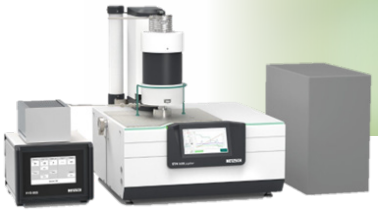
APPLICATION**NOTE**

Metals – Thermogravimetry/*H_2Secure*



Thermogravimetric Analysis of Redox Reaction of CuO and Cu by Means of the *H_2Secure* Box

Hydrogen: A Key Driver in Clean Energy Transitions

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Introduction

Hydrogen stands at the forefront of clean energy transitions, driving carbon-free industrial processes and supporting renewable energy integration. Its versatility in production, storage, and utilization highlights its role as a cornerstone of sustainable energy systems. Recent research leveraging advanced thermal analysis techniques has revealed hydrogen's broad application potential, including its role in production technologies, metallurgical processes, thermochemical energy storage, and innovative reduction/oxidation cycles. These advancements underline hydrogen's transformative impact on energy and material science.

One example is the use of thermogravimetric analysis (TGA) to study reduction/oxidation cycles of metal oxides/metals for carbon-neutral energy applications. Studies [Chen et al., 2024; Cerciello et al., 2024] have shown that repeated reduction/oxidation cycles with hydrogen in controlled atmospheres can lead to structural changes that affect reactivity. The results of these papers provide insights into structural changes under non-isothermal and isothermal conditions, revealing the effect of temperature and gas composition on reaction kinetics. In the field of thermochemical energy storage, the oxidation kinetics of Cu_2O to CuO have been analyzed [Jahromy et al., 2019].

Instrumentation

In this application note, we seek to demonstrate the capability of our new developments for the NETZSCH STA 509 series. These are designed to support advanced hydrogen research, helping to investigate kinetic changes during reversible redox reactions. The system is engineered to handle experiments in a 100% hydrogen atmosphere, addressing the challenges of hydrogen's flammability risks at temperatures up to 1600°C.

A key innovation is the integration of the *H_2Secure* system into STA devices, ensuring safe operation in up to 100% H_2 atmospheres. It includes a centralized control box for gas regulation, real-time H_2 and O_2 monitoring, and a fail-safe mechanism that purges hydrogen out with inert gas in the case of malfunctions. An optimized gas flow path ensures controlled distribution of the gas atmosphere over the sample. An internal pressure sensor enables monitoring of overpressure limits within the furnace and measurement chambers. This capability allows for the detection of accidental leakage formation during experiments, ensuring enhanced safety and system integrity.

Experimental Results and Discussion

The example in this study highlights the reversible redox reaction of copper oxide (CuO) and copper (Cu) under controlled conditions. A series of cycles were performed at 500°C using 100% H_2 for reduction and synthetic air (21% O_2) for oxidation.

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The main measurement parameters are listed in table 1.

Table 1 Measurement parameters

Instrument		STA 449[1]
Sample		CuO
Sample mass		29.975 mg
Crucible		Al_2O_3 open
Furnace		SiC
Sample carrier		TGA Plate P
Accessories		*H_2Secure* Box, H_2 Generator
	Purge 1	H_2 (150 ml/min)
	Purge 2	Ar (150 ml/min)
	Purge 3	Synthetic air (150 ml/min)
	Protective	Ar (20 ml/min)

[1] Experiments were conducted using the previous version (STA 449) of the STA 509 series instrument, which is fully compatible with the current version and provides comparable accuracy and result quality.

Figure 1 shows the TGA results obtained. The findings demonstrate the system's reversibility, with gradual kinetic changes observed over successive cycles.

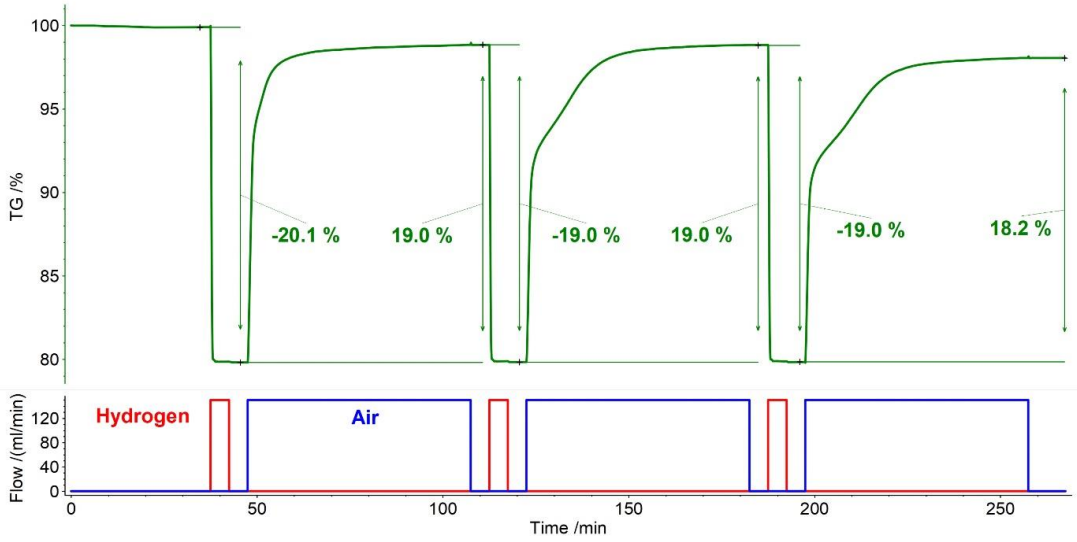
These results are discussed in the following steps.

1. Initial Heating:
The sample was heated to 500°C under a protective argon atmosphere (Purge 2 and Protective).

2. Reduction Phase:
- Once the isothermal condition was stabilized, 100% H_2 (Purge 1) was introduced for 5 minutes.
- The reduction of CuO to metallic Cu occurred rapidly, resulting in a mass stabilization at 79.9%.
- The mass loss of 20.1% matched the theoretical value of 20.11%, confirming complete reduction to pure metallic Cu powder.

3. Transition to Oxidation:
- After reduction, the purge gas was switched to argon (Purge 2) to remove the H_2 from the furnace/instrument for 5 minutes.
- This ensured safe switching to synthetic air for the oxidation step.

4. Oxidation Phase:
- After that, synthetic air (Purge 3) was introduced for 60 minutes.
- The TGA signal was continuously changing.
- A gradual mass increase was observed, but the mass gain reached 19.0% instead of the loss of 20.1% seen in the first cycle, indicating incomplete oxidation.



1 TGA results on copper oxide powder at 500°C in an alternating hydrogen (100% H_2) and synthetic air (21% O_2) atmosphere.

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Cycles

- **Reduction**

  Reduction to metallic Cu was complete for all cycles, achieving the same stabilized mass of 79.9%, indicating consistent reduction performance with 100% hydrogen.

- **Oxidation**

  Oxidation showed a decreasing trend with successive cycles: from initially 20.1% to 19.0% and then to 18.2%.

  This decline suggests surface passivation or particle agglomeration, which can inhibit complete oxidation over time and alter the kinetic mechanism of the reaction. This change is indicated by alterations in the curve shape and the total mass change between the first and the following oxidation cycles.

The results of this experiment highlight the reversible nature of the CuO/Cu redox reaction

$$CuO + H_2 \leftrightarrow Cu + H_2O$$

and demonstrate the impact of surface passivation on reaction kinetics, particularly during the oxidation step. These findings are critical for understanding material behavior under cyclic redox conditions, with implications for catalytic and energy storage applications.

Summary

The NETZSCH STA 509 *Jupiter*® in combination with the *H_2Secure* box constitutes a powerful tool for hydrogen research. The system is designed to analyze high-temperature redox reactions under controlled atmospheres, including hydrogen-rich and mixed gases. Its advanced features ensure safety and reliability during experiments while supporting a wide range of applications, including the study of reduction-oxidation cycles, the optimization of catalytic processes, and the improvement of hydrogen-based technologies in metallurgy and energy storage. By providing precise insights into reaction kinetics, phase transitions, and material stability, the STA 509 series enables researchers to enhance efficiency and sustainability in industrial and material applications, propelling innovation in hydrogen-driven processes.

References

[1] Chen, R., Hansen, B. B., Lin, W., Wu, H., & Glarborg, P. (2024). Deactivation of iron particles during combustion and reduction. Fuel, 378, 132915. https://doi.org/10.1016/j.fuel.2024.132915

[2] [2] Jahromy, S. S., Birkelbach, F., Jordan, C., Huber, C., Harasek, M., Werner, A., & Winter, F. (2019). Impact of partial pressure, conversion, and temperature on the oxidation reaction kinetics of Cu_2O to CuO in thermochemical energy storage. Energies, 12(508). https://doi.org/10.3390/en12030508

[3] Cerciello, F., Fabozzi, A., Yannakis, C., Schmitt, S., Narin, O., Scherer, V., & Senneca, O. (2024). Kinetics of iron reduction upon reduction/oxidation cycles. International Journal of Hydrogen Energy, 65, 337–347. https://doi.org/10.1016/j.ijhydene.2024.04.008"t"_new

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