

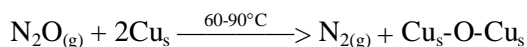
Characterization of Copper Catalysts Using Pulse Reactions and a Mass Spectrometer on the AutoChem 2910

Traditionally, catalyst metal surface areas have been characterized using chemisorption, the classic technique employing the chemical potential of the adsorbate-adsorbent interaction to determine the active metal surface area. This characterization technique can be performed in static measurement devices (often referred to as volumetric instruments) such as the Micromeritics ASAP 2010 or by using dynamic flow techniques as in the Micromeritics AutoChem 2910.

Chemisorption is a reliable technique if the adsorbate-adsorbent interaction is well known. For example, carbon monoxide selectively chemisorbs on platinum with a stoichiometry of one to one; i.e., one CO molecule chemisorbs to one surface atom of platinum. Hydrogen has also been widely used to chemisorb to metals. It is well known that H₂ dissociatively chemisorbs to platinum, one H₂ molecule chemisorbs with two platinum surface atoms.

However, chemisorption has not been regarded as an effective technique for characterizing copper catalysts. Neither CO nor H₂ has been shown to chemisorb strongly on copper. The classic method for determining copper surface areas uses the decomposition of nitrous oxide to selectively oxidize the surface copper atoms to Cu₂O^{2,3,4,5} with a stoichiometry of one oxygen

atom to two copper surface atoms^{6,7}, via the following reaction:



Samples are pretreated by reducing the copper surface with flowing hydrogen at temperatures ranging from 200-300 °C for 1-2 hours. Then the sample is cooled to the analysis temperature (60-90 °C). Pulses of nitrous oxide are then introduced to selectively oxidize the copper surface. Traditionally, a thermal conductivity detector (TCD) has been used to measure the nitrogen evolved from this reaction.

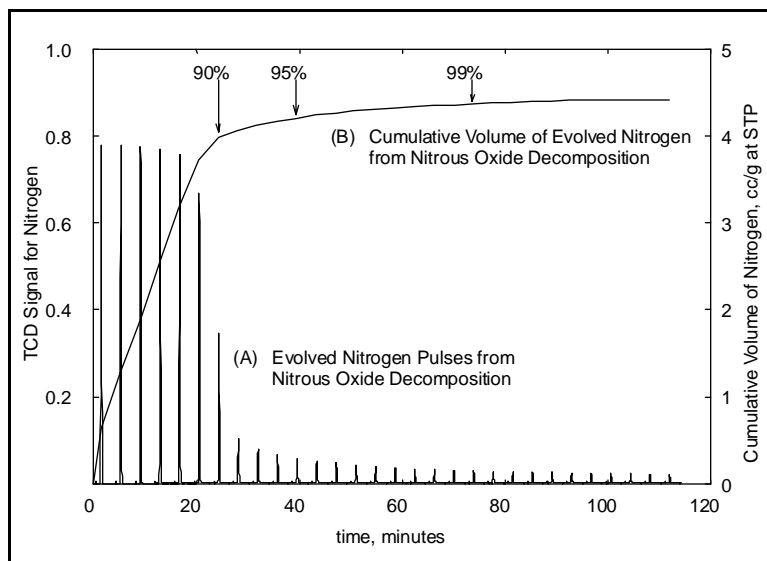


Figure 1. Decomposition of Nitrous Oxide.

Typical data from the AutoChem 2910 for the decomposition of nitrous oxide are given in Figure 1.

In this example, a mixture of 10% N₂O in helium was pulsed over copper supported on a zeolite substrate. A TCD was used to measure the peaks of evolved N₂ (Figure 1A). The cumulative volume of evolved N₂ is shown in Figure 1B. Any unreacted N₂O was removed using an IPA/LN₂ cold trap. An interesting feature of this characterization is the site-demanding nature of the reaction—two adjacent copper atoms are required for catalysis. As shown in Figure 1, the first seven pulses of N₂O reacted with 90% of the copper surface atoms. An additional four pulses (11 total) were required to reach 95% surface coverage, and nine additional pulses (20 total) were required to attain 99% coverage (Table 1). This site-demanding nature of copper characterization is typical of nearly all chemical reactions—more than one catalytic site is required.

One of the difficult aspects of the pulse technique has been the separation of the evolved nitrogen from the non-reacted nitrous oxide. The use of a TCD is restricted to detecting changes in the concentration of *one* gas. Typically, a cold trap (liquid argon, dry ice slush, or isopropyl alcohol/liquid N₂ slush) has been used to separate the N₂ from the N₂O. These are well known and accepted techniques for measuring the evolved nitrogen gas; however using a trap restricts the experimenter to

Pulse	Evolved N ₂ , cc/g at STP	% Coverage
4	2.55	58
7	3.98	90
11	4.20	95
20	4.38	99
30	4.42	100

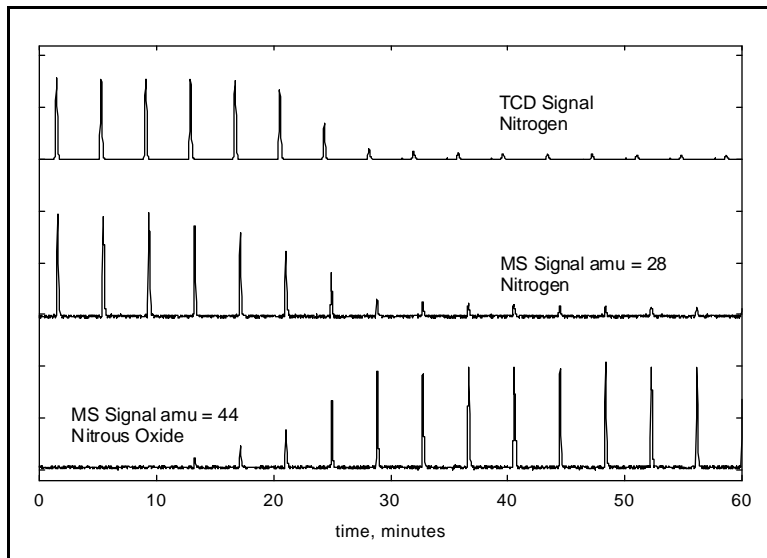


Figure 2. Evolved gas analysis of nitrous oxide decomposition.

50% of the available information. It is important to emphasize that this is a reactive technique for characterizing catalysts and it is valuable for monitoring the depletion of nitrous oxide as well as the production of nitrogen.

Using a mass spectrometer (MS) with the AutoChem 2910 provides the user with a versatile detector that can provide continuous monitoring of reactants and products. Commercial residual gas analyzers usually provide data in several formats. The most familiar mode is the analog scan or histogram where the mass spectrometer scans a user-defined mass range.

However, for pulse reactions the most useful and convenient display mode is to monitor specific ions (often referred to as amu, atomic mass units) or the partial pressure of user-specified ions. A convenient implementation of this mode is to display the data as Ion Pressure vs. time (Figure 2). This data format is very similar to the output of a TCD, but provides the added functionality of monitoring the concentration of many reactants and products.

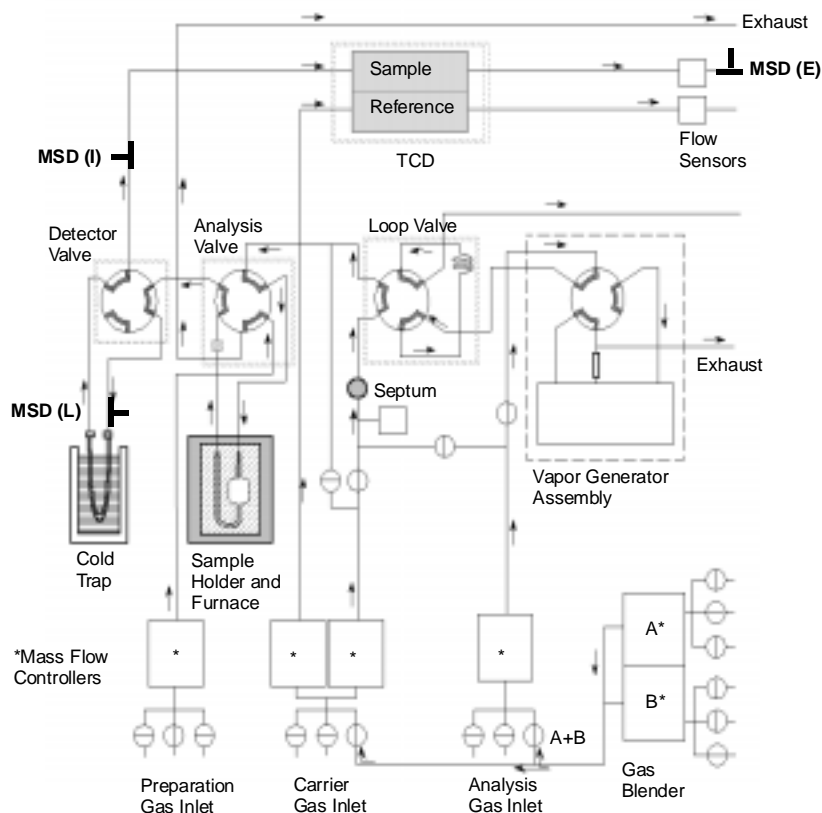
The decomposition of N₂O is a very simple reaction that demonstrates the utility of the mass spectrometer. The TCD and mass spectrometer signals

show excellent agreement for measuring the evolved nitrogen, but the mass spectrometer has the added capability of determining the unreacted pulses of nitrous oxide as the reaction proceeds.

The data generated from nearly all commercial mass spectrometers can be imported into GRAMS/32® for additional data reduction. This is accomplished by saving the data as an ASCII file, which can be read by GRAMS/32. Some commercial mass spectrometers (such as Balzers, VG, and Spectra) also support dynamic data exchange, which allows the AutoChem 2910 to communicate directly with the mass spectrometer. This option provides for even higher levels of integration.

References

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The AutoChem 2910 has tremendous flexibility and allows three options for sampling evolved gas:

MSD (I) Internal port for sampling the evolved gas *after* the cold trap. The primary use of this port is for an MS detector when it is the primary analysis detector. This port is also used as a convenient integrated port for sampling non-condensable gases.

MSD (L) External port for sampling the evolved gas *before* the cold trap. This option allows the use of both the TCD and MS detectors quantitatively. This sampling port is best suited for temperature-programmed reductions and oxidations where the TCD provides greater sensitivity for either H₂ or O₂ detection, and the MS detector is used for monitoring evolved water.

MSD (E) External port for sampling the evolved gas after the TCD detector. This sampling point allows the user to quickly connect and disconnect a portable mass spectrometer (that may be shared with other instruments) to the AutoChem 2910.