing He through saturators. The pressures of EB were in the range of 6.4-8.0 Torr. The pressure ratios of steam (or CO₂) to EB were in the range of 2.4-2.6. The major product was styrene. Toluene, benzene, ethane and methane were found as byproducts. The targets for conversion of EB and the selectivity of styrene are 60% and 97%, respectively [42]. It was found that pure fibrils have a catalytic effect on the reaction. For the reaction in the presence of steam, the conversion and selectivity were 19% and 76% respectively. While in the case of under CO₂, the conversion was 19%, but the selectivity dropped to 66%.

A. Reaction with steam

Initial tests on Mo carbide catalysts with various Mo loadings indicated that samples with low Mo loading tended to have better activities than those with higher Mo content. At 600°C in the presence of steam, the initial conversion was higher than 90% over supported nanoscale Mo carbide catalysts. The initial selectivity to styrene was, however, lower than 30%. A deactivation as a function of time on stream was observed for all the samples tested. The activity dropped very fast in the first half hour. The Mo₂C sample was oxidized by steam under reaction conditions, as identified by XRD measurements after the reaction was discontinued. This may be an explanation for the deactivation observed. The conversion was around 30-40% at steady state. The selectivity to styrene was around 90% (Figure 6.11). The catalytic activity increased as

the loading of Mo was decreased and the yield of styrene followed the same trend as well. This behavior was considered to relate to the decrease of Mo₂C particle size. The samples prepared in CH₄/H₂ mixtures showed a higher reaction rate per gram than the samples prepared in inert gases. The same phenomenon was also observed for the yield of styrene, which is in good agreement with the observation in the chemisorption measurements showing more surface sites on these samples. The XRD measurements indicate that Mo₂C was oxidized to MoO₃ by steam under reaction conditions (Figure 6.12). However, there were still some Mo₂C left for the lower Mo loading samples, which suggested that the lower Mo loading samples might have higher resistance to oxidation than the higher Mo loading samples. Furthermore, under the conditions of these experiments, there was no obvious effect on the conversion of EB and the selectivity to styrene when the loading of Mo was varied from C:Mo atom ratio 30-50:1.

In order to evaluate these catalysts in a more practical way, EB and water were pumped into a vaporizer before being introduced into the reactor. The following conditions were used: 1 gram of catalyst loading, partial pressure of EB at 2.5 psi; molar ratio of steam to EB at 5:1; LHSV of EB, 1hr⁻¹; T_{react}, 600°C. These are the industry standards, but under slightly different conditions. As shown in these experiments, the thermal conversion of EB (no catalyst) was ~11% with a selectivity to styrene ~64% in the presence of steam. XRD analyses of catalysts after running for 3-4 hours in steam showed substantial conversion of the carbide to MoO₃ indicating an inherent instability of the carbides under these conditions.

The best result was obtained with a supported Mo₂C catalyst (C:Mo ratio=50:1, prepared by intimate physical mixing of oxide and fibrils) which showed approximately stable performance over 3.5 hours in steam. The selectivity to styrene was ~96%, and the conversion of EB was ~35%. The post-reaction XRD analysis was not clear in identifying the molybdenum species present since the Mo loading was close to the detection limit of XRD.

$P_{\text{EB}}=6.2\text{-}7.6\text{ Torr}$, $\text{WHSV}=0.3\text{-}0.5\text{ hr}^{-1}$, $P_{\text{H}_2\text{O}}:P_{\text{EB}}=2.4\text{-}2.9$, balance He

$P_{\text{EB}}=6.4\text{-}8.0\text{ Torr}$, $\text{WHSV}=0.3\text{-}0.5\text{ hr}^{-1}$, $P_{\text{H}_2\text{O}}:P_{\text{EB}}=2.4\text{-}2.6$, balance He

Fig 6.11 EB dehydrogenation over Mo carbide catalysts prepared through different route. In He: 242-23-1A-He, In CH₄/H₂: 242-23-1A-CH₄a and In H₂: 242-23-1A-H₂b

Fig 6.12 XRD spectra of samples after EB dehydrogenation. 2θ diffraction peaks at 34.4° , 37.9° and 39.4° indicated presence of Mo₂C.

Decreasing the steam: EB ratio did not significantly affect EB conversion; however, selectivity decreased by about 10-20%. More cracking products were formed. Increase of LHSV of EB resulted in an increase of EB conversion ($\sim 3\%$), but was accompanied by a decrease of the selectivity to styrene ($\sim 5\%$) for the reaction at the same EB partial pressure.

B. Reaction with CO₂

This reaction was also evaluated in the presence of CO₂ in order to avoid oxidation of Mo₂C by steam. It was reported in literature that CO₂ could play the same role as steam, e.g. supplying heat, diluting EB, and avoiding coke deposition. Moreover, CO₂ could remove H₂, one of the reaction products, from the reaction system by forming CO and H₂O. This results in the increase of equilibrium yield of styrene and the decrease of the reaction temperature over an Fe-Ca catalyst [25,26]. Thus, the dehydrogenation of EB in the presence of CO₂ is also assumed to be an energy-saving process. The

dehydrogenation of EB in the presence of CO₂ was carried out at a CO₂/EB ratio of 9-14. The pressures of EB were in the range of 6.0-6.4 Torr. The WHSV of EB was about 0.33 hr⁻¹. Helium was used as balance. As compared to reaction with steam, the conversion and selectivity were slightly higher under the condition of CO₂. Formation of CO was also observed, which might be the product of the reaction between CO₂ and H₂. A gradual deactivation was observed (Figure 6.13). This is probably due to the gradual deposition of carbon and perhaps the lower carbon removal ability of CO₂ as compared to steam. Nevertheless, XRD measurements did not show the presence of MoO₂ in the samples after the reaction in the presence of CO₂. This indicates that the oxidation of Mo₂C by CO₂ did not occur under reaction conditions. Finally, samples with lower Mo loading samples once again showed higher reaction rate per gram and higher selectivity than the higher loading samples. The conversion of EB was significantly decreased when EB partial pressure was decreased. The selectivity to styrene was, however, significantly increased. This is partially due to the significant increase of the total space velocity, because more CO₂ was fed for decreasing the partial pressure of EB.

C. Effect of oxygen treatment

Effect of oxygen pretreatment on the dehydrogenation in the presence of CO₂ has also been investigated. As described in butane isomerization, oxygen treatment can play a critical role in modifying the carbide surface into oxycarbide that possess anion vacancies served as active sites. It was further found that the oxidation pretreatment on Mo₂C or fibril could also enhance the activity in dehydrogenation of ethyl benzene (Figure 6.14). The conversion of EB was increased by ~20% for the treatment on Mo₂C and ~15% for the treatment on fibril (without Mo₂C), while the selectivity was not affected.

D. Dehydrogenation of EB on fibrils supported W₂C catalysts

The initial ratio of C to W is 50. The surface area of supported W₂C measured with N₂ adsorption at 77K is 294m²/g. The XRD analysis showed that W₂C and carbon are the major components. However, the presence of small mount of WC cannot be ruled out. The hydrogen chemisorption was found on the fresh fibrils supported W₂C surface.

This is significantly different to the results obtained for fibril- supported Mo_2C , on which the hydrogen chemisorption was only observed after H_2 -pretreatment.

$P_{\text{EB}}=6.0-6.4\text{Torr}$, $\text{WHSV} \sim 0.33\text{hr}^{-1}$, $P_{\text{CO}_2}:P_{\text{EB}}=10$, balance He

$P_{\text{EB}}=6.0-6.4\text{Torr}$, $\text{WHSV} \sim 0.33\text{hr}^{-1}$, $P_{\text{CO}_2}:P_{\text{EB}}=10$, balance He

Fig 6.13 EB dehydrogenation over Mo carbides with CO_2

$P_{\text{EB}}=6.0\text{-}6.4\text{ Torr}$, $\text{WHSV}=\sim 0.33\text{ hr}^{-1}$, $P_{\text{CO}_2}:P_{\text{EB}}=10$, balance He

$P_{\text{EB}}=6.0\text{-}6.4\text{ Torr}$, $\text{WHSV}=\sim 0.33\text{ hr}^{-1}$, $P_{\text{CO}_2}:P_{\text{EB}}=10$, balance He

Fig 6.14 Effect of Oxygen treatment on the carbide activity of EB dehydrogenation

As shown in Table 6.7, an EB conversion of 29.3% and a selectivity to styrene of 88.9% was obtained for the reaction in the presence of steam at 2.5psi EB partial pressure and 600°C . This is similar to the reaction on fibril-supported Mo_2C . For the

dehydrogenation of EB in the presence of CO₂, EB conversion of 36.9% and a selectivity of 87.2% were obtained. The conversion is about 6% higher than the average conversion for the reaction on Mo₂C catalysts. A gradual deactivation was also found for W₂C.

Table 6.7 Comparison of dehydrogenation of EB over Mo and W carbides

Catalyst	Diluent	P _{EB} (psi)	Conversion (%)	Selectivity (%)	Rate (μmol/g.s)
Mo ₂ C	H ₂ O	2.5	23	86	1.3
	CO ₂	2.5	30	86	1.8
W ₂ C	H ₂ O	2.5	29	89	1.7
	CO ₂	2.5	37	87	2.1

C/Mo=C/W=50

In summary, Mo and W carbide can show modest activity in dehydrogenation of ethyl benzene as demonstrated above. However, the inherent instability of Mo carbide under reaction conditions with steam hindered further opportunities in developing proposed catalysts. Application of CO₂ as alternative to steam can stabilize the Mo carbide catalyst, however, the activity and selectivity are still lower than the desired industrial targets.

Vapor phase hydrodesulfurization of thiophene:

Thiophene was selected as the target molecule for hydrodesulfurization. A schematic diagram of the reaction path was shown in Figure 6.15. The major hydrocarbon products were n-butane, 1-butene, cis-2-butene and trans-2-butene. According to the predicted thermodynamic equilibrium, ratios for butene isomers are: cis/trans-2-butene = 0.70, and 2-butene/1-butene = 2.5.

Fig 6.15 Thiophene HDS reaction network. Numbers in parentheses are approximate rates [(mmol)/g.s] with chromia catalyst at 415°C, numbers in brackets are for Co-Mo/Al₂O₃ catalyst at 400°C [43].

All the catalyst samples were prepared at Hyperion and most of them were already calcined and converted into carbide before sent to WPI. Oxidized fibrils were generally used as catalyst support unless noted specifically. A passivation procedure with 3% O₂/Ar was applied to all catalysts in order to create a protective skin of oxide layer on top of carbide particles. Before the reaction, as-made Mo carbide catalyst (after synthesis and passivation at Hyperion) was subject to hydrogen treatment at 400°C for 30 minutes. The HDS reaction was carried out at atmospheric pressure in a continuous plug flow quartz reactor, using between 200 and 425 mg of catalyst. In each case, the mass of catalyst was adjusted in order to give approximately the same sample volume, approximately 0.7 mL for each run. The carrier gas, hydrogen, with a flow of 30 ml/min controlled by a mass flow controller was passed into a saturator/bubbler containing thiophene that was held at 0 °C using an ice-bath. 2.7 mol% of thiophene vapor was then saturated into hydrogen and flowed through the catalyst bed and the product stream was subsequently examined by GC analysis. At the beginning of the experiment, the reagent

feed was flowed through the reactor system until a steady flow had been established as evidenced by constant GC peak areas. The reactor was then heated to the reaction temperature of 400 °C over a 20-minute period, and GC analysis commenced when the reaction temperature was reached. Analyses were taken every 20 minutes over the course of the reaction.

Although the reaction was examined over a total period of 24 hours, this whole process was divided into three successive days of eight hours each. At the end of day one, the reactor was cooled under the thiophene/hydrogen flow back to room temperature. The valves to the reactor were then closed, sealing the catalyst sample in the thiophene/hydrogen mixture overnight. At the beginning of day two, the thiophene/hydrogen mix was flowed at room temperature until steady, and then the reactor was heated to 400°C and analysis begun as before. This split-time procedure is driven by safety concerns at WPI with leaving hydrogen flowing through a reactor at 400 °C unattended overnight.

A. Loading effect

The catalyst loading was simply controlled by the initial ratio of carbon to Mo. According to a stoichiometric reaction, a combination of fibrils and Mo precursor with C/Mo=3.5 will result in the formation of Mo₂C with very little unreacted fibrils left in the sample. Depending upon the preparation procedure, we are able to control the morphologies of the stoichiometric Mo carbide into “nanorods” or freestanding nanoparticles. When the C/Mo ratio is bigger than 5, most of the Mo carbide particles will be in the supported form and distributed uniformly throughout the fibril network. The particle size decreases from ~30 nm to as small as 2~3 nm when increasing C/Mo ratio from 5 to 50.

The effect of carbide loading was screened using powdered catalysts made from ammonium molybdate and oxidized fibrils using incipient wetness impregnation method with C/Mo = 3.5, 10, 20, and 30. X-ray diffraction has verified that the Mo phase was hexagonal closed packed *hcp*-Mo₂C with fairly high chemical purity.

Table 6.8A Catalyst loading: Comparison of Reaction Rates in HDS Reaction

Sample Composition	Catalyst ID	Mo ₂ C wt%	Reaction time	% Thiophene Conversion	Rate (μmol/sec.g)
C: Mo = 3.5	249-48-1B	100	t = 0 h	36.8	0.537
			t = 5 h	26.1	0.380
			t = 24 h	22.5	0.328
C: Mo = 10	1416-175-2	56.6	t = 0 h	79.9	1.109
			t = 5 h	40.6	0.563
			t = 24 h	34.8	0.481
C: Mo = 20	249-48-2B	34.0	t = 0 h	97.0	1.800
			t = 5 h	56.0	1.039
			t = 24 h	44.4	0.824
C: Mo = 30	1416-175-1	24.3	t = 0 h	41.0	0.974
			t = 5 h	30.1	0.714
			t = 24 h	26.6	0.633

Table 6.8B Catalyst loading: Final Product Distributions

Sample	i-butane (%)	n-butane (%)	1-butene (%)	trans-2-butene (%)	cis- 2-butene (%)
C: Mo = 3.5	0.3	18.9	21.7	34.7	24.4
C: Mo = 10	0.4	24.7	18.9	32.3	22.6
C: Mo = 20	0.7	32.7	16.5	28.9	20.2
C: Mo = 30	0.2	22.1	20.0	33.5	23.4

Table 6.8C Catalyst loading: Final Product Ratios for HDS of Thiophene

Sample	Cis/trans but-2-ene	But-2-ene /But-1-ene	Butene /Butane
C: Mo = 3.5	0.702	2.723	4.209
C: Mo = 10	0.699	2.949	2.687
C: Mo = 20	0.698	2.982	1.962
C: Mo = 30	0.698	2.839	3.456

As shown in Table 6.8, the correlation of reaction rate in term of $\mu\text{mol}/\text{sec.g}(\text{cat})$ versus catalyst loading appeared to be “volcano type” with the optimum catalyst composition containing $\sim 34\%$ Mo_2C . This trend was also consistent with what was found by Bussell and co-workers but with a different peak position [32]. The maximum activity occurred in their study was with 15% $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$. Meanwhile, the product distributions were found to be similar at same thiophene conversions over different samples, indicating the reactions followed the same mechanism.

B. Effect of Mo phases as HDS catalyst

Commercial HDS catalysts are usually made from Mo oxide promoted with Co or Ni. Activation of catalysts is completed via presulfidation to form Mo sulfide. Mo carbides have been reportedly used as efficient HDS catalysts [33,44,45]. However, there existed an argument on whether the formation of Mo carbide was necessary in order to become an active HDS catalyst. In the current study, three types of Mo compounds, namely MoO_3 , MoO_2 and Mo_2C , were investigated and the results are presented in Table 6.9.

Table 6.9A Supported Mo Catalysts: Comparison of HDS Reaction Rates

Sample Composition (C/Mo=20)	Sample ID	Reaction Time	% Thiophene Conversion	Rate ($\mu\text{mol}/\text{sec.g}$)
$\text{MoO}_3/\text{fibril}$	249-48-2	t = 0 h	42.9	0.856
		t = 5 h	23.5	0.468

		t = 8h	22.8	
MoO ₂ /fibril	249-48-2A	t = 0 h	50.4	1.005
		t = 5 h	36.3	0.724
		t = 8 h	33.3	
Mo ₂ C/fibril	249-48-2B	t = 0 h	97.0	1.800
		t = 5 h	56.0	1.039
		t = 24 h	44.4	0.824

Table 6.9B Supported Mo Catalysts: Final Product Distributions

Catalyst	i-butane (%)	n-butane (%)	1-butene (%)	trans-2-butene (%)	cis-2-butene (%)
MoO ₃ /fibril*	0.1	14.1	21.9	37.0	25.9
MoO ₂ /fibril*	0.2	23.8	19.2	32.9	23.0
Mo ₂ C/fibril	0.7	32.7	16.5	28.9	20.2

Table 6.9C Supported Mo Catalysts: Final Product Ratios for HDS of Thiophene

Catalyst	Cis/trans But-2-ene	But-2-ene/ But-1-ene	Butene/ Butane
MoO ₃ /fibril*	0.700	2.869	5.961
MoO ₂ /fibril*	0.701	2.909	3.122
Mo ₂ C/fibrils	0.698	2.982	1.962

*Product distribution given after 8 hours

Clearly, Mo₂C appeared to be the most active catalyst for hydrodesulfurization of thiophene. According to the some literature reports, Mo sulfide was considered as the active species on Mo catalyst during HDS. Small domains of Mo carbide and its crystal structure might lead to the formation of more active Mo sulfide species (more exposed edge sites) than MoO₃. In the current study, the catalyst particle sizes decreased from

several hundred nanometers of MoO₃, to 10~20 nm of MoO₂, and finally to 3~8 nm of Mo₂C. The results were very consistent to those in the literature.

C. W carbide catalyst in HDS

Most of HDS work in the literature was focused on the Mo-based catalysts, and only a few were found to use sulfided W or NiW. In our investigation, attempts to apply W carbide for HDS was completed over two samples with C/W = 20 and 50. The reaction data is shown in Table 6.10.

Table 6.10A W carbide: Comparison of Reaction Rates in HDS Reaction (400°C)

Sample Composition	Sample ID	Reaction Time	%Thiophene Conversion	Rate (μmol/sec.g)
C: W = 20:1	242-70-3C	T = 0 h	2.5	0.066
		T = 5 h	4.3	0.117
		T = 24 h	5.1	0.141
C: W = 50:1	249-41-3C	T = 0 h	3.2	0.118
		T = 5 h	6.8	0.252
		T = 24 h	7.0	0.255

Table 6.10B W carbide: Final Product Distributions

Sample	i-butane (%)	n-butane (%)	1-butene (%)	trans-2-butene (%)	cis-2-butene (%)
C/W = 20	0.0	5.3	31.1	37.6	26.1
C/W = 50	0.0	4.1	31.2	36.1	26.7

Table 6.10C W carbide: Final Product Ratios

Sample	Cis/trans but-2-ene	But-2-ene/ But-1-ene	Butene/ Butane
C: W = 20	0.695	2.051	18.03
C: W = 50	0.739	2.014	22.67

Compared to Mo carbide catalysts, W carbide appeared to have much lower activities in HDS reaction. In addition, the conversion of thiophene was found to increase over the reaction period instead of decrease.

D. Effect of presulfidation

Presulfidation is usually applied to generate the active sulfide species before proceeding with HDS. This process was usually done by treating catalysts with sulfur-containing compound such as thiophene, H₂S, etc. A presulfidation procedure has been tried in WPI instead of instant sulfidation during heating up the reactor within 20 minutes to the desired reaction temperature, 400°C. This experiment was carried out by heating the catalyst under thiophene/hydrogen at a rate of 2°C min to allow sufficient reaction between thiophene and Mo carbide before reaching the final temperature.

Table 6.11A Presulfidation: Thiophene conversion for different Mo/Fibril samples during sulfidation

T (°C)	% Thiophene Conversion		
	249-48-2 (MoO₃/F)	249-48-2A (MoO₂/F)	249-48-2B (Mo₂C/F)
180	0.0	0.0	0.0
220	0.0	0.0	1.9
260	0.0	0.0	6.3
300	0.0	5.3	19.6
340	0.0	26.9	52.2
380	28.1	42.4	70.4
400*	52.6	49.5	67.4

* 1st analysis at 400°C performed 10 minutes after 400°C was first reached

Table 6.11B Presulfidation: Thiophene conversion at 400°C

Time (min)*	% Thiophene Conversion		
	249-48-2 (MoO ₃ /F)	249-48-2A (MoO ₂ /F)	249-48-2B (Mo ₂ C/F)
10	52.6	49.5	67.4
30	33.4	48.4	61.0
50	27.7	47.6	58.1
70	25.7	46.9	56.7
130	23.0	45.1	54.0
310	20.0	40.0	49.8
310 + 8h	19.1	31.5	43.1
310 + 16h	17.9	28.4	40.1

*Defined as time of reading after temperature first reached 400 °C. 1st GC analysis after sample had been at 400°C for 10 minutes. Subsequent analysis every 20 minutes.

Table 6.11C Presulfidation: Major Product Distributions for 249-48-2B Mo₂C

T (°C)	Conversion (%)	n-butane (%)	1-butene (%)	Trans-2- butene (%)	Cis-2- butene (%)
220	1.9	0.0	14.7	53.3	32.0
260	6.3	20.7	14.4	39.9	25.1
300	119.6	27.4	14.3	35.1	23.1
340	52.2	33.0	14.2	31.0	20.8
380	70.4	40.7	13.6	26.0	17.9
400 (t = 0h)	67.4	38.7	14.8	26.1	118.3
400 (t = 5h)	49.8	34.2	16.0	28.0	19.6
400 (t = 13h)	43.1	30.9	17.0	29.5	20.6
400 (t = 21h)	40.1	28.8	17.7	30.5	21.3

Table 6.11D Presulfidation: Major Product Distributions for 249-48-2A MoO₂

T (°C)	Conversion (%)	n-butane (%)	1-butene (%)	Trans-2- butene (%)	Cis-2- butene (%)
300	5.3	17.7	20.1	37.4	24.8
340	26.9	17.1	18.3	38.6	26.1
380	42.4	25.7	17.6	33.1	22.9
400 (t = 0h)	49.5	32.0	16.8	29.5	20.7
400 (t = 5h)	40.0	30.6	17.5	29.9	20.9
400 (t = 13h)	31.5	26.3	19.0	31.5	22.1
400 (t = 21h)	28.4	24.6	19.6	32.0	22.6

Table 6.11E Presulfidation: Major Product Distributions for 249-48-2 MoO₃

T (°C)	Conversion (%)	n-butane (%)	1-butene (%)	Trans-2-butene (%)	Cis-2-butene (%)
380	28.1	25.0	17.3	32.9	22.6
400 (t = 0h)	52.6	23.8	18.6	32.9	23.2
400 (t = 5h)	20.0	15.1	21.6	36.6	25.6
400 (t = 13h)	19.1	15.0	23.2	35.5	25.1
400 (t = 21h)	17.9	14.3	23.8	35.5	25.1

According to the above results (Table 6.11), no significant difference appeared between the activity obtained with and without presulfidation. The sulfidation could happen instantaneous upon heating up in thiophene environment. Thiophene appeared to be a very good sulfidant.

E. Effect of catalyst precursors

Most of catalysts tested so far were made from ammonium molybdate with incipient wetness impregnation method. Early work in this program indicated that various Mo precursors could be used to make carbide under different conditions. The physical properties of these carbide particles appeared to be similar, however, the chemical properties might vary significantly. This phenomenon may have something to do with the difference in ease of carbide formation, active surface area as well as the lattice structures. In order to explore more options in catalyst formulation, Mo carbide catalysts (C/Mo=20) made from different precursors have been tested. These Mo precursors included MoO₃, ammonium heptamolybdate (A.Moly), Mo(acac)₂ (MAA), and phosphomolybdic acid (PMA). Except for the powdered sample from MoO₃, all other samples were extrudates.

Table 6.12 Mo precursor: Comparison of Reaction Rates in HDS Reaction

Sample ID	Catalyst Precursor	Reaction time	% Thiophene Conversion	Rate (μmol/sec.g)
1416-179-3	A. Moly	t = 0	59.6	1.106
		t = 5h	35.4	0.656
		t = 8h	33.7	0.626
		t = 24h	28.5	0.529

1501-21-1	PMA	t = 0	44.3	0.822
		t = 5h	24.0	0.446
		t = 8h	22.0	0.409
		t = 24h	19.6	0.364
249-48-4B*	MoO ₃	t = 0	96.9	1.932
		t = 5h	40.7	0.812
		t = 8h		
		t = 24h	36.1	0.721
1501-47-1	MAA	t = 0	49.7	0.922
		t = 5h	36.0	0.669
		t = 8h	34.6	0.641
		t = 24h	33.0	0.613

* Powder sample made from MoO₃ and oxidized fibrils.

The results (Table 6.12) clearly showed some noticeable difference in catalytic activity, which could result from the properties of carbide particles, such as morphology, surface structure, as well as interaction with extraneous P atoms.

F. Active species

In order to identify the active species, XPS studies were carried out to examine the surface of fibril-based Mo carbide catalysts. The following figure (Figure 6.16) is the spectra of the stoichiometric carbide sample, 249-48-1B (C/Mo=3.5), before and after thiophene reaction.

As expected, the catalyst underwent sulfidation during the reaction. There is an extra peak appeared after reaction in the region of 226 eV indicating an S3s signal. Meanwhile, the carbide signal was still observed after reaction with decreased intensity. Clearly, the surface has either formed a very thin layer of Mo sulfide or part of the surface has undergone this changes and left the rest of surface remain the carbide nature. Additional scan over the S2p region revealed some interesting spectra in Figure 6.17. The S2p signal exhibited some dramatic differences between 249-48-1B and 249-48-2B. Sulfate species, SO_x, was found on 249-48-2B but not on 249-48-1B. As we recalled previous results from these two samples, the thiophene conversion over the latter sample was much lower than that over the former one. As a matter of fact, the stoichiometric

carbide sample appeared to have the lowest reaction rate in term of $\mu\text{mol/sec.gcat.}$ Similar sulfur signal was also found with the samples of C/Mo=30 and 50, which exhibited better performance than C/Mo=3.5. Therefore the oxygen-associated sulfur

Fig 6.16 C1s and Mo3d regions of 249-48-1B catalyst before and after reaction.

species emerged on the sample that exhibited good activities. A blank run with fibrils has been conducted in order to identify the origin the SO_x species. Fibrils themselves didn't have any activity in converting thiophene, and the XPS result clearly indicated that thiophene is the only sulfur species found on the fibrils that has been subject to the same reaction. No sulfate species was observed. Thus, the oxygen is not likely from the fibrils. It is then possible that oxygen adsorption occurred after exposing the active Mo sulfide (or carbide) surface to air and created some SO_x species. Appearance of this species in XPS spectrum could result from some substantial amount of oxygen adsorption. Consequently, these catalysts should possess more active sites and exhibited higher activities.

Fig 6.17 Comparison of S2P signal of 249-48-1B and 249-48-2B after reaction.

Fig 6.18 Comparison of S2p and Mo3d regions of active and inactive catalysts.

In addition, the total content of surface sulfur was also found to associate with the HDS activities. Here are the S2p and Mo3d spectra of 249-48-2B (active), HCI-NMC-01 and 249-89-1 (inactive) (Figure 6.18).

Most of sulfur species is in the sulfide form, but the total sulfur content on the surface was found to be quite different. It is interesting to notice that the surface sulfur content, especially S/Mo, is well related to the catalytic activity. That is, higher S/Mo ratio resulted in better performance and vice versa. As shown in the following table (Table 6.13), the highest S/Mo was found to be 1.2~1.3 over the best sample we obtained so far. Thus it is not surprising to understand why HCI-NMC-01 and 249-89-1 exhibited low activities in HDS reaction. Carbide form was still dominant on most of the catalyst surface.

Table 6.13 Surface analysis of spent samples

Sample	HDS activity ^c ($\mu\text{mol/g.sec}$)	Mo	S	S/Mo
249-48-2B	1.04	2.4	3.1	1.3
1416-179-1	0.74	1.4	1.2	0.9
HCI-NMC-01	0.66			
249-48-1B	0.38	16.2	12.9	0.8
249-89-1	0.09	2.8	< 0.5	< 0.1
HCI-NMC-01 ^{a,d}	-	14.0	3.7	0.3
HCI-NMC-01 ^{b,d}	-	5.5	0.6	0.1

^a Exterior of extrudates

^b Interior of extrudates

^c After 5 hour's reaction with thiophene

^d After liquid phase reaction in Raytheon

Catalyst production scale-up:

In order to fulfill catalyst commercialization requirement, Hyperion Catalysis has developed a procedure to scale up the catalyst production. As described in the original proposal, Fibril nanotubes were initially oxidized by nitric acid, a procedure disclosed in US Patent 5,861,454. Then the oxidized fibrils were extruded through a Brabender single-screw extruder. Mo precursors were then loaded onto the extrudates using impregnation method and followed by calcination procedure that leads to the formation of Mo carbide nanorods or nanoparticles. This technique was applied in this program and allowed us to make large quantities of Mo carbide catalysts consisted of either nanorods or supported nanoparticles.

Catalyst evaluation using vapor phase HDS of thiophene at WPI indicated that there is no difference between lab scale powdered catalysts and bench scale extruded catalysts.

Bench-scale testing

According to original proposal, six catalysts were to be selected for further commercialization study. As indicated above, the preparation of W carbide comprise many difficulties as encountered during project period, while Mo carbide presented more success and simplicity in the preparation procedure, we concentrated on using Mo carbide in commercialization trials. Due to low activities in butane isomerization and ethyl benzene dehydrogenation, we emphasized on the application of Mo carbide in hydrodesulfurization of diesel. Six samples were synthesized and sent to Washington Group International for bench scale testing.

Initial studies by WGI indicated low activity in HDS of diesel in an autoclave liquid phase reactor. Poor sulfidation was expected to be the reason for low catalytic activity. In order to simulate the industrial sulfidation procedure, DMS was applied to presulfide the catalyst. Two Mo carbide catalysts, HCI-NMC-01 (Mo/C-1) and HCI-NMC-02 (Mo/C-2), were tested for their HDS activity after *in-situ* presulfidation. Approximately 5g of Mo carbide catalyst were loaded into a 300-ml autoclave. The catalyst was activated with pure hydrogen flow at 400°C and atmospheric pressure for at least one

hour. After the catalyst was cooled to room temperature, approximately 150 g of light gas oil (from Statoil) and 1.5 g of DMDS were charged into the autoclave for presulfidation. The autoclave was pressurized to 300 psig and subsequently heated up to 320°C under pure hydrogen flow for at least four hours. After the presulfidation was finished, the autoclave was cooled to room temperature. The reaction liquid was drained and replaced with fresh gasoil. The autoclave was then brought to desired experimental condition (300 psig and 320 or 340°C). The feed sample was taken once the experimental temperature was reached. During the experiment, product sample was taken periodically for sulfur and aromatic analysis.

Fig 6.19 Bench scale testing of Liquid phase HDS with Mo carbide catalysts

The sulfur concentration profiles in diesel fuel are shown in Figure 6.19 for the two catalysts (Mo/C-1 and Mo/C-2). Initially, the sulfur conversion increased almost linearly but seemed leveling off after 3-4 hours. It is conceivable that those easy sulfur species usually reacted first. Therefore, the difficulty to desulfurize the remaining sulfur species will increase through the course of the run. As shown in Figure 6.15, the HDS activity increases with reaction temperature. However, the HDS activity of Mo/C-2 catalyst seems to show much stronger dependency on temperature that that of Mo/C-1. The concentration profiles of aromatics are shown in Figure 6.20. Although the aromatic conversion showed slight fluctuation, the reduction of aromatics over time was clear. The conversion of di-aromatics and polyaromatics are slightly higher than that of total is expected because di-aromatics and polyaromatics are usually easier to be hydrogenated than monoaromatics.

Fig 6.20 Profiles of aromatic compound during liquid phase HDS.

However, such low aromatic conversions suggest that both catalysts have only weak activity to aromatic saturation under the experimental conditions. Their weak hydrogenation activity probably affects negatively their ability to convert those difficult sulfur species (mainly substituted dibenzothiophenes) present in diesel.

Above all, we have demonstrated to be able to successfully synthesized nanoscale Mo carbide catalysts with two different morphologies, supported nanoparticles and freestanding nanorods respectively. This Mo carbide was found to behave very similar to noble metals in several reactions. In butane isomerization, Mo carbide exhibited striking similarity as compared to untreated commercial Pt/Al₂O₃ catalyst with low activity and high selectivity. Nanoeffect was also seen during ethyl benzene dehydrogenation where smaller carbide particles not only had better activity and selectivity but also stronger oxidation resistance. Mo carbide catalyst also appeared to be better than fibril supported MoO₃ (MoS₂) during HDS work. Although the performance of these carbide catalysts need to be further improved in order to match and surpass that of current industrial catalysts, the fibril based nanoscale Mo carbide catalysts have proved to have a great potential in industrial applications.

6.2 Advantages of new nanoscale Mo carbide catalysts:

There are several methods reported in the literature to make nanoscale Mo carbides. One of them is inherited from metallurgical industry, where carbon black was reacted with Mo oxides under inert environment at temperatures of 1200~1300°C. Another common method operates at lower temperatures (700~850°C) is to carburize Mo oxides (mostly supported) using methane and hydrogen. Chemical vapor deposition method was also used by some people to make fine carbide powder, but high temperature and difficulty to scale up restrict this method in industrial application.

Our goal is to synthesize highly active Mo and W carbide with nanoscale dimensions. As summarized previously, we developed an innovative method under a separate program and applied it to synthesize nanoscale Mo carbide catalysts. The method was

based on using carbon nanotube as template that might exerted the so-called memory effect. By utilizing the nanoscale dimension of carbon nanotube, it was demonstrated to achieve easy control of fine dispersion of Mo carbide particles. The size range varied from a few to less than 30 nanometers. Compared to other synthetic methods reported in the literature, the solid-state synthesis has demonstrated to be the easiest with most energy saving.

- The current process was mostly carried out at temperatures lower than 800°C, a sharp decrease from metallurgical synthetic conditions, e.g. 1200°C.
- The synthesis doesn't require hydrogen as part of reactant. This is in fact a great cost-saving process in catalyst production.

The reaction between Mo precursors and Fibrils is very unique. The product distributions and morphologies are very different than reactions with activated carbon or commercial graphite. The latter give only low conversions to micron-sized mixed particles of Mo carbides and oxides.

The prepared Mo carbide catalysts inherited the rigid porous structures of fibril nanotubes either as nanoparticles distributed inside fibril network or as nanorods. Like fibril nanotubes, the porous assemblages possess only macropore and mesopore. The lack of microporosity makes this catalytic material very attractive in certain applications where steric limitation becomes the rate-determining step.

Finally, the nanoscale Mo carbide catalysts were found to have mild hydrogenation activity. During HDS of diesel, the unsaturated C=C bonds were found to have minimum hydrogenation conversion to saturated C-C bonds. This property may be more useful in term of selective hydrogenation in chemical refinery and pharmaceutical synthesis.

6.3 Problem encountered

As described in previous summary, the method we proposed to prepare Mo carbide appeared to be unsuccessful. The method was based on our patent work on making Si

carbide and nitride from carbon nanotubes and volatile reactant such as SiO. The problem of using this method in making Mo carbide appeared to be the facile deposition of Mo-suboxide. Under any practical conditions, this deposition occurs at a much faster rate than the desired reaction, resulting in a heavy coating of oxides on the surface of Fibrils and eventually limiting the diffusion of carbon in Mo phase to form Mo carbide.

In order to solve this problem, we adopt an innovative technique called stepwise solid-state synthesis developed prior to the DOE program. This method has been proved to be very promising in making carbon nanotube-based catalysts using carbon as both reducing agent and support. The evaporation of Mo oxides and facile deposition were controlled to allow the formation of Mo carbide with nanometer dimensions. Therefore, this problem has been solved and the program moved forward as scheduled.

6.4 Problem remained

During the course of program, we encountered several problems that still remained. Some of the problem are associated with the inherent nature of starting materials such as fibril nanotubes, catalyst precursors, and other problems could be solved but, outside the scope of current program.

Although we are able to make highly dispersed Mo carbide catalysts, we haven't made tungsten carbide within the same caliber. This was due partially the inherent properties of tungsten oxides that have a very high melting temperature and low vapor pressure. The tungsten precursor was also found to favor agglomerating rather than wetting the surface of carbon nanotubes possibly due to poor interaction between these precursors and carbon surface. In addition, the W carbide we made had lower activities than Mo carbide, this was also partially due to the dimensions of W carbide particles being much bigger. It is hard to conclude at this point whether W carbide exhibits better or worse catalytic performance as compared to Mo carbide.

Another problem existed as the application of Mo carbide in butane isomerization. Untreated Mo or W carbides exhibited very low catalytic activity in the hydrocarbon

skeleton isomerization. The activity obtained from Mo carbide was, however, very similar to that of untreated Pt/Al₂O₃, where the hydrogenolysis or cracking reactions were favored over selective isomerization. Comparison of the carbide catalysts with reported results for monofunctional Pt/Al₂O₃ catalysts were impressive. Conversions for the monofunctional Pt catalysts are too low for commercial applications, while conversions of n-butane and selectivities to i-butane obtained over the carbide catalysts were comparable to monofunctional Pt, although the carbide catalysts required a higher temperature to operate. It is only when the Pt catalysts are made bi-functional by strongly increasing the acidity that conversions are sufficiently high for commercialization. These levels of activity for the carbide catalysts were not achieved by the activation methods used in the current program. The main reason (we suspect) for the poor performance of the carbide catalysts is that the reported oxidative procedures for increasing the acidities on these catalysts for higher paraffin chain isomerization is insufficient to drive the butane isomerization reaction. Furthermore, butane is considerably more difficult to isomerize than higher paraffins. Our reaction tests have been conducted near atmospheric pressure, while commercial butane isomerization proceeds at 250 psig. While there is no obvious reason to expect that higher pressures will increase reaction rate, these effects are not always understood on a theoretical basis. Research to find new procedures for increasing acidity is beyond the scope of the proposed work. However, this remains a potential area for further exploratory work.

As shown in many scientific papers as well as our studies, transition metal carbides exhibit excellent activity in hydrogenation and hydrogenolysis. However, chemisorption of hydrogen on these catalysts was much lower than that of CO. Till now, there is no fundamental explanation on the exact cause. Further investigation into the adsorption properties of transition metal carbides remains as an attractive direction.

The application of ethyl benzene dehydrogenation appeared to be impractical due to the deactivation problem. This problem was mostly resulted from carbon deposition, oxidation of Mo carbide and fibril support under steam at elevated temperatures. After we adjusted the reaction conditions as CO₂ was introduced to replace steam as diluent, the oxidation of Mo carbide and fibril support appeared to be avoided. However, the

carbon deposition still seemed hindered the catalytic activity since CO₂ has weaker ability to remove generated carbon.

Hydrodesulfurization is the most promising application for our nanoscale Mo carbide catalyst. However, our carbide catalysts appeared to have moderate hydrogenation activity as compared to commercial Co-Mo and Ni-Mo catalysts, therefore, possess lower activity to remove sulfur in deep HDS process. Addition of promoters to increase the hydrogenation ability can be one of solutions to improve the overall HDS activity. In addition, it was found that the nanoscale Mo carbide need much less hydrogen than commercial catalysts during HDS process and was able to remove sulfur without hydrogenate the unsaturated C=C bonds. This property is very useful in refining naphtha where minimum hydrogenation of C=C bonds is desired.

6.5 Unexpected or serendipitous results

None.

Reference

1. R. B. Levy and M. Boudart, *Science*, **187**, 547 (1973)
2. M. R. A. Blomberg, P. E. M. Siegbahn and M. Svensson, *J. Phys. Chem.*, **96**, 9794 (1992).
3. F. Zaera, *Chem. Reviews*, **95**, 2651 (1995).
4. G. A. Gaziev et. al., *Dokl. Akad. Nauk. SSSR*, **140**, (1961)863
5. J. M. Muller and F. G. Gault, *Bull. Soc. Chem. Fr.*, **2**, 416 (1970)
6. J. H. Sinfelt and D. J. C. Yates, *Nature*, **229**, 27 (1971)
7. L. E. Toth, "Transition Metal Carbides and Nitrides", Academic Press, p8, 1971
8. T. Hyeon, M. Fang, and K. S. Suslick, *J. Am. Chem. Soc.*, **118**, 5492 (1996)
9. L. LeClercq, K. Imura, S. Yoshida, T. Barvee, M. Boudart, Preparation of Catalysts II, Elsevier, Amsterdam, 1978.
10. S. T. Oyama, The Chemistry of Transition Metal Carbides and Nitrides, Blackie Academic & Professional, Glasgow, 1996.
11. H. Tennent, *US Patent*, 4,663,230.
12. S. Iijima, *Nature*, **354**, 56 (1991).
13. M. S. Hoogenvaad, et. al., in "Proceedings of 6th International Conference on Scientific Basis for the Preparation of Heterogeneous Catalysts", Brussels, 1994.
14. A. Fischer, et. al., *US Patent*, 6,203,814.
15. C. M. Niu et. al., *Mat. Res. Soc. Symp. Proc.*, **410**, 179 (1996)
16. H. Dai et. al., *Nature*, **375**, 769 (1995)
17. W. M. H. Sachtler, in "Recent Advances in Basic and Applied Aspects of Industrial Catalysts" (T. S. R. Prasada Rao and G. Murali Dhar, eds.), *Stud. Surf. Sci. Catal.*, **113**, 41 (1998).
18. G. Martino, *Stud. Surf. Sci. Catal.*, **130**, 83 (2000).
19. K. J. Ware and A. H. Richardson, *Hydrocarbon Process*, **11**, 161 (1972).
20. L. Leclercq, M. Provost, H. Pastor and G. Leclercq, *J. Catal.*, **117**, 384 (1989).
21. F. H. Ribeiro, R. Dalla Betta, M. Boudart, J. Baumgartner and E. Iglesia, *J. Catal.*, **130**, 86 (1991).
22. C. Bouchy, C Pham-Huu, B. Heinrich, C. Chaumont and M. J. Ledoux, *J. Catal.*, **190**, 92 (2000)

23. M. K. Neylon, S. Choi, H. Kwon, K. E. Curry and L. T. Thompson, *Appl. Catal.*, **183**, 253 (1999)
24. J. S. Lee, B. J. Song, S. Li, and H. C. Woo, in “The Chemistry of Transition Metal Carbides and Nitrides”, (S. T. Oyama, ed.), p398, Blackie Academic & Professional, Glasgow, 1996.
25. N. Mimura, I. Takahara, M. Saito, T. Hattori, K. Ohkuma and M. Ando, *Catalysis Today*, **45**, 61 (1998).
26. N. Mimura and M. Saito, *Catalysis Today*, **55**, 173 (2000).
27. K. Tanaka and T. Okuhara, *Catal. Rev.-Sci. Eng.*, **15**, 249 (1977).
28. P. Grange, *Catal. Rev.-Sci. Eng.*, **21**, 135 (1980).
29. R. Prins, V. H. J. De Beer and G. A. Somorjai, *Catal. Rev.-Sci. Eng.*, **31**, 1 (1989).
30. P. T. Vasudevan and J. L. Fierro, *Catal. Rev.-Sci. Eng.*, **38**, 161 (1996)
31. G. C. Stevens and T. Edmonds, in “Preparation of Catalysts II”, Elsevier, Amsterdam, 1979, p. 507.
32. K. R. McCrea, J. W. Logan, T. L. Tarbuck, J. L. Heiser and M. E. Bussell, *J. Catal.*, **171**, 71 (1997);
33. P. A. Aegerter, W. W. C. Quigley, G. J. Simpson, D. D. Ziegler, J. W. Logan, K.R. McCrea, S. Glazier and M. E. Bussell, *J. Catal.*, **164**, 109 (1996)
34. Y. Xie and Y. Tang, *Adv. Catal.*, **37**, 1 (1990).
35. J. S. Lee, S. T. Oyama and M. Boudart, *J. Catal.*, **106**, 125 (1987).
36. S. Siffert, J. Schmitt, and F. Garin, *J. Catal.*, **184**, 19 (1999)
37. W. Souverijns, A. Houvenaghel, P.A. Jacobs, *J. Catal.*, **174**, 201 (1998)
38. S. R. Vaudagna, R. A. Comelli, N. S. Figoli, *React. Kinet. Catal. Lett.*, **63**, 33 (1998)
39. M. C. Clark, and B. Subramaniam, *Chem. Eng. Sci.*, **51**, 2369 (1996)
40. H. Y. Chu, M. P. Rosynek, J. H. Lunsford, *J. Chinese Chem. Soc. (Taipei)*, **45**, 481 (1998)
41. F. D. Rossini, in “Physical Chemistry of the Hydrocarbons”, (A. Farkas, ed.), vol.1, p 1950.
42. Communication with Washington Group.
43. P. J. Owens and C. H. Allmberg, *Adv. Chem. Ser.*, **33**, 182 (1961); *Can. J. Chem.*, **40**, 941 (1962); *ibid*, **40**, 947 (1962).

44. S. Li and J. S. Lee, *J. Catal.*, **178**, 119 (1998).
45. E. J. Markel, S. E. Burdick, M. E. Leaphart and K. L. Roberts, *J. Catal.*, **182**, 136 (1999)

Section 7 Commercialization Report

A. Follow On Funding Commitments.

Since last October, Hyperion has continued to pursue research on this family of catalysts. This research addresses the question of whether modifications to the catalysts might make them more suitable to address the reactions originally proposed to the DOE and also explores new potential reactions that these catalysts might address. Since last October we have spent approximately over \$150,000 dollars on the molybdenum carbide family of catalysts. None of this money was from leveraged sources.

No commercialization activity related to the continuing work has been undertaken, because we have not yet demonstrated performance in a commercially interesting target reaction. We expect to continue working in this area using our own funds, spending at about the same rate, through the end of 2002. Depending upon the results of that work, funding may continue longer. If promising results are achieved, we would seek a partner to participate in the project and provide a commercialization path. They would, in essence, fill the role that Washington Group, our funding partner played in the DOE program.

B. Products or Processes based upon the results of this work.

No products or processes are currently available based upon the work of this project. A number of presentations have drawn at least in part on the DOE funded work which has been appropriately acknowledged. These include: 218TH American Chemical Society Meeting at New Orleans in 1999; American Institute of Chemical Engineers Annual Meeting at Los Angeles in 2000; 17TH North American Catalysis Society Conference at Toronto in 2001; and CatCon 2002 at Houston in 2002.

C. Revenues, Commercialization efforts

Because no product based on this work is yet available there have been no revenues and there has been no commercialization activity.

D. Market Opportunity

Hyperion believes that the market opportunity for the reactions originally targeted has not significantly changed. We believe that the chance of a molybdenum carbide family catalyst finding use in ethyl benzene dehydrogenation is minimal. Both butane isomerization and diesel HDS remain viable targets for the technology, but will not be achieved with the catalysts in their present form. The kinds of modification required to address these targets are beyond the scope of work originally proposed to DOE. These kinds of catalyst modifications are the subject of our continuing internally funded work.

We also believe that these catalysts may find application in reactions other than those originally proposed to DOE. This is also part of our internally funded program.

Section 8 Appendix

Reports from Battelle Pacific Northwest National Lab

Battelle

Pacific Northwest Laboratories
Battelle Boulevard
P.O. Box 999
Richland, Washington 99352
Telephone (509) 375-2759

Dec 17, 1999

fax (509) 375-3864
e-mail dean.matson@pnl.gov

Mr. David Moy
Hyperion Catalysis International
38 Smith Place
Cambridge, MA 02138

Dave:

Enclosed is a brief letter report summarizing the results of XPS analysis on your samples done at our EMSL lab. I've also enclosed hardcopies of the XPS spectra and some of the raw analyses of Mo/C ratios, etc. Please let me know if you have any comments/questions regarding the analyses or the report. I'm hoping to get you some TEM results soon as well.

Regards,

Dean W. Matson
Senior Research Scientist
Materials Resources Division

Enclosures

Report on XPS Analysis of As-Received and Sputtered Carbided Hyperion Samples

12/99

<u>Sample #</u>	<u>Hyperion ID#</u>
1	242-8-2B
2	1327-103-3A
3	242-50-3

XPS analyses were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe at the Environmental and Molecular Science Laboratory (EMSL) at PNNL. Initial survey scans were performed on the as-received samples from 0 to 1300 eV at 117.4 eV pass energy. High resolution scans were also taken for each of the samples in the Mo3d (222 to 244 eV), C1s (278 to 298 eV), and O1s (425-445 eV) regions at 35.5 eV pass energy. The area of analysis was 1.5 mm x 0.2 mm. Each sample was then Ar ion sputtered at 2KeV for the equivalent time required to remove 50 Å based on a calibrated SiO2/Si standard.

Initial survey scans and high resolution scans of the Mo3d, C1s, and O1s regions were consistent with Hyperion's description of the samples and with the XPS analysis of the 1327-103-3 sample performed at Harvard. As expected, the #1 sample exhibited a much lower initial Mo/C ratio than the other two. The Mo3d region was dominated by MoO3 peaks with a small carbide peak and a very weak MoO2 component. After sputtering, the dominant peaks in this region shifted to MoO2, probably due to the reducing effect of the Ar sputtering process, and a significant Ar peak was detected due to incorporation of Ar into the sample during sputtering. The peak shapes and magnitude in the C1s and O1s regions of the spectrum changed little as a result of sputtering on this sample.

Initial scans of both the calcined samples indicated a significant Mo⁶⁺ (MoO6) component, with smaller peak near 228 eV attributed to Mo2C. The spectrum of the #3 sample also contained a significant peak near 229 eV attributed to MoO2 that was present to a smaller extent in the spectrum of sample 2. After sputtering, the spectra of both calcined samples showed a dramatic decrease in Mo⁶⁺ and a corresponding increase in relative intensity of the Mo2C peak, suggesting an increased exposure of the carbide phase as a result of the sputtering process. Intensity at energies associated with the MoO2 peaks also increased as a result of the sputtering process, although clear peaks are not present. Again, this is probably at least partially a result of reduction from the sputtering process itself.

Peaks in the C1s area of the spectra of the calcined samples were also significantly changed as a result of the sputtering process. Initial spectra in this region were dominated by a peak at 284.6 (graphite or hydrocarbon). After sputtering the dominant peak in this region shifted to 282.7 eV, indicative of the Mo2C species. In the spectrum of sample 2, the 284.6 eV peak remained as an identifiable peak but was lower in intensity than the 282.7 eV peak. In the spectrum of sample 3, the 283.6 eV peak was

reduced to an unresolved shoulder on the 282.7 eV peak. Essentially no change in peak shape was noted in the O1s region of the spectra as a result of the sputtering process. Mo/C ratios derived from the spectra of the samples before and after sputtering are summarized in the table below:

Sample #	Mo/C before sputtering	Mo/C after sputtering
1	0.1/1	0.2/1
2	1/1	1.7/1
3	1.57/1	2.95/1

In summary, the results the XPS analysis before and after sputtering indicates that for the calcined material, a carbon-rich (graphite or hydrocarbon) phase is associated with carbide species in the as-received samples. An oxide layer is also present. These additional layers on the carbide are at least partially removed by the sputtering process, exposing more of the underlying carbide phase.

#1

Atomic Concentration Table

FileName	AreaComment	C1s	O1s	Mo3d	Mo/c
		[0.314]	[0.733]	[3.544]	
XPS0585.spe	#1 242-8-2B	95.19	3.54	1.27	0.01/1
XPS0598.spe	#1 242-8-2B	96.01	2.29	1.70	0.02/1
		95.60	2.91	1.49	Mean
		0.58	0.89	0.30	Standard Deviation

Intensity Table

FileName	AreaComment	C1s	O1s	Mo3d	
		[0.314]	[0.733]	[3.544]	
XPS0585.spe	#1 242-8-2B	22655.29	2111.36	3830.17	
XPS0598.spe	#1 242-8-2B	33112.64	1976.59	7403.98	
		27883.96	2043.98	5617.08	Mean
		7394.46	95.29	2527.07	Standard Deviation

MoO₃ REDUCED BY AR SPUTTER TO MoO₂

#2

Atomic Concentration Table

FileName	AreaComment	C1s	O1s	Mo3d	
		[0.314]	[0.733]	[3.544]	
XPS0586.spe	#2 1327-103-3A	24.40	51.47	24.12	
XPS0597.spe	#2 1327-103-3A	21.39	41.79	36.82	
	3.5:1 C:Mo	22.89	46.63	30.47	Mean
		2.13	6.85	8.98	Standard Deviation

Mo/C

1/1
1.7/1

Intensity Table

FileName	AreaComment	C1s	O1s	Mo3d	
		[0.314]	[0.733]	[3.544]	
XPS0586.spe	#2 1327-103-3A	2510.98	13275.34	31359.88	
XPS0597.spe	#2 1327-103-3A	3111.55	15239.63	67673.39	
		2811.27	14257.49	49516.63	Mean
		424.66	1388.96	25677.53	Standard Deviation

SAME RESULT AS SAMPLE #2 LESS MOOZ ~~7.11.05~~

#3

Atomic Concentration Table

FileName	AreaComment	C1s	O1s	Mo3d	Mo/c
		[0.314]	[0.733]	[3.544]	
XPS0587.spe	#3 242-50-3	17.23	55.74	27.03	1.57/1
XPS0595.spe	#3 242-50-3	12.78	49.52	37.70	2.95/1
		15.00	52.63	32.37	Mean
		3.14	4.40	7.55	Standard Deviation

Intensity Table

FileName	AreaComment	C1s	O1s	Mo3d	
		[0.314]	[0.733]	[3.544]	
XPS0587.spe	#3 242-50-3	4083.52	33120.48	80953.47	
XPS0595.spe	#3 242-50-3	3237.80	31448.70	120686.59	
		3660.66	32284.59	100820.03	Mean
		598.01	1182.13	28095.56	Standard Deviation

MIXTURE OF MO₂C, MO_{0.2}, AND MOO₃
SPUTTER SOA^o TO SHOW MORE MO₂C

INITIAL

XPS0575.spe: Dean Matson

EMSL

1999 Nov.29 Al mono 100.9 W 100.0 μ 45.0° 117.40 eV

7.7529e+04 max

14.56 min

Survey/Area1: #1 242-8-2B/1 (SG5)

AFTER 50 Å SPUTTER

XPS0599.spe: Dean Matson

1999 Dec 2 Al mono 100.9 W 100.0 μ 45.0° 117.40 eV

8.3969e+04 max

EMSL

9.70 min

Su/Area10: #1 242-8-2B/1 (SG5)

INITIAL

XPS0576.spe: Dean Matson

EMSL

1999 Nov 29 Al mono 100.9 W 100.0 μ 45.0° 117.40 eV

5.5338e+04 max

14.56 min

Survey/Area2: #2 1327-103-3A/1 (SG5)

AFTER 50 Å SPUTTER

XPS0600.spe: Dean Matson
1999 Dec 2 Al mono 100.9 W 100.0 μ 45.0° 117.40 eV
Su/Area9: #2 1327-103-3A/1 (SG5)

EMSL

9.70 min

9.0483e+04 max

XPS0600.spe

INITIAL

XPS0577.spe: Dean Matson

EMSL

1999 Nov 29 Al mono 100.9 W 100.0 μ 45.0° 117.40 eV

1.6295e+05 max

14.56 min

Survey/Area3: #3 242-50-3/1 (SG5)

#3

AFTER 50A⁰ SPUTTER

XPS0601.spe: Dean Matson
1999 Dec 2 Al mono 100.9 W 100.0 μ 45.0° 117.40 eV
Su/Area8: #3 242-50-3/1 (SG5) EMSL
1.5287e+05 max 9.70 min

EMSL

13.00 min

1.0000e+00 max

XPS0585.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV

Mo3d/Area1: #1 242-8-2B/1

XPS0585.spe

EMSL

XPS0598.spe: Dean Matson

1999 Dec 2 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV

C1s/Area10: #1 242-8-2B/1.

1.0000e+00 max

2.89 min

XPS0585.spe

XPS0585.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV
O1s/Areal: #1 242-8-2B/1
EMSL
1.0000e+00 max
13.00 min

XP50586.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV
Mo3d/Area2: #2 1327-103-3A/1
1.0000e+00 max
13.00 min
EMSL

XP50586.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV
C1s/Area2: #2 1327-103-3A/1
EMSL

XP50586.spe

XPS0586.spe: Dean Matson

1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV

O1s/Area2: #2 1327-103-3A/1

1.0000e+00 max

13.00 min

EMSL

XPS0586.spe

XPS0587.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV
Mo3d/Area3: #3 242-50-3/1
EMSL
1.0000e+00 max
13.00 min

XPS0587.spe: Dean Matson

1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV

1.0000e+00 max

EMSL

13.00 min

C1s/Area3: #3 242-50-3/1

XPS0587.spe

XPS0587.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV
Ots/Area3: #3 242-50-3/1
EMSL
1.0000e+00 max
13.00 min

XPS0585.spe: Dean Matson
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV
C1s/Area1: #1 242-8-2B/1

INITIAL

EMSL

1.0000e+00 max

13.00 min

XPS0585.spe

AFTER SPUTTER 50A°

XPS0598.spe: Dean Matson

1999 Dec 2 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV

9.9755e-01 max

EMSL

2.89 min

C1s/Area10: #1 242-8-2B/1 (SG5)

XPS0598.spe

INITIAL

XP50585.spe: Dean Matson	1.0000e+00 max	EMSL
1999 Nov 30 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV		
Mo3d/Areal: #1 242-8-2B/1		13.00 min

AFTER SPUTTER 50A⁰

XPS0598.spe: Dean Matson

1999 Dec 2 Al mono 100.9 W 100.0 μ 45.0° 23.50 eV

1.0000e+00 max

EMSL

2.89 min

Mo3d/Area10: #1 242-8-2B/1

XPS0598.spe

Battelle

Pacific Northwest Laboratories
Battelle Boulevard
P.O. Box 999
Richland, Washington 99352
Telephone (509) 375-2759

Aug. 16, 2000

fax (509) 375-3864
e-mail dean.matson@pnl.gov

Mr. David Moy
Hyperion Catalysis International
38 Smith Place
Cambridge, MA 02138

Dave:

Enclosed are the results of Auger electron spectroscopy analysis of the last batch of three tungsten carbide catalyst samples you sent in March. On this batch of samples we decided to go with Auger rather than XPS in order to resolve analyses of individual particles.

Results of analyses performed on sample 242-72-3B2 are included in the attached summary report prepared by the instrument operator. These analyses suggested the presence of iron and aluminum contamination associated with some of the features in the sample. Subsequent discussions with you suggested that this contamination wasn't unexpected and was likely an artifact of the sample preparation. Tungsten concentrations varied depending on the type of feature analyzed, but in general were apparently higher than in the other two samples.

Analyses of the other two samples (242-72-3C2 and 272-72-3D) were performed more recently and after the instrument had had some service performed that allowed some slightly different analytical capabilities. A large area survey scan was performed on each of these samples to assess overall C/W and those results are included in the first two pages of the summaries. These are followed by analyses of individual features within the samples, which indicated that the tungsten distribution was much more heterogeneous than in the first sample, with background areas that contained low concentrations of W. The final pages of these analyses include elemental maps of carbide carbon (as opposed to elemental carbon) and tungsten. As expected, these appear to correlate closely.

I'm also working on getting some TEM work done on these samples. My TEM operator recently left the lab for another job, which I guess explains why he was so nonresponsive in my requests to do your samples. Just last week I identified another operator and then was told that the instrument would be down for two weeks for maintenance. I'll get those results to you as soon as they are available. Please call if you have questions regarding the Auger results.

Regards,

Dean W. Matson
Senior Research Scientist
Materials Resources Division

Enclosures

File	Type	Beam	Mag	location	acquisition comments
WC242c1	survey	10nA20kV	4kX	Full	
WC242c2	survey	10nA20kV	15kX	1: 169/84	long rod
			2: 364/153	short rod	
			3: 385/415	large particle	
			4: 175/298	flat background	
WC242c3	sem	10nA20kV	15kX	Image: WC242c2 survey, WC242c4 W map & WC242c5 C multiplex	
WC242c4	map	10nA20kV	15kX	W2: 1731-1755eV (20swps)	
WC242c5	multiplex	10nA20kV	15kX	1: 169/84	long rod
			2: 175/298	flat background	
WC242d1	survey	10nA20kV	20kX	Full	
WC242d2	survey	10nA20kV	20kX	1: 245/35	rod near top
			2: 248/194	rod in middle	
			3: 277/364	rod near bottom	
			4: 145/275	flat background on left	
			5: 365/195	flat background on right	
			6: 82/135	flat amorphous area on left	
WC242d3	sem	10nA20kV	20kX	Image for WC242d2 survey and WC242d4 W map	
WC242d4	map	10nA20kV	20kX	W2: 1731-1755eV (20swps)	

Tungsten carbide powder (242-72-3B2 3.5:1 A) was mounted on indium foil for analysis. Although reference data of the indium foil was taken, no Auger peaks attributable to indium were observed. Hence all data is representative of the tungsten carbide powder exclusively.

The first analysis was done using a 10nA10kV electron beam at magnification of 20kX. While this beam did not provide the best imaging conditions, data was still taken. Area 1 and 3 appear to be from locations that are not on these 'rods or needles' comprised of 'particles strung together'. In these two areas, there is a large source of 'contamination'. As much as 30% aluminum is detected in addition to iron and phosphorous contamination. While area 3 does not show any evidence of carbide, area 1 does show the presence of carbide. Area 2 does appear to be on one of these needles. This area does not appear to have aluminum or iron contamination, but does have some phosphorous contamination. This area has the highest tungsten and carbon content and the carbon is in the form of carbide.

Analysis #1

Atomic Concentration Table

C	O	Al	P	Fe	W	Location
24.12	17.55	24.53	4.46	1.8	27.54	Area 1
31.51	12.61	---	1.6	---	54.28	Area 2
12.24	11.46	32.08	2.38	1.98	39.86	Area 3

The second analysis was performed on a different particle with a 10nA20kV beam at 15kX. Better imaging capabilities were obtained with this beam. Auger spectra were taken at 5 different locations. Location 1 is on what appears to be an amorphous region. Locations 2, 4, and 5 are on rods and location 3 is on a plate-like area. The composition of the amorphous location shows a significant aluminum content. There is also significantly more oxygen and tungsten and less carbon than in the rod locations. The carbon peak also shows little evidence of carbide. The plate-like location shows much more carbon and much less tungsten than in the rod locations. Here, too, there is little evidence of carbide. Locations 2,4, and 5 (rods) all have similar compositions and the carbon peak is indicative of a carbide.

Analysis #2

Atomic Concentration Table

C	O	Al	W	Location
29.3	24.21	9.1	37.38	Area 1
50.93	15.22	<1.59	32.26	Area 2
73.05	15.04	<1.64	10.26	Area 3
52.28	15.3	<1.60	30.82	Area 4
50.87	16.26	<1.41	31.46	Area 5

The third analysis was also performed on a different particle with a 10nA20kV beam at 15kX. Auger spectra were taken at 5 different locations. Locations 1, 2, and 4 appear to be on rods, whereas location 3 appears to be at an amorphous region and location 5 appears to be on an amorphous particle. On two of the rod locations (1 and 4) there is little aluminum and concentrations of carbon, oxygen and tungsten similar to those found on the rods in analysis #2. On the other rod location (2), there is significant aluminum (4%) and a lower tungsten content (22%). And while there is significant carbide at locations 1 and 4, there is less at location 2. Locations 3 and 5 show a high aluminum content (8%) and an even lower tungsten concentration (18%). There is very little evidence of carbide in these locations.

Analysis #3

Atomic Concentration Table

C	O	Al	W	Location
51.99	12.44	1.13	34.43	Area 1
57.59	16.55	4.19	21.68	Area 2
59.56	14.55	8.05	17.84	Area 3
52.12	16.73	2.47	28.69	Area 4
52.64	21.23	8.52	17.6	Area 5

acwc2423c1

242-72-3C2, Large Area Survey, 7500X, 10nA20kV

File Information

File Name: WC242c1.spe

File Type: AES SPECTRUM

Comment: Tungsten Carbide, survey, 10nA20kV, 7500X, 242-72-3C2

Atomic Concentration Table

C1	O1	W1
[0.076]	[0.212]	[0.091]
93.84	3.61	2.55

WC242c1.spe: Tungsten Carbide, survey, 10nA20kV, 7500X,242-72-3C2
100 May 26 20.0 keV 0 FRR
Surf1/Full1 (S9D5)

8.3564e+003 max

Company Name
15.84 min

Spectrum Skip Auto by 1

acwc242c2

242-72-3C2, 7500X, Point survey, 50swps, 10nA20kV

File Information

File Name: WC242c2.spe

File Type: AES SPECTRUM

Comment: Tungsten Carbide, survey, 10nA20kV, 7500X, 242-72-3C2

Atomic Concentration Table

C1	O1	Fe3	W1
[0.076]	[0.212]	[0.178]	[0.091]
80.39	3.03	1.73	14.84
81.48	2.39	0.82	15.32
95.29	1.90	<0.66	2.15
95.55	2.14	<0.31	<2.00

WC242c2.spe: Tungsten Carbide, survey, 10nA20kV, 7500X, 242-72-3C2
100 May 26 20.0 keV 0 FRR
Sur1/Area1/2 (S9D5)

Company Name
12.67 min

1.1617e+004 max

WC242c2.spe

x 10⁴

Spectrum Skip Auto by 1

WC242c2.spe: Tungsten Carbide, survey, 10nA20kV, 7500X,242-72-3C2
100 May 26 20.0 keV 0 FRR
Sur1/Area1/3 (S9D5)

1.3578e+004 max

Company Name
12.67 min

Spectrum Skip Auto by 1

WC242c2.spe: Tungsten Carbide, survey, 10nA20kV, 7500X, 242-72-3C2
100 May 26 20.0 keV 0 FRR
Sur1/Area1/4 (S9D5)

Company Name
12.67 min

5.7773e+003 max

WC242c2.spe

Spectrum Skip Auto by 1

15kX
~~SEM~~ SEM

WC242d1.spe: Tungsten Carbide survey, 10nA20kV, 20000X, 242-72-3D
100 Jun 2 20.0 keV 0 FRR
Surf1/Full1 (S9D5)

1.2372e+004 max

Company Name
31.68 min

File Information

File Name: WC242d2.spe

File Type: AES SPECTRUM

Comment: Tungsten Carbide survey, 10nA20kV, 20000X, 242-72-3D

Atomic Concentration Table

C1	O1	W1	
[0.076]	[0.212]	[0.091]	
85.36	3.36	11.28	Area 1
74.22	7.11	18.67	Area 2
80.93	2.86	16.21	Area 3
96.66	1.35	2.00	Area 4
96.88	1.63	1.49	Area 5
94.86	1.86	3.28	Area 6

WC242d2.spe: Tungsten Carbide survey, 10nA20kV, 20000X, 242-72-3D
100 Jun 2 20.0 keV 0 FRR
Sur1/Full/1 (S9D5)

1.5694e+004 max

Company Name
15.84 min

Spectrum Skip Auto by 1

WC242d2.spe: Tungsten Carbide survey, 10mA20kV, 20000X, 242-72-3D
100 Jun 2 20.0 keV 0 FRR
Surf1/Area1/2 (S9D5)

1.6712e+004 max

Company Name
15.84 min

WC242d2.spe: Tungsten Carbide survey, 10nA20kV, 20000X, 242-72-3D
 100 Jun 2 20.0 keV 0 FRR
 Sur1/Area1/3 (S9D5)

Company Name
 1.6718e+004 max
 15.84 min

Company Name
15.84 min

Spectrum Skip Auto by 1

WC242d2.spe: Tungsten Carbide survey, 10nA20kV, 242-72-3D
100 Jun 2 20.0 keV 0 FRR
Surf1/Area1/5 (S9D5)

1.5376e+004 max

Company Name
15.84 min

WC242d2.spe: Tungsten Carbide survey, 10mA20kV, 20000X, 242-72-3D	Company Name
100 Jun 2 20.0 keV 0 FRR	15.84 min
Surf1/Area1/6 (S9D5)	1.5849e+004 max

20kx SEM

WC242d3.sem: SEM: Tungsten Carbide survey, 10nA20kV, 20000X, 242-7281 Company Name
100 Jun 2 20.0 keV 0 FAT
SEM/Full

227

SEM

105

20kX SEM

WC242d4.map: Tungsten Carbide survey, 10nA20kV, 20000X, 242-72-3D Company Name
100 Jun 2 20.0 keV 0 FRR 109.23 min
W2/Full

20kX TUNGSTEN MAP

Battelle

Pacific Northwest Laboratories
Battelle Boulevard
P.O. Box 999
Richland, Washington 99352
Telephone (509) 375-2759

Oct. 19, 2000

fax (509) 375-3864
e-mail dean.matson@pnl.gov

Mr. David Moy
Hyperion Catalysis International
38 Smith Place
Cambridge, MA 02138

Dave:

I'm finally getting you some TEM photos of your samples labeled 242-72-3B2, -3C, and -3D. The photos, in .tif format are on the enclosed zip disk (PC format). I'm assuming you have access to a zip drive. If not, let me know and I'll print out hard copies. The files are much too big to copy to floppy disks. I had difficulty opening the files by simply clicking on them, but dragging them onto the Quicktime player icon they popped right up. I was provided no additional information about what we are looking at in the photos other than the sample number.

Also enclosed with this packet is some EDS elemental data on a couple of areas of each sample and some d-spacing analysis done by the TEM operator that indicate the presence of WC.

Let me know if you have any specific questions about the pictures or data and I'll try to dig up the answers.

Regards,

Dean W. Matson
Senior Research Scientist
Materials Resources Department

Enclosures

Operator : alice
Client : Dean Matson
Job : 242-72-3C
3B2 - large (9/21/00 11:13)

cps

Operator : alice
Client : Dean Matson
Job : 242-72-3C
3C- tubes area (9/21/00 14:57)

242-72-3C

d=2.1A

Operator : alice
Client : Dean Matson
Job : 242-72-3D
3Dhr4 (9/22/00 12:02)

Operator : alice
Client : Dean Matson
Job : 242-72-3D
3D particles in tubes (9/22/00 12:15)

cps

242-72-3B2

Operator : alice
Client : Dean Matson
Job : CN 242-72-3B2
3B2 "finger" (9/7/00 17:26)

Operator : alice
Client : Dean Matson
Job : CN 242-72-3B2
3B2 large particle (9/7/00 17:15)

cps

Operator : alice
Client : Dean Matson
Job : CN 242-72-3B2
3B2 light material (9/7/00 17:23)

Operator : alice
Client : Dean Matson
Job : CN 242-72-3B2
3B2 thin carbon film (9/7/00 18:01)

Operator : alice
Client : Dean Matson
Job : CN 242-72-3B2
3B2Hr1 (9/7/00 15:01)

Operator : alice
Client : Dean Matson
Job : CN 242-72-3B2
3B2Hr2 (9/7/00 17:03)

Dohnalkova, Alice

To: Matson, Dean W
Subject: TEM

Dean,

I did a little search based on measurements of the d-spacing found in those samples:

In 242-72-3B2 I found on several occasions lattice fringes with d lines 2.8 Å, which points clearly towards WC (none of the other ratios W:C has this characteristic).

Samples 3C and D look very similar, both have lots of tubes - the whole sample is virtually bunches of tubes with W/C containing material trapped in. The free particle size varies from 5nm to about a hundred nm, with d-spacing 2.1 to 2.3 Å, which are unfortunately the most common characteristics for all the tungsten carbides. W₂C, W₃C (?), even the tungsten itself has (110) on 2.24. Lots of nice "finger-like" structures though.

Enclosing the Jade PDFs, let me know if you need more info, Alice.

Tungsten Carbide

W2C

Radiation=CuK α 1

Lambda=1.5405981

Filter=Graph

Calibration=Internal(W)

d-Cutoff=17.7

I/Ic(RIR)=

Ref= Natl. Bur. Stand. (U.S.) Monogr. 25, 21 128 (1984)

CAS#12070-13-2

Hexagonal - Powder Diffraction, P-3m1 (164)

Z=1

mp=

Cell=2.997x4.7279

Pearson=hP3 (\$GA Cd I2)

Density(c)=17.144

Density(m)=17.27A

Mwt=379.71

Vol=36.78

F(22)=92.9(.0085,28)

Ref= Metcalfe, A.

J. Inst. Met., 73 591 (1947)

NOTE: The sample was obtained from CERAC, Incorporated, Milwaukee, WI, USA. The mean temperature of data collection was 23.5 C. To replace 2-1134.

Color: Dark gray

Strong Line: 2.28/X 2.60/3 2.36/2 1.75/2 1.50/1 1.35/1 1.27/1 1.25/1 0.96/1 1.14/1

22 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = Peak Height

#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	2.5959	25.0	1	0	0	34.523	17.262	0.1926	12	1.0756	2.0	1	0	4	91.469	45.735	0.4648
2	2.3643	22.0	0	0	2	38.028	19.014	0.2115	13	1.0018	3.0	2	0	3	100.507	50.253	0.4991
3	2.2757	100.0	1	0	1	39.568	19.784	0.2197	14	0.9811	1.0	2	1	0	103.468	51.734	0.5096
4	1.7478	17.0	1	0	2	52.299	26.149	0.2861	15	0.9607	5.0	2	1	1	106.610	53.305	0.5205
5	1.4986	14.0	1	1	0	61.859	30.930	0.3336	16	0.9281	3.0	1	1	4	112.185	56.092	0.5387
6	1.3469	14.0	1	0	3	69.767	34.883	0.3712	17	0.9061	1.0	2	1	2	116.447	58.224	0.5518
7	1.2975	2.0	2	0	0	72.837	36.418	0.3854	18	0.8884	2.0	1	0	5	120.234	60.117	0.5628
8	1.2657	12.0	1	1	2	74.977	37.488	0.3951	19	0.8738	1.0	2	0	4	123.645	61.822	0.5722
9	1.2514	10.0	2	0	1	75.982	37.991	0.3996	20	0.8651	1.0	3	0	0	125.836	62.918	0.5779
10	1.1821	2.0	0	0	4	81.325	40.663	0.4230	21	0.8329	3.0	2	1	3	135.292	67.646	0.6003
11	1.1377	3.0	2	0	2	85.225	42.613	0.4395	22	0.8124	2.0	3	0	2	142.923	71.462	0.6154

Tungsten Carbide

W2 C

Radiation=CuKa

Lambda=1.5418

Filter=

Calibration=

d-Cutoff=

$$I/I_c(RIR)=$$

Ref= Rudy, St. Windisch.

J. Am. Ceram. Soc., 50 272 (1967)

CAS#12070-13-2

Orthorhombic - Powder Diffraction, Pbcn (60)

 $Z=4$

mp=

Cell=4.728x6.009x5.193

Pearson=0P12 (O2 Pb)

Density(c)=17.090

Density(m)=17.27A

Mwt=379.71

Vol=147.54

$$F(28)=1.9(0.094, 158)$$

Ref= Ibid.

NOTE: Mo2C(\$GA) isomorphous (\$GZ-Fe2 N type sublattice). W-C (32.6 atomic %C) quenched in tin after equilibration at 2360 C. Impurities: O, 130ppm; N, 60ppm; Fe, 30ppm; Si, 40ppm; Ni and Mo not determined; others, <200ppm.

Strong Line: 2.28/X 2.60/4 1.35/4 0.96/5 0.89/5 0.83/5 0.93/5 1.27/4 0.81/4 0.79/4

33 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = (Unknown)

[illegible]

Tungsten

W

Radiation=CuK α 1

Lambda=1.5405

Filter=Ni

Calibration=

d-Cutoff=

I/Ic(RIR)=18.00

Ref= Swanson, Tatge.

Natl. Bur. Stand. (U.S.), Circ. 539, I 28 (1953)

CAS#7440-33-7

Cubic - Powder Diffraction, Im3m (229)

Z=2

mp=

Cell=3.1648

Pearson=cl2 (W)

Density(c)=19.265

Density(m)=19.20A

Mwt=183.85

Vol=31.70

F(8)=107.7(.0093,8)

Ref= Ibid.

NOTE: Sample prepared at Westinghouse Electric Corp. Analysis of sample shows Si O₂ 0.04%, K 0.05%, Mo, Al₂ O₃ and 0.01% each. Pattern taken at 26 C. Merck Index, 8th Ed., p. 1087.

Color: Gray metallic

Strong Line: 2.24/X 1.29/2 1.58/2 0.85/2 1.00/1 1.12/1 0.91/1 0.79/1 0.00/1 0.00/1

8 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = (Unknown)

#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	2.2380	100.0	1	1	0	40.264	20.132	0.2234	5	1.0008	11.0	3	1	0	100.647	50.324	0.4996
2	1.5820	15.0	2	0	0	58.274	29.137	0.3161	6	0.9137	4.0	2	2	2	114.924	57.462	0.5472
3	1.2920	23.0	2	1	1	73.195	36.598	0.3870	7	0.8459	18.0	3	2	1	131.178	65.589	0.5911
4	1.1188	8.0	2	2	0	87.021	43.511	0.4469	8	0.7912	2.0	4	0	0	153.590	76.795	0.6320

W

Filter=

$$I/I_c(RIR)=$$

J. Electrochem. Soc., 138 767 (1991)

mp=

Pearson=cP8 (\$GB Cr3 Si)

$$F(9)=999.9(.0002,14)$$

Ref= Ibid.

Cl₂, Na Cl and W Cl₆ and 350 mv and a total deposition charge of 25 coulombs/cm².

9 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = (Unknown)

[illegible]

CW3

Filter=

$$I/I_c(RIR)=$$

Thin Solid Films, 95 105 (1982)

mp=

Pearson=cP8 (Cr3 Si)

$$F(12)=12.0(0.050,20)$$

Ref= Ibid.

NOTE: Thin film.

Strong Line: 2.25/X 2.05/X 1.34/9 1.10/5 0.93/5 1.40/4 2.52/4 1.26/4 0.92/3 1.13/3

13 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = (Unknown)

[illegible]

Tungsten Carbide

W C1-x

Radiation=CoKa

Lambda=1.7902

Filter=Fe

Calibration=

d-Cutoff=

I/Ic(RIR)=

Ref= Krainer, Robitsch.

Planseeber. Pulvermetall., 15 46 (1967)

CAS#12070-12-1

Cubic - Powder Diffraction, Fm3m (225)

Z=4

mp=

Cell=4.2355

Pearson=cF8 (C1 Na)

Density(c)=17.121

Density(m)=15.13A

Mwt=195.86

Vol=75.98

F(8)=4.7(0.242,7)

Ref= Ibid.

NOTE: Phase homogeneity from 37.5 atomic % C (at 2525 C) to 50 atomic % C (at 2785 C). Formed by spark erosion. cf. 20-1309.

Strong Line: 2.11/X 1.28/5 2.43/4 0.97/4 0.95/4 1.50/3 1.06/2 1.22/1 0.00/1 0.00/1

8 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = (Unknown)

#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	2.4290	40.0	1	1	1	36.977	18.489	0.2058	5	1.2210	10.0	2	2	2	78.227	39.114	0.4095
2	2.1070	100.0	2	0	0	42.887	21.443	0.2373	6	1.0610	15.0	4	0	0	93.103	46.552	0.4713
3	1.4950	30.0	2	2	0	62.027	31.013	0.3344	7	0.9730	40.0	3	3	1	104.681	52.340	0.5139
4	1.2770	50.0	3	1	1	74.198	37.099	0.3915	8	0.9480	40.0	4	2	0	108.688	54.344	0.5274

WB C2.54

Filter=

$$I/I_c(RIR)=11.06$$

ICDD Grant-in-Aid

mp=

Pearson=hP8.54 (\$GE-Fe2 N)

$$F(23)=35.2(.0093, .70)$$

Acta Chem. Scand., Ser. A, 32 891 (1978)

23 Lines. Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = Peak Height

[illegible]

Unnamed mineral, syn [NR]

W C

Radiation=CuK α 1

Lambda=1.54056

Filter=

Calibration=

d-Cutoff=

I/I_c(RIR)=

Ref= Bind, McCarthy, G., Penn State Univ, University Park, PA, USA.

ICDD Grant-in-Aid (1973)

CAS#12070-12-1

Hexagonal - Powder Diffraction, P-6m2 (187)

Z=1

mp=

Cell=2.9062x2.8378

Pearson=hP2 (C W)

Density(c)=15.664

Density(m)=15.13A

Mwt=195.86

Vol=20.76

F(14)=28.6(0.035,14)

Ref= Ibid.

NOTE: Sample obtained from General Electric, type KB, lot no. 131412. To replace 5-728. Described as a mineral from Mengyin, Shadong and Danba, Sichuan, China. Zianhong, Z., Guojie, Y., Zhaojni, L., Acta Mineral. Sinica, 6 344-349 (1986).

Strong Line: 2.52/X 1.88/X 2.84/5 1.24/3 1.29/3 1.45/2 1.15/2 0.90/2 1.26/1 1.02/1

14 Lines, Wavelength to Compute Theta = 1.54056A(Cu), I%-Type = (Unknown)

#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(A)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	2.8400	45.0	0	0	1	31.474	15.737	0.1761	8	1.2360	30.0	1	0	2	77.101	38.550	0.4045
2	2.5180	100.0	1	0	0	35.626	17.813	0.1986	9	1.1510	20.0	2	0	1	84.015	42.007	0.4344
3	1.8840	100.0	1	0	1	48.266	24.133	0.2654	10	1.0150	14.0	1	1	2	98.734	49.367	0.4926
4	1.4540	20.0	1	1	0	63.979	31.990	0.3439	11	0.9510	10.0	2	1	0	108.186	54.093	0.5258
5	1.4200	6.0	0	0	2	65.701	32.851	0.3521	12	0.9460	1.0	0	0	3	109.026	54.513	0.5285
6	1.2940	25.0	1	1	1	73.064	36.532	0.3864	13	0.9420	10.0	2	0	2	109.712	54.856	0.5308
7	1.2590	14.0	2	0	0	75.442	37.721	0.3971	14	0.9020	20.0	2	1	1	117.292	58.646	0.5543