Research paper

High heating rate decomposition dynamics of copper oxide by nanocalorimetry-coupled time-of-flight mass spectrometry

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A R T I C L E   I N F O

A B S T R A C T

The thermodynamics and evolved gases were measured during the rapid decomposition of copper oxide (CuO) thin film at rates exceeding 100,000 K/s. CuO decomposes to release oxygen when heated and serves as an oxidizer in reactive composites and chemical looping combustion. Other instruments have shown either one or two decomposition steps during heating. We have confirmed that CuO decomposes by two steps at both slower and higher heating rates. The decomposition path influences the reaction course in reactive Al/CuO/Al composites, and full understanding is important in designing reactive mixtures and other new reactive materials.

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1. Introduction

Accurate measurements of the thermal decomposition of CuO at high heating rates is directly related to developing a deeper understanding of energetic composites [1,2], chemical looping combustion [3,4] and solar thermochemical fuel production [5]. In contrast, CuO is also widely used as a catalyst, but catalytic applications are primarily interested in avoiding the decomposition of CuO [6]. In traditional slow heating rate studies using thermogravimetric analysis and differential scanning calorimetry (TGA/DSC), CuO decomposes to Cu_2O, then to Cu in a two-step decomposition process. However, in a recent article [7], only one oxygen evolution event was observed when CuO was rapidly heated at heating rates between 1.5×10^5 K/s and 6.5×10^5 K/s, which suggested the possibility of a different decomposition mechanism: two decomposition steps for low heating rates and one decomposition step for high heating rates; we have investigated this materials system further with our new instrument to provide more detailed data.

Nanocalorimeters are MEMS-based thermal sensors capable of measuring thermodynamic properties of very small amounts of sample with high sensitivity under very fast heating rates [8–11] up to 10^6 K/s. Recently, a newly developed instrument integrating a nanocalorimeter into a time-of-flight mass spectrometer (ToF-MS) has been demonstrated to simultaneously measure thermal properties and evolved gas phase species of rapid reactions [12].

As will be described below, CuO films were deposited directly onto the nanocalorimeter by sputtering from a CuO target with a thin layer of alumina as a diffusion barrier between the silicon nitride sensor membrane and the sample. X-ray diffraction was used to confirm the deposited phase and valence state before starting the experiments. The nanocalorimeter-TOF MS instrument was used to measure the decomposition process and capture decomposition temperatures and evolved species information.

2. Method and experiments

2.1. Sample preparation

The CuO and Al films were prepared using sputter deposition with a copper backed CuO target (Kurt Lesker, 99.7% purity) and an Al target (Kurt Lesker, 99.9995% purity) under a pressure of 5 mTorr of argon. RF power of 300 W was used for CuO sputtering and DC power of 300 W was used for aluminum sputtering. The nanocalorimeter sensor fabrication and calibration have been described previously [13]. It has a 100 nm thick platinum heater suspended on a 100 nm thick silicon nitride membrane in a silicon frame. CuO films are deposited on the silicon nitride side of the nanocalorimeter sensor with a thin alumina barrier layer between the sample and sensor.

2.2. Nanocalorimetry-coupled time-of-flight mass spectrometry measurements

The integration of the nanocalorimeter into a time-of-flight mass spectrometer (ToF-MS) has recently been described [12].

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Briefly, the nanocalorimeter sensor was positioned at the ionization region of the ToF-MS using a linear motion feedthrough with a 3D printed adapter. These reactions were typically completed within 10 ms. The ToF-MS was sampled at 100 µs per spectrum (10 kHz), with 100 spectra obtained post-triggering for each run. Gas phase reaction products were ionized for 3 µs using an electron gun operated at 70 eV and 1 mA.

3. Results and discussion

3.1. Copper (II) Oxide phase confirmation

Copper is multivalent and can form CuO, Cu_4O_3 and Cu_2O. Typically, copper oxide films are deposited by sputtering from either Cu or CuO targets, and their final chemical form would depend on the oxygen availability and other sputtering parameters. In this case, the target material is CuO and no reactive gas (oxygen) is introduced. Fig. 1 shows the X-ray diffractogram of the deposited film. The patterns and relative intensities of the diffraction peaks match with JCPDS data for CuO (PDF 00-048-1548). The main diffraction peaks of 35.3° and 38.3° correspond to the lattice plane of $(-1\ 1\ 1)$ and $(1\ 1\ 1)$ respectively. Therefore, the result here confirmed the sputtered film is CuO. A previous article [14] reported that a Cu_4O_3 film was formed while sputtering from a CuO target, but we did not see this in our samples. It is likely due to differences in the sputtering tool or parameters. First, the base pressure in that report was 1.9×10^{-7} Torr, lower than in this work (3×10^{-6} torr), therefore more oxygen was available for our samples. Second, that substrate was water-cooled but our substrate was not temperature controlled.

3.2. Decomposition of CuO film

The decomposition of CuO is believed to occur in two steps: CuO first decomposes to Cu_2O and O_2, followed by the decomposition of Cu_2O to Cu and O_2 at a higher temperature. This process has been reported previously [15,16] and measured at slow rates using differential scanning calorimetry of CuO nanoparticles (data not shown). However, a recent article[7] suggests only one oxygen release event during rapid heating (from 1.5×10^5 K/s to 6.5×10^5 K/s) based on observations in a mass spectrometer. A change in the number of peaks suggests kinetic limitations or

Fig. 1. X-ray diffraction data of a CuO film prepared by RF magnetron sputtering using CuO target. The indexed peaks are based on ICDD PDF 00-048-1548 for Copper Oxide (CuO).

different mechanisms comparing faster heating rates to slow heating rates.

To prevent the possible reaction between oxygen released from the sample and the silicon nitride sensor membrane at temperatures over 1000 °C [17], a 40 nm barrier layer of alumina is deposited between sample and silicon nitride. Nanocalorimetry results shown in Fig. 2 provide the first insights into these materials – the peak expected for Cu_4O_3 decomposition to CuO and Cu_2O would have occurred in a broad exothermic reaction with a peak temperature at 427 °C [14], but this peak is absent, which supports the x-ray diffraction data showing the deposited material is CuO instead of Cu_4O_3.

As shown in Fig. 2a, two endothermic signals are observed with peak temperatures of 975 °C and 1112 °C respectively, indicating two step decompositions of CuO. However, as is true for the previous mass spectrometer results, there is only one broad oxygen evolution event that spans the temperature range of the two endothermic thermal signals. Therefore, identifying this reaction as one step or two steps based solely on mass spectrometer data depends on the rate of removal of oxygen from the system and the temporal resolution of the mass spectrometer. We see two peaks in the nanocalorimeter data due to this instrument's greater temporal resolution.

Efforts were made to further separate the oxygen release events. The heating and measurement duration was varied from 10 ms to 50 ms. As shown in Fig. 2b, two consecutive endothermic signals were observed accompanied by only one oxygen release event in the TOF-MS data. The oxygen signal spans the two endothermic peaks even though the time between the two signals is increased to $\approx$2 ms from less than 1 ms. Here, we also see the tradeoff between the mass spectrum signal sensitivity and heating rate. The gap between the two decomposition events is only a few milliseconds in the thermal data and yet is not resolved in the mass spectrometer signal.

To further study the decomposition of CuO, a sample was rapidly heated to a maximum temperature below the onset of the second endotherm. These results are shown in Fig. 3, the sample was heated to 1005 °C, which is just below the onset temperature of the second decomposition step. No nitrogen was detected (meaning the barrier layer prevented a reaction with the membrane) and no exothermic signal is observed. The only oxygen source is from the first decomposition step and the peak temperature of oxygen release is at 982 °C, which is lower than the peak oxygen release temperature (1070 °C) for the sample heated up to 1270 °C, as shown in Table 1. The results from the sample heated to 1270 °C covers the temperature range of both the decomposition steps and shows the oxygen is from both decomposition steps. These further confirm the proposed mechanism: CuO decomposes by two steps at heating rates up to 150,000 K/s. The second decomposition endotherm contributes to a significant gaseous oxygen release at higher temperatures and the mass spectrometer alone cannot always resolve the two closely spaced oxygen release events.

These experiments also show that the peak temperature of oxygen release depends on the heating rate. As shown in Table 1, the peak temperature of oxygen release shifts from 990 °C to 1070 °C as the heating rate increases from 60,000 K/s to 150,000 K/s. These results agree with the recent report [7]. At high heating rates, atomic diffusion plays an important role during the reactions [2,7,18,19]. At high heating rates, the oxygen diffusion in the solid state during the decomposition of CuO may be a limiting step that increases the peak temperature of oxygen release as the heating rate increases; additional studies are needed to address this question.
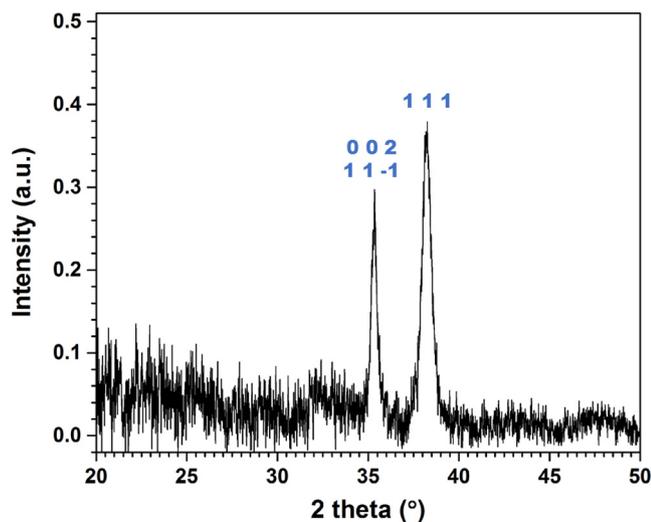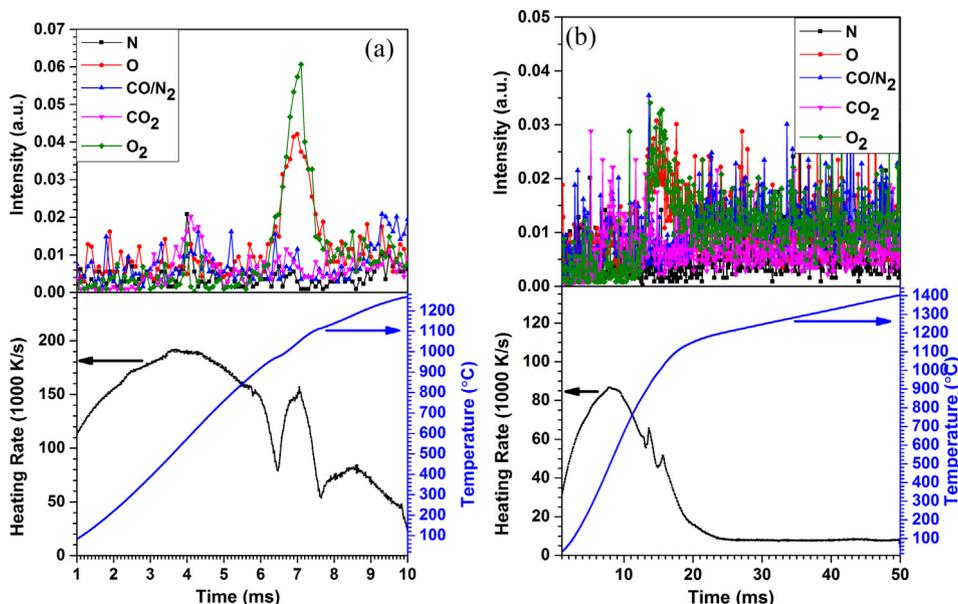
Fig. 2. Mass spectra and nanocalorimetry data of the decomposition of CuO using a 40nm alumina barrier layer. Experiments with heating duration of (a) 10 ms, and (b) 50 ms.
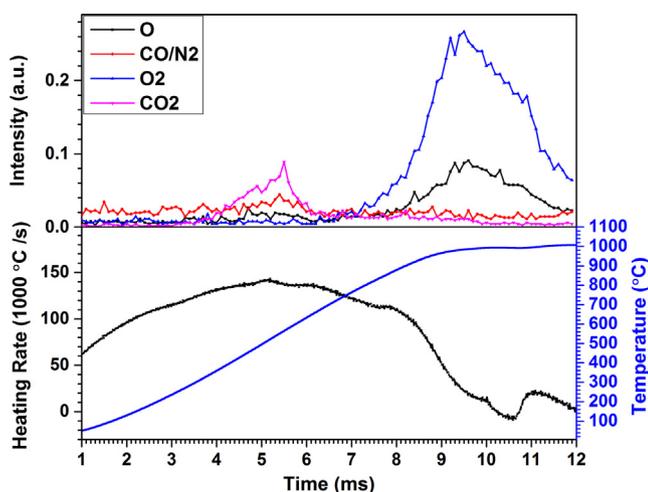

Fig. 3. Mass spectra and nanocalorimetry data of the decomposition of CuO film heated only to the temperature of the first decomposition step.

Table 1
Heating rate dependence of the O_2 release peak temperatures.

Sample	CuO thin film		
Maximum temperature (°C)[*]	1005	1270	1400
Heating rate [*] (1000 K/s)	130	150	60
O_2 peak temperature (°C)[**]	982	1070	990

[*] Heating rate is not constant due to the rapid reactions. The reported value is determined at the onset of the first decomposition of CuO.

[**] Peak temperature is determined from the peak of the ToF-MS signal.

3.3. CuO decomposition in Al/CuO/Al nanolaminates

The reactions of Al/CuO/Al nanolaminates [2] were also measured using this approach, and two reaction steps were observed in the nanocalorimeter data for the temperature range expected for the decomposition of CuO. For a fuel-lean sample (twice the CuO needed, based on the stoichiometric ratio for the expected

reaction of $2Al + 4CuO \rightarrow 2Cu_2O + Al_2O_3$) shown in Fig. 4, the first reaction occurs between 300 °C and 500 °C. This temperature range implies that reaction starts in the solid phase and is therefore less energetic than the reaction that occurs around the melting point of aluminum. In part because the CuO wasn't fully consumed, a second, larger exotherm is seen that spans a broad temperature range roughly from the melting temperature of Al to the decomposition temperature of CuO (red solid line in Fig. 4).

Since this sample is fuel-lean, not all the CuO is consumed in the reaction with Al, leaving the remaining Cu_2O to decompose at even higher temperatures. We believe the last exothermic signal is due to the reaction of SiN_x, as mentioned above, with oxygen from decomposition of Cu_2O [17], which is further confirmed by the similar position of the peaks of the last exothermic reaction and the second step of the decomposition of CuO.
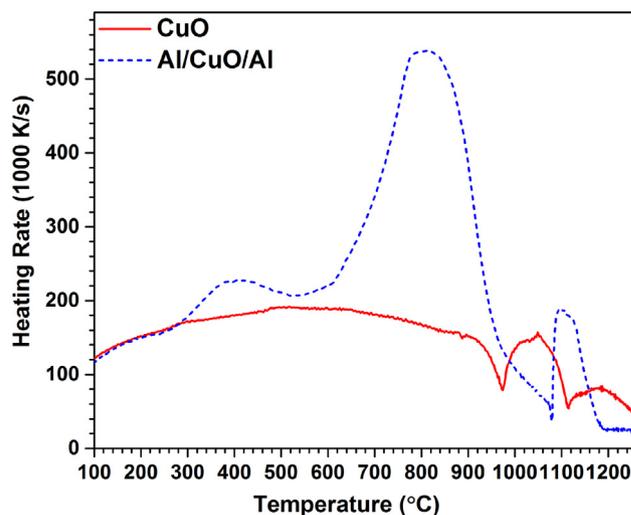

Fig. 4. Nanocalorimetry data for decomposition of a CuO film (50 nm, red solid line) with 40 nm alumina barrier and Al/CuO/Al nanocomposite film (80 nm total thickness, blue dashed line) with 10 nm alumina barrier. Note: heating duration is 10 ms for both samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

The combined nanocalorimeter ToF-MS instrument can resolve previously unknown details of very rapid reactions including the decomposition of nanomaterials. We used this instrument to measure the decomposition of CuO and reactions of Al/CuO/Al nanocomposites. With heating rates on the order of 10^5 K/s, the decomposition of CuO occurs in two steps. Both decomposition steps play an important role in the reactive composites that use CuO as an oxidizer – the initial decomposition step at lower temperatures is associated with a solid phase reaction and minor gaseous release; the second decomposition step is more energetic and associated with significant gaseous release in compositions with excess oxidizer.

Acknowledgements

Conflict of interest

None.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2017.09.066.

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