Thermal Programmed Reduction and Desorption System

Standard Operating Procedure

Lab: Flaherty Research Group, Davenport Hall 270

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Section 1: Overview

Type of SOP: ☐Process ☐Hazardous Material ☐Hazardous Class of Materials ☐Equipment

Synopsis:

The TPR system can run thermal programmed desorption, oxidation, and reduction as well as nitrous oxide titrations over a packed bed for catalyst characterization. These tests are done with MFC regulated gas flows of He, O_2, CO_2, H_2, and NH_3 through a temperature regulated reactor. The Pfeiffer quadrupole mass spectrometer (ThermoStar) measures product gas feed compositions which are analyzed to characterize catalyst acid/base sites, oxidation and reduction profiles, fractional dispersion, and average particle diameter. This SOP should familiarize the reader with the system procedures as well as potential hazards with the system.

Section 2: Risk Assessment Summary (Hazards and control measures)

Information obtained from performing a risk assessment should be entered into this section.

Materials:

Material (name, CAS #, other ID)	Hazards
Hydrogen	Extremely flammable gas, gas under pressure should not be heated
Ammonia	Flammable gas, toxic if inhaled, can cause skin or eye burns
Carbon Dioxide	Gas under pressure, Can cause suffocation
Compressed Air	Gas under pressure, may support combustion
Nitrous Oxide	May cause or intensify fire, gas under pressure, may cause suffocation
Helium	Gas under pressure, may cause suffocation
Acetone	Highly flammable liquid and vapor, causes serious eye irritation, can cause dizziness or drowsiness

Relevant References for Material Hazards:

Hydrogen
http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=295396&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F295396%3Flang%3Den
Ammonia
http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=294993&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F294993%3Flang%3Den
Carbon Dioxide
http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=295108&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F295108%3Flang%3Den
Compressed Air
http://airgas.com/msds/001002.pdf
Nitrous Oxide
http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=295590&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F295590%3Flang%3Den
Helium
http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=295345&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F295345%3Flang%3Den
Acetone
http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=320110&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F320110%3Flang%3Den

Equipment Hazards:

The furnace which heats the TRP cell can reach high temperatures. Caution should be taken when handling the furnace and cell inside. Be sure to use a quartz reactor cell rather than Pyrex. Pyrex has a lower melting point. The mass spectrometer also can be at high temperatures. Caution should be taken when near the Mass Spectrometer. The Mass Spectrometer has a mode for "Bake Out" to bake any water or residue out of the system. If the Mass Spectrometer is set in this mode then the filament should not be turned on. The instrument will reach high temperatures.

Hazardous Conditions:

The furnace can reach high temperatures. Be sure to use thermal gloves when working with the furnace or the cell heated by the furnace.

The ventilation of vapors or gases coming out from the system is on the lab ventilation. Make sure the vent is routed properly

Technique Hazards:

When closing furnace and setting a temperature, be sure to place the thermocouple in the correct position.
When changing the valves on the system to and from reactor and bypass, be sure that the valves are set to either both reactor or both bypass. If they are not the same, the feed gas could cause a pressure build up in the cell, and it could explode from high pressures.
It is good practice to change the valves to bypass when changing gas flow. Then there will be no contamination of unwanted gas in the reactor cell.

Be sure to wear gloves when handling the test sample, especially if the material is hazardous.

Personal Protective Equipment

Be sure to always wear safety glasses. When handling equipment at high temperatures, wear thermal gloves.

Engineering Controls

If any toxic gases, such as nitrous oxide, are being used, the proper exhaust equipment should be used. If the gas is being purged, the exhaust arm should be in place to remove any gas released into the air.

Section 3: Procedures

Thermal Programmed Desorption:

1. Switch to bypass by turning the valves upstream and downstream of the reactor so that the arrows are pointing away from the reactor.
2. Take the cell out, dump old catalyst into a vial, wash cell with acetone, and dry.
3. Load the cell with desired amount of sample and fasten it back into the system. Be careful that the cell is properly installed and there are no chips or cracks in the cell.
4. Switch upstream valve to the cell. Ensure that the pressure in cell increases. Do not let the pressure get over 10 psi or the cell may explode. If the pressure does not increase, then there may be a leak.
5. Switch the downstream valve to the cell. The pressure should decrease back to normal.
6. Set desired flow rate for helium.
7. On computer, open [M1] PFEIFFER VACUUM QUADSTAR 32-bit Measurement.
8. Go to File, Load, test.mip in PAP folder. Go to File, save cycle data, set to the maximum amount of cycles, click save measure-data only, save the file.
9. Ensure the thermocouple is properly positioned in cell. Close the furnace and set to 500°C. The furnace has a preset ramp rate of 5°C/min.
10. On computer, open [D4] Display Saved Values. Go to File, Open, and select the .mdc file created in step 8. In order to update the data throughout the experiment, go to File and click Reload Cycles.
11. There should be signals as the gases desorb from the catalyst. By time the furnace reaches 500°C, the signals should stabilize. Once the signals are stable, turn off the furnace and open it to let the cell cool down to 50°C.
12. Once the cell has reached 50°C, switch to the bypass.
13. Change flow rates of desired gas to adsorb onto catalyst. Let the gas flow through the bypass for a while to flush out any unwanted gases.
14. Switch valves back to the reactor. Wait for the signals to stabilize.
15. Once the signals are stable, close the furnace and set to desired temperature for desorption (~500-700°C). Take note of the cycle number at which heating began.
16. As the cell heats up, there should be peaks of gas desorbing from the catalyst.
17. Once the furnace reaches the desired temperature and the signals have stabilized, shut off the heat and open the furnace to allow the cell to cool. Take note of the cycle number at which heating was stopped.
18. To export data, on [D4] click file, Convert to ASCII, save the file.

Thermal Programmed Oxidation and Reduction

Similar procedures and precautions should be taken for the TPR. A more generic description will be given for this procedure.

- Follow steps 1-5 for loading the sample
- Set the desired flow rates for oxidation by switching to air at the backside of the panel
- Follow steps 7 and 8, but load TPR.mip instead of test.mip
- Begin heating to desired oxidation temperature and take note of cycle number when heating started
- Once final temperature is achieved, stop air flow and purge with Helium
- The reactor is then cooled for 40-60 min.
- Keeping the He flow on, switch to bypass so that the cell is filled with the inert gas
- Set control loop temperature in the EZ zone software to -200 C
- Start the Hydrogen and helium flow through the bypass
- Take the liquid nitrogen tank and attach the nozzle to the vent
- Vent the liquid nitrogen vapors on the reactor to cool the reactor to < -15C by keeping an eye on the temperature readout on the temperature controller
- As soon as reactor temperature reached 0 C (this will happen within 30-60 sec.), switch to reactor and start the temperature profile immediately
- Ideally, mass spec should be recording the profile since oxidation
- Note down the cycle and time when the valves were switched to the reactor
- Save cycles as in step 18.

<u>Nitrous Oxide Titration</u>
Procedures and precautions are similar to TPR and TPD.

- Follow steps 1-5 for loading the sample.
- Set Helium flow rate at lowest possible for the MFC (~2.00 mL/min)
- Follow steps 7 and 8 but load N2O Titration.mip instead of test.mip
- Be sure the syringe used for titrations is cleaned of any contaminants
- Open the nitrous oxide feed valve. Insert syringe completely into nitrous oxide feed line. Draw out desired amount of gas for injection.
- Release any unwanted gas into the exhaust arm and not into the lab air.
- Insert syringe completely into reactor and inject the nitrous oxide
- Record the cycle number and injection description
- Once a desired amount of titrations is complete, close the nitrous oxide feed valve

<u>Shutdown Procedures</u>

- Turn off the furnace and open the furnace
- Switch valves to the bypass and remove the cell
- Transfer the sample into a vial and label the sample. Clean the reactor cell with acetone and let dry.
- Turn off any feed gas flow rates and close gas feed valves
- Turn off MS-SPEC filament

Section 4: Waste Disposal/Cleanup

All samples removed from the reactor cell should be transferred to vials and properly labeled. Usually samples are saved, but if not they should be disposed of in a solid waste container.
Any unused nitrous oxide in a syringe should be released in a fume hood or exhaust arm.
For guidance on disposal procedures, see the "Waste Management" menu on the DRS webpage.

Section 5: Emergency Response

Emergency Response should be a component of the Laboratory Safety Plan.

Section 6: Additional Information

Advice:

This section should be updated regularly by the researchers performing the procedure. This section can be a list of things to never do when working with the hazard or quick tips for using a material in a safe manner. The points in this section should be read regularly to see if they should be highlighted in another section (e.g., procedure). Examples for this section may include:

1. *Scale ups with this chemical may result in an exotherm. Have ice bath ready.*
2. *Centrifuge secondary containment is necessary for this process.*
3. *Dry solvents are absolutely necessary for this process.*
4. *Weighing out this solid on humid days resulted in quick decomposition of the material.*

Checklist:

A checklist can be written in the SOP as a reminder for the steps needed to take in order to perform the procedure. Potential checklist items include:

☐*Read (Material) Safety Data Sheets.*

☐*Proper fire extinguisher is nearby.*

☐*Another researcher is nearby and knows the hazards present.*

☐*All calculations are done prior to beginning the procedure.*

☐*The required glassware is of the proper size to accommodate all steps of the procedure.*

☐*Received necessary immunizations.*

References:

Add any references to literature, previous SOPs, or lab specific references such as lab notebook entries.

Training Documentation
Signing this document means that you have read and understand all aspects of this Standard Operating Procedure. The supervisor is the person that acknowledges you took the training and understand the procedure. They can be a lab manager or researcher assigned by the PI to oversee this particular SOP.

Name (Printed)	Name (Signed)	Supervisor	Date