

Impact of the high pressure of H₂ as compared to the impact of the high flow of the reductive gas on the reduction of copper oxide

By: Elizabeth Karivelil and Patrick Aghadiuno
The Gwinnett School of Mathematics, Science and Technology
Supervised by Dr. Simon Yunes, Micromeritics instruments Corporation

Introduction:

In continuation to our previous application note No.31, higher reduction temperature material was tested to prove that the reduction temperature will shift even more to lower temperature as the partial pressure of the reducing gas increases.

Copper oxide was selected for these experiments due to its abundance in nature and economic accessibility in the market as well as its very wide application in the industry of catalysis⁽¹⁾. Copper being a transition metal that can easily change its oxidation state makes it a good catalyst for hydrogenation and dehydrogenation of many organic compounds. It is also used in wastewater treatment and water gas shift process. Due to its excellent conductive properties it is also widely used in wiring and motor industries⁽²⁾. Copper is also used as a good catalyst for synthesis of ammonia industry, and in many other applications well detailed in the literature⁽³⁾.

The main goal of this application note is to study the reduction of copper oxide and see how the high pressure of H₂ as well as the high flow of the H₂ mixture can affect the TPR profile of this important oxide. Also the experimentation has been intended to see if the high pressure of H₂ can alter the mechanism of reduction of this oxide.

Reduction of copper oxide is not an easy and straight forward reaction because it forms several transition states during reduction, some are stable while others are not. The reduction step can be summarized according to the following equation:



While Cu₃O₄ is not a stable species, Cu₂O is, and this complicates the TPR profile of the original oxide. The TPR profile presents essentially two main peaks, the Cu₄O₃ species being not stable will rapidly reduce toward the formation of Cu₂O and, as temperature keeps increasing, this species ultimately reduces to Cu⁽⁴⁾.

These two reduction peaks are highly affected by either the higher pressure of H₂ or by increasing the flow of the hydrogen mixture which increases the partial pressure of H₂ over the oxide while being reduced.

Our experiments indicate that as the pressure of the reducing mixture increases the reduction profile of the CuO starts shifting toward a lower reduction temperature. This fact of lowering the reduction temperature has a very positive impact in catalysis as it minimizes sintering of active species in any kind of catalyst. Moreover, it has been observed from the experiments that the high pressure of H₂ alters the mechanism of reduction of the oxide. While, at atmospheric pressure, the first reduction peak was only a shoulder, at high pressure of H₂ the first peak is much more defined while the second reduction peak starts to flatten out progressively as the pressure increases.

Experimental:

The equipment used for these experiments was a modified PID EFFI to include the MCCTC option that has been detailed in the application note No.30.

An amount of approximately 0.25g of material was used in each experiment. This amount was properly determined by the use of an appropriate equation described by Mallet et al⁽⁵⁾, which permits the use of a sufficient amount of oxide and prevents the depletion of H₂ during reduction.

The temperature of the reactor was raised at a rate of 10°C per minute up to 550°C. All TPR profiles were recorded by an MKS Cirrus II mass spectrometer following mass 2.

Results and Discussion:

The basic TPR profile that was used for comparison was carried out by using 50 ml of a 10% H₂ balance Argon at atmospheric pressure. (Top 1 on figure 1). This TPR profile showed one shoulder at 240°C that could correspond to the transformation of CuO into the unstable species Cu₄O₃ that rapidly goes into the formation of a rather stable species, Cu₂O. A second well-defined peak appears at 320°C and could correspond to the reduction of Cu₂O into metallic copper, Cu. As the pressure was increased by either raising the absolute pressure over the sample or by raising the mixture flow, results showed not only a shift on the reduction temperature (220°C compared to 240°C, and 237°C compared to 320°C), but also a transition on the reduction mechanism. The first peak now becomes well-defined compared to the shoulder seen at the basic TPR profile. This first peak undergoes a significant change and becomes better defined as the pressure approaches 20 bar as seen in all figures (Figures 1 and 2).

Figures 1 shows the TPR profiles of CuO shifting as the pressure increases from atmospheric up to 20 bar, while figures 2 correspond to the same effect when the H₂ mixture

flow increases from 50 up to 950ml/minute. Both cases show almost the same impact on the original reduction profile; both reduction peaks shift toward lower reduction temperature. While increasing the flow of the reducible mixture displaces the TPR profile (Figure 4) and improves the reduction peak on the first step of the reaction, the high pressure shows the same shift (Figure 3) but also improves even more than the first peak of reduction, making it a much better defined and pronounced peak.

Conclusion:

Definitely, adding the MCCTC option to the PID EFFI expands this instrument to be a critical tool in catalysis. This option is capable of showing catalyst behavior under high pressure and high temperature reaction conditions.

All obtained results shown in application note 30 and in this one demonstrate the positive effect of both the high pressure as well the high flow of the reducible mixture on significantly reducing the reduction temperature of the different oxide species present in a catalyst. Sintering of active species, which often occurs during reduction of the oxide, can be highly improved by reducing temperature of the reducible species; hence, a higher dispersion that leads to a better activity and selectivity of the catalyst.

Finally, no significant impact on reducing the reduction temperature was observed in these experiments, regardless of whether high pressure or high flow of the reducible mixture was used. The outstanding result here, however, is to take advantage of the fact that all oxide species on catalysts that can be reduced – almost all of them due to the negative free energy of the reduction – are to be reduced at a lower possible temperature.

APPLICATION NOTE 032

References:

- 1 – Chemical Kinetics of Copper Oxide Reduction with Carbon monoxide. Eli A. Goldstein, Reginald E. Mitchel., ScienceDirect, Proceedings of the Combustion Institute (2010)
- 2 – Indirect Phase Transformation of CuO to Cu₂O on a Nanowire Surface. Fei Wu, Sriya Banerjee, Huafang Li, Yoon Myung, and Parag Banerjee., Langmuir 2016, 32 (18), 4485-4493
- 3 – Reduction of CuO and Cu₂O with H₂: H Embedding and Kinetic Effects in the Formation of Suboxides. Jae Y. Kim, Jose A. Rodriguez, Jonathan C. Hanson, Anatoly I. Frenkel, and Peter L. Lee., JACS 2003
- 4 – Formation of Stable Cu₂O from Reduction of CuO Nanoparticles. Jenna Pike, Siu-Wai Chan, Feng Zhang, Xianquin Wang, Jonathan Hanson., Applied Catalysis A: General 303 (2006), 273-277
- 5 – The selection of Experimental Conditions in Temperature-Programmed Reduction Experiments. Pilar Mallet and Alfonso Caballero., J. Chem. Soc., Faraday Trans. 1, 1988, 84(7), 2369-2375

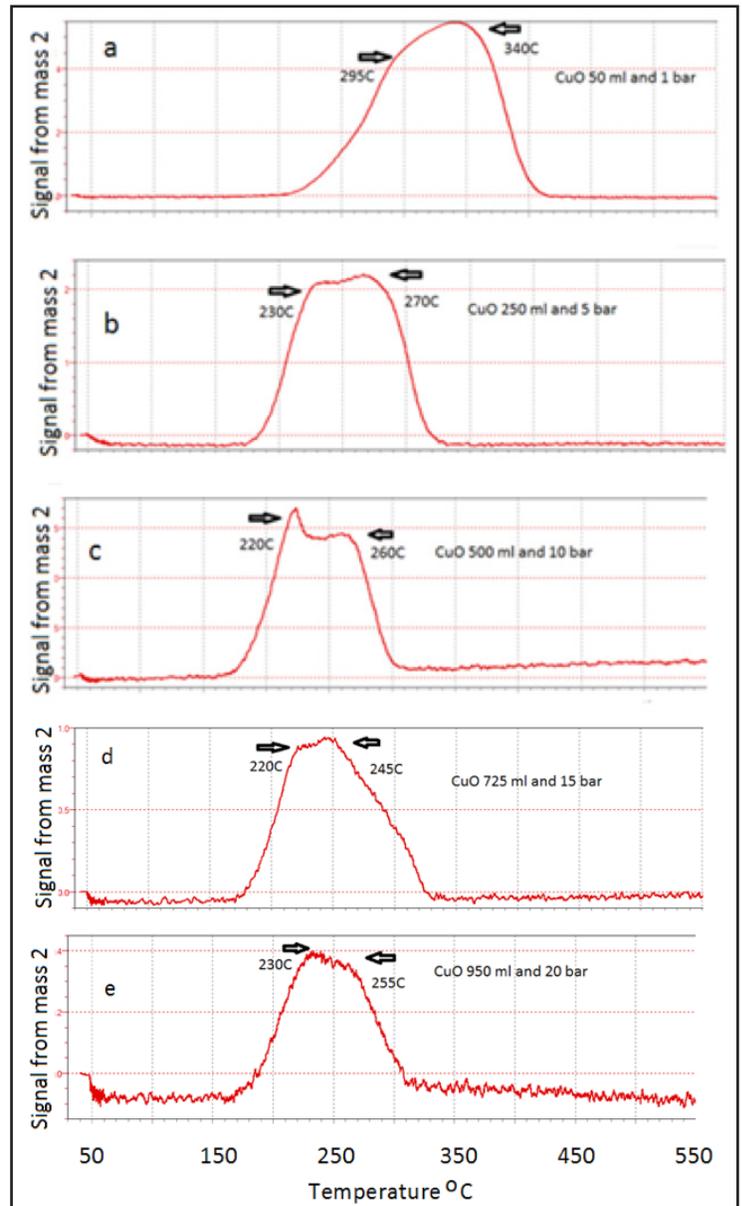


Figure 1: Profiles from a to e represent the shift as function of increasing pressure

APPLICATION NOTE 032

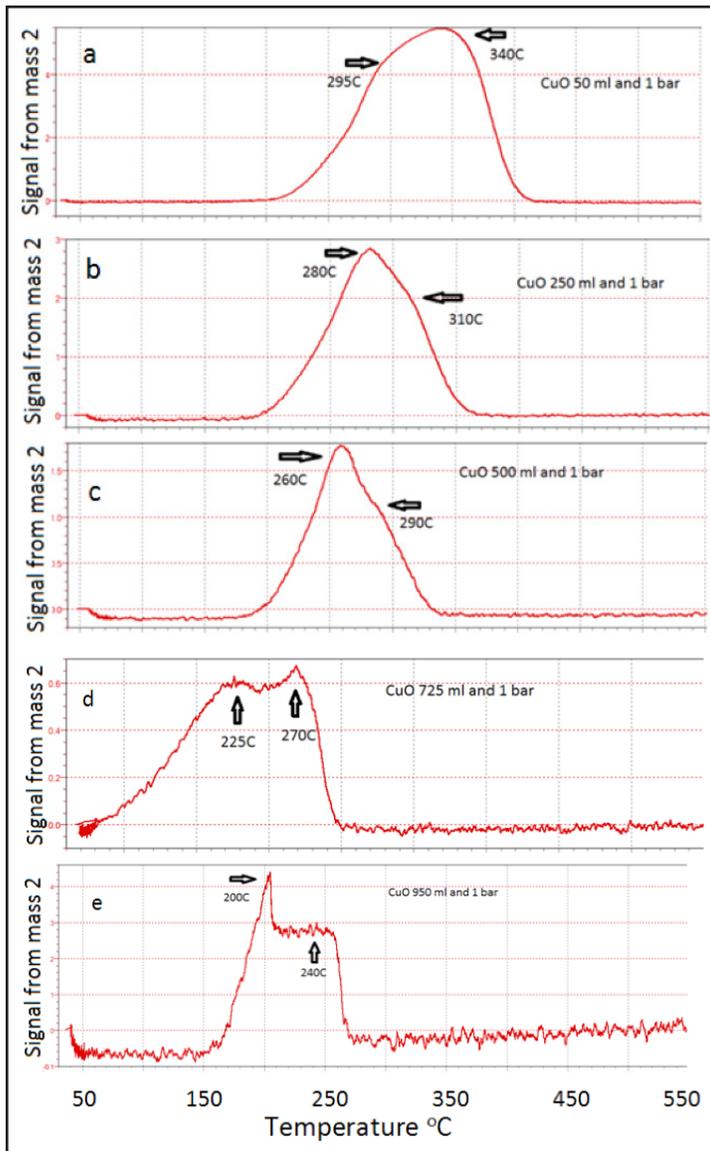


Figure 2: Profiles from a to e represent the shift as function of increasing flow of the reducible mixture

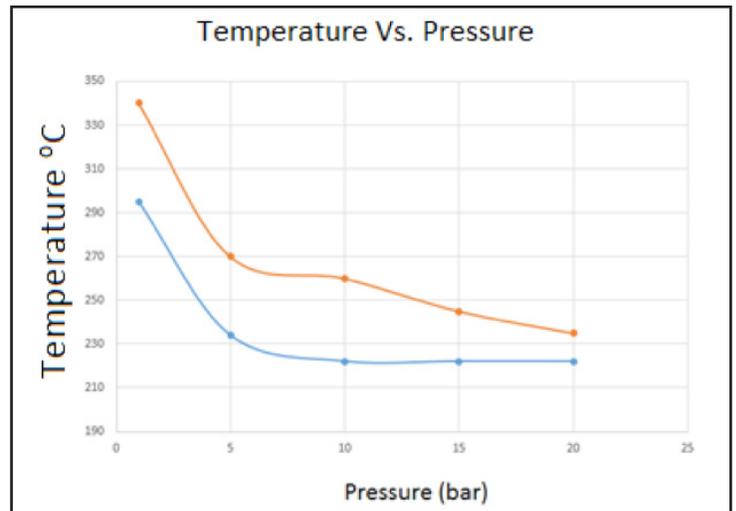


Figure 3: This figure represents the temperature trend as function of increasing pressure

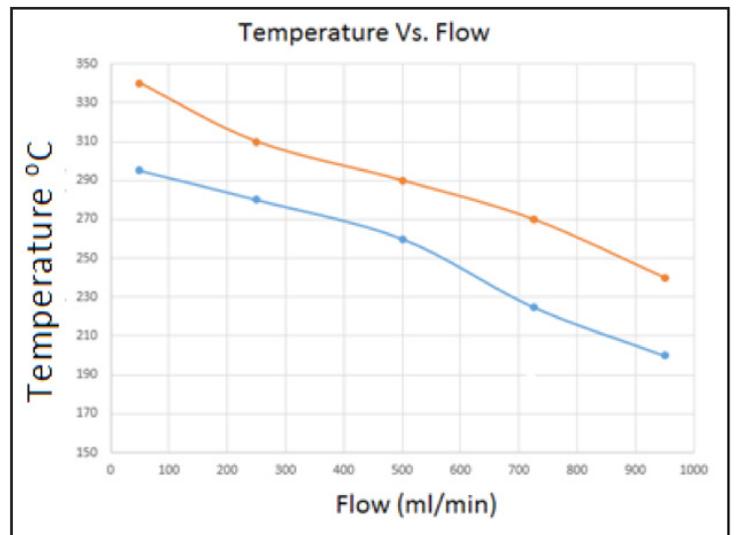


Figure 4: This figure shows the change in the reduction temperature as a function of increasing flow of the reducible mixture.