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Characterization and investigation of molybdenum carbides on activated carbon as hydrogenation catalysts

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Characterization and Investigation of Molybdenum Carbides on Activated Carbon
as Hydrogenation Catalysts

By

Christopher H. Clark

A THESIS

Submitted to the College of Engineering and Mineral Resources
at West Virginia University
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Master of Science
in
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Edwin L. Kugler, Chair
Dady B. Dadyburjor
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temperature-programmed-reaction, carbon-monoxide chemisorption

Abstract

Characterization and Investigation of Molybdenum Carbides on Activated Charcoal as a Hydrogenation Catalysts

Christopher H. Clark

The formation of Mo_2C and MoC supported on activated carbon was investigated in three different flowing reaction gas environments: H_2 , He , and CO . Additionally, benzene hydrogenation activity was studied for the catalysts reduced in each of these three different gas environments.

It was found through in-situ x-ray diffraction (XRD) that reducing in H_2 , ammonium heptamolybdate impregnated on activated carbon yielded 1-3 nm Mo_2C particles. When the same material was calcined in inert, 9 nm Mo_2C particles were formed. If the reduction gas were CO , MoC particles having size less than 3 nm were formed. In all three reduction environments, the in-situ XRD revealed that MoO_2 reduced to molybdenum carbide, without the appearance of Mo^0 . Data from temperature programmed reaction (TPR) spectra compared to the in-situ XRD patterns indicates that the carbon support is the source for carburization.

Only the catalyst reduced in H_2 has significant activity for benzene hydrogenation. Furthermore, these Mo_2C -on-carbon catalysts have only a small range of reduction temperatures, 675-825°C, for which they are active. Additionally, as soak time at reduction temperature increases, the catalyst's initial activity decreases. Activity seems to be correlated to the appearance of graphitic carbon in the XRD patterns of the spent catalyst.

Dedicated to my grandfather, Paul Franklin

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1. Introduction

In recent years, West Virginia University, along with many schools across the country and around the world, have sought to investigate the synthesis, characteristics, and potential reaction niches of molybdenum-based catalysts. One such reaction is the platinum-like behavior of molybdenum carbide for hydrogenation reactions (1). Due to its low cost, in comparison to platinum, molybdenum carbide is worthy of further investigation.

There are currently several proposed methods for preparing molybdenum carbides. The specific method of interest involves the reduction of ammonium heptamolybdate impregnated on activated carbon (2,3). Using H_2 as a reduction gas, this method has been shown to form small particles of Mo_2C between 700-800°C. Through Debye-Scherrer peak-broadening analysis of the x-ray diffraction pattern, the Mo_2C formed has been shown to have average particle sizes of 3 nm (2). Further studies done at the Université de Pierre et Marie Curie and West Virginia University show that larger-particle Mo_2C can be formed between 750-850°C by using the same impregnation method for catalyst preparation, but the catalyst pretreatment environment is changed from H_2 to Ar (2). Work done to date at West Virginia University has revealed that MoC, a cubic crystal-structure form of molybdenum carbide referenced less often than Mo_2C , can also be formed. This MoC on activated carbon catalyst is prepared using the same impregnation method, but the pretreatment gas is changed to CO and the MoC is formed between 550-650°C.

It is the purpose of this research to characterize these molybdenum-on-carbon catalysts prepared under three different flowing gas environments: H_2 , inert, and CO. Methods of characterization include x-ray diffraction for identification of bulk phases, CO chemisorption for

titration of the surface reaction sites, and kinetic studies of the benzene hydrogenation reaction to provide evidence of noble-metal-like activity.

2. Literature Review

2.1 Molybdenum Carbide Preparation Methods

Investigation of Group VI B transition metal carbides was pioneered by Boudart's group at Stanford University. This group proposed that these carbides could be made through the direct carburization and reduction of unsupported MoO_3 by flowing a gas mix of 20% CH_4 (balance H_2) over the sample at high temperature (4). This reduction method yields hexagonal Mo_2C at a temperature of approximately 700°C . This reduction was first observed through a temperature-programmed reaction (TPR) in 20% CH_4 (balance H_2) performed from room temperature to 825°C at 60°C per hour (4). The Stanford group later reported that this process yields Mo_2C particles of 11.5 nm, as found from XRD peak broadening (5). In this work done at Stanford, there is much care taken to keep graphitic carbon from occluding the molybdenum carbide surface. Equation 1 is the mechanism for the carburization of MoO_3 to Mo_2C , as proposed by Boudart's group (4). Equation 2 gives a possible side reaction thought to cause catalyst deactivation by graphitic carbon formation. Figure 1 shows the equilibrium relationship between Equation 1 and Equation 2 at atmospheric pressure as shown by Lee et al. (4). In Figure 1, curve (a) represents equilibrium data for Equation 1 and curve (b) represents equilibrium data for Equation 2. Where the x-axis is temperature in K and the y-axis is % CH_4 (balance H_2). For carburization conditions on the left of curve (a) only Mo and CH_4 should be observed. If temperature is increased, and carburization conditions move beyond curve (a), but below curve

(b) only Mo_2C and CH_4 should be observed. Finally, if temperature is high, where carburization conditions are above line (b), Mo_2C and graphite should be observed.

Figure 1: Plot of Equilibrium Conditions for Equation 1 and Equation 2. Plot constructed by Lee et al. (4)

From Figure 1, it was reported that the optimum balance between molybdenum carbide formation from Mo^0 and prevention of graphite formation on the Mo_2C occurred at a 20% CH_4 (balance H_2). Conditions were chosen for carburization to stay in the phase regime of Mo_2C and CH_4 .

Other methods of molybdenum carbide formation proposed by the Stanford Group include the preparation of cubic MoC through doping MoO_3 with a low concentration of Pt and performing the same TPR in 20% CH_4 (balance H_2) (5). This method formed MoC at

approximately 700°C. The particles formed in this method are very small, 3.4 nm as measured by x-ray line broadening.

Yet another method proposed by the Stanford Group for forming cubic MoC, is first to form Mo₂N with flowing 20% NH₃ (balance H₂) up to 700°C. After initially forming Mo₂N, one can form MoC using TPR in 20% CH₄ (balance H₂). This method forms MoC at approximately 700°C (5). As these particles are 6 nm, as measured by x-ray line broadening, it is postulated that small MoC particles are formed from small Mo₂N precursors (5).

Similar TPR methods with 20% CH₄ (balance H₂) have been used to form Al₂O₃ - supported Mo₂C (6). This involves first impregnating γ -Al₂O₃ with ammonium heptamolybdate (AHM), then calcining in air at 500°C for 5h. The catalyst is then carburized using TPR in 20% CH₄/balance H₂ up to 900°C. This method yields 7.8 nm Mo₂C particles, as measured by x-ray line broadening. These supported Mo₂C nanoparticles are formed at approximately 700°C (6).

More recently, another method of Mo₂C preparation was discovered by a group at Université of Pierre et Marie Curie(2). This method does not utilize methane or MoO₃. Instead the Mo₂C is prepared by impregnating activated carbon with AHM and then heating the sample to 700°C in flowing H₂ (2,3). In yet unpublished work, x-ray diffraction peak broadening predicts that the Mo₂C particles formed by the West Virginia University group are 3 nm in size. Furthermore, larger particles of Mo₂C can be formed by simply pretreating the molybdenum impregnated carbon catalyst in flowing inert gas.

Mordent et al. propose the following mechanism for the reduction of MoO₂ on activated carbon to Mo₂C in inert gas (2):

It is proposed that water is present in the carbon support material reacts with carbon to form carbon monoxide. The water then reacts with carbon monoxide, in Equation 4, to produce the hydrogen needed for reduction. Methane can then be formed by the hydrogenation of carbon (Equation 6) or the hydrogenation of CO (Equation 7). Finally, the methane and hydrogen react with the molybdenum dioxide (Equation 8) to form Mo_2C . The reaction in Equation 8 is similar to that proposed for unsupported MoO_3 particles (4).

The reaction scheme proposed by Mordenti et al. (Paris Group), Equations 3-8, is significantly different than that proposed by the Stanford Group. The Paris Group's mechanism has Mo_2C formed from MoO_2 . However, the Stanford Group has Mo_2C formed from Mo^0 .

A recent unpublished investigation by the West Virginia University group has revealed that cubic MoC can be formed by a new synthesis method. MoC is formed through the reduction of a molybdenum-on-carbon catalyst in 5% CO (balance inert). The molybdenum –on-carbon precursor material is prepared by impregnating AHM on activated carbon. Preliminary estimates of particle size by x-ray peak broadening have shown that these particles are 3 nm or less (7).

The review of the literature shows that the study of molybdenum carbide catalysts has focused on unsupported Mo_2C having particle sizes ranging from 3.4-to-11.5 nm (5,6). It is then interesting that the carbon-supported molybdenum-carbide catalysts of West Virginia University have a smaller particle size, 1-3 nm size evident by scanning tunneling micrographs, on a support that can offer high pore volume and surface area.

2.2 Molybdenum Carbide as a Catalyst

Boudart's group at Stanford concluded that molybdenum carbide behaved in many ways like a Group VIII metal (1), but noted that the activity of the catalyst was limited by the surface area (4). They advocated that a synthesis method should be developed that yields high-surface-area carbides (4).

Since this initial investigation, a myriad of reactions have been tested for activity over molybdenum carbide. The most prominent reactions reported in the literature are: Fischer-Tropsch synthesis (1), alkene hydrogenation (7-10), aromatic hydrogenation (6,11-14), hydrodenitrogenation (15-19), hydrodesulfurization (8,20-21), hydrocarbon reforming (22-26), isomerization (27-28), aromatization (29-31), and ammonia synthesis (32). To insure only pertinent background is provided, only Fischer-Tropsch synthesis, alkene and aromatic hydrogenation, hydrodenitrogenation, and hydrodesulfurization will be surveyed.

Like most noble metals, molybdenum carbides have been shown to be active hydrogenation catalysts (1). As mentioned previously, this was initially studied on CO hydrogenation reactions, generally termed Fischer-Tropsch synthesis (1). Lee et al. (6) report that molybdenum and tungsten carbides have better initial activities for this reaction than ruthenium-on- Al_2O_3 . However, all molybdenum carbide catalysts tested for hydrocarbon and aromatic hydrogenations deactivated very quickly (6,9,11-13). Unsupported Mo_2C catalysts, prepared by the CH_4/H_2 TPR method, are active for aromatic hydrogenation and can be regenerated (9,12). Further, the degree of carburization has a significant effect on activity (13). The effect of degree-of-carburization on aromatic hydrogenation was performed by varying CH_4/H_2 ratio and temperature (13). This study showed, that for the unsupported Mo_2C , there is an optimum temperature and CH_4/H_2 ratio that leads to the highest aromatic hydrogenation

activity and density of CO chemisorption sites (13). Unsupported and Al_2O_3 -supported Mo_2C catalysts were comparable to an Al_2O_3 -supported Ru catalyst for benzene hydrogenating activity at room temperature (6,13). Other research groups have studied molybdenum carbide activity for alkene hydrogenation. One such group at Université Henri Poincaré concluded that Mo_2C was very active for propene hydrogenation and could be regenerated with no significant change in activity (6).

Another reaction that Mo_2C has been reported to catalyze is the hydrodenitrogenation of nitrogen containing aromatics, such as indole and quinoline (15-16). Schlatter et al. report that unsupported Mo_2C , prepared by the method proposed by the Stanford group, uses less H_2 than the commercial Ni-Mo/ Al_2O_3 (15). Additionally, the unsupported Mo_2C catalyst retains its activity longer in the presence of sulfur. Although this is a promising result, on an equal mass of metal basis, the unsupported Mo_2C is about half as active as the commercial Ni-Mo/ Al_2O_3 catalyst at the desired selectivity of propylbenzene to propylcyclohexane, the two major products of the quinoline hydrodenitrogenation (15).

MoC has been tested with limited success for the hydrodesulfurization of thiophene. It was determined (through differences in chemisorbed CO concentration before and after the reaction) that the surface was being sulfided, even though XRD shows the bulk is unchanged. Although the reaction rate is high in the initial hours of the reaction, once the catalyst surface is sulfided, the reactivity is comparable to Mo/ Al_2O_3 (21).

The reactions cited above give a wealth of information about reaction conditions and catalytic behavior. The literature proposes that molybdenum carbides are excellent hydrogenation catalysts, with activity comparable to supported Group VIII metals. Further studies on hydrodenitrogenation and hydrodesulfurization reactions show that molybdenum

carbide is marginally susceptible to sulfide poisoning. Review of the literature further suggests that few studies have been performed on carbon-supported molybdenum carbide catalysts.

2.3 Characterization Techniques

For this study, four different catalyst characterization techniques were used. The goal of this study was to characterize the catalyst bulk, to characterize the catalyst surface, and correlate the two characterizations to catalytic performance for benzene hydrogenation. The characterization techniques proposed are: temperature programmed reaction (TPR), CO chemisorption, H₂ chemisorption, and XRD. Basic theory and usage will be provided for each.

Powder x-ray diffraction seeks to probe the major crystalline phases in the bulk of a material, in this case the catalyst. X-ray diffraction is the uniform interaction of x-rays with crystalline materials. Strong X-ray diffraction is observed when the x-ray wavelength approaches the interatomic distances in a molecule (33). When this material is a single crystal, the diffraction has less secondary diffraction, leading to little or no interference. This gives a noiseless diffraction of spots on an x-ray image plate. The more amorphous a material is, the more interference there is in the diffraction.

A powder diffraction pattern is normally a plot of the scanning angle 2θ on the ordinate vs. intensity on the abscissa. When analyzed using theoretical calculations for simple crystalline material and measured values for more complex crystal structures, one can match the peaks and determine the major crystalline components of the bulk phase (33). One example of a powder diffraction apparatus used for in-situ experiments at the National Synchrotron Light Source (NSLS) is given in Figure 2.

Figure 2: Schematic of Powder Diffraction Measurement at NSLS Beamline X7B (figure provided by Jonathan Hanson at NSLS)

In Figure 2, the sample is in a single-crystal sapphire tube. The synchrotron x-rays then bombard the sample and are scattered to the image-plate detector. Since sapphire is a single crystal, it diffracts x-rays as spots through Bragg diffraction while the powder diffracts as rings. The spots are subtracted as background and the rings averaged and analyzed (34). The setup, shown in Figure 2, allows the use high temperature, high pressure, and gas flow in experimentation, making it useful for in-situ material science and catalysis studies (35).

Temperature-programmed reaction (TPR) is the heating of a material at a specific rate in an environment with a reactant gas, usually CO, CH₄, or H₂, to observe when the reactant gas is consumed. The temperature at which a reducing agent is consumed usually corresponds to a reduction in oxidation state in a metal. Through proper use of this method, multiple reduction steps can be characterized. TPR is an excellent starting point when exploring the proper preparation method for a test system or a preliminary probe into oxidation state transitions (2-4). It should be noted that analysis of simple systems is fairly easy, as metallic oxide reduction temperatures are prominent in catalysis and metallurgy literature, but more complex systems

require either a TPR apparatus attached to a mass spectrometer or a way of modeling the underlying peak structure (2,3).

The characterization methods discussed thus far can be used to characterize the bulk of the material. However, catalyzed reactions occur on the surface or in the pores of the catalyst. The proposed method of characterizing the surface seeks to measure the amount of a chemisorbing species, either CO or H₂, taken up by the catalyst.

In the pulse chemisorption method, an activated catalyst sample is placed in inert flow at a fixed temperature. Usually, the exit gas is analyzed by a gas chromatograph or mass spectrometer and set as a background. Then, a known-volume pulse of absorbing gas is injected into the flow system and allowed to adsorb on the catalyst. This pulse procedure is repeated until the measured pulse-peak areas become constant. This occurs when surface sites are saturated. The amount of adsorbate gas taken up by the catalyst is calculated as the difference between the measured peak areas and the peak areas expected if no gas is adsorbed (36).

3. Materials and Methods

3.1 Catalyst Preparation

Samples were prepared by first impregnating activated carbon (from Sigma-Aldrich) with a 0.100 g/L aqueous solution of ammonium heptamolybdate (Sigma-Aldrich, P.A. grade), followed by drying in air at 100°C. Multiple impregnations were used in achieving the desired loading (37). All temperature-programmed-reaction studies and benzene hydrogenation studies were performed on catalyst having an approximate Mo metal loading of 13%. In-situ XRD studies were carried out on molybdenum-on-carbon samples in which the AHM was

predecomposed in N_2 at 500°C. The Mo loadings for the catalysts used for in-situ XRD were between 18% and 24% (37). This high metal loading allowed for clearer XRD patterns.

3.2 Benzene Hydrogenation Reaction Setup

A simple gas-phase, down-flow tubular reactor was constructed in which to carry out low-temperature benzene hydrogenation experiments. Figure 3 is a flow diagram of the constructed unit. The reaction was carried out in an 11.5" long stainless-steel tube with an outside diameter of 1/4". A quartz wool plug was placed 7" down the reactor and the catalyst bed was directly above. An Omega 1/16" type K thermocouple, placed at the top of the catalyst bed, was used for temperature control. The reactor bed was heated by an Applied Test Systems clam-shell-style tube furnace controlled by an 8 segment Yokogawa 351A temperature controller. Gas flow through the reactor was controlled using three Brooks 5890 mass flow controllers (MFC). The MFC used to control H_2 flow was calibrated for 0-50 sccm of He flow. This controller was tested and a correction factor applied for ultra high purity (UHP) H_2 . The MFC's used for He and 10%CO (balance He) were calibrated for 0-100 sccm of He. These controllers were also calibrated and a correction factor applied. The calibrations for these controllers can be found in Appendix A.

3.3 Reduction and Calcination of Benzene Hydrogenation Catalysts

Molybdenum-on-carbon samples were reduced in the reactor where the sample was not exposed to air between reduction and benzene hydrogenation. During either reduction or inert-gas calcination, gas flow was 34 sccm, as measured by a "bubble" type flow meter and a stop watch. The catalyst sample was purged for approximately 5 minutes with the gas flow prior to

Figure 3: Flow diagram of catalyst test unit constructed for use in testing benzene hydrogenation activity

heating. The sample was then heated to desired reduction temperature, always at 10°C per minute.

3.4 Benzene Hydrogenation Procedure

Sigma-Aldrich (99.9%) benzene was introduced into the system using a 25 mL glass saturator, hand blown by Sherman Adams in the WVU chemistry department, and held at 1°C. This saturator allowed the reaction gas to bubble through the liquid benzene. The saturator was connected to the system through the use of ¼" Cajon compression fittings with viton o-rings to prevent gas leaks. The saturator was purged for no less than 36 h with UHP H₂ before a series of reaction studies. This long purge was an attempt to remove all dissolved air from the benzene. During benzene hydrogenation reactions, the saturator was kept at 1°C.

The effluent gas was sampled using a Valco six-port valve and a Valco 2-mL sample loop. The sample was analyzed by the thermal conductivity detector (TCD) of a Hewlett Packard 5890 Series II gas chromatograph. A 6' 35% BC-150 on 100/120 Chromosorb P AW 1/8" stainless steel packed column was used to separate the analytes (cyclohexane and benzene); this column is designed for aromatic analysis of gasoline. The results of a test separation of cyclohexane and benzene are provided in Appendix B. The GC oven was kept isothermal at 120°C with a typical analysis time being 5 minutes.

For all benzene hydrogenation tests, benzene conversions were kept below 12%, in most cases below 5%, to use the differential reactor model for calculating reaction rate.

3.5 X-ray Diffraction (XRD)

Time resolved (in-situ) x-ray diffraction and powder x-ray diffraction of molybdenum-on-carbon samples were carried out at beamline X7B at the National Synchrotron Light Source

Figure 4: Labeled pictorial diagram of in-situ XRD flow cell (35)

(NSLS) at Brookhaven National Laboratory (BNL) in Upton, NY. Simultaneous temperature-programmed reaction and XRD were carried out in a fixed-bed-sapphire-tube micro-reactor shown in Figure 4 (35). The micro-reactor was designed and machined by the catalysis group at BNL.

Temperature control for the apparatus was provided using an un-insulated 24 AWG Kanthal wire coiled around the sample, functioning as a simple resistance heater. A small loop is placed in the wire to prevent the Kanthal wire from interfering with x-ray diffraction. Gas flow through the sapphire tube was kept at approximately 20 mL per minute for all in-situ XRD runs. The synchrotron x-rays used had an approximate wavelength of 0.92 angstroms. The distance from the sample to the image plate detector varies, but was calibrated each visit using a LaB₆ standard (34). All x-ray calibration data is provided in Appendix C.

Spent catalyst samples, used in benzene hydrogenation experiments, were run in 0.5 mm quartz micro-capillaries using beamline X7B with an image plate detector. Spent catalysts were run ex-situ, with no flowing gas, or heating element.

3.6 Temperature Programmed Reaction (TPR)

Temperature programmed reaction (TPR) was carried out in a Micromeretics AutoChem 2920 with the effluent gas analyzed by a ThermoONIX Prima dB scanning sector mass spectrometer. This apparatus was set up and is operated by the catalyst characterization group at the National Energy Technology Laboratory (NETL) in Morgantown, WV. A block flow diagram of the experimental setup is shown in Figure 5. These experiments were carried out using 150 mg of catalyst under 50 sccm of flowing H₂/Ar (5/95), CO/He (10/90), and Ar (Linde UHP 99.999%).

Figure 5: Flow diagram of TPR-MS apparatus at the National Energy and Technology Laboratory in Morgantown, WV.

3.7 CO Chemisorption

Measurements of chemisorbed CO were made on both commercial Pt/Al₂O₃ catalyst (manufactured by Pressure Chemical) and molybdenum-on-carbon catalysts. CO chemisorption was performed on a unit constructed “in-house” for use in TPR experiments (3). A flow diagram of the apparatus is provided in Figure 6. During the operation of the apparatus shown in Figure 6, reduction gas flows first through the reference of the TCD of a Hewlett Packard 5890 Series II gas chromatograph (GC), then through the sample. Upon exit of the reference of the GC, but prior to the sample, the gas flows through a six-port dosing valve. Through the use of this valve, known volumes of a gas (such as CO or H₂) can be used to titrate the catalyst sample. The sample off-gas is then measured by GC.

Before chemisorption measurement, the samples are first reduced in approximately 30 ccm of flowing reduction gas, either 5%H₂ (balance Ar), UHP H₂, or 10%CO (balance Ar). The samples are then cooled in Ar flow (30 ccm) to 100°C. Once cooled, pulses of 250 µL of either 5%H₂ (balance Ar) or 10% CO (balance Ar) are dosed over the sample. The dosing is performed using a Valco six-port valve and a Valco 250µL loop. The sample is dosed with CO or H₂ until the gas concentration eluted from the sample was constant. Constant gas concentration is determined by monitoring the eluted peaks using a GC-TCD. Once the eluted peak area is found to be constant the sample is said to be saturated and dosing is terminated (36).

Figure 6: Flow diagram of chemisorption and TPR apparatus constructed in the West Virginia University reactions engineering laboratory

3.8 Safety

The chemicals used in these experiments are ammonium heptamolybdate, activated carbon, benzene, acetone, 5% H₂ gas (balance inert), 5% CO gas (balance inert), 10% CO gas (balance inert), UHP H₂, UHP He, UHP Ar, and cryogenic solid CO₂. The MSDS for ammonium heptamolybdate state that exposure to the skin should be avoided and ingestion prohibited. For activated carbon, skin exposure and ingestion of large quantities should be avoided. Benzene safety precautions include a warning against skin contact and a prohibition of ingestion or inhalation. Benzene is a flammable liquid so that it should keep away from open flames and other ignition sources. Great care must be taken to prevent inhalation, ingestion, or skin exposure as benzene is a suspected carcinogen. Acetone safety precautions include a warning against skin contact and a prohibition of ingestion, but go on to include flammability precautions that state one should keep it away from open flames and other ignition sources. All of the gases pose certain inhalation hazards, but the CO permissible exposure limit (PEL) is 50 ppm (39). Electronic monitoring is present near the work area to warn of exposure. He, Ar, CO₂ and 5% H₂ (balance inert) are asphyxiators so that they pose a danger if they displace air from the lab. Hoods eliminate inert-gas hazard by bringing fresh air into the lab. UHP H₂ is flammable, but 5% CO (balance inert), 10% CO (balance inert), and 5% H₂ (balance inert) are not flammable. The gas cylinders, 5% H₂ (balance Ar), 5% CO (balance He), 10% CO (balance Ar), UHP H₂, UHP He, and UHP Ar, are secured to the walls by chains and connected with stainless steel tube. Periodic checks for leaks are made. Additionally, the reactor outlet after gas sampling is plumbed directly to the hood to prevent any gas or vapor inhalation. For solid cryogenic CO₂, proper attire is worn, cryogenic gloves, goggles, and a lab coat, and a Dewar flask was used for cryogenic transport.

4. Results and Discussions

4.1 Benzene Hydrogenation

Benzene hydrogenation was carried out in the reactor shown in Figure 3 and described in Section 3.2. Reduction and benzene hydrogenation were carried out by methods described in Section 3.3 and Section 3.4. All molybdenum-on-carbon catalysts were approximately 13 wt.% molybdenum (metal basis), in the form of AHM, on the activated carbon support.

Figure 7 is a plot of the rate of disappearance of benzene for all catalysts prepared in a UHP H₂ reduction environment with a soak time of 15 minutes. The rate of disappearance of benzene is defined by the design equation for a differential reactor, Equation 9 (40).

$$-r_{benzene} = \frac{F_{Benzene\ 0} X_{benzene}}{W} \quad (9)$$

Where, $-r_{benzene}$ is the rate of consumption of benzene, $F_{benzene\ 0}$ is the inlet molar flow of benzene, $X_{benzene}$ is benzene conversion based on gas chromatography, and W is the weight of catalyst used in the experiment. Detailed calculations of $-r_{benzene}$ are given in Appendix D.

The major notable feature of Figure 7 is that all molybdenum-on-carbon catalysts, reduced in UHP H₂, have rates of reaction one order-of-magnitude less than that of the commercial 5% Pt/Al₂O₃. When looking at Figure 8, where the commercial Pt/Al₂O₃ catalyst is not displayed, it is clearly seen that reduction temperature is a key variable in catalyst preparation. However, there is an optimum reduction temperature, 825°C, above which the molybdenum-on-carbon catalysts are less active. The effect of changing soak time at the optimum reduction temperature, 825°C, is shown in Figure 9. As soak time increases the catalyst activity decreases. Once the soak time reaches 1 h, benzene hydrogenation is not observed.

Figure 7: Effect of time on stream and final reduction temperature on the rate of disappearance of benzene for molybdenum-on-carbon Samples reduced in UHP H₂ and held at final temperature for 15 minutes (for data comparison for commercial 5% Pt/Al₂O₃ is also shown)

Figure 8: Effect of time on stream and final reduction temperature on the rate of disappearance of benzene for molybdenum-on-carbon Samples reduced in UHP H₂ and held at final temperature for 15 minutes

Figure 9: Effect of time on stream and soak time at final reduction temperature (825°C) on the rate of disappearance of benzene for molybdenum-on-carbon catalysts

All catalysts in Figures 7,8,and 9 deactivated quickly. This is consistent with findings in the literature for Al_2O_3 supported and unsupported Mo_2C (6, 11-13). This deactivation is most likely due to residual air dissolved in the benzene (12). This air is undetectable to the GC-TCD as its concentration is below the sensitivity limits of the detector. This oxygen is expected to passivate the surface with unreactive MoO_2 (4).

No benzene hydrogenation activity was observed for molybdenum-on-carbon catalysts calcined in He (presumed Mo_2C) or reduced in CO (presumed MoC). Calcination possibly leads to uncontrollable build-up of surface carbon. This phenomenon will be discussed further in Section 4.4. Additionally, if CO reduction is used for preparation, chemisorbed CO could block reaction sites (12).

4.2 XRD of Spent Benzene Hydrogenation Catalysts

Post-run XRD was performed for the catalysts reduced in UHP H_2 and subsequently tested for benzene hydrogenation. This analysis was revealing as to the nature of the benzene hydrogenation deactivation as either reduction temperature or soak time at temperature increased.

Figure 10 shows the analysis of XRD performed on a spent-catalyst reduced at 825°C and held at 825°C for 1h, and then tested for benzene hydrogenation activity. XRD was performed at beamline X7B at the National Synchrotron Light Source at Brookhaven National Laboratory, by methods described in Section 3.5. Clear lines for Mo_2C are found between 2θ values of 20° and 28° . Strong lines for SiO_2 impurities appear at 2θ values of 12° and 16° . Additionally, a weak line for graphite appears at a 2θ value of 26° . Although this assignment for graphite seems difficult, the peak at 26° 2θ could not be assigned to any other structure with Mo, Si, O, or C through use of the International Center for Diffraction Database and the XRD

Figure 10: XRD pattern of molybdenum-on-carbon catalyst tested for benzene hydrogenation, catalyst was reduced at 825°C and held at 825° C for 60 minutes

analysis software JADE. Since no other significant impurities have been seen in XRD or elemental analysis, it is believed this assignment is correct. The small intensity of the peak is most likely due to the weak scattering of carbon due to its small molecular weight (33). Of the catalysts tested, this one had the most intense peaks for graphite and for Mo₂C, but had no catalytic activity for benzene hydrogenation.

Figure 11 shows the analysis of XRD performed on a catalyst reduced at 825°C for 15 minutes. Clear, strong lines are found for Mo₂C between a 2θ value of 20° and 28°. Lines for the SiO₂ impurities appear at 2θ values of 12° and 16°. Interestingly, there is only an extremely weak, arguably non-existent, peak for graphite at a 2θ value of 26°. Unlike the catalyst in Figure 10 which has strong lines for Mo₂C and much more intense lines for graphite, but was inactive for benzene hydrogenation, the catalyst in Figure 11 is the most stable and the second-most active for benzene hydrogenation.

Figure 12 shows the growth of the graphite peak at a 2θ value of 26.2° with soak time at 825°C in UHP H₂. Clearly the longer the molybdenum-on-carbon sample stays at high temperature the more prevalent this XRD line for crystalline graphite is. It is theorized that this crystalline graphite is occluding the Mo₂C surface preventing reaction. This is similar to graphitization proposed by the Stanford Group on unsupported Mo₂C (4).

Figure 13 shows the analysis of XRD performed on a catalyst reduced at 775°C for 15 minutes. Again, XRD on this sample was performed at beamline X7B at the National Synchrotron Light source at Brookhaven National Laboratory using methods described in section 3.2. When looking at this, sample lines for the SiO₂ impurities are the only distinguishable lines that appear. The non-existence of Mo₂C lines is strange due to the significant benzene hydrogenation activity observed on this sample.

Figure 11: XRD pattern of molybdenum-on-carbon catalyst tested for benzene hydrogenation, catalyst was reduced at 825°C and held at 825° C for 15 minutes

Figure 12: Plot illustrating growth of graphite XRD peak at $26.2^\circ 2\theta$ with increasing time at maximum reduction temperature (825°C)

Figure 13: XRD Pattern of molybdenum-on-carbon catalyst tested for benzene hydrogenation, catalyst was reduced at 775°C and held at 775°C for 15 minutes

When comparing XRD patterns in Figure 12 and benzene hydrogenation data for the same catalyst in Figure 9, it appears that graphite XRD lines grow as the catalyst becomes less active for benzene hydrogenation, to the point where no activity is observed. Inverse to this, Mo₂C line intensities increase with reduction temperature and length of soak time at reduction temperature, even when the catalyst has no reactive surface. It is, therefore, possible that small surface particles, barely visible or invisible to XRD, play the key role in Mo₂C hydrogenation activity. Analyzed XRD patterns for all spent catalysts found to have benzene hydrogenation activity are found in Appendix E.

4.3 In-situ XRD

On an October 2003 visit to the National Synchrotron Light Source (NSLS) by Edwin Kugler, experiments were carried out to measure the phase transitions of molybdenum-on-carbon (Mo/C) catalysts reduced in H₂. Figure 14 shows the results of the in-situ XRD of 18% Mo/C reduced in H₂. This sample was heated from 25-825°C at a rate of 5°C per minute then held at 825°C for 1 hour. Each XRD scan in Figure 14 was taken in a 5 minute interval, thus, each scan represents 25°C of heating.

Two major changes can be seen in the XRD patterns in Figure 14. First at ~500°C, where there is a background shift in the low 2θ angles. Furthermore, at ~700°C the peaks for MoO₃, between 2θ values of 18° and 28°, disappear and broad peaks for Mo₂C appear. Figure 14 shows that during the transition to Mo₂C there is no formation of Mo⁰, instead there is a direct transition from MoO₃ to Mo₂C. Possibly, excess carbon prevents the transition of the material to Mo⁰ and instead drives the transition to Mo₂C.

Figure 14: In-situ XRD scans of the reduction of 18% Mo/C to 825° at 5°C per minute in 5% H_2 (balance He). Each scan represents 25°C of heating

Figure 15 shows the peak fitting of the bulk structures of the predominant materials at the end of reduction in H_2 . This analysis was performed using the XRD analysis software JADE. Through peak matching of The International Centre for Diffraction Data (ICDD) database, a database of experimental and calculated crystal diffraction patterns, the XRD analysis reveals that the predominant structures found in the sample are that of hexagonal Mo_2C and SiO_2 . SiO_2 is an impurity found in the activated carbon purchased from Sigma-Aldrich. This impurity is useful as a marker due to its persistence throughout reduction. From Debye-Scherrer line broadening of the x-ray diffraction pattern, it is found that the average Mo_2C particle size is 2 nm. It should be noted that 2 nm lies within the lower limit of the effectiveness of the line-broadening technique (33).

On another visit to NSLS in March 2004, experiments were carried out by Edwin Kugler, Christopher Clark, and James Wright, this time to measure phase transitions of molybdenum-on-carbon catalysts calcined in He. Figure 16 shows these results of the in-situ XRD of 24% Mo/C calcined in He. This sample heated from 25-825°C at a rate of 5°C per minute then held at 825°C for 1 hour. Each XRD scan in Figure 16 was taken in a 5-minute interval, thus each scan represents 25°C of heating.

Two major changes can be seen in the XRD patterns in Figure 16. The first of these changes is the growth of intensity of MoO_2 peaks at between a 2θ value of 18° and 28°. This change from weak broad peaks to sharp intense peaks is indicative of larger particles (13). This particle growth can be seen starting at ~500°C and continuing to 800°C. The second change happens suddenly at ~800°C where the relatively intense peaks for Mo_2C appear between a 2θ value of 20° and 25°. Similar to the case of H_2 reduction, no Mo^0 is seen. However, even without the presence of H_2 the material transitions to Mo_2C .

Figure 15: XRD Profile, with peak fitting, of final product of in-Situ reduction of 18% Mo/C in 5% H₂ (balance He)

Figure 16: In-situ XRD scans of the reduction of 24 % Mo/C to 825° at 5°C per minute in He. Each scan represents 25°C of heating up to 825°C then held at 825° for 30 minutes

Figure 17 shows the peak fitting of the bulk structures of the predominant materials at the end of calcination in He. This analysis was performed using the XRD analysis software JADE. Through peak matching using JADE and the ICDD database, the XRD analysis reveals that the predominant structures are found to be that of hexagonal Mo_2C , and SiO_2 . From line broadening, the average Mo_2C particle size is found to be 9 nm. During calcination in He, the particles formed are much larger, and the transition happens at higher temperatures, in comparison to the case of H_2 reduction. In this case of calcination in He the particles are larger due to the formation of large MoO_2 precursors prior to the transition to Mo_2C .

On an April 2004 visit to NSLS, experiments were carried out by Edwin Kugler to measure the phase transitions of molybdenum on carbon catalysts reduced in 5% CO (balance He). During this visit, a curious new transition was measured. Figure 18 shows the results of the in-situ XRD of Mo/C reduced in CO. This sample was heated from 25°C-825°C at a rate of 5°C per minute then held at 825°C for 1 hour. Each XRD scan in Figure 18 was taken in a 5-minute interval, thus each scan represents 25°C of heating. Only one major transition occurs in this material, a shift at approximately 650°C from MoO_2 to MoC. This transition is marked by disappearance of MoO_2 peaks found at 2θ values of 20° and 28 and the sudden appearance of very broad MoC peaks between 2θ values of 17° and 28°. The very broad nature of the MoC peaks is indicative of very small particle size.

Figure 19 shows the peak fitting of the bulk structures of the predominant materials at the end of reduction in 5% CO (balance He). This analysis was performed using the XRD analysis software JADE. Again, through peak matching using JADE and the ICDD database the predominant structures are those of cubic MoC and SiO_2 .

Figure 17: XRD profile, with peak fitting, of final product of in-Situ calcination 24% Mo/C in He

Figure 18: Plot of in-situ XRD scans of the reduction of 21% Mo/C to 825° at 5°C per minute in 5% CO (balance He). Each scan represents 25°C of Heating

Figure 19: Profile, with peak fitting, of final product of in-Situ calcination 21% Mo/C in 5%CO (balance He)

4.4 Temperature Programmed Reaction-Mass Spectrometry (TPR-MS)

Temperature programmed reaction (TPR) experiments, where the gas effluent was measured using a mass spectrometer, have been performed at the National Energy Technology Laboratory (NETL) by Todd Gardner. These experiments used a Micromeritics Autochem 2920 Catalyst Characterization System with the sample off-gas analyzed by a ThermoONIX Prima $\delta\beta$ magnetic sector mass spectrometer, described in Section 3.6. TPR was performed on Mo/C samples pretreated in flowing H₂, CO, and Ar.

Figure 20 illustrates the observed TPR-MS pattern of Mo/C reduced in 5% H₂ (balance Ar). The sample was heated at 10°C/min. to 900°C. At approximately 500°C, H₂ is consumed with carbon monoxide evolved at near 800°C. Trace amounts of NH₃ are evolved at ~200°C in the breakdown of the ammonium heptamolybdate complex, but only trace amounts of CO₂ are produced. Additionally, H₂ seems to be produced at high temperatures. This can be seen as the value of H₂ mol% in Figure 20 increases as temperature reaches 900°C. When comparing the H₂ consumption in Figure 20 to transitions observed in the in-situ XRD in Figure 14, one sees that the largest H₂ consumption in the TPR correlates to only a background shift in the XRD pattern. It is believed that this XRD background shift is the formation of small MoO₂ precursors. Furthermore, if we correlate the CO evolution in Figure 20 to the in-situ XRD in Figure 14, we see that the CO evolution roughly correlates to the transition from MoO₂ to Mo₂C.

Figure 21 illustrates the observed TPR pattern of Mo/C, now calcined in Ar. As above, the sample was heated at 10°C/min. to 900°C and then held at 900°C for 130 minutes. At near 850°C, CO is evolved with H₂ being evolved at approximately 900°C. When comparing Figure 21 (calcination in Ar), to Figure 20 (reduction in 5% H₂ (balance Ar), one finds that CO evolution occurs at a higher temperature (850°C) in the case of calcinations in Ar.

Figure 20: TPR-MS Spectra of Mo/C Reduced in 5% H₂ (balance Ar) from 25°C to 900°C at 10°C per minute

Figure 21: TPR-MS Spectra of Mo/C calcined in Ar from 25°C to 900°C at 10°C per minute, then held at 900°C for 130 minutes (plot of only 40 minutes of 130-minute temperature soak at 900°C)

Trace amounts of NH_3 are evolved in the breakdown of the ammonium heptamolybdate complex at $\sim 400^\circ\text{C}$, with only small quantities of CO_2 produced. It is interesting to note that NH_3 is produced at a slightly higher temperature during calcinations than during reduction in H_2 . When comparing Figure 21 and the in-situ XRD for TPD in inert found in Figure 16, one can correlate CO evolution to the formation of Mo_2C . However, there is no change in the XRD pattern correlating to the evolution of H_2 at high temperatures.

Figure 21 signifies that reduction of the MoO_2/C catalyst does not occur from the gas environment, but is instead carburized directly from the activated carbon support. One possible mechanism for this reduction is:

For this proposed mechanism, it is of interest to see how well the TPR-MS data compare to that predicted by thermodynamics. For the gas phase reaction shown in Equation 11, the equilibrium CO_2 concentration was calculated by:

$$\Delta G_r = -RT \ln(K_a) \quad (12)$$

$$K_a = \frac{(y_{\text{co}})^2 P}{y_{\text{co}_2}} \quad (13)$$

where ΔG_r is the Gibbs free energy of reaction for Equation 12 calculated using tabulated data (40), R is the gas constant, T is temperature in Kelvin, K_a is the equilibrium constant, P is total pressure, y_{co} and y_{co_2} are the equilibrium mole fraction of CO and CO_2 . This calculation is shown in detail in Appendix F. The equilibrium value for CO_2 corresponding to the observed maximum CO concentration, occurring at 875°C , has been calculated. When CO is at its observed maximum concentration of 4.5 mole %, the equilibrium concentration of CO_2 is 0.0066

mole %. When we compare this equilibrium calculation to the experimental data in Figure 21 they are consistent, there is no significant observed or equilibrium CO_2 produced at 875°C . Indeed, the equilibrium for Equation 11 explains the large CO evolution and the absence of CO_2 . However, when one looks at the equilibrium CO and CO_2 concentrations prior to 875°C in Figure 21, it is difficult to say anything about the reaction mechanism as both CO and CO_2 are in small concentrations. It should be noted that the equilibrium constant for the reaction in Equation 11 is equal to one at approximately 700°C , and possible error in this temperature is associated with extrapolation of the Gibbs free energies of formation for CO and CO_2 given only to 1000K (41).

During a discussion with Jae-Soon Choi (42), a researcher working on unsupported molybdenum carbides, he noted that when preparing unsupported molybdenum carbide in CH_4/H_2 one needs to take great care in not using high temperatures or CH_4/H_2 molar ratios exceeding 1/9. Going to high temperatures or exceeding 10% $\text{CH}_4/\text{balance H}_2$ would lead to carbon build up on the surface. It is believed that a similar phenomenon is present in the carbon supported system, but one has little or no control over carbon sources for carburization.

Figure 22 illustrates the observed TPR pattern of Mo/C reduced in CO. As before, the sample was heated at $10^\circ\text{C}/\text{min}$ to 900°C , and then held at 900°C for 130 minutes. At approximately 600°C , CO is consumed with CO_2 being evolved proportional to the CO being consumed. Trace amounts of NH_3 are not evolved in this sample, and this sample only, due to pre-calcination of the 13% Mo/C in N_2 at 500°C . When comparing TPR spectra in Figure 22 with the in-situ XRD spectra, Figure 19, it is seen that CO consumption begins at approximately the same temperature, 625°C , that MoO_2 converts to MoC.

Figure 22: TPR-MS spectra of Mo/C calcined in 10% CO (balance Ar) from 25°C to 900°C at 10°C per minute, then held at 900°C for 130 minutes (plot of only 20 minutes of 130-minute temperature soak at 900°C)

4.5 CO Chemisorption

CO chemisorption was attempted on all catalysts found to be active for benzene hydrogenation. However, good chemisorption data could not be obtained for active Mo/C catalysts. For commercial 5% Pt/Al₂O₃, purchased from Pressure Chemical, the chemisorption apparatus described in Section 3.4 consistently yielded data comparable to literature values (6, 43). Data for pulse CO chemisorption over 5% Pt/Al₂O₃ is provided in Figure 23. Figure 23 indicates that the 5% Pt/Al₂O₃ sample is saturated with CO after 16 doses. This value corresponds to a CO uptake of 111 $\mu\text{mol/g-sample}$.

A sample prepared to be MoO₂-on-carbon (by calcination in Ar) consistently gave good data revealing no CO uptake. Pulse chemisorption of CO over MoO₂-on-carbon is provided in Figure 24. In many cases where CO chemisorption was attempted on what should be an active Mo₂C-on-carbon surface, the data showed strange behavior for CO uptake. Pulse chemisorption of CO over Mo/C, prepared through reduction in flowing H₂ to 825°C at 10° per minute and held at 825°C for 15 minutes, is provided in Figure 25. CO chemisorption data in Figure 25 showed odd peak heuristics for the Mo₂C-on-carbon catalyst. However, pyrophoric behavior was observed upon removal from the TPR-chemisorption unit. This pyrophoric behavior of the Mo/C catalyst is independent evidence for activity. It is, therefore, strange that good CO chemisorption, similar to that obtained for Pt catalysts, was not observed.

4.6 Active Site Determination

To counter this problem, CO chemisorption data were collected for the 5% Pt/Al₂O₃, as shown in Figure 23. This was then combined with benzene hydrogenation rate data, to give a number for rate-per-active-site, or average turn-over-frequency (TOF). TOF is defined by:

Figure 23: Pulse CO chemisorption over 0.1078g Pressure Chemical 5% Pt/Al₂O₃ reduced in H₂ to 425°C

Figure 24: Pulse CO chemisorption over 0.1074 g molybdenum-on-carbon calcined in flowing Ar to 615°C

Figure 25: Pulse CO chemisorption over 0.1258 g molybdenum-on-carbon, prepared through reduction in flowing UHP H₂ to 825°C at 10° per minute and held at 825°C for 15 minutes

$$TOF = \frac{-r_{benzene}}{[S]} \quad (14)$$

Where $-r_{benzene}$ is the initial rate of benzene consumption calculated by Equation 14, $[S]$ is surface site concentration, and TOF is site time yield. An average TOF was first calculated for 5% Pt/Al₂O₃. This value is 3.80 (reactions/site-min), for an average $-r_{benzene}$ of 4.24×10^{-4} (mol*min⁻¹(g-catalyst)⁻¹). Once TOF was calculated for Pt/Al₂O₃, it was assumed to be constant for the benzene hydrogenation reaction. This number could therefore be applied to other catalysts. Surface site concentration was then calculated for Mo/C samples by Equation 14 (44).

Table 1 gives calculated values for surface site concentration for catalysts found to be active for benzene hydrogenation. Values for $(-r_{benzene})_0$ were found by fitting curves to the experimental data for $-r_{benzene}$ and extrapolating to zero time (12). Fitting of the $-r_{benzene}$ data as well as the precise calculation method for $[S]$ from this data can be found in Appendix D. The data in Table 2 serve to quantify the activity effects of reduction temperature and soak time as discussed in Section 4.1. It should be noted that Table 1 contains only calculated CO adsorption site concentrations.

Table 1: Surface Site concentrations as measured by either by benzene hydrogenation

Catalyst	Reduction Temperature (°C)	Heating Rate (°C/min)	Soak Time at Reduction Temperature (min)	Initial $-r_{\text{benzene}}$ as extrapolated from experimental data (mol/(min*g-catalyst))	Surface Site Concentration ($\mu\text{mol/g-catalyst}$)
13% Mo/C	675	10	15	2.50×10^{-6}	0.76
13% Mo/C	725	10	15	2.45×10^{-5}	7.45
13% Mo/C	775	10	15	3.25×10^{-5}	9.88
13% Mo/C	825	10	15	6.98×10^{-5}	21.2
13% Mo/C	875	10	15	3.77×10^{-5}	11.5
13% Mo/C	825	10	0	9.95×10^{-5}	30.3
13% Mo/C	825	10	30	5.45×10^{-6}	1.66
13% Mo/C	825	10	60	0	0

5. Conclusions

The molybdenum-on-carbon catalysts reduced in UHP H_2 clearly have benzene hydrogenation activity, but do not have activity comparable to a commercial Pt/ Al_2O_3 catalyst. Additionally, the Mo/C catalysts deactivate quickly, possibly due to residual oxygen in the benzene feed, compared to the commercial Pt catalyst. However, molybdenum-on-carbon has some interesting features that could lend themselves to further development and fundamental insight.

In-situ XRD patterns indicate that the MoO_2 reduces to Mo_2C or MoC between 650°C and 750°C in all reduction cases. When correlating these transitions to benzene hydrogenation, one finds that only during the transitions to molybdenum carbide is the catalyst active. Upon completion of the TPR, some phenomenon passivates the surface. Independent evidence for this passivation was found during CO chemisorption experiments over the catalysts. For CO chemisorption on catalysts having the highest benzene hydrogenation activity, pyrophoric behavior was observed on disposing of the catalyst. Previous to this, no molybdenum carbide-

on-carbon catalyst had shown this tendency to violently oxidize in air (burn). When the catalysts that had no benzene hydrogenation activity were handled in a similar manner, no burning was observed. This lends evidence to the presence of surface poison occurring at high temperatures or long soak times.

The benzene hydrogenation reaction was used to determine metal surface site concentration. It was found through this method that the best surface site concentration per gram of catalyst for any of the Mo/C samples was approximately 25% of that measured for the commercial 5% Pt/Al₂O₃ catalyst. Additionally, this chemisorption study yielded the first observation of pyrophoric Mo/C, observed on catalyst disposal.

Taking into account the observed deactivation with reduction temperature and soak time at reduction temperature, it is believed that a carbon layer is occluding the active surface. Three possible mechanisms for this are: carbon lay-down from CH₄ formed (Equation 1), carbon laydown from CO formed (Equation 5), or mobile carbon used in the reduction of the Mo₂C that migrates to the surface. Evidence for one or all of these mechanisms can be found in the formation of graphite, as seen by XRD, as the catalyst becomes increasingly inactive.

When looking at the formation of molybdenum carbides in H₂, inert, and CO, one finds that in none of the cases is Mo⁰ observed. This is shown clearly in the in-situ XRD patterns, Figures 17, 19, and 21. It is interesting that Mo⁰ is not seen as this is the carburization mechanism proposed by the Stanford Group, as seen in Equation 2. Instead MoO₂ is the starting material, after the initial decomposition of ammonium heptamolybdate, which then reduces at high temperature to Mo₂C.

Additionally, for the case of Mo₂C formation in H₂ or inert, one finds that CO is evolved during the reduction of MoO₂ to Mo₂C. This CO evolution implies that the reaction path to

Mo₂C does not use methane as the reducing agent, as proposed by Lee et al. (4), but instead is using the carbon support. This is seen in correlating the TPR-MS, Figure 21, and in-situ XRD, Figure 16. From the TPD-MS in inert gas, it seems clear that the Mo/C samples are reduced to Mo₂C-on-carbon by the carbon support, not the gas environment. This is supported by the equilibrium calculation (Equation 11). For the case of the reduction in 5% CO (balance inert), the consumption of CO and production of CO₂, seen in the TPR-MS spectra Figure 22, corresponds to the same temperature as the transition of MoO₂ to MoC, seen in Figure 18. In all cases, active carbon appears to be the reducing agent.

Molybdenum carbide shows promise as a hydrogenation catalyst, but needs further materials refinement to optimize hydrogenation activity. This study has observed that noble metals and unsupported molybdenum carbides outperform carbon-supported molybdenum catalysts.

6. Recommendations

Future work should involve the probing of the surface of Mo₂C-on-carbon. Understanding the mechanism and rate of carbon build up on the particle surface should lead to forming a more stable and more active catalyst. Infrared (IR) spectroscopy or x-ray near edge spectroscopy should lend itself to this pursuit. One should be able to observe the surface carbon build-up by these methods.

Furthermore, when reducing the Mo₂C catalyst formed in UHP H₂, the hydrogenation activity could be improved by increasing H₂ concentration to assure that the metal surface is clean. Due to limitations in the apparatus constructed for these experiments, high H₂ pressures could not be reached, but future work should reduce these Mo/C catalysts under higher H₂ pressures. This high H₂ concentration should drive carbon off the surface as CH₄ by the reaction

in Equation 1 and leave a clean metal surface. Finally, with MoC reduced in CO, the study of co-feeding CO₂ might reveal that surface carbon can be cleaned up and catalytic activity achieved. The reaction in Equation 5 lends evidence to this phenomenon.

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Appendix A: Mass Flow Controller Calibration

This appendix provides calibration curves for the Brooks mass flow controllers used for reduction and reaction in the benzene hydrogenation reactor shown in Figure 3.

Figure 26: Calibration of MFC for UHP H₂ Flow

Figure 27: Calibration of MFC for 5% CO/balance He

Appendix B: GC Separations

This appendix provides test separations and column specifications for the 35% BC-150 on 100/120 Chromosorb P AW column used to separate cyclohexane from benzene. For the test separation, 1 μL of an approximately 50/50 weight % mixture of benzene and cyclohexane was injected into the Hewlett Packard 5890 series II gas chromatograph.

Figure 28: Chromatograph of 1 μL injection of a 1/1 mixture of benzene and cyclohexane, where the GC oven was kept isothermal at 120°C and data was collected for 5 min.

Appendix C: XRD Calibrations

In this appendix LaBa₆ standards run for X7B distance and wavelength calibrations for data collected in: October 2003, March 2004, April 2004, and August 2005, is provided. This data is used in the integration of a circular diffraction image, as seen in Figure 2, to the standard 2-dimensional XRD pattern (Intensity vs. 2θ) (34).

Table 2: Data Collected through the Analysis of a LaBa₆ Standard to Calibrate Experimental Conditions for XRD data Collected at NSLS.

	10/2003		3/2004		4/2004		8/2005	
Sum of Squares	4.0471		8.4712		15.907		0.044527	
Number of Rejected Coordinates	0		0		0		0	
Refined Beam Center (Pixels)	1169.090	1153.449	1169.535	1155.183	1169.768	1152.535	1164.453	1153.268
Refined Beam Center (mm)	175.364	173.017	175.430	173.277	175.465	172.880	174.668	172.990
Refined Sample to Detector Distance (mm)	145.240		148.324		167.763		152.321	
Refined Wavelength (Å)	0.92246		0.92130		0.92233		0.92042	
Energy (keV)	13.44075		13.45765		13.44268		13.47057	
Refined Tilt Plane Rotation Angle (°)	126.960		-61.278		-69.676		142.716	
Refined Tilt Angle (°)	0.161		-0.223		-0.206		0.144	
ROT X (°)	-0.090		-0.107		-0.072		-0.115	
ROT Y (°)	0.133		0.195		0.193		0.087	
Stability Indicator (proportional to D-spacing; Angstroms)	1.55327		1.57611		1.73669		1.60687	

Appendix D: Benzene Hydrogenation and CO Chemisorption Data and Calculations

This appendix provides calculations and raw data for benzene hydrogenation and CO chemisorption experiments.

Known Values:

$$P_{benzene}^* = 32.44 \text{ mm Hg}$$

$$V_0 = 34 \frac{\text{mL}}{\text{min}}$$

W = varies with catalyst tested, but known

$$\text{Thermal Response}_{benzene} = 100 - \text{from Dietz (43)}$$

$$\text{Thermal Response}_{cyclohexane} = 114 - \text{from Dietz (43)}$$

$$T_s = 274 \text{ K}$$

$$[S]_{Pt / Al_2O_3} = 111 \frac{\mu\text{mol}}{\text{g} - \text{catalyst}}$$

Measured Variables:

$$\text{TCD Peak Area}_{benzene}$$

$$\text{TCD Peak Area}_{cyclohexane}$$

Gas Constant Used:

$$R = 82.057 \frac{\text{ml} - \text{atm}}{\text{mol} - \text{K}}$$

Finding Initial Benzene Concentration:

$$C_{benzene0} = \frac{P^*}{RT_s}$$

Finding Outlet Benzene Concentration by Gas Chromatograph:

$$y_{benzene} = \frac{C_{benzene}}{(C_{benzene} + C_{cyclohexane})} = \frac{RF_{benzene}}{(RF_{benzene} + RF_{cyclohexane})} \text{ - from Dietz, Fogler (43, 40)}$$

$$RF = \frac{TCD \text{ Peak Area}}{Thermal \text{ Response}} \text{ - from Dietz (43)}$$

Assuming 100% Carbon Balance and a differential reactor model (conversion <15%):

$$X_{benzene} = \frac{1 - y_{benzene}}{y_{benzene} \varepsilon + 1}$$

$$\varepsilon = \delta y_{benzene0}$$

$$\delta = \text{Stoichiometric Coefficients of Products} - \text{Stoichiometric Coefficients of Reactants} = -3$$

$$y_{benzene0} = \frac{C_{benzene0} RT_{ambient}}{P_{ambient}}$$

$$-r_{benzene} = \frac{X_{benzene} C_{benzene0} V_0}{W} \text{ - from Fogler (40)}$$

$$TOF = \frac{-r_{benzene}}{[S]} \text{ - from Fogler (40)}$$

Since we know $[S]_{Pt/Al_2O_3}$, TOF_{Pt/Al_2O_3} can be found:

$$TOF_{Pt / Al_2O_3} = \frac{(-r_{benzene})_{Pt / Al_2O_3}}{[S]_{Pt / Al_2O_3}}$$

Assuming that TOF is constant for benzene hydrogenation on all catalysts, $[S]_{Mo/C}$ can be found:

$$[S]_{Mo / C} = \frac{(-r_{benzene})_{Mo / C}}{TOF_{Pt / Al_2O_3}}$$

Table 3: Raw Gas Chromatograph Data for Benzene Hydrogenation tested on Mo/C reduced in UHP H₂ to 675°C at 10°C/min, then held at 675°C for 15 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
12.00	1574	410130
20.50	1575	395460
30.25	3061	329886
35.50	1280	397047
54.00	1223	356783

Table 4: Raw Gas Chromatograph Data for Benzene Hydrogenation tested on Mo/C reduced in UHP H₂ to 725°C at 10°C/min, then held at 725°C for 15 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
9.00	10682	403251
18.00	8277	408328
36.50	7235	378942
42.00	7302	372981
48.00	6019	367499
64.50	3921	367740
85.00	2577	363060
103.25	1240	360758
120.00	875	424706

Table 5: Raw Gas Chromatograph Data for Benzene Hydrogenation tested on Mo/C reduced in UHP H₂ to 775°C at 10°C/min, then held at 775°C for 15 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
10.00	23667	380848
23.75	12710	393037
41.75	10753	392546
58.00	10305	373181
78.00	7834	415611
120.00	4866	410296

Table 6: Raw Gas Chromatograph Data for Benzene Hydrogenation tested on Mo/C reduced in UHP H₂ to 825°C at 10°C/min, then held at 825°C for 0 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
10.00	45702	324129
22.00	15759	377022
46.00	5619	425333
59.25	3867	431511

Table 7: Raw Gas Chromatograph Data for Benzene Hydrogenation tested on Mo/C reduced in UHP H₂ to 825°C at 10°C/min, then held at 825°C for 15 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
10.00	40271	347487
25.75	34037	336843
45.75	28625	336960
60.75	20376	412885
74.50	23776	332521
120.00	16648	387253

Table 8: Raw Gas Chromatograph Data for Benzene Hydrogenation tested on Mo/C reduced in UHP H₂ to 825°C at 10°C/min, then held at 825°C for 30 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
10.50	3237	390515
32.75	995	435798
46.25	1081	380210
62.00	783	453991

Table 9: Raw Gas Chromatograph Data for Benzene Hydrogenation Data tested on Mo/C reduced in UHP H₂ to 825°C at 10°C/min, then held at 825°C for 60 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
11.00	0	415599
16.00	0	406853

Table 10: Raw Gas Chromatograph Data for Benzene Hydrogenation Data tested on Mo/C reduced in UHP H₂ to 875°C at 10°C/min, then held at 875°C for 15 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
10.50	12235	390361
29.50	2140	443576
44.50	910	379648
60.50	431	371463

Table 11: Raw Benzene Hydrogenation Data for Pt/Al₂O₃ reduced in UHP H₂ to 425°C at 10°C/min, then held at 875°C for 0 minutes

Time on Stream (min.)	Cyclohexane TCD Peak Area	Benzene TCD Peak Area
12.50	14149	391179
33.25	17856	384264
48.25	18686	382485
63.25	17653	381567

Figure 29: Effect of time-on-stream on the rate of disappearance of benzene for Mo/C catalysts with varying final reduction temperature with exponential curve fitting to find initial rate of benzene disappearance

Figure 30: Effect of time on stream on rate of disappearance of benzene for Mo/C catalysts with varying soak time at final reduction temperature (825°C) with exponential curve fitting to find in rate of benzene disappearance

Appendix E: XRD Analysis of Spent Benzene Hydrogenation Catalysts

Analysis of XRD patterns of spent catalysts found to have benzene hydrogenation activity will be provided in this appendix.

Figure 31: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 675°C and held at 675° C for 15 minutes

Figure 32: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 725°C and held at 725° C for 15 minutes

Figure 33: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was Reduced at 775°C and held at 775° C for 15 minutes

Figure 34: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 825°C and held at 825° C for 0 minutes

Figure 35: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 825°C and held at 825° C for 15 minutes

Figure 36: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 825°C and held at 825° C for 30 minutes

Figure 37: XRD pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 825°C and held at 825°C for 60 minutes

Figure 38: XRD Pattern of Mo/C catalyst tested for benzene hydrogenation, catalyst was reduced at 875°C and held at 875° C for 15 minutes

Appendix F: Reaction Equilibrium Calculations

Detailed calculations involving the equilibrium between CO and CO₂ during the transition from MoO₂ to Mo₂C, described in Section 4.4.

$$\Delta G_r = 2(\Delta G_f)_{CO_2} - (\Delta G_f)_{CO}$$

$$\Delta G_r = -RT \ln(K_a)$$

$$K_a = \frac{(y_{CO})^2 P}{y_{CO_2}}$$

Table 12: Gibbs' Energy of Formation and Reaction from Yaws' Handbook for CO and CO₂ (41)

T (K)	$\Delta G_{f, CO_2}$ (kJ/mol)	$\Delta G_{f, CO}$ (kJ/mol)	ΔG_r (kJ/mol)
700	-393.06	-172.659	47.742
800	-392.97	-181.573	29.824
900	-392.87	-190.476	11.918
1000	-392.76	-199.367	-5.974
1100	-392.63	-208.247	-23.864
1200	-392.50	-217.115	-41.600