

Catalytic oxidation of hydroxyarenes over silica-supported bimetallic noble metal catalysts

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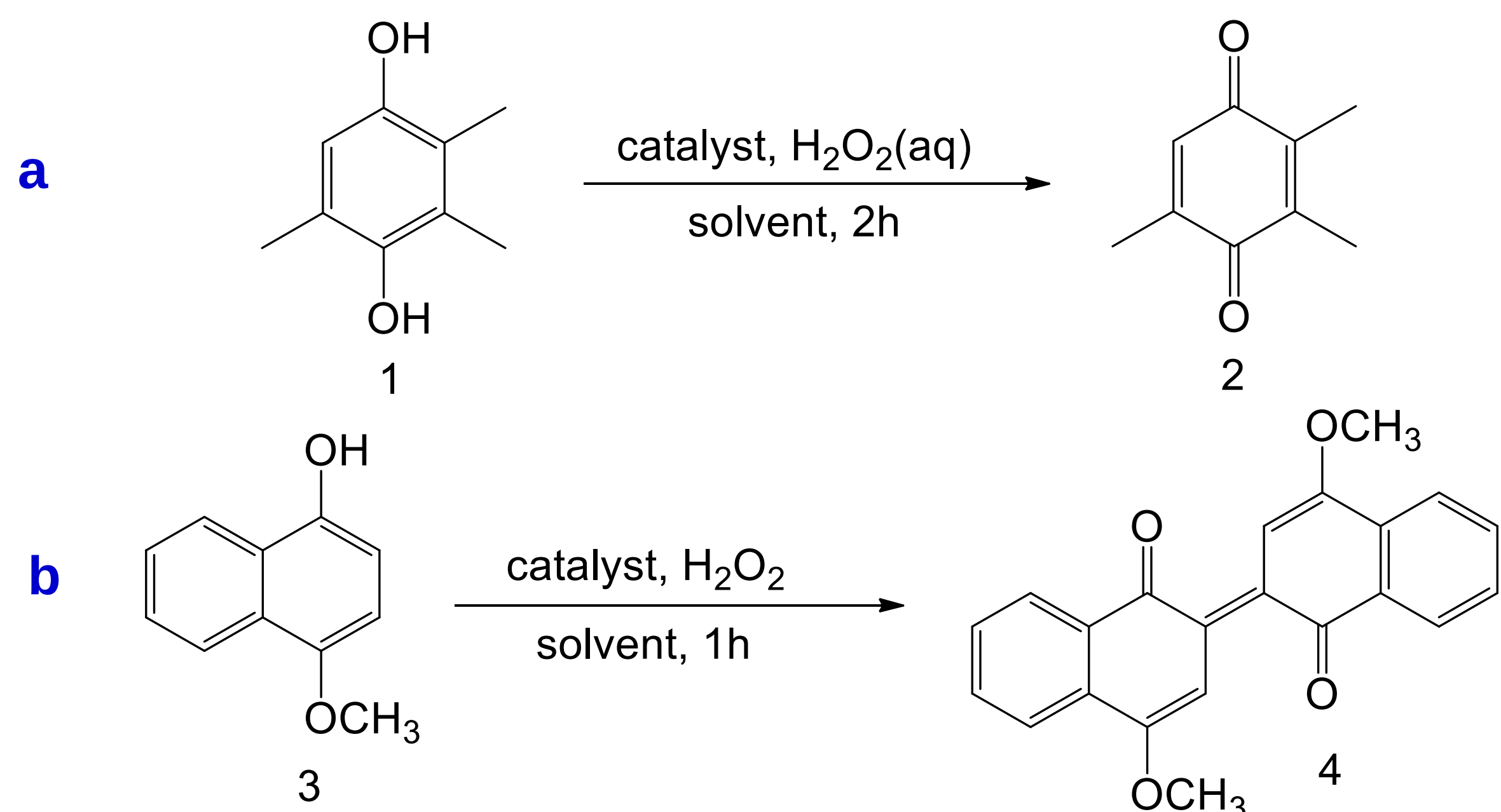
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INTRODUCTION

The catalytic oxidation of hydroxyarenes is an important goal in the synthesis of organic compounds [1]. The products obtained such as quinones and binaphthones, serve as the elementary building blocks for several classes of complex molecules that play a role in biological systems [2]. Conventional methods such as the use of stoichiometric oxidants have served as primary synthesis routes for numerous years to obtain quinones and binaphthones. However, these methods have become synonymous with low yields, poor oxidation and coupling selectivity, production of byproducts and reduced oxidants that have adverse effects on the environment [3, 4]. Therefore, a need to substitute these methods with greener, efficient and environmentally friendly methods is of paramount importance. In this work, the oxidation of hydroxyarenes (phenols and naphthols) were carried out using bimetallic noble metal Ru-Bi/SiO₂, Au-Ru/SiO₂ and Au-Bi/SiO₂ catalysts.

REACTION ROUTES



Oxidation of trimethylhydroquinone (a) and 4-methoxy-1-naphthol (b) over Au-Bi, Ru-Bi and Au-Ru catalysts prepared by microwave-assisted loading (MW) and deposition (DP).

RESULTS & DISCUSSION

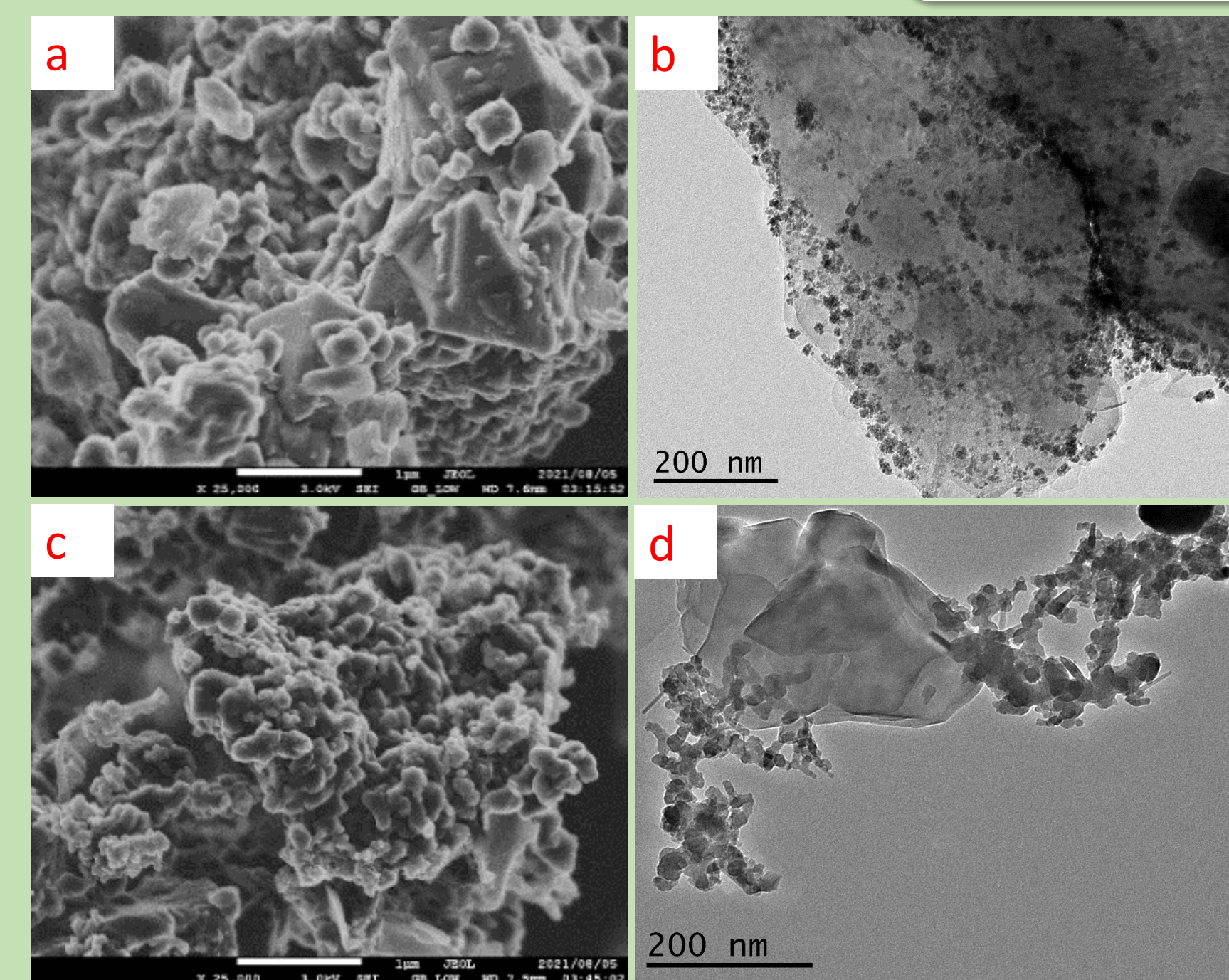


Figure 1. SEM and TEM images of 5%Au-5%Ru/SiO₂-MW (a) and (b), and 5%Au-5%Ru/SiO₂-DP (c) and (d). SEM and TEM images of MW-Au-Ru catalyst showed the presence of some agglomerated metal nanoparticles. The DP-Au-Ru catalyst showed agglomerated nanochains on the surface of SiO₂ support and this was also confirmed by EDX mapping (Figure 2).

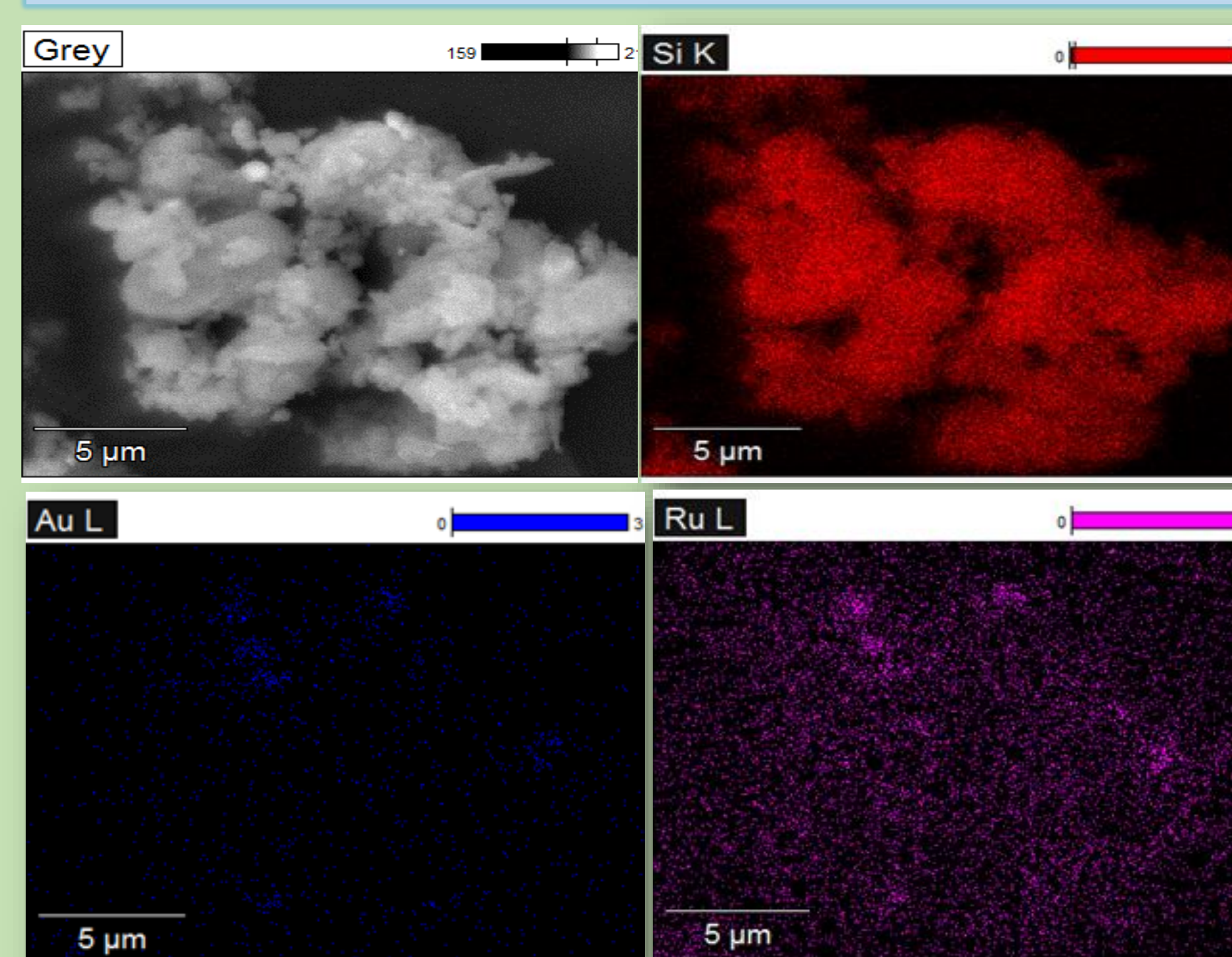


Figure 2. EDX mapping analysis for 5%Au-5%Ru/SiO₂-MW

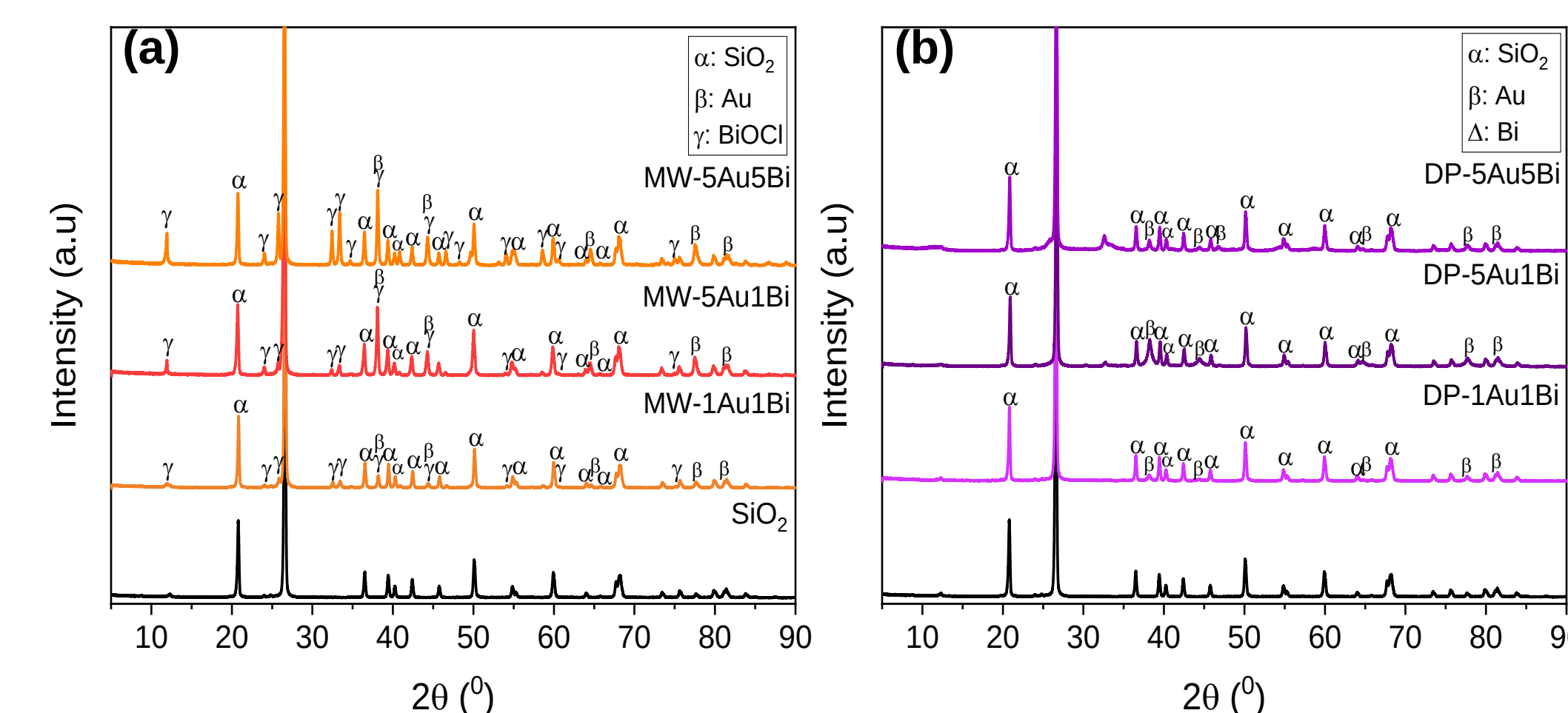


Figure 3. XRD patterns of (a) MW Au-Bi, and (b) DP Au-Bi catalysts.

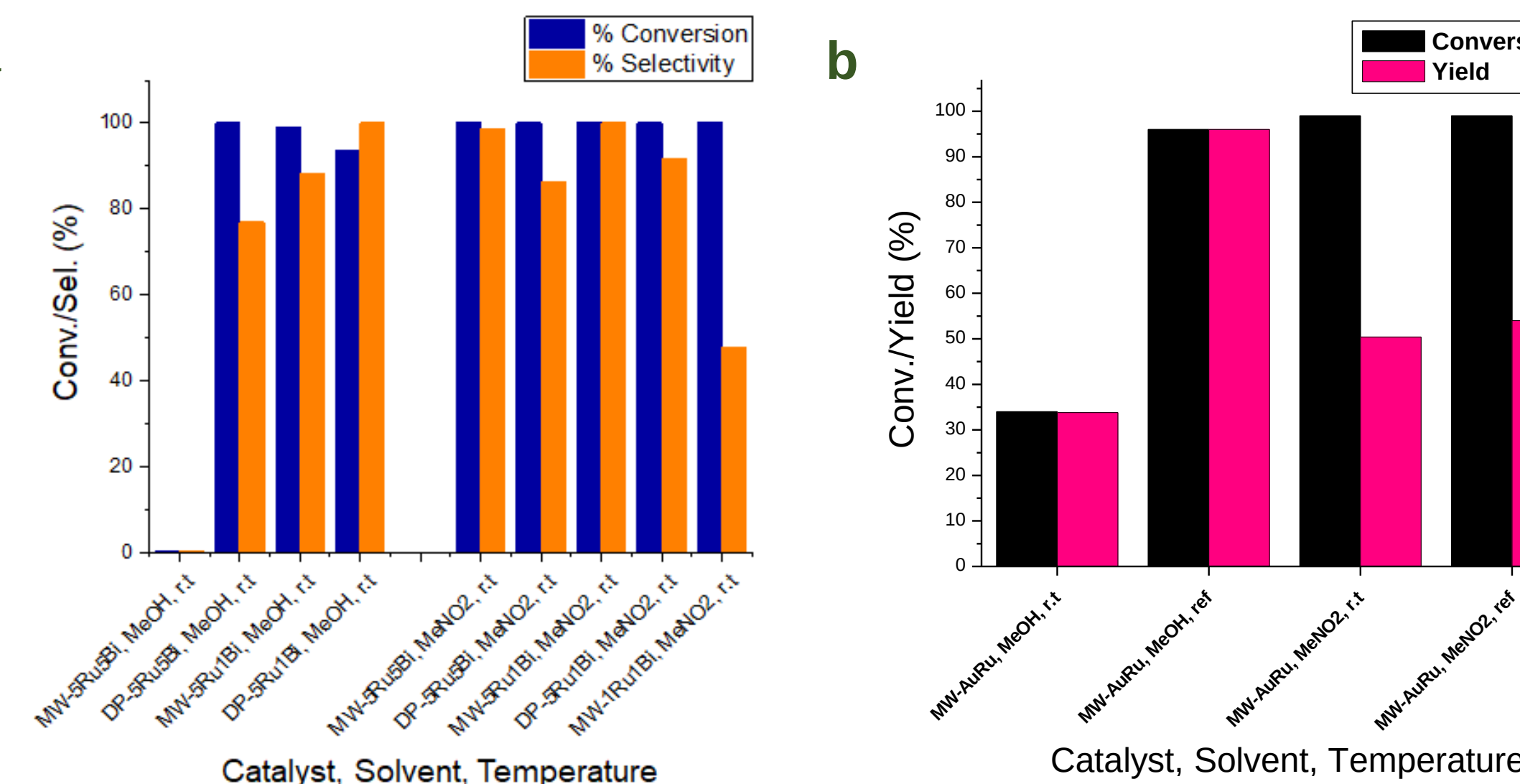


Figure 4. Conversions and selectivities obtained for the oxidation of trimethylhydroquinone over silica-supported Ru-Bi (a) and conversions and yields obtained for the oxidative coupling of 4-methoxy-1-naphthol (b) in various solvents under different temperature conditions.

- High conversions are always observed in MeNO₂ and MeOH, 88-100%, for trimethylhydroquinone oxidation and at high temperatures, higher yields (82-100%) and conversions (99-100%) are observed in both MeOH and MeNO₂.
- High conversions and yields are also observed at r.t. in both MeOH and MeNO₂, except for MW-Au-Ru catalyst which shows low to moderate yields in both solvents (35-52%).
- High conversions are always observed in MeNO₂, 99-100%, for oxidation of 4-methoxy-1-naphthol, although with moderate yields.
- Relatively low conversions are achieved in MeOH (34%), albeit there is a significant increase at high temperatures (>90%).
- High conversions are always observed at high temperatures, 95-100%, and moderate yields are observed at lower temperatures, 34-50%.

CONCLUSION

- Bimetallic silica-supported Au-Bi, Au-Ru, and Ru-Bi catalysts were synthesized successfully with microwave (MW) and deposition (DP) methods.
- The presence of metal nanoparticles was confirmed with characterization by XRD, TEM, SEM and EDX.
- Au-Ru and Ru-Bi catalysts are more active compared to Au-Bi catalysts.
- Au-Bi and Ru-Bi catalysts are not active in trimethylhydroquinone oxidation when the reactions are carried out in MeOH.
- MeOH and MeNO₂ promote high conversion, yield and selectivity and at higher temp in trimethylhydroquinone oxidation, regardless of catalyst composition or preparation method.
- MeNO₂ promotes high conversions in 4-methoxy-1-naphthol oxidation compared to MeOH, although MeOH has better selectivity than MeNO₂.
- Higher temperatures promotes high conversions in 4-methoxy-1-naphthol oxidation.

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