

Using the Modified PID EFFI Microactivity Reactor for the Characterization of Catalysts via Thermo-Programmed Techniques

Simon Yunes, Andrew D'Amico, and Jason Exley

Introduction

The PID EFFI (Efficiency) microactivity reactor can be re-configured and connected to a mass spectrometer for temperature-programmed and pulse chemisorption techniques used to characterize and test catalysts *in situ*. This innovative research tool, known as the “Micro Catalyst Characterization and Testing Center” (MCCTC), allows for multiple catalyst characterization experiments and activity testing at pressures ranging from atmospheric up to 100 bar or 200 bar (depending on instrument configuration). Characterization techniques including temperature-programmed reduction, oxidation, and desorption can be used as a point of reference prior to testing the performance of the catalyst. The capability to then follow the transient activity of the catalyst on-line provides important information about the behavior of the catalyst’s active life and deactivation. Re-characterization of the catalyst after activity testing provides critical information about the parameters which potentially cause loss in activity of the catalyst. The combination of characterization and performance testing in a single apparatus provides important and accurate information about catalytic behavior for specific applications.

The Instrument

Figure 1 shows the MCCTC configuration of the PID EFFI, designed for catalyst characterization and catalytic testing to determine activity and selectivity of the specimen. The essential components of this instrument include mass flow controllers (MFCs) for the carrier and active gases, three (3) six-port valves to dictate flow pathways and pulsing through the reactor, a heated reactor zone able to reach temperatures up to 1100°C using various ramping rates, and a quadrupole mass spectrometer for on-line analysis of gas mixtures. All plumbing, valves, and the liquid evaporator (for cases involving liquid feeds), are enclosed in a hot box heated up to 200°C ensuring excellent mixing of gases and the prevention of condensation within the system. Heated vapors which condense at atmospheric conditions are cooled and separated from the gas phase using the patented Liquid/Gas separator.

These liquid products can be collected for further studies and the dry gas proceeds to the mass spectrometer for composition analysis.

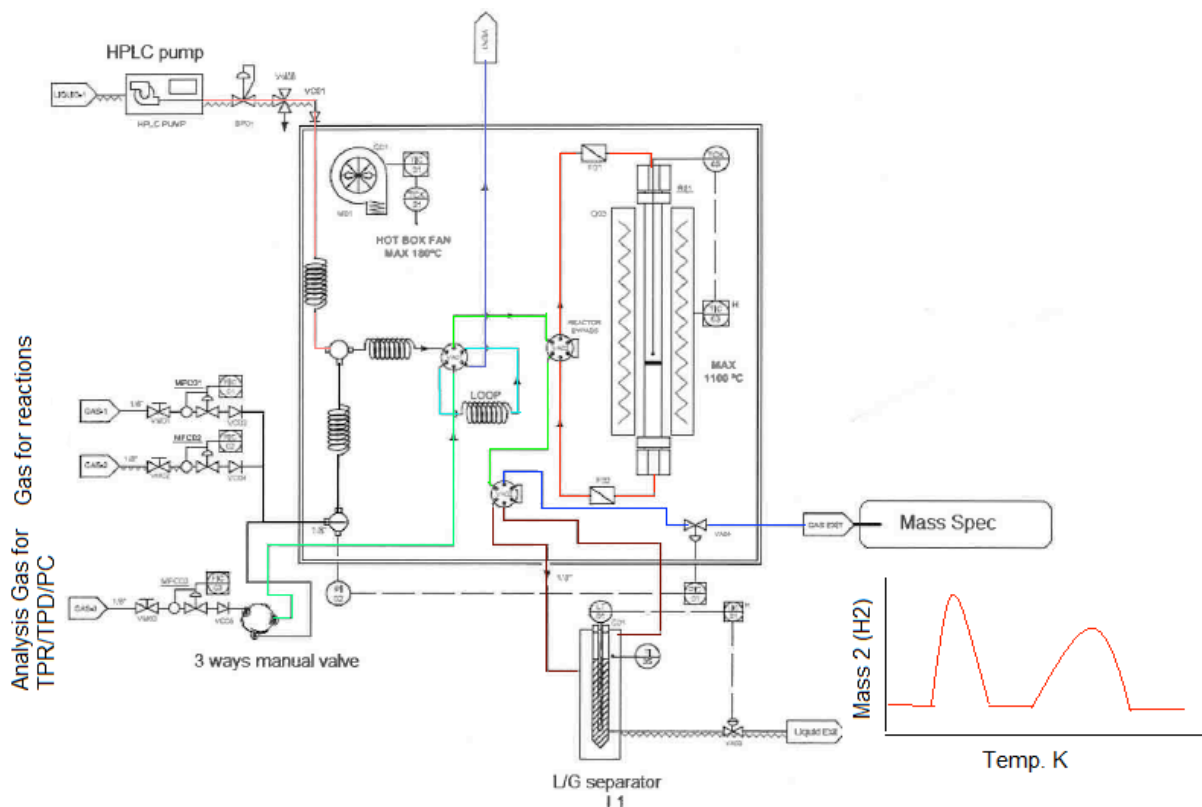


Figure 1: Flow Diagram of the MCCTC Connected to a Mass Spectrometer

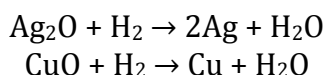
Experiment 1: Temperature-Programmed Reduction (TPR)

Temperature-programmed reduction is used for characterizing the reducible species existing in the catalyst as well as determining the effect of the catalyst support on the dispersion of active metal(s). In this particular case, the effect of the H₂ pressure on the reduction profile of a catalyst was studied by acquiring TPR profiles at two distinctly different pressures, 1 bar and 25 bar. Approximately 80mg of a silver (I) oxide and copper (II) oxide catalyst mixture (50/50 approx.) was selected for this study. A flow of 50 sccm of a 10% hydrogen balance nitrogen mixture was used for species reduction and a flow of 100 sccm nitrogen was supplied as a carrier gas and diluting agent. The furnace temperature was ramped at a rate of 10°C/min up to 500°C to generate complete TPR profiles.

First, temperature-programmed reduction was performed on the silver/copper oxide mixture at atmospheric pressure like most TPR studies are traditionally executed. The atmospheric pressure TPR profile can be seen in Figure 2 and portrays a sharp inverted peak at 163°C and a broader inverted peak at 320°C,

indicating the activation temperatures of the silver oxide and copper oxide, respectively. Next, the same TPR analysis was performed at a pressure of 25 bar.

The 25 bar pressure TPR profile can be seen in Figure 3 and includes a sharp inverted peak at 150°C and a broader inverted peak near 250°C. The inverted peaks show the decrease of H₂ in the exhaust gas downstream of the catalyst being reduced. During reduction hydrogen is consumed and combines with the oxygen atoms in the metal oxide following the chemical reactions:



It is clear that the high pressure of H₂ over the catalyst significantly decreases the reduction temperature as expected. The increased pressure provides a higher driving force for hydrogen and oxide interaction, specifically regarding porous catalyst supports. This principle is very valuable in industry because reduction of catalysts at lower temperatures greatly decreases the chance of sintering and ultimately allows for higher catalytic activity. Since TPR is a bulk reaction, a quantitative analysis can be made with the mass spectrometer data to determine the total amount of reducible species present in the catalyst.

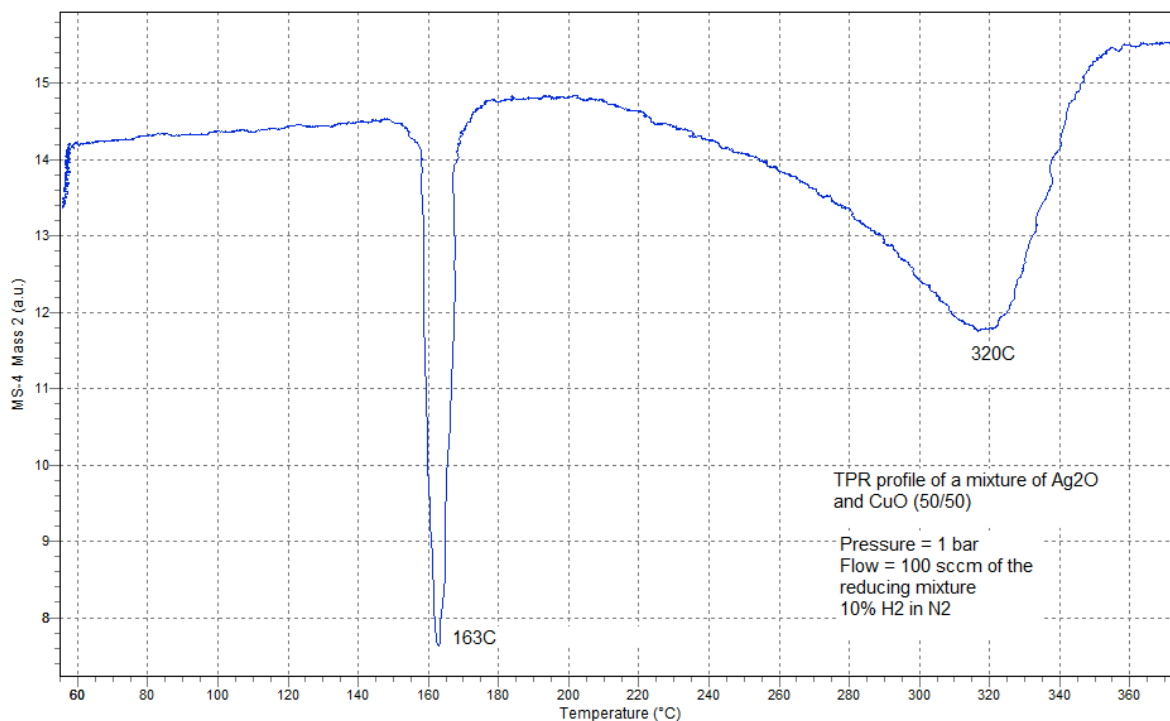


Figure 2: TPR Profile Performed at Atmospheric Pressure

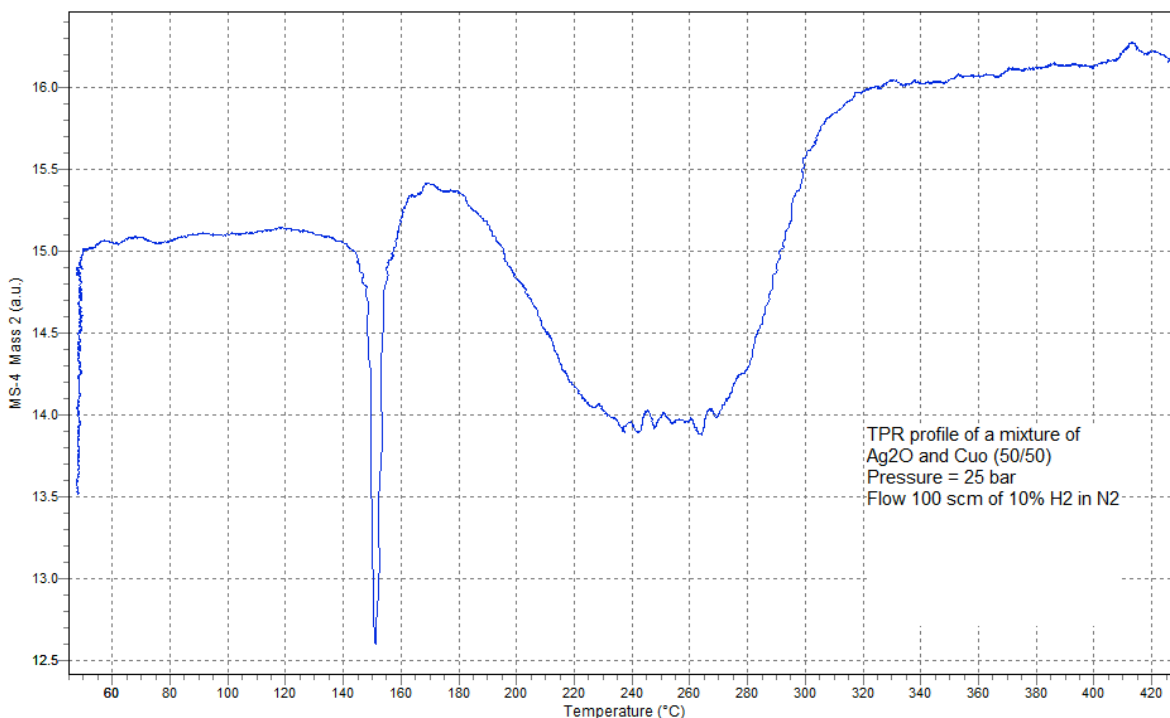


Figure 3: TPR Profile Performed at 25 bar Pressure

Experiment 2: Pulse Chemisorption (PC)

Pulse chemisorption (PC) is an analytical technique used to determine the dispersion, or accessible active species present on the surface, of a catalyst. An active gas such as CO or, in this case, H₂, is pulsed onto the catalyst at room temperature and the quantity of active gas adsorbed is determined. For this experiment, the active gas was pulsed by using a six-way valve with a 0.5 mL STP loop in intervals of approximately 3 minutes. The 10% hydrogen balance nitrogen mixture was fed through the loop at a flow rate of 20 sccm to ensure complete filling within 1 minute. Atmospheric pressure nitrogen was fed at a constant rate of 50 sccm through the system to act as a carrier gas. Approximately 800mg of 0.5 wt% Pt/Al₂O₃ was the studied catalyst. Figure 4 is the data obtained from the mass spectrometer during the duration of the experiment and the five separate peaks indicate the five separate pulses. The last three peaks are identical and represent pulses after the catalyst has been saturated and are used as a baseline to back-calculate the amount of gas adsorbed from the first two pulses. Almost all of the active gas is adsorbed in the first pulse and some of the active gas is adsorbed in the second pulse. By integrating the peaks and combining this data with the known

pulsed volume, the total amount of adsorbed gas is known. The percent dispersion of the catalyst is determined using the following equation:

$$D_{\%} = \frac{V_{ads} F_s W_a}{V_{mol} M_{\%}} \cdot 100 \cdot 100$$

Where $D_{\%}$ is the percent dispersion, V_{ads} is the total volume of gas chemisorbed, F_s is the stoichiometry factor, in this case 2 for diatomic hydrogen, W_a is the atomic weight of the active metal, 195 AMU for platinum, V_{mol} is the molar volume of the adsorptive (22.414 liters/mol), and $M_{\%}$ is the percent of active metal by weight as grams of metal per gram of sample.

The studied catalyst, 0.5 wt% Pt/Al₂O₃, is a well known standard used for Micromeritics Chemisorption instruments such as the Autochem II 2920 and has a reported dispersion of 35% ± 5%. The percent dispersion calculated from the data collected by the MCCTC and mass spectrometer yielded 36%.

If the PC experiment is performed at elevated pressures, more active species will be adsorbed and thus, the percent dispersion of the catalyst will be proportionally higher. It is known that catalysts characterized at atmospheric pressure exhibit higher activity than indicated when screened at elevated pressures required for industrial chemical reactions.

Furthermore, other parameters can be determined by the PC technique such as active metal surface area and the size of the active particles. Large active particle size indicates sintering, or growth, of the active particle. Generally, as the active particle size increases, the activity of the catalyst decreases.

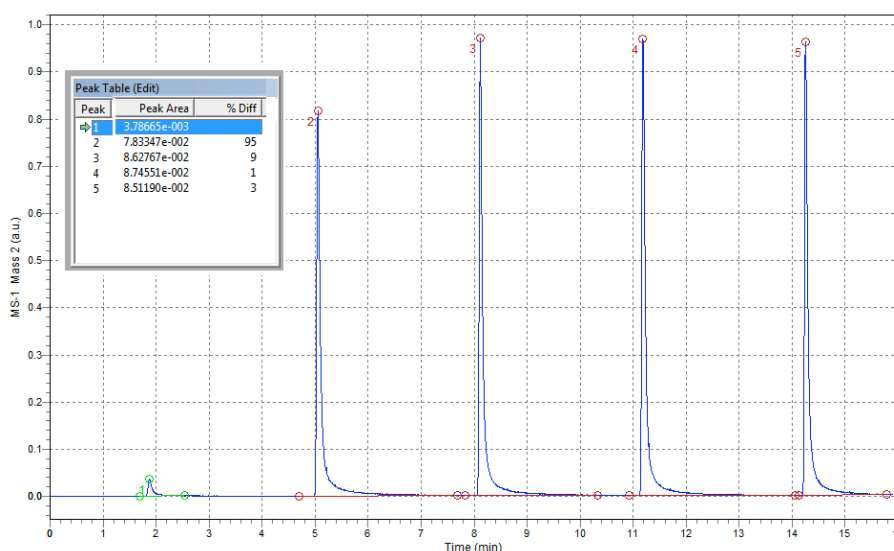


Figure 4: Pulse Chemisorption Profile of H₂ on 0.5 wt% Pt/Al₂O₃

Additional Catalyst Characterization Experiments Using the MCCTC

Temperature-Programmed Desorption (TPD)

This technique monitors the amount of gas desorbed from the surface of a catalyst during a linear temperature ramp after the surface has been saturated by an active gas. The strength of interaction of adsorbed molecules bonded to the active species is evaluated and surface coverage may also be quantified. In addition, the portion of adsorbed molecules present on the catalyst surface up to the reaction temperature can be determined. For example, if hydrogen is retained on a catalyst such as platinum up to the desired reaction temperature, the catalyst will be capable of performing the hydrogenation reaction.

To illustrate this analysis, a TPD profile of hydrogen on platinum collected on the Autochem II 2920 is considered here in Figure 5. The Autochem II 2920 uses a thermal conductivity detector (TCD) to quantify the amount of hydrogen in the exhaust stream and the MCCTC paired with a mass spectrometer will provide the same TPD profile. The increasing signal intensity indicates the release of hydrogen from the surface of the catalyst, seen here occurring at three separate temperature peaks. The multiple peaks indicate different active sites of the catalyst; peaks occurring at higher temperatures reflect sites with higher adsorption enthalpies. TPD can be performed at elevated pressures using the MCCTC but should only be considered if the catalyst was reduced at the same pressure.

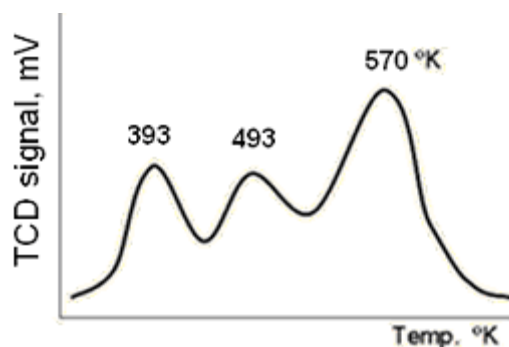


Figure 5: TPD Profile of H₂ on a Platinum Supported Alumina Catalyst

Temperature-Programmed Oxidation (TPO)

This technique is mainly used to determine the degree of reduction of active species present on the catalyst. Combining this technique with TPR allows for estimating the number of regeneration cycles that a catalyst can undergo before completely deactivating

TPO is also used for characterizing de-NO_x catalysts such as V₂O₅ and TiO₂. These catalysts are widely used in industry for transforming dangerous NO_x contamination into other non-pollutant components. Typically these catalysts promote the reaction of NH₃ with NO_x to safely produce water and nitrogen.

Figure 6 shows an example of a typical TPO profile of the pre-reduced de-NO_x catalyst, V₂O₅. The TPO profile includes three oxidation peaks, two of them well defined at 500°C and 860°C and the third is a “shoulder” near 960°C. Peaks appearing at such high temperatures indicate stability of the reduced species that will be active for the reaction. This particular catalyst was reported to have a 95% conversion rate during activity testing, an exceptional yield for a de-NO_x catalyst.

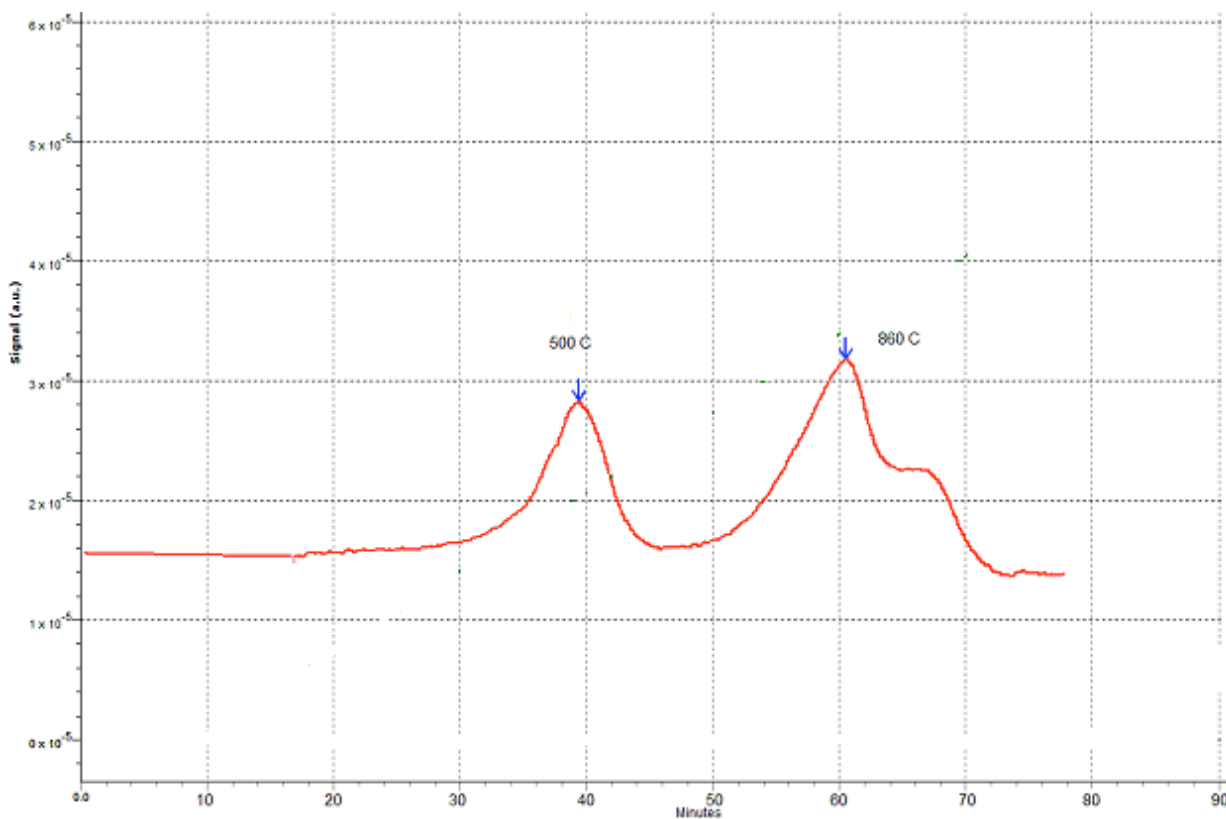


Figure 6: TPO Profile of V₂O₅, a de-NO_x Catalyst



Conclusion

The MCCTC is an innovative piece of equipment that combines almost every simple catalyst characterization technique with catalytic activity testing. This combination reduces overall costs by eliminating the need for multiple pieces of equipment by performing the same tasks in just one instrument. Also, the ability to characterize catalysts at different experimental pressures and temperatures is extremely valuable due to the fact that the catalyst can undergo preliminary characterization and testing using the same industrial reaction conditions. This fact

predicts the catalyst behavior at the pre-set experimental conditions prior to activity testing and can determine the cause of catalyst deactivation through post activity testing characterization. Ultimately the user saves time and money by electing to characterize and test catalytic activity using one system.