Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Plastically Deformed Cu-Based Alloys as High-Performance Catalysts for the Reduction of 4-Nitrophenol

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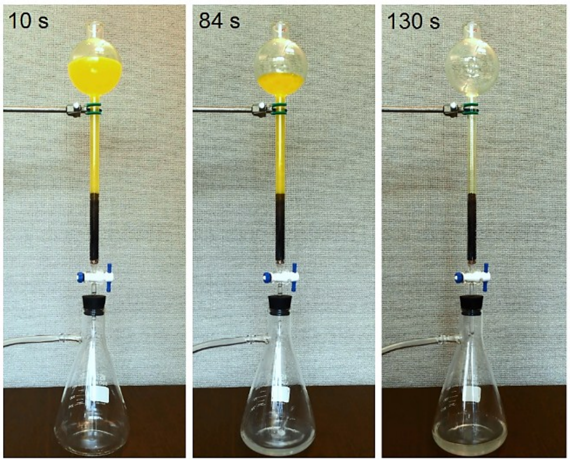
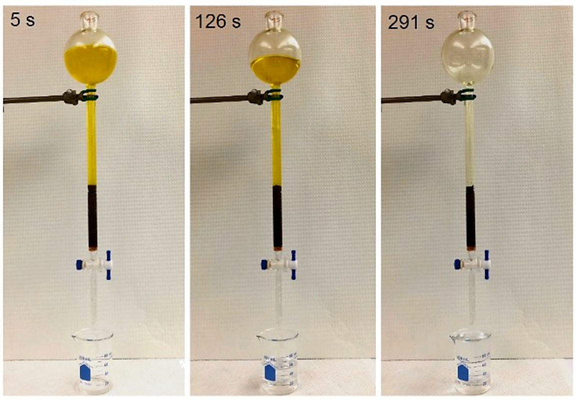
1. Supplementary Information Videos. Accompanying this Supplementary Information document are two videos showing an operating fixed-bed catalytic reactor. Images from the video and reactor operating characteristics are provided below:
Video 1: An operating fixed-bed catalytic reactor where suction is applied to the output.



Operating Characteristics:
Catalyst: Plastically deformed and etched bronze
Reactants: 20 mM 4-NP and 2 M $NaBH_4$
Volume Reacted: 125 mL
Flow Rate: 63 mL min^{-1}

Video 2: An operating fixed-bed catalytic where no suction is applied to the output.



Operating Characteristics:
Catalyst: Plastically deformed and etched bronze
Reactants: 20 mM 4-NP and 2 M $NaBH_4$
Volume Reacted: 110 mL
Average Flow Rate[1]: 23 mL min^{-1}

[1] The flow rate diminishes over time as the bulb at the top of the column empties since the weight of the fluid forcing the liquid through the fixed-bed is reduced (i.e., the hydraulic head is reduced). The flow rate at the beginning of the reaction is, hence, significantly higher than the average while the flow rate near the end is slower.

2. The Shearing Parameters used to Obtain Plastically Deformed Metal Chips.

Table S1. The table lists the metal catalyst produced, the rotational speed of the metal rod during cutting, the depth to which the cutting tool penetrates the rod, the rate at which the cutting tool is advanced in the horizontal direction, the typical dimensions of the metal chips produced, and an estimate of the catalyst surface area normalized to its mass.

Material	Rotation Speed (rpm)	Horizontal Feed (mm/min)	Cutting Depth (mm)	Chip Dimensions $l \times w \times h$ (mm)	Catalyst Surface Area (10^{-3} m^2/g)
Copper	500	25	0.025	15 × 0.15 × 0.04	4.7
Brass	500	50	0.1	2.3 × 0.2 × 0.08	2.5
Bronze	400	50	0.15	2.9 × 0.2 × 0.05	2.4

3. Additional Characterization of the Catalysts

3.1 Percent Conversion Data. Figure 3c of the report shows the percent conversion of 4-NP to 4-AP observed for seven reaction cycles carried out on consecutive days using a plastically deformed and etched bronze contained within the fixed-bed catalytic reactor. Figure S1 shows the equivalent data for the other metal catalysts investigated. Note than none of the catalysts show any signs of deterioration over the 7 day period.

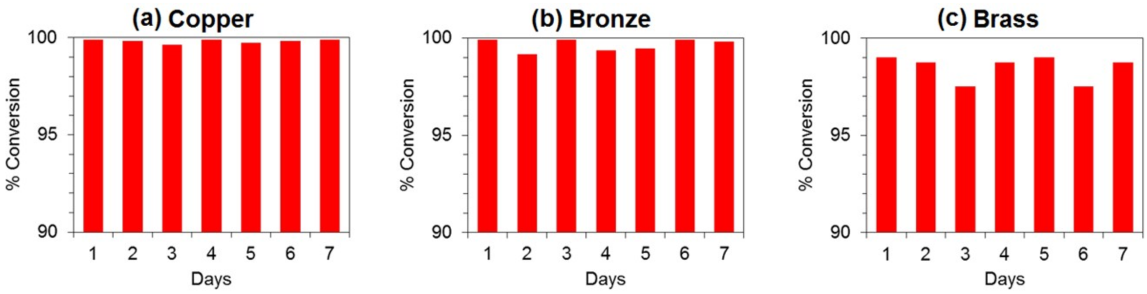


Figure S1. Percent conversion of 4-NP to 4-AP when using plastically deformed (a) copper, (b) bronze, and (c) brass for a continuous flow catalytic reactor operated on seven consecutive days. None of these catalysts underwent an etching procedure.

3.2 Temperature Dependence of k_{app}. Figure S2 shows the dependency of $\ln(k_{app})$ on the reciprocal of the reaction temperature. The plot shows Arrhenius behavior with an activation energy of 42 kJ/mol.

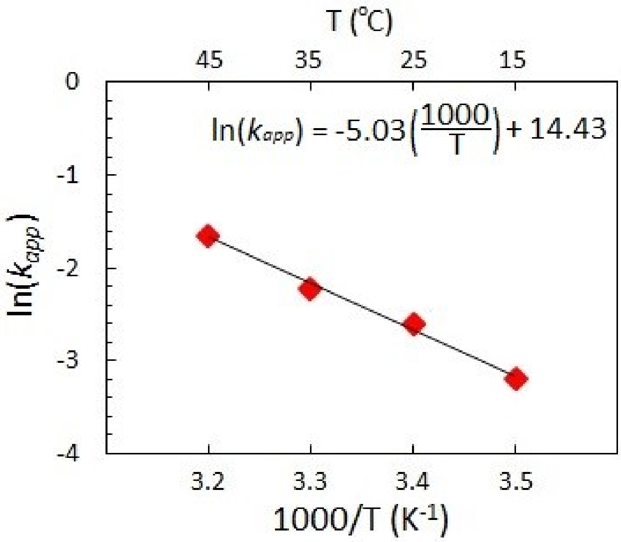


Figure S2. The dependency of the natural logarithm of the reaction rate constant on the reciprocal of the reaction temperature (T).

3.3. Elemental Maps of the Bronze Catalyst after Etching. Figure 4a of the report shows elemental maps for the serrated convex surface of the plastically deformed bronze catalyst before and after it is etched with 2 M nitric acid for 10 min. Figure S3 shows the analogous data for the convex surface which shows a relatively smooth morphology.

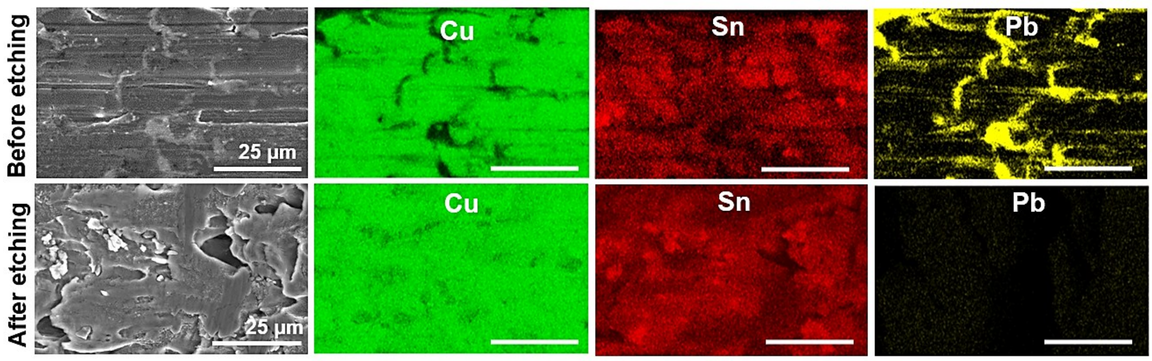


Figure S3. SEM images and the associated elemental maps of the convex surface of the plastically deformed bronze chips before and after being exposed to a nitric acid etch. The results are consistent with ICP-MS analysis which shows significantly less Pb in the 4-AP product when using the etched catalyst.

3.4 Passivation of the Back and Side Surfaces of the Cu Single Crystals. In order to obtain the k_{app} values for the various single crystal surfaces of Cu (Figure 1d) it was required that that the sides of the crystal and the unpolished back surface be rendered catalytically inactive by coating them with a lacquer. The effectiveness of this lacquer was verified in a separate experiment by coating all the surfaces of a catalytically active Cu foil. Figure S4 shows the time-dependent absorbance of the 400 nm 4-nitrophenolate peak before and after surface passivation. Note that the absorbance remains unchanged when the Cu surface is passivated with the lacquer.

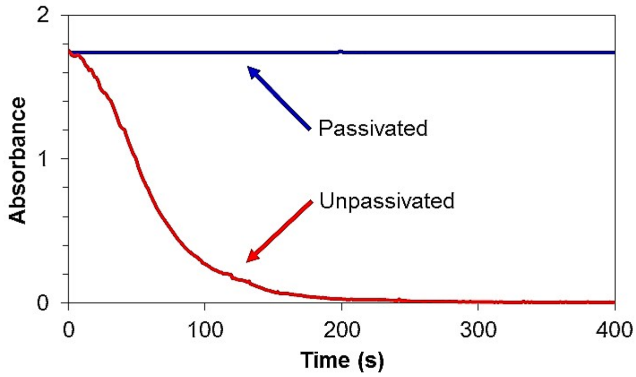


Figure S4. Time-dependent absorbance of the 400 nm 4-nitrophenolate peak for a catalytically active Cu foil (red) and the same foil after all surfaces are passivation with a lacquer (blue).

3.5 Catalysis Data showing that Elemental Pb and Sn are Catalytically Inactive. Figure S5 shows the time-dependent absorbance of the 400 nm 4-nitrophenolate peak for plastically deformed Pb and Sn. The fact that the absorbance is near constant over a 600 s interval indicates that neither of these elements show any meaningful catalytic activity towards the reduction of 4-NP.

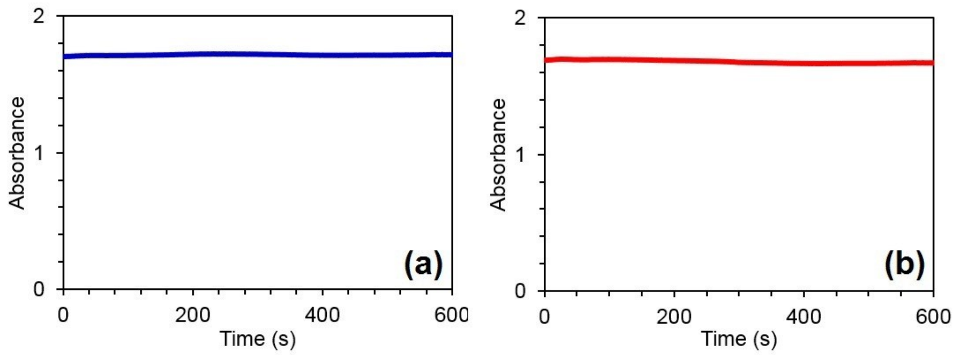


Figure S5. The time-dependent absorbance of the 400 nm 4-nitrophenolate peak for plastically deformed (a) Pb and (b) Sn.

3.6 AFM Image of the Bronze Catalyst. The surface morphology of the bronze chips used in the continuous flow reactor were characterized using atomic force microscopy. Presented in Figure S6 is an AFM image of the surface of a chip formed through plastic deformation and then etched in nitric acid.

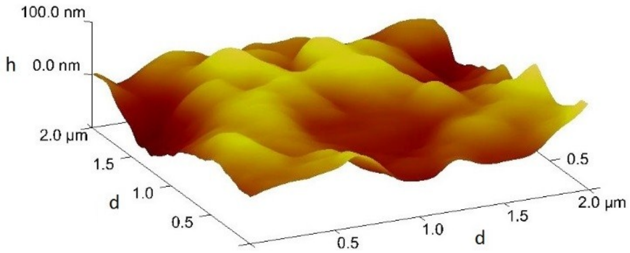


Figure S6. AFM image of the plastically deformed and etched bronze catalyst.

3.7 The Reaction Rate Constant (k_{app}). Figures 4b, 4d, and 4f show the linear portion of the -ln(A/A$_o$) vs. time plots from which the reaction rate constant is extracted. Figure S7 shows the same data, but where the non-linear regions, which are characteristic of the early- and late-stages of the reaction, are included.

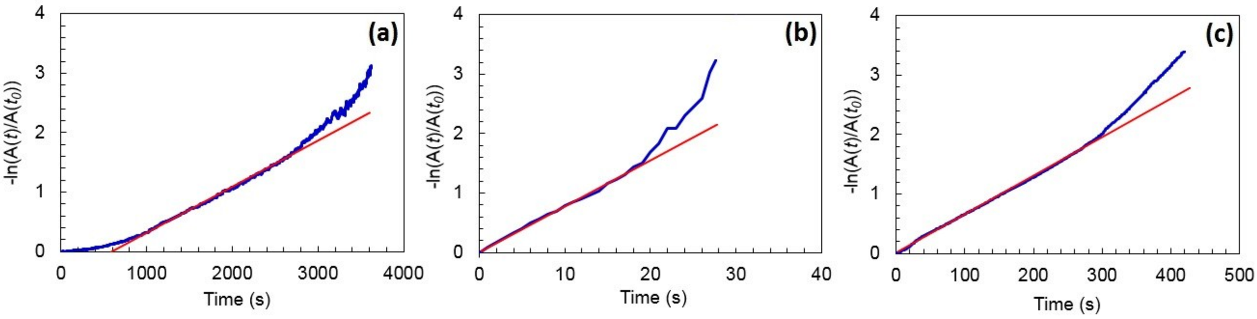


Figure S7. Plots of -ln(A/A$_o$) vs. time for (a) an unetched bronze catalyst, (b) an etched bronze catalyst, and (c) an etched Pb-free bronze catalyst. For each case the red line denotes the fit to the linear region.