

CuNi/Co composites prepared by electroless deposition: Structure and catalytic activity for the oxidation of cyclohexene with oxygen

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Experimental Section

1. Ni-ELD/Co-5 composite preparation

In a typical synthesis, 0.7355 g Co powder (300 meshes, 99.5%), 0.2076 g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), 1.875 g $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ($\geq 99.0\%$), 1.4 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ($\geq 99.0\%$) and 80 mL distilled water were added into a 250 mL round bottom flask and the pH value was adjusted to 10 with NaOH ($\geq 96\%$). The reaction was allowed to continue for 1 h at 333 K under stirring. The precipitate was filtered, washed with distilled water three times and air-dried at 373 K for 3 h. The color of precipitate was gray.

2. CuCo-ELD/Co-5 composite preparation

In a typical synthesis, 0.7355 g Co powder (300 meshes, 99.5%), 0.192 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($\geq 99\%$), 0.086 g $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), 1.875 g $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ($\geq 99.0\%$), 1.4 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ($\geq 99.0\%$) and 80 mL distilled water were added into a 250 mL round bottom flask and the pH value was adjusted to 9 with NaOH ($\geq 96\%$). The reaction was allowed to continue for 1 h at 333 K under stirring. The precipitate was filtered, washed with distilled water three times and air-dried at 373 K for 3 h. The color of precipitate was changed from Co gray to Cu red.

3. CuNi-ELD/Al-5 composite preparation

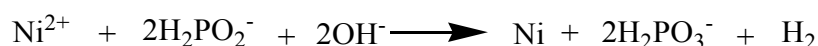
In a typical synthesis, 0.3272 g Al powder (500 meshes, 99.9%), 0.192 g CuSO₄·5H₂O (≥99%), 0.08 g NiSO₄·6H₂O (≥98.5%), 1.875 g NaH₂PO₂·H₂O (≥99.0%), 1.4 g Na₃C₆H₅O₇·2H₂O (≥99.0%) and 80 mL distilled water were added into a 250 mL round bottom flask and the pH value was adjusted to 9.5 with NaOH (≥96%). The reaction was allowed to continue for 2 h at 333 K under stirring. The precipitate was filtered, washed with distilled water three times and air-dried at 373 K for 3 h. The color of precipitate was changed from Al silvery to Cu red.

4. Cu-ELD/Co-5 composite preparation

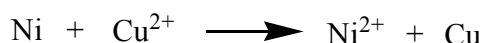
In a typical synthesis, 0.7355 g Co powder (300 meshes, 99.5%), 0.192 g CuSO₄·5H₂O (≥99%), 0.4 g EDTA-2Na (≥99%), 1.5 mL formaldehyde (36.7%), 2 mg 2,2'-bipyridyl (≥99.0%) and 80 mL distilled water were added into a 250 mL round bottom flask and the pH value was adjusted to 12.5 with NaOH (≥96%). The reaction was allowed to continue for 0.5 h at 333 K under stirring. The precipitate was filtered, washed with distilled water three times and air-dried at 373 K for 3 h. The color of precipitate was changed from Co gray to Cu red.

Main reactions:

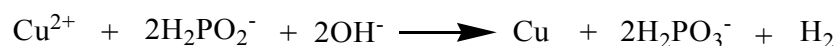
Ni²⁺ oxidizes H₂PO₂⁻ in alkaline condition and Ni deposition:



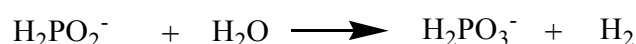
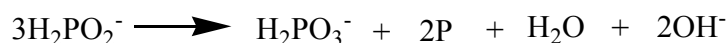
Ni replaces Cu reaction:



Adding above two equations:



Side reactions:



Scheme S1. The chemical equations of copper electroless deposition using sodium hypophosphite as a reducing agent and Ni²⁺ as a catalyst.

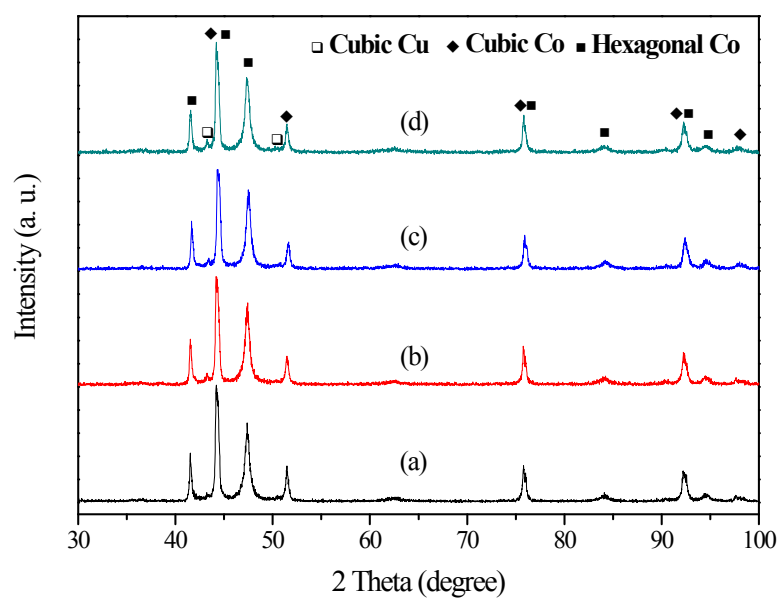


Fig. S1 XRD patterns of mixture of commercial Cu nanoparticles and Co powder: (a) 1.7 wt% Cu and 98.3 wt% Co; (b) 2.2 wt% Cu and 97.8 wt% Co; (c) 3.3 wt% Cu and 96.7 wt% Co; (d) 4.3 wt% Cu and 95.7 wt% Co.