

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 09-11-2017		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 18-Apr-2016 - 17-Apr-2017	
4. TITLE AND SUBTITLE Final Report: Chemisorption as a versatile tool to characterize multifunctional materials			5a. CONTRACT NUMBER W911NF-16-1-0166		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611103		
6. AUTHORS			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Wisconsin - Madison The Board of Regents of the University of Wisconsin S Suite 6401 Madison, WI 53715 -1218			8. PERFORMING ORGANIZATION REPORT NUMBER 1.00		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 68570-CH-RIP.4		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Ive Hermans
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 608-262-4966

RPPR Final Report

as of 11-Jun-2018

Agency Code:

Proposal Number: 68570CHRIP

Agreement Number: W911NF-16-1-0166

INVESTIGATOR(S):

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DUNS Number: 161202122

EIN: 396006492

Report Date: 17-Jul-2017

Date Received: 09-Nov-2017

Final Report for Period Beginning 18-Apr-2016 and Ending 17-Apr-2017

Title: Chemisorption as a versatile tool to characterize multifunctional materials

Begin Performance Period: 18-Apr-2016

End Performance Period: 17-Apr-2017

Report Term: 0-Other

Submitted By: Ive Hermans

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 6

STEM Participants: 10

Major Goals: In our proposal entitled, "Chemisorption as a versatile tool to characterize multifunctional materials", we requested and received funding for a chemisorption setup, specifically a Micromeritics Autochem II. We proposed several "routine" experiments using this instrument which would immediately push our research forward. These are repeated below.

1. Controlled synthesis of metal nanoparticles (and core-shell particles), in particular bimetallic systems like RhRe/C and PtMo/C, important catalysts in biomass chemistry (BETO project). It is currently assumed that the active sites are at the interface of the two metals. This implies that one should synthetically aim at depositing small amounts of the oxophilic metal (e.g., Re and Mo) to the noble metal (e.g., Rh or Pt), rather than to the exposed support surface between the metal nanoparticles. The decrease in probe adsorption can be connected with the deposition of the oxophilic metal on the noble metal, rather than on the support, provided that the particles did not sinter (which needs to be verified with microscopy) and the probe molecule does not bind to the oxophilic metal sites.
2. Zeolites are a class of materials used in a number of our projects, related to biomass, as well as important commodities chemistry like Bayer-Villiger oxidations and epoxidations. Determining their acid/base properties would allow a correlation of these properties with the catalytic activity of different materials. These materials are not always stable with time-on-stream and tend to deactivate. An analysis of the acid/base properties before and after reaction would help in understanding such effects better. Furthermore, it is common to postsynthetically modify zeolites, e.g. by steaming, a process that is still poorly understood. Also here, the effects of different parameters during the steaming on the acid/base properties could be studied.
3. Our group is working on the synthesis of ternary metal oxides prepared with controlled dispersion. As an example, we are interested in understanding synergetic effects between Ti(IV) and V(V) (Ti-V/SiO₂) in the oxidative dehydrogenation of propane. Comparing the TPR-TPO-TPR profiles of V/SiO₂, Ti/SiO₂ and Ti-V/SiO₂ materials would provide valuable information on the influence of the titanium species on the redox cycling of the vanadium, assumed to be an important descriptor of this reaction. This can then be correlated with 51V NMR (monitoring the influence of the Ti on the V chemical shift) and catalytic activity measurements.

Following various stages during material synthesis, in particular oxidation (calcination) and reduction steps. An important question that we are trying to answer is, for instance, why does the ramp rate during catalyst calcination influence the catalytic performance (E.g. methanol synthesis catalyst)? The outlined chemisorption techniques would allow us to conveniently investigate the influence of this parameter on 1) the metal dispersion (e.g. copper in case of the methanol synthesis catalyst), and/or 2) the amount and strength of acid sites.

Accomplishments: 2 publications have been completed, with one additional submitted for review. We now go through the results of each of the "routine" experiments discussed in the original proposal, numbered as they are

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above.

1. We have performed these experiments on a number of catalysts, contributing to two publications since this instrument was obtained.^{1,2} Specifically, we used CO as a probe molecule for adsorption on RhRe/C and PtW/TiO₂ to see whether the oxophilic additive (e.g., W or Re) covered metallic sites (e.g., Pt or Rh) during synthesis. CO adsorbs to exposed metallic sites, but not to exposed oxophilic sites. Therefore, metal coverage by an oxophilic additive would be shown by a higher CO uptake in Rh/C as compared to RhRe/C and, likewise, a higher CO uptake in Pt/TiO₂ as compared to PtW/TiO₂. Indeed, this is what we see with Rh/C and RhRe/C, but not with Pt/TiO₂ and PtW/TiO₂. This indicates that Re does cover Rh sites on RhRe/C, but W does not cover Pt sites on PtW/TiO₂.

Without this instrument, we would have had to take STEM-EDX measurements of each of our catalysts to obtain the same information. There are two instruments on the UW-Madison campus that can carry out these experiments. Each of these instruments charges \$60/hr for student use, and requires a student/post-doc with years of experience to operate properly. We tested close to 100 samples for these studies alone, which would have cost ~\$6000 for instrument time, and would have required the training of a new graduate student. The chemisorption setup we now have costs essentially nothing to operate, and a student can be trained in the course of a day.

2. We tested postsynthetically-modified zeolites with the Temperature Programmed Desorption of NH₃ (NH₃-TPD) to analyze the acid properties of the zeolite, contributing heavily to another publication.³ NH₃ binds to acid sites on the zeolite, and a TPD of NH₃ quantifies the amount and strength of these acid sites. In this study, we correlated the quantity and strength of acid sites (determined with our chemisorption setup) with zeolite catalytic activity measured elsewhere in the lab.

Without this instrument, we could have quantified the number of acid sites on each catalyst by FTIR of adsorbed pyridine after calibrating the pyridine signal to a standard with a known amount of acid sites. This technique is possible in our labs, but it is much less precise than with our chemisorption setup. Moreover, the FTIR method will provide very little information on the strength of the acid sites, which was quickly and easily calculated by our chemisorption setup.

3. While the exact experiment described in this portion of the proposal was not used for publication, we did study ternary metal oxides with other experiments with this chemisorption setup, contributing to publication.⁴ Specifically, we studied the acid properties of a Ag-Zr-BEA catalyst by NH₃-TPD. In this study, we determined that Ag atoms/particles blocked acidic sites in Zr-BEA, which was crucial to the reactivity of the catalyst.

Similar to point 2, without this instrument, we could have studied this effect by quantitative FTIR of pyridine adsorption, but this would have provided less precise data and would have been much more labor intensive.

4. These experiments are not published yet, so we will not go into as much detail. We are currently synthesizing core-shell catalysts, where the core strongly adsorbs H₂, but the shell does not. We are using H₂ chemisorption to confirm that the "shell" covers the H₂ adsorption sites on the "core", as this is going to be necessary for high activity and selectivity in our reaction of interest. Analogous to point 1, the catalyst without the shell should (and does) show higher H₂ uptake than the catalyst with the shell. Moreover, we are currently using the H₂ uptake of these catalysts to help determine the thickness of the shell we have synthesized.

Similar to point 1, without this instrument, we would require STEM-EDX measurements to obtain the same information. This instrument is expensive to use and requires years of training for a graduate student or post-doc to use properly.

Training Opportunities: No less than 3 post-doctoral researchers, 6 graduate students, and 5 undergraduate students have been trained on the instrument purchased from this grant. Each have benefitted from knowledge gained about his or her samples, as discussed in the "Accomplished" section.

Results Dissemination: 1. Karanjkar, P., Burt, S. P., Chen, X., Barnett, K. J., Ball, M., Kumbhalkar, M., Wang, X., Miller, J. B., Hermans, I., Dumesic, J. A., & Huber, G. W. Effect of Carbon Support on Rh-Re Bifunctional Catalysts for Selective Hydrogenolysis of Tetrahydropyran-2-methanol, (2016). *Catalysis Science and Technology*, 6, 7841-7851.

2. Burt, S. P., He, J., Zhang, L., Ball, M., Hermans, I., Dumesic, J. A., & Huber, G. W., Synthesis of 1,6-Hexanediol from cellulose derived molecules with Pt-MOx/TiO₂ catalysts, submitted.

3. Burt, S. P., Barnett, K. J., McClelland, D. J., Wolf, P., Dumesic, J. A., Huber, G. W., & Hermans, I. Production of 1,6-hexanediol from tetrahydropyran-2-methanol by dehydration-hydration and hydrogenation, (2017). *Green Chemistry*, 19, 1390-1398.

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Honors and Awards: Jan. 14, 2016 - Prof Hermans receives Postdoc Mentoring Award
July 3-8, 2016 - Dr. Carlos Carrero (Postdoc in Hermans group) receives Young Scientist Prize at the 16th International Congress on Catalysis
May 10, 2017 - Professor Ive Hermans receives Vilas Mid-Career Investigator Award

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Ive Hermans

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: Y

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Carlos Carrero

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Alessandro Chierogato

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Somphonh Peter Phivilay

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Samuel Peter Burt

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

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Participant Type: Graduate Student (research assistant)
Participant: Juan Mauricio Venegas
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Joseph Grant
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Sarah Specht
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Philipp Mueller
Person Months Worked: 13.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Patrick Wolf
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Fangying Huang
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N

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Other Collaborators:

Participant Type: Undergraduate Student

Participant: Kurtis Casperson

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Jack Micka

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Faisal Bin Salem

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Allison Arinaga

Person Months Worked: 4.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

ARTICLES:

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Catalysis Science and Technology

Publication Identifier Type:

Publication Identifier:

Volume:

Issue:

First Page #:

Date Submitted: 11/9/17 12:00AM

Date Published: 9/12/16 5:00AM

Publication Location:

Article Title: Effect of carbon supports on RhRe bifunctional catalysts for selective hydrogenolysis of tetrahydropyran-2-methanol

Authors: Pranav U. Karanjkar, Samuel P. Burt, Xiaoli Chen, Kevin J. Barnett, Madelyn R. Ball, Mrunmayi D. Kuml

Keywords: Biomass, 1,6-hexanediol, heterogeneous catalysis

Abstract: Tetrahydropyran-2-methanol undergoes selective C–O–C hydrogenolysis to produce 1,6-hexanediol using a bifunctional RhRe (reducible metal with an oxophilic promoter) catalyst supported on Vulcan XC-72 carbon (VXC) with >90% selectivity. This RhRe/VXC catalyst is stable over 40 h of reaction in a continuous flow fixed bed reactor. The hydrogenolysis activity of RhRe/VXC is two orders-of-magnitude higher than that of RhRe supported on Norit Darco 12X40 activated carbon (NDC). STEM–EDS analysis reveals that, compared to the RhRe/VXC catalyst, the Re and Rh component metals are segregated on the surface of the low activity RhRe/NDC catalyst, suggesting that Rh and Re in close proximity (“bimetallic” particles) are required for an active hydrogenolysis catalyst. Differences in metal distribution on the carbon surfaces are, in turn, linked to the properties of the carbons: NDC has both a higher surface area and surface oxygen content.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Green Chemistry

Publication Identifier Type:

Publication Identifier:

Volume:

Issue:

First Page #:

Date Submitted: 11/9/17 12:00AM

Date Published: 2/6/17 6:00AM

Publication Location:

Article Title: Production of 1,6-hexanediol from tetrahydropyran-2-methanol by dehydration–hydration and hydrogenation

Authors: Samuel P. Burt, Kevin J. Barnett, Daniel J. McClelland, Patrick Wolf, James A. Dumesic, George W. Hul

Keywords: Biomass, 1,6-hexanediol, heterogeneous catalysis

Abstract: In this work we present an alternate method for the conversion of tetrahydropyran-2-methanol (THP2M), a cellulose-derived renewable building block, to 1,6-hexanediol (1,6-HDO). Our method is composed of three consecutive steps that either use relatively inexpensive catalysts or no catalyst at all. First, THP2M is catalytically dehydrated to 2,3,4,5-tetrahydrooxepine (THO) in up to 40% yield. THO is then hydrated to 2-oxepanol (OXL) and 6-hydroxyhexanal (6HDHX) with a combined yield of 85% in the absence of a catalyst. OXL and 6HDHX are then quantitatively hydrogenated to 1,6-HDO over a commercially available Ni/C or Ru/C catalyst. Various silicoaluminates were screened for the first acid-catalyzed reaction, and it was found that K-BEA shows the highest THO yield (40% over fresh catalyst, 20% after 25 h on stream). An overall 1,6-HDO yield of 34% from THP2M was obtained.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

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as of 11-Jun-2018

Publication Type: Journal Article

Peer Reviewed: Y

Publication Status: 4-Under Review

Journal: ACS Catalysis

Publication Identifier Type:

Publication Identifier:

Volume:

Issue:

First Page #:

Date Submitted: 11/9/17 12:00AM

Date Published:

Publication Location:

Article Title: Synthesis of 1,6-Hexanediol from cellulose derived tetrahydrofuran dimethanol (THFDM) with Pt-WO_x/TiO₂ catalysts

Authors: Jiayue He#, Samuel P. Burt#, Madelyn Ball, Dongting Zhao, Ive Hermans, James A. Dumesic, and Gec

Keywords: Biomass, 1,6-hexanediol, heterogeneous catalysis

Abstract: Cellulose-derived tetrahydrofuran dimethanol (THFDM) can be converted over Pt-WO_x/TiO₂ catalysts to 1,6-hexanediol (1,6-HDO) with up to 70% yield. This reaction involves ring-opening of THFDM to 1,2,6-hexanetriol (HTO) and then hydrogenolysis of HTO to 1,6-HDO. Hydrogen spills over from Pt sites onto WO_x/TiO₂ to reduce the W=O functional group and create Brønsted acid sites. Similar catalytic activity for THFDM conversion can be obtained with a physical mixture of Pt/TiO₂ and WO_x/TiO₂ due to hydrogen spillover over spatially separate Pt and WO_x when a reducible support (TiO₂) is used.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

Statement of the Problem Studied

In our proposal entitled, “Chemisorption as a versatile tool to characterize multifunctional materials”, we requested and received funding for a chemisorption setup, specifically a Micromeritics Autochem II. We proposed several “routine” experiments using this instrument which would immediately push our research forward. These are repeated below.

1. Controlled synthesis of metal nanoparticles (and core-shell particles), in particular bimetallic systems like RhRe/C and PtMo/C, important catalysts in biomass chemistry (BETO project). It is currently assumed that the active sites are at the interface of the two metals. This implies that one should synthetically aim at depositing small amounts of the oxophilic metal (*e.g.*, Re and Mo) to the noble metal (*e.g.*, Rh or Pt), rather than to the exposed support surface between the metal nanoparticles. The decrease in probe adsorption can be connected with the deposition of the oxophilic metal on the noble metal, rather than on the support, provided that the particles did not sinter (which needs to be verified with microscopy) and the probe molecule does not bind to the oxophilic metal sites.
2. Zeolites are a class of materials used in a number of our projects, related to biomass, as well as important commodities chemistry like Bayer-Villiger oxidations and epoxidations. Determining their acid/base properties would allow a correlation of these properties with the catalytic activity of different materials. These materials are not always stable with time-on-stream and tend to deactivate. An analysis of the acid/base properties before and after reaction would help in understanding such effects better. Furthermore, it is common to postsynthetically modify zeolites, *e.g.* by steaming, a process that is still poorly understood. Also here, the effects of different parameters during the steaming on the acid/base properties could be studied.
3. Our group is working on the synthesis of ternary metal oxides prepared with controlled dispersion. As an example, we are interested in understanding synergetic effects between Ti(IV) and V(V) (Ti-V/SiO₂) in the oxidative dehydrogenation of propane. Comparing the TPR-TPO-TPR profiles of V/SiO₂, Ti/SiO₂ and Ti-V/SiO₂ materials would provide valuable information on the influence of the titanium species on the redox cycling of the vanadium, assumed to be an important descriptor of this reaction. This can then be correlated with ⁵¹V NMR (monitoring the influence of the Ti on the V chemical shift) and catalytic activity measurements.
4. Following various stages during material synthesis, in particular oxidation (calcination) and reduction steps. An important question that we are trying to answer is, for instance, why does the ramp rate during catalyst calcination influence the catalytic performance (*E.g.* methanol synthesis catalyst)? The outlined chemisorption techniques would allow us to conveniently investigate the influence of this parameter on 1) the metal dispersion

(*e.g.* copper in case of the methanol synthesis catalyst), and/or 2) the amount and strength of acid sites.

While these proposed experiments were more or less hypothetical at the time of their writing, we have completed and even published experiments very similar to those described in the proposal. We discuss these experiments individually in the next section.

Summary of the most important results

We now go through the results of each of the “routine” experiments discussed in the original proposal, numbered as they are above.

1. We have performed these experiments on a number of catalysts, contributing to two publications since this instrument was obtained.^{1,2} Specifically, we used CO as a probe molecule for adsorption on RhRe/C and PtW/TiO₂ to see whether the oxophilic additive (*e.g.*, W or Re) covered metallic sites (*e.g.*, Pt or Rh) during synthesis. CO adsorbs to exposed metallic sites, but not to exposed oxophilic sites. Therefore, metal coverage by an oxophilic additive would be shown by a higher CO uptake in Rh/C as compared to RhRe/C and, likewise, a higher CO uptake in Pt/TiO₂ as compared to PtW/TiO₂. Indeed, this is what we see with Rh/C and RhRe/C, but not with Pt/TiO₂ and PtW/TiO₂. This indicates that Re does cover Rh sites on RhRe/C, but W does not cover Pt sites on PtW/TiO₂.

Without this instrument, we would have had to take STEM-EDX measurements of each of our catalysts to obtain the same information. There are two instruments on the UW-Madison campus that can carry out these experiments. Each of these instruments charges \$60/hr for student use, and requires a student/post-doc with years of experience to operate properly. We tested close to 100 samples for these studies alone, which would have cost ~\$6000 for instrument time, and would have required the training of a new graduate student. The chemisorption setup we now have costs essentially nothing to operate, and a student can be trained in the course of a day.

2. We tested postsynthetically-modified zeolites with the Temperature Programmed Desorption of NH₃ (NH₃-TPD) to analyze the acid properties of the zeolite, contributing heavily to another publication.³ NH₃ binds to acid sites on the zeolite, and a TPD of NH₃ quantifies the amount and strength of these acid sites. In this study, we correlated the quantity and strength of acid sites (determined with our chemisorption setup) with zeolite catalytic activity measured elsewhere in the lab.

Without this instrument, we could have quantified the number of acid sites on each catalyst by FTIR of adsorbed pyridine after calibrating the pyridine signal to a standard with a known amount of acid sites. This technique is possible in our labs, but it is much less precise than with our chemisorption setup. Moreover, the FTIR method will provide

very little information on the strength of the acid sites, which was quickly and easily calculated by our chemisorption setup.

3. While the exact experiment described in this portion of the proposal was not used for publication, we did study ternary metal oxides with other experiments with this chemisorption setup, contributing to publication.⁴ Specifically, we studied the acid properties of a Ag-Zr-BEA catalyst by NH₃-TPD. In this study, we determined that Ag atoms/particles blocked acidic sites in Zr-BEA, which was crucial to the reactivity of the catalyst.

Similar to point 2, without this instrument, we could have studied this effect by quantitative FTIR of pyridine adsorption, but this would have provided less precise data and would have been much more labor intensive.

4. These experiments are not published yet, so we will not go into as much detail. We are currently synthesizing core-shell catalysts, where the core strongly adsorbs H₂, but the shell does not. We are using H₂ chemisorption to confirm that the “shell” covers the H₂ adsorption sites on the “core”, as this is going to be necessary for high activity and selectivity in our reaction of interest. Analogous to point 1, the catalyst without the shell should (and does) show higher H₂ uptake than the catalyst with the shell. Moreover, we are currently using the H₂ uptake of these catalysts to help determine the thickness of the shell we have synthesized.

Similar to point 1, without this instrument, we would require STEM-EDX measurements to obtain the same information. This instrument is expensive to use and requires years of training for a graduate student or post-doc to use properly.

Moreover, we have completed Temperature Programmed Reduction experiments on a number of catalysts, which will likely soon contribute to publication. These experiments would be especially difficult without the use of our chemisorption setup. In fact, we tried to complete these experiments in the past, before purchasing this instrument. In these experiments, we put a catalyst (our sample) in a reactor, and performed a TPR on it with a mass spectrometer (MS) at the outlet. We tried to use the decrease in the H₂ signal of the MS to measure H₂ uptake and obtain a TPR curve. Unfortunately, the H₂ uptake in a typical catalyst of ours is not significant enough to be detected as a decrease in the MS signal. Therefore, our TPR curves were hopelessly noisy, and we obtained no valuable data from them. As you can see in Figure 1, recently-obtained TPR curves feature a high signal-to-noise ratio even when using a small amount of sample (<100 mg) using our chemisorption setup. These experiments take advantage of the accurate control of the furnace temperature program, the programmable functions, and the high sensitivity of the gas detectors available with the Autochem.

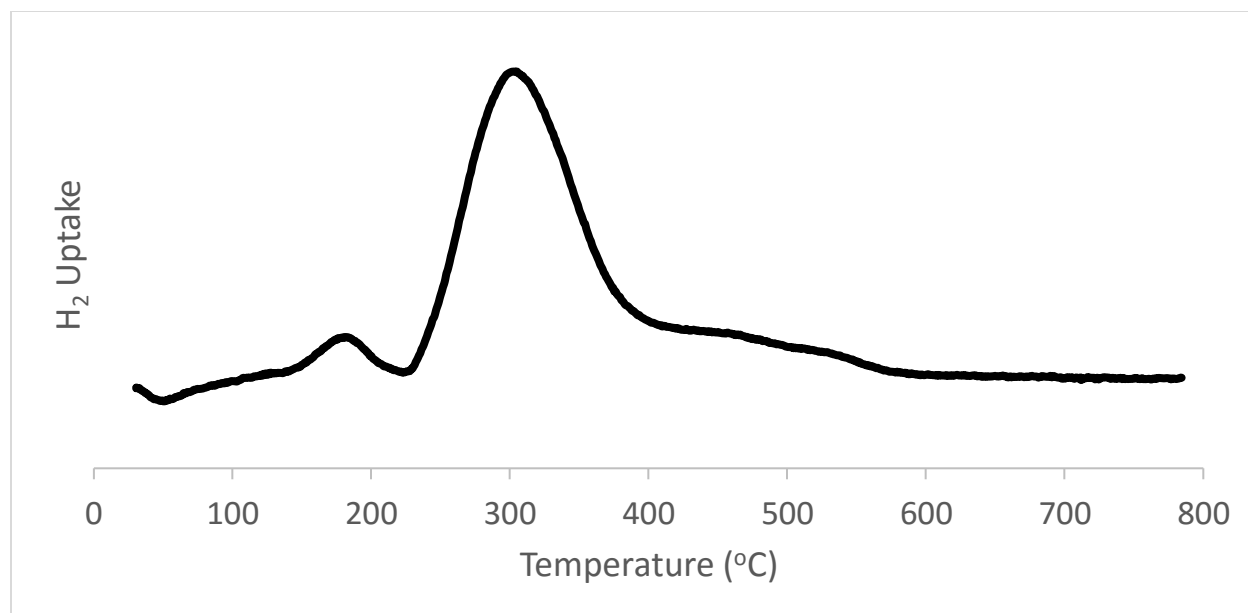


Figure 1: Recently-obtained TPR profile of metal catalyst (<100 mg used as sample) with chemisorption setup.

Future Work

We also discussed in the original proposal more advanced experiments that we wished to carry out with this instrument. Most of these experiments are currently in the planning phase. We are particularly excited about future experiments on catalysts for propylene oxidation, as was discussed in the original proposal, as well as catalysts for oxidative dehydrogenation of alkanes, which is a growing area of interest in our group.

Ongoing study in our group of a Ag catalyst (Ag/CaCO_3) for aerobic epoxidation of propylene is an ideal candidate for some of the more complex chemisorption experiments that we envision. Kinetic studies by our group have shown that high concentrations of propylene have an inhibitory effect on the rate of propylene oxide production over our catalyst. We hypothesize that this is due to the competitive adsorption between the propylene substrate and the oxide product and/or the inability of propylene to displace propylene oxide at the surface after it is formed. Therefore, we propose to use chemisorption studies to investigate these hypotheses, beginning with TPD of propylene and propylene oxide on the catalyst. TPD would allow us to compare the adsorption strengths of propylene and propylene oxide separately from one another to determine which maintains a stronger interaction with the Ag surface in a more controlled environment than in the reactor setup used for kinetic experiments. Furthermore, consecutive adsorption of propylene and propylene oxide (and *vice versa*) onto the catalyst should yield insight on the competitive behavior, such as whether propylene can displace propylene oxide. Such study of the catalyst will enhance our understanding of the origin of the kinetic behavior of the catalyst.

As we referenced in our original proposal, chemisorption studies on aerobic propylene epoxidation catalysts have previously been used to show that the reaction relies on surface oxygen sites, rather than lattice oxygen sites.⁵ We propose to perform similar studies on our Ag catalyst, which has been treated under various conditions proposed in the literature that lead to different activity results. For example, Ag catalysts have been treated with alkyl chlorides to enhance selectivity at the cost of conversion, with nitrogen oxides to improve conversion and selectivity to a moderate degree, and with alkali metal salts to improve selectivity. We propose to use chemisorption studies to understand (i) how the catalyst treated under different conditions adsorbs and activates oxygen differently and (ii) how those oxygen sites contribute to selectivity. Experiments to explore (i) can be performed using a combination of TPR, to prepare the surface for oxygen activation, and TPD of oxygen, to observe the type and strength of oxygen surface sites. We postulate that the different treatments and modifications will lead to variations in both the strength and number of surface oxygen sites. To investigate (ii), the different catalysts will be reduced and exposed to oxygen to generate the sites observed in the previous experiment, followed by pulses of propylene at reaction temperature to react with the active oxygen sites on each catalyst, the products of which will be measured with an online mass spectrometer. We expect to see that different treatment conditions lead to different ratios of CO₂ and propylene oxide products. A final study of the different catalysts would include an investigation of the competitive adsorption of propylene and propylene oxide, using a similar procedure to that proposed in the previous paragraph.

Another area of interest where we envision this instrument being very useful is understanding the formation of active catalytic surface species and their formation. Our group has discovered that boron containing catalysts for the oxidative dehydrogenation (ODH) of alkanes have an increased surface oxygen content after reaction, as observed by X-ray photoelectron spectroscopy (XPS).⁶⁻⁹ We attribute the high selectivity of these materials to their ability to activate oxygen, which we believe is evidenced by the surface oxygen content of spent catalysts. We hypothesize that initially the catalyst activates oxygen and generates a considerable amount of surface oxygen sites which are highly selective to propylene. In order to understand this phenomenon at a fundamental molecular level, we propose to use Temperature Programmed Surface Reaction (TPSR) measurements on the chemisorption instrument. Similar experiments have been previously used to elucidate mechanistic information on the ODH of ethane over NiO-based catalysts,¹⁰ and we hope to use such experiments to expand our understanding of boron containing materials for ODH. As a representative reaction to begin, we will examine ODH of propane using hexagonal boron nitride (h-BN) as the catalyst. The instrument setup would use dilute feeds of C₃H₈ in He and O₂ in He as the reactant gases, and online MS will be used to observe product formation. The fresh h-BN catalyst would first be exposed to a dilute C₃H₈ feed in the instrument while heating to 600 °C. The fresh h-BN sample would possess only trace amounts of surface oxygen species, leading to no reactivity until not

catalytic, gas-phase thermal cracking and dehydrogenation reactions begin to occur. Next, a new fresh h-BN sample would be exposed a feed of both dilute C₃H₈ and O₂ and heated to 600 °C to mimic ODH conditions, and the product distribution would be monitored by MS. Based on our previous ODH publications[add Science, C4, and borides], we expect that this environment will lead to catalytic activity at lower temperatures due to the activation of oxygen to form reactive surface species. Following the fresh catalyst experiments, we will examine a spent h-BN catalyst that already shows evidence of increased surface oxygen content. The spent catalyst will first be fed dilute C₃H₈, followed by both C₃H₈ and O₂ in a subsequent experiment. We expect to see the temperature at which the reaction takes place to decrease compared with the fresh catalyst, since the surface is already functionalized with active oxygen species. Furthermore, under oxygen-free conditions, we hypothesize that the spent catalyst will show some activity due to the presence of surface oxygen. We aim to gain insight on the kinetics of surface oxygen formation as well as the reactivity of said species with this set of experiments, which would not be possible without the capabilities of the Autochem instrument.

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