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Temperature-Programmed Deoxygenation of Acetic Acid on Molybdenum Carbide Catalysts

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TITLE:

Temperature-Programmed Deoxygenation of Acetic Acid on Molybdenum Carbide Catalysts

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SHORT ABSTRACT:

Presented here is a protocol for the operation of a micro-scale temperature-programmed reactor for evaluating the catalytic performance of molybdenum carbide during acetic acid deoxygenation.

LONG ABSTRACT:

Temperature programmed reaction (TPRxn) is a simple yet powerful tool for screening solid catalyst performance at a variety of conditions. A TPRxn system includes a reactor, furnace, gas and vapor sources, flow control, instrumentation to quantify reaction products (e.g., gas chromatograph), and instrumentation to monitor the reaction in real time (e.g., mass spectrometer). Here, we apply the TPRxn methodology to study molybdenum carbide catalysts for the deoxygenation of acetic acid, an important reaction among many in the upgrading/stabilization of biomass pyrolysis vapors. TPRxn is used to evaluate catalyst activity and selectivity and to test hypothetical reaction pathways (e.g., decarbonylation, ketonization, and hydrogenation). The results of the TPRxn study of acetic acid deoxygenation show that

molybdenum carbide is an active catalyst for this reaction at temperatures above ca. 300 °C and that the reaction favors deoxygenation (i.e., C-O bond-breaking) products at temperatures below ca. 400 °C and decarbonylation (i.e., C-C bond-breaking) products at temperatures above ca. 400 °C.

INTRODUCTION:

Temperature programmed reaction (TPRxn) is one of many temperature programmed methods, including desorption (TPD), oxidation (TPO), and reduction (TPR), and proceeds via exposure of a catalyst to a reactant concurrent with or followed by a steady increase in temperature.¹⁻³ TPRxn is a transient technique that provides information about catalyst activity and selectivity as a function of reaction temperature.⁴⁻⁶ It is also a popular technique: a search of the keywords 'temperature programmed reaction' in the literature yields over 1,000 sources citing its use.

TPRxn experiments are typically performed in a microreactor system, equipped with a mass spectrometer (MS) for real-time analysis of the reactor effluent and correlation of performance with temperature. Reactant gases can be introduced using mass flow controllers and liquids can be introduced via a syringe pump or as vapors by bubbling inert gas through a liquid. The catalyst is often pre-treated *in situ* to form the desired catalytic phase for the reaction. Some systems are equipped with additional analytical equipment, beyond the typical mass spectrometer, to provide quantitative or qualitative information about the catalyst selectivity, surface species present on the catalyst, or reaction mechanism. For example, temperature programmed *in situ* Fourier Transform Infrared Spectroscopy (FTIR) provides information about the evolution of surface species with varying reaction temperature.^{7,8} The TPRxn system demonstrated in this work is equipped with a gas chromatogram (GC) in addition to the more typical MS. This GC, equipped with four parallel columns, allows for more accurate quantification of the reaction products, but is limited in analysis frequency by the time it takes the products to elute through the columns. Thus, the combination of MS and GC can be particularly useful for coupling real-time identification with accurate quantification of reactants and products.

Here, we apply the TPRxn methodology to study the deoxygenation of acetic acid on molybdenum carbide catalysts. This is an interesting and important reaction in catalyst research, as acetic acid is a useful analog for the many carboxylic acids present in biomass pyrolysis vapors.⁹ The high oxygen content in biomass pyrolysis vapors necessitates oxygen removal to produce hydrocarbon fuels,¹⁰⁻¹² and molybdenum carbide catalysts have shown promising deoxygenation performance for many biomass pyrolysis vapor model compounds, including furfural, 1-propanol, phenolics and acetic acid.^{9,13-16} However, the activity and selectivity of molybdenum carbide catalysts in deoxygenation reactions is dependent on the catalyst structure and composition, the reacting species and the reaction conditions.

The data collected from TPRxn of acetic acid shows that molybdenum carbide catalysts are active for deoxygenation reactions above ca. 300 °C, and when combined with catalyst characterization information allows for quantification of the catalyst activity as a function of

temperature via the calculation of acetic acid turnover rates. The TPRxn results show that deoxygenation (i.e., C-O bond-breaking) products are favored at temperatures below ca. 400 °C and decarbonylation (i.e., C-C bond-breaking) products are favored at temperatures above ca. 400 °C. Additionally, TPRxn studies illustrate the changes in the activity and selectivity of molybdenum carbide catalysts produced using various synthetic procedures (i.e., the production of different molybdenum carbide catalyst structures and compositions). Still, the value of this information and, more generally, the successful application of TPRxn experimental data toward catalyst design and process optimization is a function of the quality of the data obtained. Careful consideration and knowledge of the potential difficulties and limitations highlighted throughout the TPRxn procedure is paramount.

PROTOCOL:

CAUTION: Consult safety data sheets (SDS) for all chemicals used prior to operation. Flammable gases may present explosion hazards if combined with air or oxygen and an ignition source. Hydrogen is an extremely flammable gas. Acids are corrosive, and in the case of skin or eye contact, are irritants and may produce burns. Acetic acid is a flammable liquid and vapor and thus may ignite and/or explode in the presence of open flames, sparks and oxidizing agents, in addition to potentially causing severe skin burns and eye damage. When not in a closed system or container, acetic acid should be handled inside of a chemical fume hood. The hazards of nanomaterial catalysts are not well-understood, thus these materials should be handled inside local exhaust enclosures (i.e., a chemical hood) to reduce exposure. Personal protective gear (safety glasses, nitrile gloves, lab coat, closed-toed shoes, long pants) should be worn while handling any of these materials.

NOTE: The quadrupole mass spectrometer (MS) used in this work is equipped with a Faraday cup detector and operates at an ionization energy of 70 eV. For quantification of all reaction products, the micro gas chromatograph (μ GC) includes a total of four independent columns each equipped with a thermal conductivity detector (TCD). For column types refer to the Specific Equipment/Materials list. Clean gas filters are used on the μ GC carrier gases (He, Ar) to prevent column degradation due to H₂O, and to improve the performance of the thermal conductivity detectors. Briefly, μ GC units are typically less expensive and have shorter sample times than conventional gas chromatograph systems, but are restricted in the compounds that can be analyzed (i.e., most effective for permanent gases, short chain hydrocarbons and low molecular weight oxygenates) and are limited to thermal conductivity detectors.

1. System Preparation

1.1) Equipment Startup

1.1.1) Verify the MS and μ GC are powered on, stabilized, tuned, and the μ GC is calibrated. For tuning and method development of the MS and μ GC, refer to the operating manual of the analytical equipment. Detailed procedures for μ GC calibration are published elsewhere¹⁷⁻²¹, and an overview of the specific calibration process used here is presented in the note below.

NOTE: Compounds were identified through retention time comparison with known standards.

Quantitative analysis was carried out using TCDs, which were calibrated with standards of known concentrations. Briefly, each gas standard was fed to the μ GC with a two-stage regulator and the concentrations were allowed to stabilize. Once gas concentrations stabilized as evidenced by stabilization in the chromatogram peak areas, at least three samples of the calibration gas standard were taken. The process was repeated for all relevant gas standards. Response factors for each species were generated from the line of best fit of the peak areas from the triplicate calibration samples as a function of the known gas standard concentrations. The species and concentration ranges observed in the experiment, and thus needed for calibrations, are outlined in Table 1. In general, a minimum of three calibration points for each species, spanning the entire expected range, is preferable. For relatively non-volatile (i.e., low vapor pressure) species such as acetic acid, obtaining gas calibration standards with appropriate concentrations may be difficult, and thus single-point calibrations may be the only option.

1.1.2) To prevent condensation of gas phase reactants and products in the system lines, ensure that the system lines from the reactor to the MS, and from the MS to the μ GC are heated to 84 °C and 105 °C, respectively, using insulated heat tapes (Figure 1A) and a heat tape temperature controller. These temperatures are chosen based on the boiling points of the reactant and product species, manufacturers specifications for the maximum allowable temperature for gas fed to the μ GC, and the need to maintain a sufficiently low MS vacuum pressure.

NOTE: All system lines are 316/316L stainless steel unless otherwise noted. VCR and compression type fittings are used exclusively throughout the system, with one exception at the reactor thermocouple. The fittings connecting the quartz “U-tube” reactor to the system tubing are VCR; however, Ultra-Torr fittings would also be applicable under the conditions employed in this work. Such a fitting is used for the reactor thermocouple, in conjunction with a bored-through union, allowing the position of the thermocouple to be adjusted. An acetic acid compatible o-ring (perfluoroelastomer) is used for this fitting.

1.1.3) Use a roughing pump to decrease the MS pressure below 1×10^{-4} Torr.

1.1.4) Power on turbo vacuum pump for the MS and allow the vacuum pump sufficient time to reach desired vacuum pressures ($<1 \times 10^{-7}$ Torr).

1.1.5) Fill saturator (Figure 1B) with glacial acetic acid in an appropriate ventilated fume hood.

1.1.5.1) Carefully pour the acetic acid into the saturator; minimize contact between the acid and the stainless steel “cutting edge” that will be used to complete the fitting with the copper gasket.

1.1.5.2) Place a copper gasket on the bottom half of the saturator unit, and align the top half of the saturator in place.

1.1.5.3) Insert the bolts through the flange holes, and hand-tighten into the washers. Use a

wrench to tighten the bolts further, alternating bolts after each half turn to ensure a uniform seal across the copper gasket.

1.1.6) Install saturator on TPRxn system.

NOTE: When installing the saturator, ensure the orientation of the saturator is correct. Helium should flow through the stainless steel tubing into the liquid acetic acid, with the vapors exiting the saturator through the headspace. Improper installation could result in liquid acetic acid entering the system lines.

1.2) Reactor Loading

1.2.1) Remove a clean, dry, quartz “U-tube” reactor (Figure 2) from a storage/drying oven (nominally kept at 110-150 °C).

1.2.2) Once the reactor has cooled to room temperature, load a small amount of quartz wool into the reactor. Use the minimum amount of quartz wool needed to support the catalyst bed.

1.2.3) Using a clean, stiff, metal wire packing rod (*e.g.*, 3/32” OD, 316/316L stainless steel), gently push the wool down the quartz tube to the end of the straight section of the tube.

1.2.4) Weigh 50 mg catalyst, and mix with 200 mg quartz chips to prevent channeling and to ensure consistent temperature through the catalyst bed. Prior to use, sieve quartz chips to a particle size similar (*i.e.*, 180-300 μm) to that of the catalyst (*i.e.*, 150-250 μm) to limit inhomogeneity of the physical mixture.

NOTE: Sieving the quartz chips to a smaller particle size may result in a larger pressure drop across the catalyst bed.

1.2.5) Using weigh paper and a clean funnel, pour catalyst/quartz chip mixture into the reactor, such that the catalyst bed sits on top of the quartz wool support.

1.2.6) Gently push a second small piece of quartz wool on top of the catalyst bed, securing the catalyst bed in place.

1.3) Reactor Installation

1.3.1) Clean reactor thermocouple with acetone to remove any residue from previous experiment.

1.3.2) Install the reactor by first connecting and tightening the fitting on the upstream side of the catalyst bed (*i.e.*, the straight section of the quartz reactor tube).

1.3.3) Connect and tighten the fitting on the downstream side of the catalyst bed. The short section of flexible stainless steel tubing used for this fitting in the system demonstrated here mitigates potential breaks in the delicate “U-tube” reactors during reactor installation and

removal.

1.3.4) Adjust the reactor thermocouple position by pushing the thermocouple through a bored-through fitting so that the tip of the thermocouple sits on the top edge of the catalyst bed. The thermocouple should be pushed through the quartz wool located on top of the catalyst bed.

NOTE: A perfluoroelastomer (FFKM) o-ring is compatible with reactants and products present in this experiment and is therefore recommended for sealing the fitting.

1.3.5) Carefully raise the furnace (Figure 1C) to the highest level allowed by the “U-tube” reactor, such that the top edge of the furnace does not touch the reactor. Do not allow the bottom of the reactor to contact the bottom of the furnace.

1.3.6) Wrap the exposed sections of the “U-tube” reactor above the furnace with insulation.

2. Reactor Startup

2.1) Inert Purge

NOTE: The reactor system and analytical equipment must vent to a safe location such as a fume hood so that people and other lab equipment are not exposed to harmful gases and vapors. Prior to starting flow of any gas, the respective compressed gas cylinder and two-stage regulator delivery valves should be opened. If needed, the regulator delivery pressure should be adjusted to the inlet pressure at which the associated mass flow controller (MFC) was calibrated. The delivery pressure from the MFCs should not exceed 140 kPa, a limit defined by the maximum allowable pressure at the inlet of the μ GC.

2.1.1) Open the shut-off valve between the ultra-high purity (UHP) He MFC and the reactor (this valve is present to prevent backflow to the He MFC), and ensure the three-way valve is routing gas from the reactor to the local exhaust ventilation line (Figure 3).

NOTE: Unless otherwise specified, all pressures are given relative to local barometric pressure (gauge pressures). The addition of water traps to each gas feed line is recommended to remove any trace water from the gas.

2.1.2) Flow UHP He gas at 40 standard cubic centimeters per minute (sccm) through the calibrated MFC. This flow rate has been empirically determined to effectively purge the system of air and residual gases within a reasonable time frame (ca. 45-60 min).

NOTE: Valves have been placed immediately downstream of the MFCs to prevent backflow of residual acetic acid vapors, which may result in damage to the MFCs. When starting gas flow, it is important to start flow through the MFCs immediately after opening these system line valves.

2.1.3) Verify that the system pressure does not rise to more than 7 kPa.

NOTE: A higher system pressure may indicate that a valve is closed or that the pressure drop

through the catalyst bed is higher than acceptable. If the latter, increasing the amount of quartz chips mixed with the catalyst may decrease the pressure drop across the catalyst bed.

2.1.4) Using the computer software associated with the MS, start the online MS. Set the MS to scan from mass-to-charge (m/z) ratios of 0 to 100.

NOTE: Using a scan mode is preferred to using a selective ion monitoring (SIM) mode as it allows for detection of unknown products. The scan range is chosen based on limitations of the MS and a scan over the range of 0-100 (m/z) is typically sufficient for analysis of the major acetic acid reaction products. If equipment allows a larger range, scanning up to 102 would be desirable to include detection of any acetic anhydride produced.

2.1.5) Open the MS gas sampling orifice valve to allow the vacuum of the MS system to draw gas through the 1 μm orifice.

NOTE: A 2 μm filter incorporated into a VCR gasket is installed just upstream of the 1 μm orifice to limit plugging of the 1 μm orifice.

2.1.6) Purge air from the acetic acid saturator with UHP He by opening the inlet and outlet saturator valves, and subsequently closing the saturator-bypass valve. Continuous bubbling through the liquid acetic acid indicates that the system line valves are in the correct position and that the saturator was installed with the correct flow orientation. Allow the saturator to purge while monitoring the MS signal until N_2 and O_2 ($m/z = 28$ and 32 , respectively) are no longer present.

NOTE: Step 2.1.6 may be skipped if it has been performed in previous experiments.

2.1.7) Stop the saturator purge by opening the saturator bypass valve and closing the saturator inlet and outlet valves.

2.1.8) Continue purging the system with UHP He until all m/z signals except He ($m/z = 4$) are no longer present (may require 45-60 min depending on system volume).

NOTE: System may remain under UHP He flow until ready to begin subsequent steps.

3. Catalyst Pretreatment

3.1) *In-Situ* Hydrogen Pretreatment

NOTE: At this point, the catalyst exists as molybdenum carbide and was synthesized *ex-situ* via methods published elsewhere.^{9,22} The *in-situ* hydrogen pretreatment step is included to remove surface oxygen (often resulting from the oxygen passivation following synthesis), and/or to remove organic ligands that may be present on the catalyst surface as a result of synthesis.

3.1.1) Continue UHP He flow at 40 sccm.

3.1.2) Open the H₂ tank cylinder valve. Adjust the two-stage regulator delivery pressure if needed, and open the regulator needle valve (see NOTE in 2.1.1).

3.1.3) Begin H₂ flow by opening the H₂ system line shut-off valve just downstream of the H₂ MFC and setting the MFC to flow at 1.3 sccm. Adjust UHP He flow to 36 sccm.

NOTE: A 3.5% H₂/He gas mix is chosen to keep the H₂/He composition below the lower explosive limit of hydrogen (4%). The flow rate of 37.3 sccm is chosen to achieve the desired mix composition given the flow range limitations of the MFCs on our system, to ensure a steady supply of H₂ during the catalyst pre-treatment, and to maintain a system pressure below 140 kPa.

3.1.4) Allow the gas phase concentrations of H₂ and He to stabilize (30-45 min) by monitoring the MS signals $m/z = 4$ and 2 for He and H₂, respectively.

3.1.5) Enter the temperature program into the furnace controller. A typical temperature program is as follows: ramp from room temperature to 400 °C at 5 °C/min, holding at 400 °C for 2 h.

NOTE: The reduction temperature and holding time are often material dependent and empirically determined. Here, these values were determined based on previous temperature programmed reduction studies of molybdenum carbide catalysts which indicate when O₂ removal by H₂ as H₂O is complete. As an example, for bulk orthorhombic β -Mo₂C, the O₂ removal was complete following 2 h at 400 °C. The ramp rate of 5 °C/min is sufficiently slow to ensure the pre-treatment is not destructive to the catalyst and sufficiently fast to complete in a reasonable time period.

3.1.6) Begin the temperature program.

3.1.7) When the program ends, allow the reactor to cool to ambient temperature in flowing 3.5% H₂/He.

4. Acetic Acid Temperature Programmed Reaction (TPRxn)

4.1) Starting an Experiment

4.1.1) Continue flowing UHP He and H₂ at flowrates of 36 and 1.3 sccm, respectively.

4.1.2) Begin the flow of acetic acid vapors through the reactor by opening the inlet and outlet saturator valves, and subsequently closing the saturator-bypass valve.

4.1.3) Route gas flow to the μ GC by switching the three-way valve downstream of the reactor from its current position (sending gas from the reactor to the local exhaust vent) to the μ GC position.

NOTE: System pressure should begin to increase. This pressure increase is due to the pressure

drop through the 1/16" tubing used in the μ GC unit and should not be allowed to exceed 140 kPa (this limitation is based on the maximum allowable pressure at the inlet of the μ GC).

4.1.4) Allow the system pressure and gas phase concentration of acetic acid to stabilize (requires 60-90 min depending on system volume).

NOTE: Acetic acid concentration may be tracked on the MS by visualizing the real-time data from $m/z = 43$ and 60. System pressure typically stabilizes at approximately 130 kPa.

4.1.5) Program the furnace temperature controller to ramp from room temperature to 600 °C at 10 °C/min.

NOTE: The ramp rate of 10 °C/min is sufficiently slow to obtain well-resolved data as a function of temperature and to avoid any destruction to the catalyst, but sufficiently fast to complete the experiment within a reasonable period, and without substantial catalyst deactivation.

4.1.6) Begin collecting μ GC samples as frequently as possible.

NOTE: The μ GC method used here allows for sampling once every 5.5 min. The MS data should include temperature vs. time data and the μ GC data should include synchronized time stamps such that both the MS and μ GC data can be correlated with temperature.

4.1.7) Begin the temperature program immediately after starting the μ GC samples.

4.2) Stopping an Experiment

4.2.1) When the temperature program has completed, stop the μ GC sequence.

4.2.2) Using the computer software associated with the MS, turn the MS off.

NOTE: Leave the MS turbo pump 'on' if the MS is to be used in subsequent experiments.

4.2.3) Close the 1 μ m MS orifice valve.

4.2.4) Load a μ GC method that sets the column temperatures to their maximum allowable limit, as recommended by the manufacturer.

NOTE: Carrier gases to the μ GC must remain on. This 'bakeout' method is recommended by the manufacturer to remove (clean) oxygen, water, and high-boiling compounds from the μ GC columns.

4.2.5) Shut off hydrogen flow by setting the H₂ MFC to 0 sccm and closing the H₂ shut-off valve.

4.2.6) Allow the reactor to cool to ambient temperature while purging the system with flowing UHP He at 40 sccm.

4.2.7) When cool, turn off UHP He flow, and allow the system to reach ambient pressure.

4.2.8) Once at ambient pressure, route gas to the local exhaust vent using the three-way valve.

5. Reactor Unloading

5.1) Uninstalling a Reactor

5.1.1) Stop UHP He flow by setting the He MFC to 0 sccm. Close the UHP He line shut-off valve located immediately downstream of the He MFC.

5.1.2) Loosen the Ultra-Torr thermocouple fitting and pull the thermocouple up and away from the catalyst bed to facilitate reactor removal.

5.1.3) Uninstall the reactor by first disconnecting the fitting on the downstream side of the reactor (*i.e.*, the fitting connected to the flexible stainless steel tubing).

5.1.4) Disconnect the fitting on the upstream side of the reactor.

5.1.5) Remove the reactor from the system and transport to a chemical fume hood.

5.2) Reactor Cleaning

5.2.1) Working in a chemical fume hood, use a clean, corrosive resistant wire (*e.g.*, 24 gauge nichrome wire) to remove the piece of quartz wool on the top of the catalyst bed.

5.2.2) Pour the used catalyst into a sample vial to keep in case post-reaction characterization is desired at a later time.

5.2.3) As in 5.2.1, use the wire to remove the remaining piece of quartz wool.

5.2.4) Clean the inside of the reactor with acetone.

NOTE: A pipe cleaner may be used in conjunction with acetone to scrub the inside of the reactor if any residual carbon is present.

5.2.5) Store the reactor in an oven at 110 °C to remove any residual water. If an oven is not available, the reactor can be blown dry using a compressed air line in a chemical fume hood and stored in a desiccator.

6. Data Analysis

6.1) MS Deconvolution

Note: The method for MS deconvolution is briefly outlined here. Refer to recently published literature for a complete summary of the deconvolution of acetic acid TPRxn MS data.^{9,23}

6.1.1) Using the MS software, download individual m/z ratio data as a function of reaction

temperature.

6.1.2) Adapting a method used by Zhang, *et al.*²⁴, correct for overlapping MS signals using mass fragmentation patterns for individual species (see discussion section below).

6.1.3) Correct the deconvoluted MS data similar to the method described by Ko, *et al.*,²⁵ for relative differences in ionization efficiency, quadrupole transmission and electron multiplier gain.

6.1.4) Use the normalized and corrected data to gain semi-quantitative information regarding catalyst performance.

6.2) μ GC Data Integration and Analysis

6.2.1) Using the μ GC software, integrate chromatogram peaks.

6.2.2) Using the response factors generated from the μ GC calibration discussed in section 1.1.1, transform peak area counts into molar composition data for each species observed.

6.2.3) Refer to recent literature for a detailed explanation of the μ GC data analysis procedure and the quantitative information it can provide.²²

REPRESENTATIVE RESULTS:

The online MS provides the capability to analyze the gas composition at the reactor outlet in real-time. The online MS is not coupled with any device to separate products prior to analysis, and thus species identification is challenging when differentiating between compounds with overlapping mass fragmentation patterns. As shown in Table 2, many of the common products from acetic acid TPRxn experiments are characterized by multiple common m/z signals. Deconvolution of the MS data ($m/z = 1 - 100$ as a function of temperature) allows for semi-quantitative data to be obtained because the MS signal intensity for a given species is roughly proportional to the partial pressure of that species.^{26,27} Following deconvolution, the data are normalized and corrected, and thus may be used semi-quantitatively to gather information such as reactant conversion and relative product concentration as a function of reaction temperature (Figure 4).

A μ GC is also included with the system for more accurate quantification of reactants and products, while maintaining the temporal resolution required for analyzing TPRxns. The μ GC method used by our group limits the frequency of sample collection to intervals of approximately 5.5 min (at a 10 °C/min ramp rate, this corresponds to a sample approximately every 55 °C). The time between samples is limited by the method required to achieve both carbon monoxide elution and separation between H₂ and He in column 1 of the GC. Figures 5 and 6 show representative data for a study comparing the acetic acid deoxygenation activity and selectivity of molybdenum carbide catalysts with varying structures, morphologies and compositions. In that work, nanoparticle MoC_{1-x} (NP-MoC_{1-x}) were synthesized with and without an SBA-15 template and compared with bulk MoC_{1-x} and bulk Mo₂C. Figure 5 illustrates the use

of μ GC data, combined with catalyst characterization information, to generate acetic acid (Figure 5A) and H_2 (Figure 5B) turnover rates (TOR) as a function of reaction temperature. The results show that the templated NP-MoC_{1-x}/mSBA demonstrated greater acetic acid TOR, and thus greater catalytic activity, compared to the untemplated NP-MoC_{1-x}, and similar acetic acid TOR compared to the bulk molybdenum carbide catalysts below 400 °C. Above 400 °C, the templated catalyst demonstrated greater acetic acid TOR than any of the other catalysts studied. The H_2 TOR was lower on the nanoparticle catalysts than on the bulk catalysts at all temperatures studied. Figures 6A and 6B show data for the reaction selectivity to decarbonylation and decarboxylation (DCO, sum of selectivities to CH_4 , CO_2 , and CO) and ketonization (KET, selectivity to acetone), respectively, as a function of reaction temperature obtained from μ GC sampling during TPRxn experiments. Both nanoparticle materials (NP-MoC_{1-x} and NP-MoC_{1-x}/mSBA) demonstrated higher selectivity to KET above 400 °C than their bulk counterparts. In light of acid and H-site titration data, the authors concluded that the higher KET selectivity was attributed to an increase in the fraction of strong acid sites relative to the bulk materials. Furthermore, based on these results, the ratio of acid sites to H-sites was identified as a key property in determining acetic acid deoxygenation performance. In Figures 5 and 6, error bars for each data point are based on data collected for at least 3 replicate experiments.

Figure 1. TPRxn Equipment.

(A) Wrapped heat tape. The heat tape is taped to the stainless tubing with high temperature electrical tape and covered with two layers of thermal insulation. (B) Acetic acid saturator. (C) Ceramic furnace (D) Knockout vessel at low point in the TPRxn system upstream of the μ GC.

Figure 2. Quartz “U-tube” reactor.

(A) Installed quartz “U-tube” reactor used for acetic acid TPRxn. (B) Close-up of molybdenum carbide catalyst bed and thermocouple.

Figure 3. Process flow diagram.

The process flow diagram for the TPRxn system.

Figure 4: Representative analysis of MS data after deconvolution.

(A) Conversion of acetic acid and hydrogen and the (B and C) relative concentrations of products during acetic acid TPRxn using a molybdenum carbide catalyst. Reprinted with permission from [9]. Copyright 2016 American Chemical Society.

Figure 5: Acetic acid and hydrogen turnover rate from μ GC data.

The (A) acetic acid and (B) hydrogen turnover rate (TOR). The TOR values were calculated by normalizing acetic acid and hydrogen conversion by the number of acid- and H-sites, respectively, on the catalytic materials. Error bars were determined from at least 3 replicate experiments and represent the standard error in the data. Adapted with permission from [22]. Copyright 2016 Angewandte Chemie International Edition.

Figure 6: Selectivity during acetic acid TPRxn experiments.

The selectivity to (A) decarbonylation and decarboxylation (DCO) and (B) ketonization (KET) products during acetic acid TPRxn experiments over various molybdenum carbide catalysts. Error bars were determined from at least 3 replicate experiments and represent the standard error in the data. Adapted with permission from [22]. Copyright 2016 Angewandte Chemie International Edition.

Table 1: Reactant and product species with corresponding calibration concentrations.

The typical concentration ranges for reactants and products during acetic acid TPRxn. Calibration standards for the μ GC should be designed to span the range of observed concentrations.

^aIf a single concentration is shown, it may be assumed the lower range of the observed concentration range is 0 mol%.

Table 2: Mass fragmentation pattern.

The fragmentation patterns of reactants and products during acetic acid TPRxn. Fragmentation patterns are used in the MS deconvolution algorithm to produce normalized species concentration data. Reprinted with permission from [9]. Copyright 2016 American Chemical Society.

^aThe mass fragment intensities, highlighted in bold, have been identified as the primary mass fragments for each compound. ^bAll m/z values from 1 – 100 are collected during TPRxn experiments; only a selected subset is shown here corresponding to only those m/z values used in deconvolution. ^cMass fragmentation patterns are collected by introducing pure compound vapor into the MS for all compounds except ethane. The mass fragmentation pattern for ethane is obtained from the NIST Chemistry WebBook database.²⁸

DISCUSSION:

The TPRxn method is a powerful tool for screening of catalytic materials, providing information about the activity and selectivity of a catalyst as a function of reaction temperature. Other temperature-programmed methods such as TPD, TPO and TPR can provide information on the adsorption strength of reactants, number of adsorption sites, and appropriate catalyst pre-treatment procedures, but do not provide direct catalytic performance data. It is important to note that the TPRxn method detailed in this work does not measure steady-state reaction rates, and thus, reaction data may include the effects of catalyst stabilization, deactivation and transport limitations. However, TPRxn studies are often higher throughput than steady-state experiments, providing initial insight into catalyst activity and selectivity that can motivate and inform more rigorous future studies. While deoxygenation of acetic acid over molybdenum carbide catalysts under specific reaction conditions is detailed in this work, the TPRxn method is applicable to a broad range of reactant compounds (*e.g.*, ethanol, methanol, crotonaldehyde), catalytic materials (*e.g.*, zeolites, noble metals, metal oxides) and reaction conditions (*e.g.*, reactant concentrations, pre-treatment procedures, pressures). With the system setup described in this work, limitations in reactant molecules studied are primarily the volatility (*i.e.*, boiling point) of the reactant molecule and compatibility with the analytical equipment. For use in the saturator, the reactant must be volatile enough to achieve sufficient concentrations in the vapor phase as dictated by thermodynamic principles (*i.e.*, vapor-liquid-equilibrium). The

use of higher-boiling point compounds can be accomplished with the addition of a controlled heating device to the saturator, such as a heated mineral oil bath.

The ability to monitor the reactor effluent gas in real-time using the online MS allows the user to monitor reaction progress and to verify that the system is performing correctly, thus improving the efficiency of the TPRxn method. Use of the MS simplifies the system operation, as monitoring primary fragmentation peaks (Table 2) eliminates the guesswork in operations such as purge steps, in which it is important to know when the system is clear of contaminants that may affect the experiment. Although rigorous quantitative data is difficult to achieve from a MS, semi-quantitative data is attainable despite the complexity of observed product fragmentation patterns (Table 2). For optimal MS performance, it is critical to allow the turbo vacuum pump enough time to reach sufficiently low pressures at the ion source. Similarly, the 1 μm orifice valve that controls gas flow to the MS must be firmly shut in order for the turbo pump to function properly between experiments (*i.e.*, reach a sufficiently low pressure). The persistence of $m/z = 18$ (water) in MS data is one potential indicator that the turbo pump is not functioning properly or that more time is needed for the vacuum pump to purge the vacuum chamber prior to beginning an experiment.

An additional key to achieving reliable MS data is the collection of mass fragmentation patterns for relevant pure compounds prior to performing experiments. Mass fragmentation patterns are known to be instrument specific.²⁹⁻³¹ If semi-quantitative data of reaction products is desired, collecting pure compound mass fragmentation patterns for each species, as shown in Table 2, will dramatically improve the quality and reliability of results. If semi-quantitative data is not needed, mass fragmentation patterns obtained from the NIST Chemistry WebBook database may suffice.²⁸

Continuous monitoring of the MS ion source pressure and the system pressure during the reaction are important factors in troubleshooting any potential discrepancies in the data. In general, the system pressure positively affects the ion source pressure within the MS, and the ion source pressure directly affects the m/z signal intensity. Thus, changes in system pressure may lead to changes in MS signal intensity. An indication that this pressure effect was present during an experiment is a uniform increase in all m/z intensities. To mitigate this problem, ensure that the pressure drop across the reactor is low throughout the experiment. This can be achieved via dilution of the catalyst bed with quartz chips of the appropriate particle size as described in step 1.2.4.

A critical factor in achieving optimal quantitative performance of the μGC is maintenance of instrument calibration data. Complete recalibration can be infrequent (*i.e.*, annually or biannually); however, repeating a single standard calibration weekly will help to identify and correct any drift in the detector signal. Another phenomenon to be mindful of is retention time drift, particularly if chromatograms have peaks eluting near the end of the method (the shortest effective method run time is advantageous in maintaining high temporal resolution). Should retention times shift to later times, compound peaks may begin to decrease in area (due to backflush timing), or disappear altogether. Running sample calibration standards frequently

will help identify this issue. An additional procedure that has improved the quality and reproducibility of our μ GC data is to hold the μ GC columns at their maximum allowable temperatures and pressures when the instrument is not in use (*i.e.*, “bakeout” mode). This “bakeout” helps to remove oxygen, water, acetic acid and other contaminants from the μ GC columns and prepares the μ GC for the next experiment.

Various engineering controls have improved the overall functionality and performance of our acetic acid TPRxn system. A 2 μ m solids filter was placed upstream of the 1 μ m MS orifice. This filter has dramatically reduced the frequency of turbo pump shutdowns to manually clear blockage in the MS orifice. By reducing the frequency of orifice blockage, the solids filter has reduced the overall downtime of the system. Heat tapes are used on tubing sections to prevent vapors from condensing. This serves to protect the analytical equipment from damage and to maintain accurate analysis of the gas composition. Additionally, a small, unheated knockout vessel is located upstream of the μ GC. This knockout vessel (Figure 1D) is located at a low point in the system and serves as a redundant measure to reduce the possibility of liquid products entering the μ GC, which would cause damage to the columns. Clean gas filters are used on the μ GC carrier gases to remove any water and oxygen contaminants from the ultra high purity (UHP) carrier gases. Water traps are also used on the H₂ and UHP He gas feeds into the reactor system to prevent trace amounts of water from complicating the interpretation of experimental results.

Additional “soft-use” measures help to ensure collection of the highest quality data. For example, when using the μ GC the system pressure will increase from ambient to approximately 130 kPa. It is important to refrain from switching the three-way valve from its ‘ μ GC’ position to the ‘local exhaust vent’ position while at a system pressure greater than 14 kPa, as the abrupt change in pressure will move the catalyst bed, pushing it into the system tubing. As a second example, diligent note taking will assist in data analysis and system troubleshooting, particularly notation of the system pressure and the temperature at which μ GC injections occur during the acetic acid TPRxn. The former is needed to calculate the actual flow rate of acetic acid across the catalyst bed (based on vapor-liquid-equilibrium principles), and the latter is important in accurately assigning μ GC data to a given temperature.

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DISCLOSURES:

The authors have nothing to disclose.

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Figure 1

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Figure 2

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Figure 3

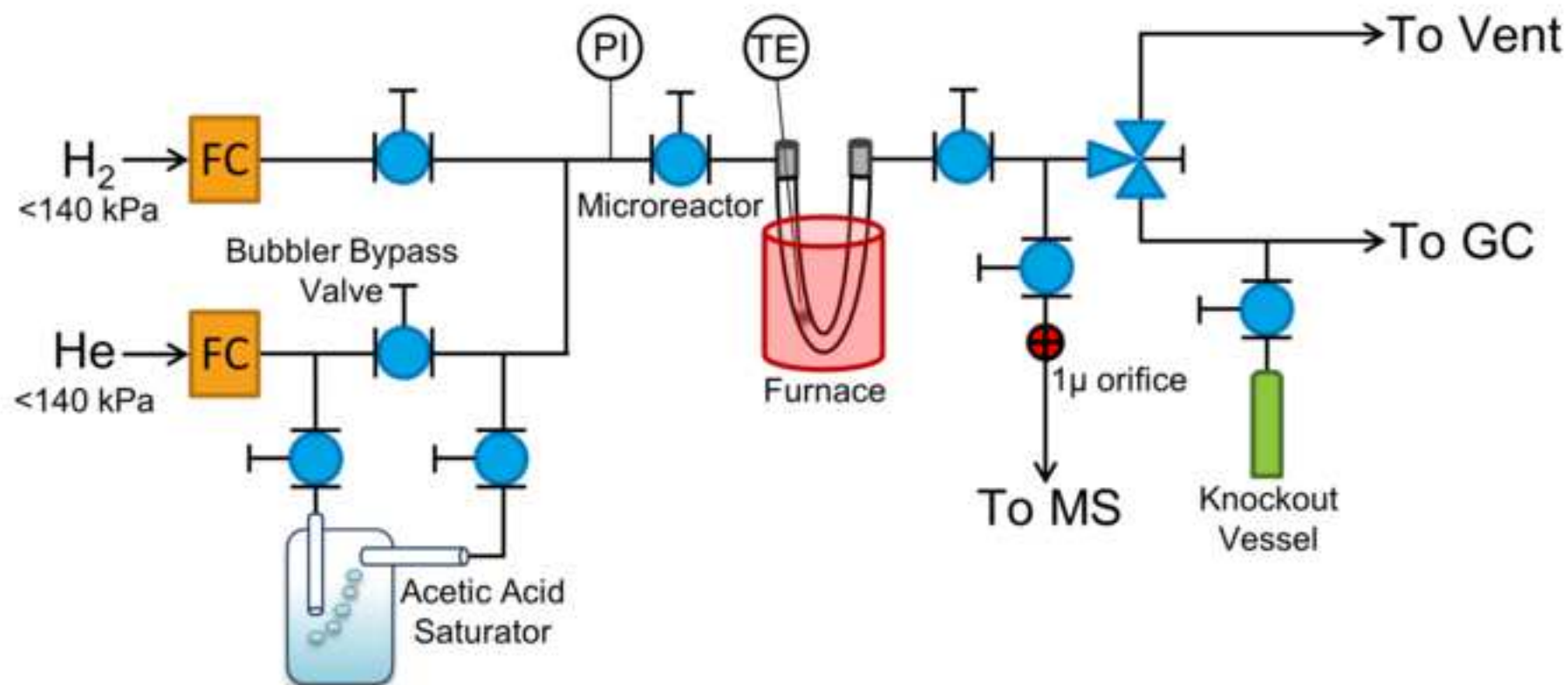
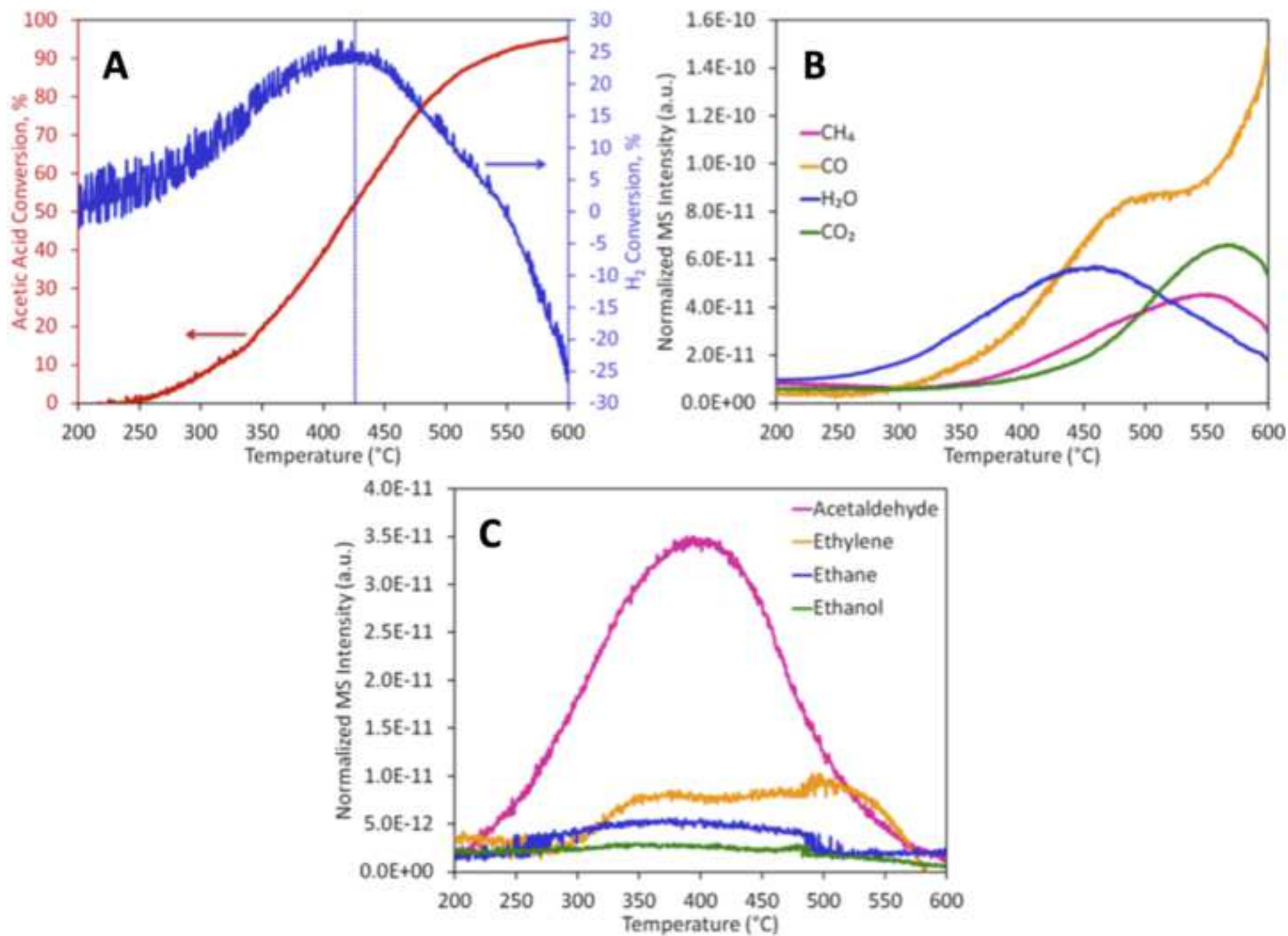
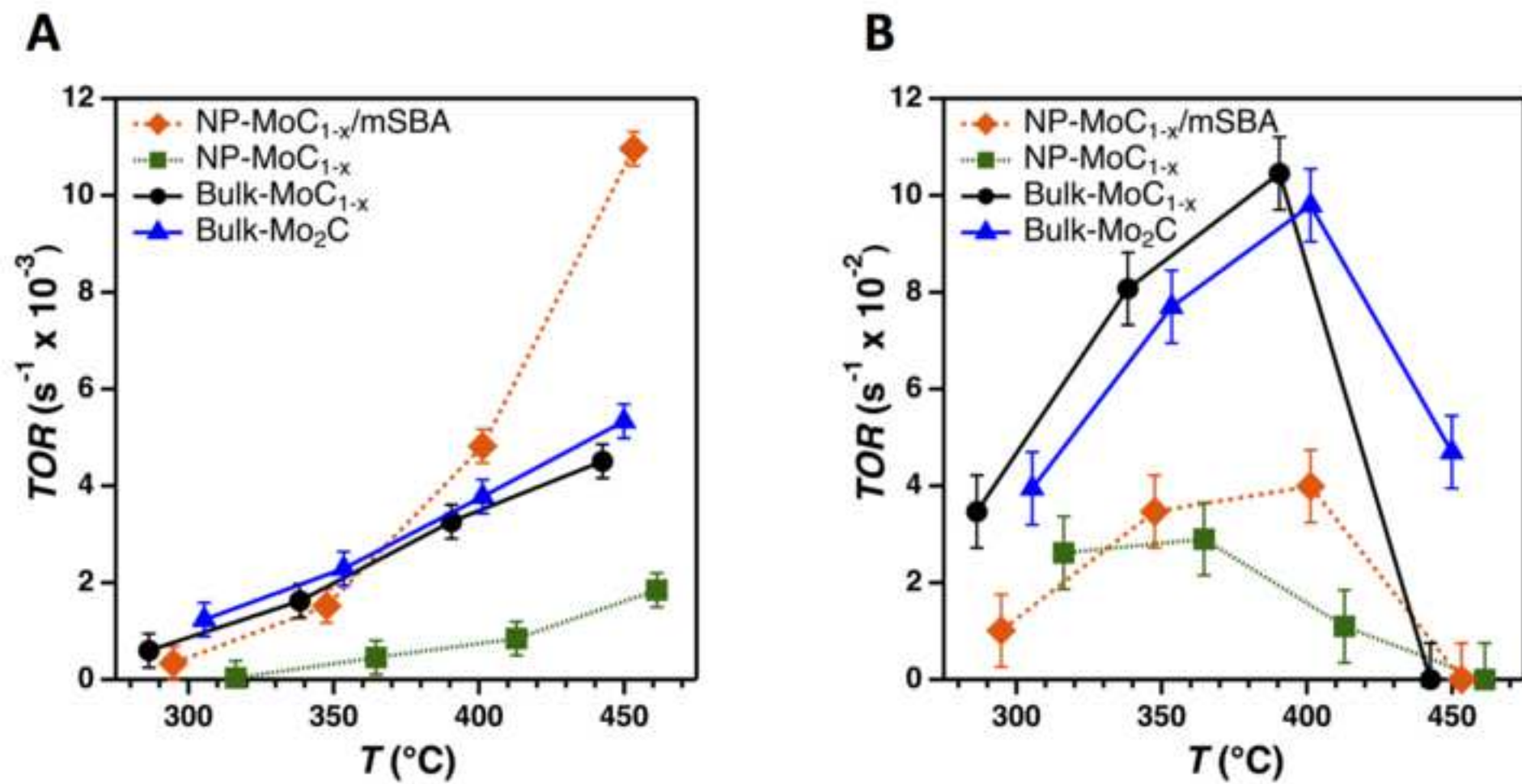
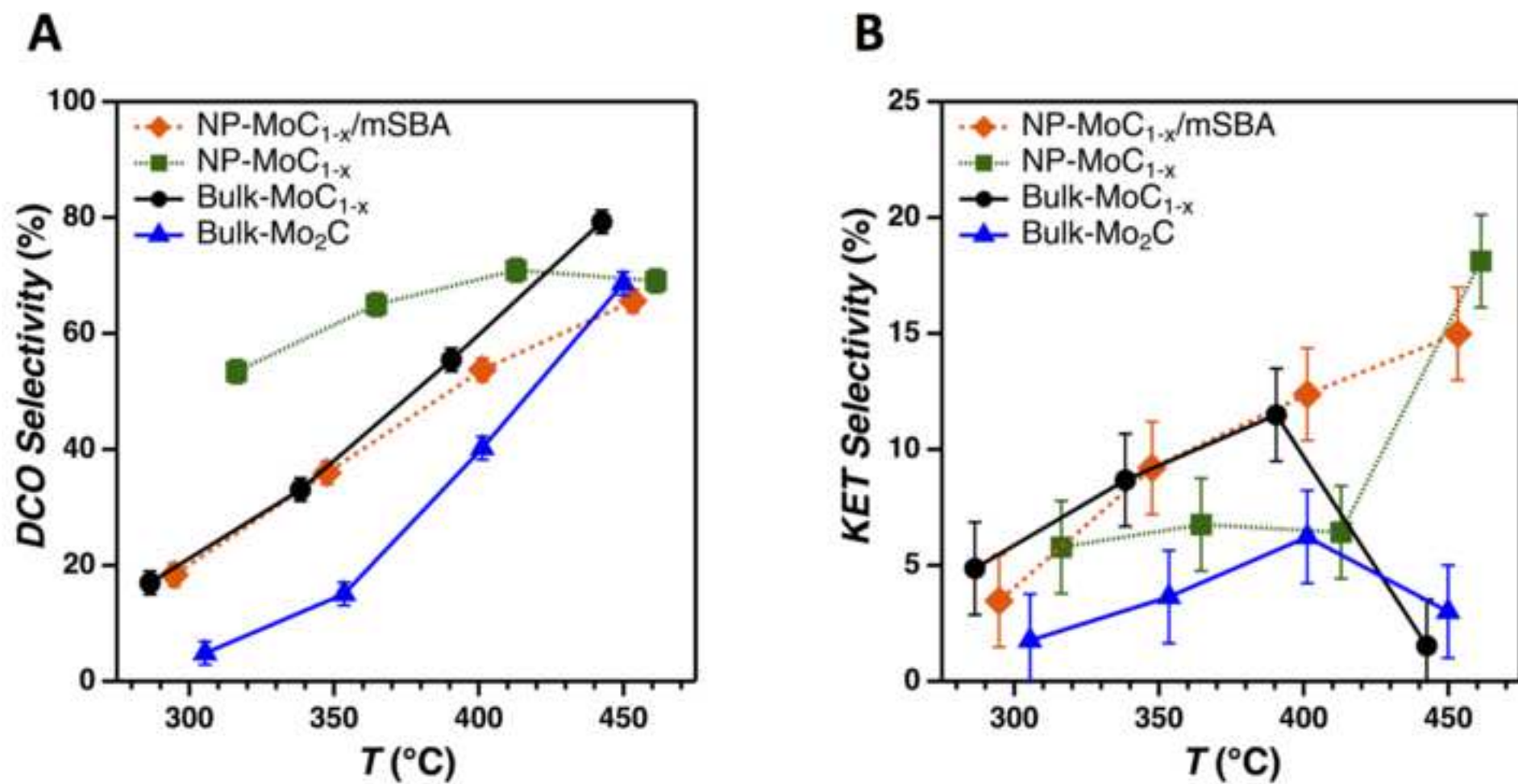


Figure 4

[Click here to download Figure Figure4_.tiff](#)





Species	Concentration, mol%
He	80-90
H ₂	10
Acetic Acid	6
CO	2
H ₂ O	1
CH ₄	0.6
CO ₂	0.6
Acetaldehyde	0.3
Acetone	0.2
Ethane	0.1
Ethylene	0.1
Propane	0.1
Propylene	0.1
Ethanol	<0.1

[illegible]

17	16	15	14	13	12	4	2
-	-	34	24	-	-	-	-
-	9	-	-	-	3	-	-
-	1	24	5	1	-	-	-
1	1	9	5	2	1	-	-
-	-	4	3	-	-	-	-
1	10	66	26	11	5	-	-
-	2	-	-	-	3	-	-
-	-	1	4	2	1	-	-
24	3	1	-	-	-	-	-
2	100	76	13	6	2	-	-
-	-	-	-	-	-	100	-
-	-	-	-	-	-	-	100

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
glacial acetic acid	Cole-Parmer	EW-88401-62	alternate supplier acceptable if ACS purity grade. See caution statement in protocol for safety information
UHP H ₂	Airgas	HY R300	alternate supplier acceptable if >99.99% purity
UHP He	Airgas	HE R300SS	alternate supplier acceptable if >99.99% purity
UHP Ar	Arigas	AR R200	alternate supplier acceptable if >99.99% purity
acetone	VWR International	BDH1101-4LP	alternate supplier acceptable if >99.5% purity
quartz chips	Powder Technology Inc.	Crushed Quartz	sieved 180-300 µm, calcined in air at 500 °C overnight
mass spectrometer - turbo vacuum pump	Pfeiffer Vacuum	TSU 071	mass spectrometer is controlled with LabVIEW 2010 software package (National Instruments)
mass spectrometer - turbo vacuum pump	Stanford Research Systems	RGA100	
micro gas chromatograph	Agilent	CP740388	490 Micro GC; 4-channel system Channel 1: 494001360 Molseive 10m, heated backflush Channel 2: 494001460 PPU 10m, heated backflush Channel 3: 490040 AL2O3/KCL 10+0.2m, heated backflush SPECIAL Channel 4: 492005750 5CB 15m, heated
GC software	Aglient	OpenLAB CDS EZChrom Edition	
clean gas filters	Agilent	CP17974	for use on GC carrier gases (He, Ar)
quartz "U-tube" reactor	n/a		hand blown glass, custom built to order
bubbler	n/a		custom built to order
ceramic furnace	Watlow	discontinued	Similar furnace part #: VC401J12A-B000R
heat tape controller	n/a		custom built with Watlow EZ-zone parts
heat tape	Omega	FGH051-060	alternate supplier for extreme temperature heat tape acceptable
heat tape insulation	JEGS	710-80809	alternate supplier acceptable
thermocouple	Omega	<i>e.g.</i> , KMQSS-062U-18	K-type thermocouples; alternate sizes may be required
thermocouple o-ring	Swagelok	VT-7-OR-001-1/2	perfluoroelastomer(fluorocarbon FKM) o-ring
2 µm solids filter, VCR gasket	Swagelok	SS-4-VCR-2-2M	
1 µm orifice, VCR gasket	Lenox Laser	SS-4-VCR-2	for mass spectrometer orifice
316/316L stainless steel tubing and fittings	Swagelok	Varies	See Swagelok 'VCR Metal Gasket Face Seal Fittings' and 'Stainless Steel Seamless Tubing and Tube Support Systems' catalogs for more information
316/316L stainless steel tubing and fittings	Swagelok	Varies	See Swagelok 'Integral-Bonnet Needle Valves', 'Bellows-Sealed Valves' and 'One-Piece Instrumentation Ball Valves' catalogs for more information



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Article Title: Temperature-Programmed Deoxygenation of Acetic Acid on a Molybdenum Carbide Catalyst

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We thank the editors and reviewers for their constructive feedback. Our responses are provided below in red under each set of comments.

Editorial comments:

The manuscript has been modified by the Science Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (553314_R0_080516.docx) is located in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions.

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.
2. Please abbreviate all journal titles.
3. Please obtain explicit copyright permission to reuse any figures from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure must be cited appropriately in the Figure Legend, i.e. "This figure has been modified from [citation]."
4. Grammar: 6.2.3 – Please convert to a note or use imperative tense.
5. Results: Please discuss the interpretation of the data in Figures 5 & 6 in the Results section. What do the results shown mean?
6. Discussion: Please discuss the significance with respect to alternative methods. Please also discuss the future applications of the method.

1. We have thoroughly proofread the manuscript and corrected all spelling and grammar issues.
2. All journal titles are now abbreviated.
3. Explicit permissions have been uploaded for all reused figures and the citations in the manuscript are per instructions from the respective journals.
4. Converted 6.2.3 to the imperative tense.
5. Discussion of the interpretation of the results in Figures 5 and 6, specifically the relative activity and selectivity of the various catalysts, has been added to the results section.
6. The significance with respect to other temperature-programmed methods, as well as alternative catalyst evaluation methods, has been added to the discussion section. Future

applications of the method, such as the use of alternative reactant molecules, catalytic materials and reaction conditions have also been added to the discussion section.

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

This manuscript details the use of temperature programmed reaction (TPRxn) equipment for the study of reaction pathways of acetic acid on MoC-based catalysts. The authors provide enough detail such that potential readers could construct and operate a TPRxn unit.

Major Concerns:

N/A

Minor Concerns:

The following minor revisions should be considered before final publication.

- Line 112: The authors first use the abbreviation "mGC" in line 112 but don't define the abbreviation until line 123. They should define the abbreviation in Line 112, and perhaps add a brief explanation of the difference between a micro GC and a conventional GC.
- Section 1.1.1: It would be helpful to include a reference here for GC/MS tuning and calibration because not all of the readers may be familiar with GC-MS equipment.
- Section 1.1.5: I suggest using the term "saturator" instead of "bubbler". Also, could the authors provide some details of how they filled the saturator? These details would be helpful to readers trying to reproduce this saturator and who do not have experience with the flange connecting the stainless steel components to the glass components.
- Section 1.3: The fittings connecting the quartz reactor to the stainless steel feed lines appear to be VCR fittings. Is this correct? It may be useful to provide this detail as well as information about the type and locations of different fittings (i.e., ultra-torr, compression, VCR, etc.)
- I suggest using the term "condenser" instead of "knockout" in the Discussion and Figure caption.

Additional Comments to Authors:

N/A

Line 112: We have now defined μ GC in line 112 and removed the definition from line 123. A brief explanation of the difference between a μ GC and a conventional GC has been added to the text near line 117.

Section 1.1.1: References for detailed descriptions of gas chromatograph calibration are now included. In addition, a brief overview of the specific calibration method used in this work has been added to the NOTE below Section 1.1.1. The reader is referred to their analytical equipment operating manuals for tuning methods, as these are often instrument/manufacturer specific.

Section 1.1.5: All instances of the term "bubbler" have been replaced with the term "saturator." Additional details of the procedure used to fill the saturator have been added to 1.1.5

Section 1.3: The fittings connecting the quartz reactor to the stainless steel feed lines are VCR fittings, but this is not a strict requirement, as Ultra-Torr fittings are also suitable for this application. The only Ultra-Torr fitting currently on the system is used with the reactor thermocouple and a bored-through tee union. A brief description of the fittings used and required throughout the system has been added to the NOTE following 1.1.2.

The term “condenser” generally refers to a heat exchanger intended to condense a gas. The knockout vessel used in our application is intended to collect any already condensed gas to prevent it from entering the μ GC. Thus, we think that “knockout” is the appropriate term for our system. The purpose of the vessel is described in the Discussion section.

Reviewer #2:

Manuscript Summary:

This manuscript describes the details associated with measuring the activity of molybdenum carbide catalysts on the deoxygenation of acetic acid. This detailed report is based off of measurements the same group reported in recent Angew. Chem. and ACS Catalysis publications. This is a well written, detailed explanation of the measurements, an important contribution because this measurement is unique and not associated with an instrument that can be easily obtained from a commercial source and was likely "home-built".

- * Why are some of the steps highlighted in the draft? There does not seem to be an explanation of how the highlighted steps differ from the non-highlighted text.

- * Perhaps the authors could explain what the state of the catalyst is in the pretreatment step. For many applications of molybdenum carbide catalysts there is an in situ carburization step but it appears that the catalyst is going into the reactor as a molybdenum carbide already.

- * The steps are clear and sound and, without actually doing the measurement, they appear to be complete.

- * The abstract is missing the second parenthesis after "spectrometer".

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

N/A

1. The highlighted steps indicate the protocol text we want featured in the video, per JOVE author instructions.

2. Information regarding the general state of the catalytic materials has been included in a NOTE following 3.1. Because of the difference in the various molybdenum carbide materials used (i.e., crystal structure, morphology, and composition as a result of the particular synthetic method used), we chose not to include this specific information regarding the precise state of the catalyst materials. The appropriate references were included to direct the reader to the synthetic methods

and corresponding characterization data. A justification for the hydrogen pretreatment has been added.

3. The parenthesis after “spectrometer” has been added. The authors apologize for the error.

Reviewer #3:

Manuscript Summary:

This paper presents work regarding an experimental system of temperature-programmed reaction as well as its application for the deoxygenation of acetic acid on molybdenum carbide catalysts. The paper is well-written for providing clear and detailed demonstration for the setup and use of this system using acetic acid deoxygenation as an example. This paper indicates that the system with both GC and MS equipped is a powerful tool for catalyst testing in various ways in terms of temperature-programmed techniques. I recommend accepting the manuscript as is. It will be a valuable reference for other researchers who are having similar needs for catalyst performance testing.

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

N/A



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