

Oxidative transformation of phenols and naphthols on metal-oxide supported bimetallic noble metal nanocatalysts

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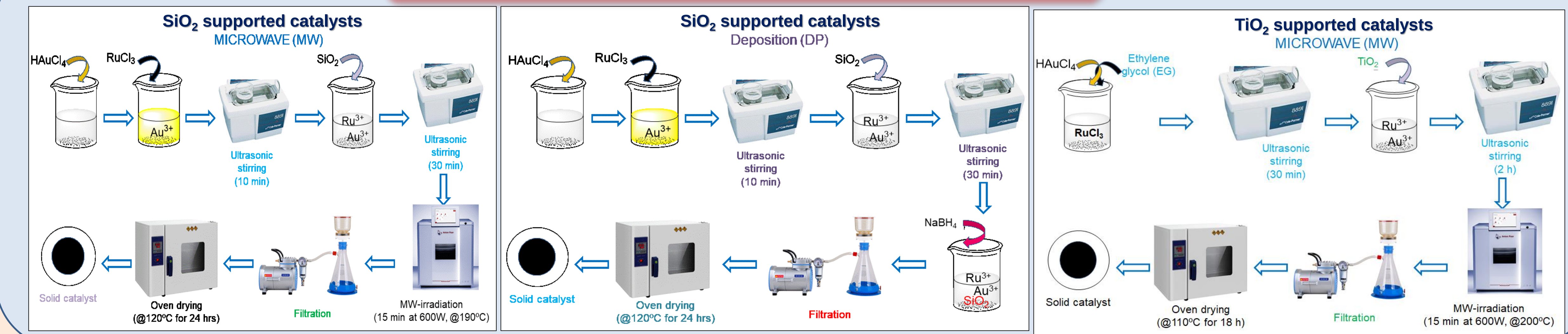
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INTRODUCTION

Oxidation of phenols and naphthols is an important goal in fine chemical synthesis [1]. These reactions are essential for the formation biologically active compounds, which are central building blocks for many synthetic and natural products [2]. The products obtained from these reactions, quinones, phenoxazinones and binaphthones, are a class of natural and synthetic compounds with pharmaceutical applications due to their biological activities [3]. Stoichiometric oxidants and homogeneous catalysts have been used for numerous years to synthesize quinones, phenoxazinones and binaphthones. However, these methods often lead to low yields, poor oxidation and coupling selectivity and produce byproducts and reduced oxidants that are harmful to the environment [4]. The need to substitute these traditional methods with more efficient and environmentally friendly catalytic methods is of high importance. In this work, the oxidation of phenols and naphthols were carried out using heterogeneous Ru-Au/TiO₂, Ru-Pd/TiO₂, Ru-Bi/SiO₂, Ru-Au/SiO₂ and Au-Bi/SiO₂ catalysts.

CATALYST PREPARATION METHODS



CATALYST CHARACTERIZATION RESULTS

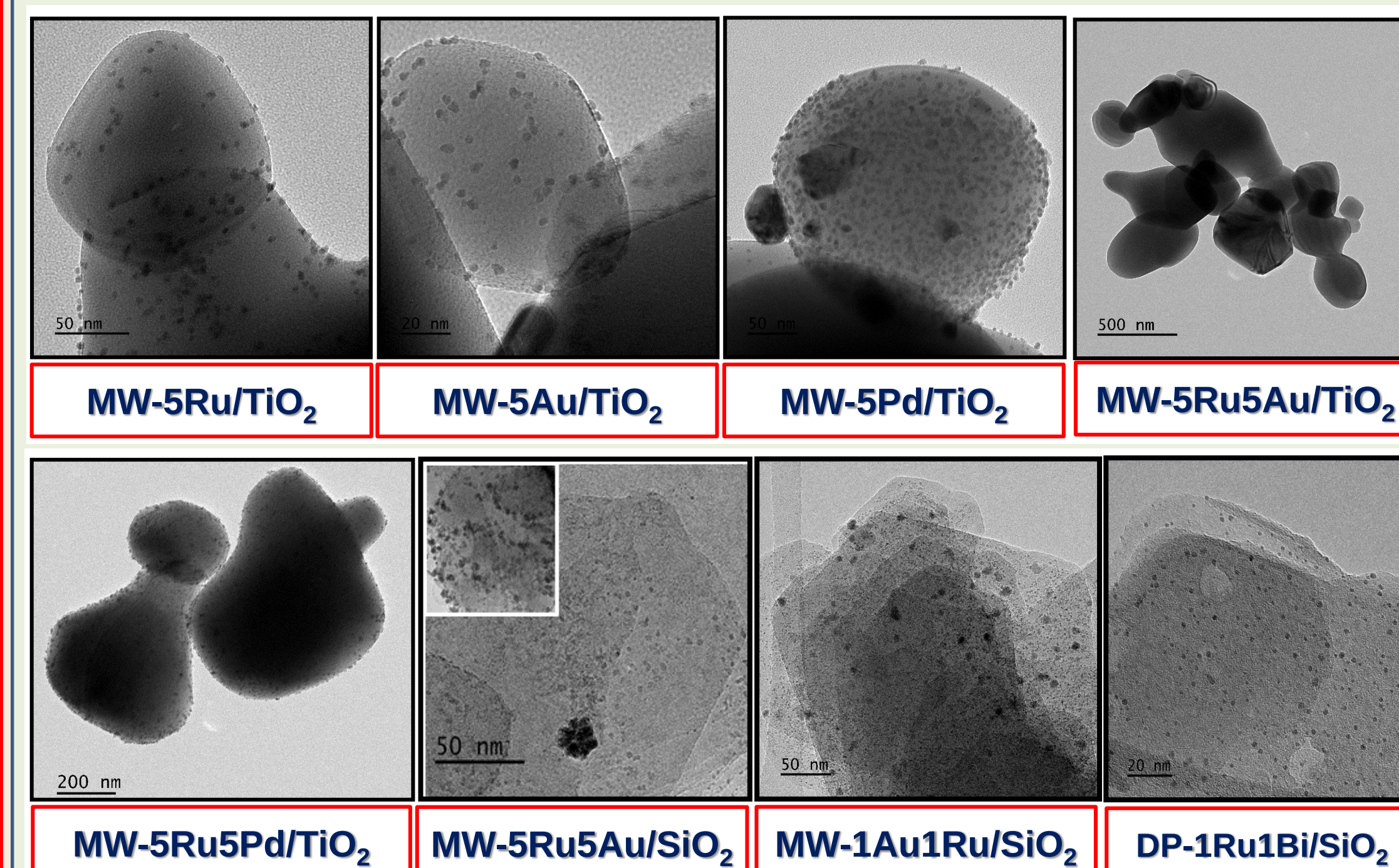


Figure 1: TEM images of TiO₂ and SiO₂ supported catalysts

TiO₂ and SiO₂ supported monometallic and bimetallic catalysts with for each metals metal nanoparticles dispersed on the surface of TiO₂.

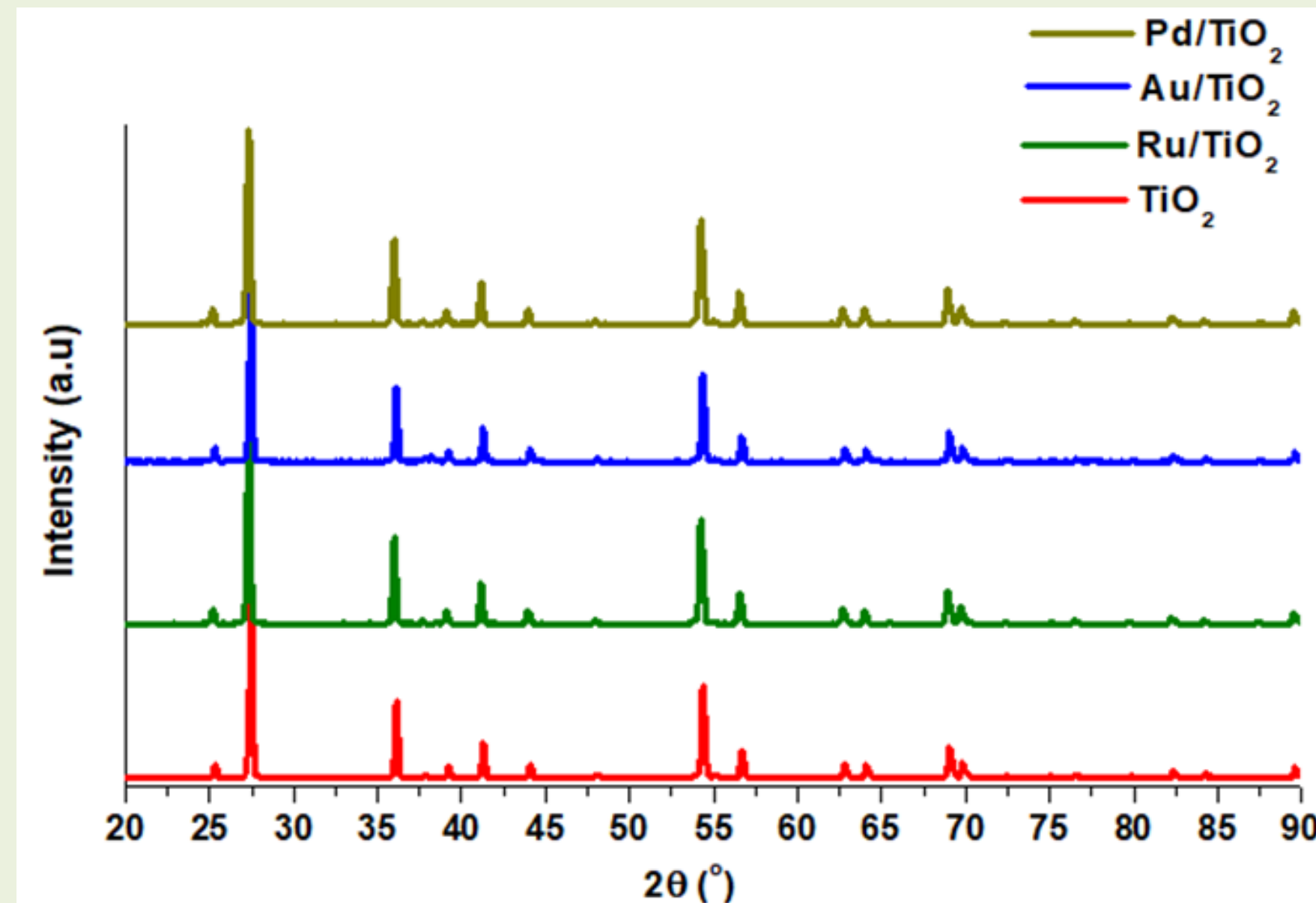


Figure 2: XRD pattern of TiO₂ and TiO₂ supported catalysts

- ✓ The diffraction peaks for both catalyst shows the presence of the support-Rutile.
- ✓ There is a slight shift of the Ru-Pd diffraction peaks to the left, due to the change in lattice parameters.
- ✓ No diffraction peaks of metals were observed. However, Ru-Au showed a weak intensity broad peak at 2θ=38.3°, which could be due to the presence of larger metallic particles.

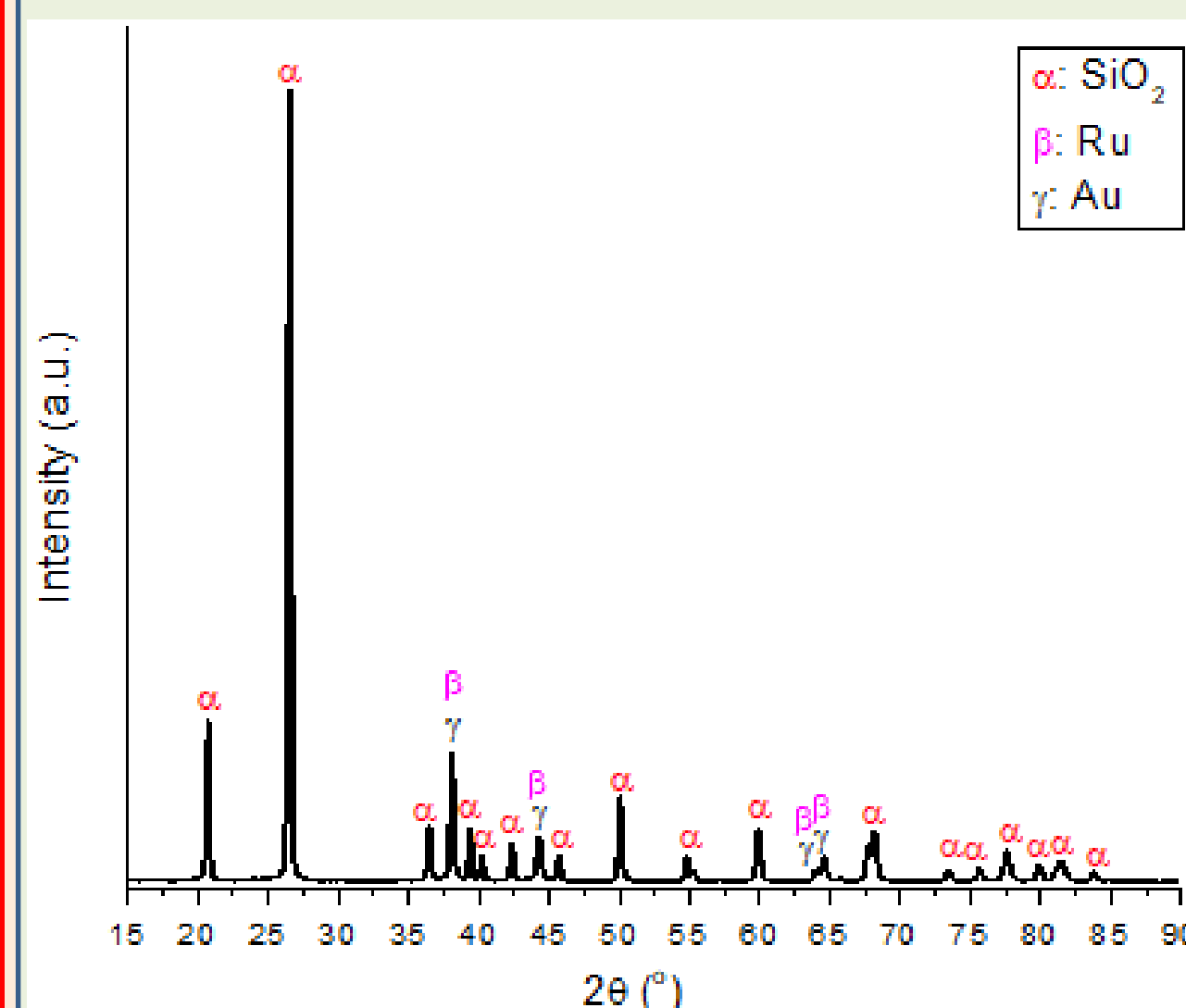


Figure 3: XRD diffraction pattern of MW-5Ru5Au/SiO₂

- ✓ The diffraction peaks for quartz were observed for silica.
- ✓ Both Au and Ru are presents as face centered cubic crystals

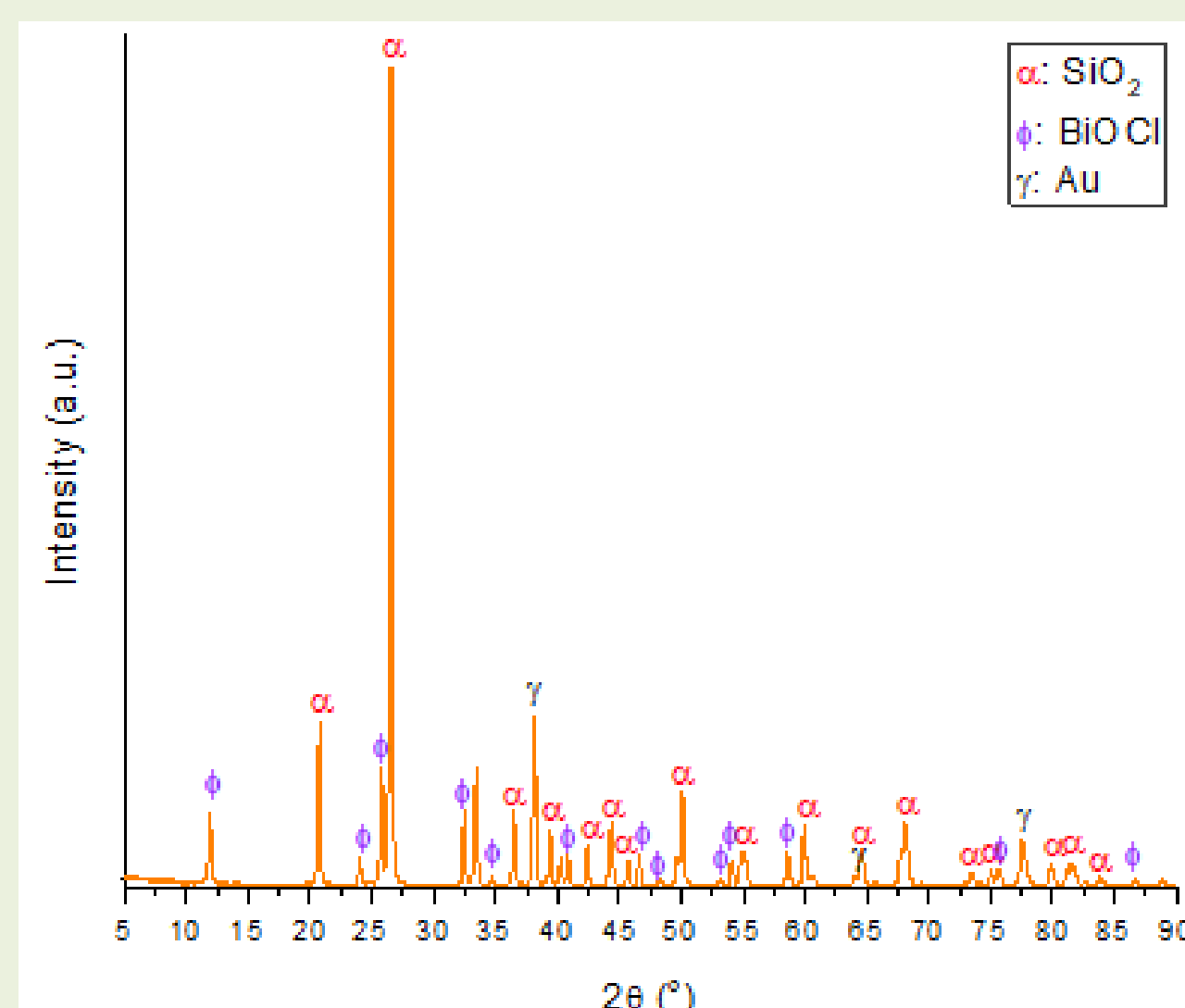


Figure 4: XRD diffraction pattern of MW-5Au5Bi/SiO₂

- ✓ The diffraction peaks for quartz were observed for silica.
- ✓ Both Au is present as face centred cubic crystals while Bi formed BiOCl sheets on silica

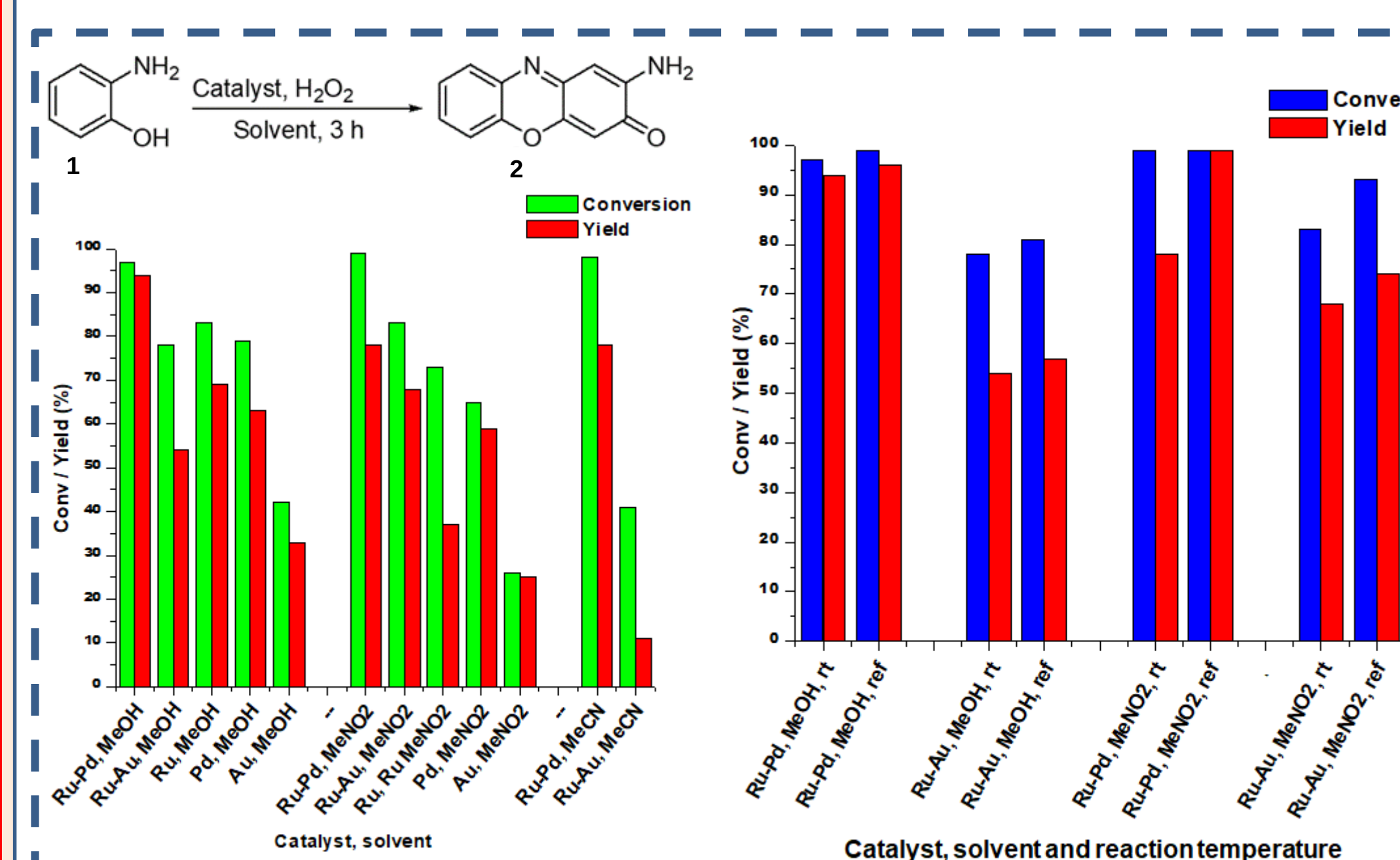


Figure 5: Oxidation of 1 on TiO₂ supported catalysts at room temperature. (The loading is 1% for each metal)

- ✓ Ru-Pd has a good catalytic activity in all solvents as compared to other catalysts- High yields ~94%.
- ✓ Ru-Au is also active- efficient in nitromethane- conversion increased from 78-83%.
- ✓ Catalysts with Au have a decreased activity.
- ✓ Acetonitrile showed a lower activity for both bimetallic catalysts.

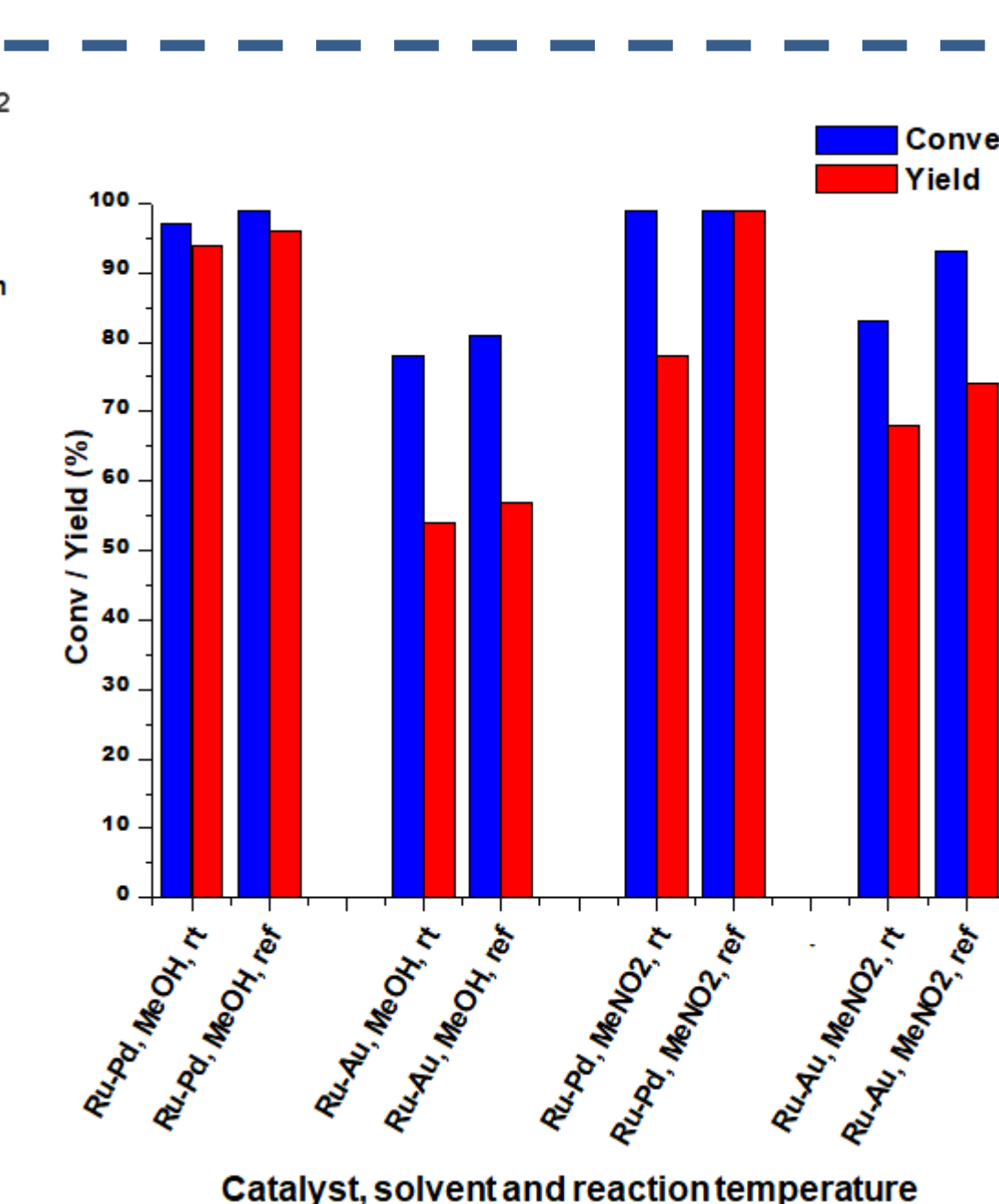


Figure 6: Catalytic outcomes for the oxidation of 1 on TiO₂ supported catalysts at different temperatures using various catalysts and solvents. (ref: solvent reflux temperature. The loading is 1% for each metal)

- ✓ Ru-Pd shows good catalytic activity in both solvents- High conversions ~99%.
- ✓ Ru-Au has lower activity compared to Ru-Pd.
- ✓ The increase in temperature improves the efficiency of Ru-Au- High conversions ~93%.

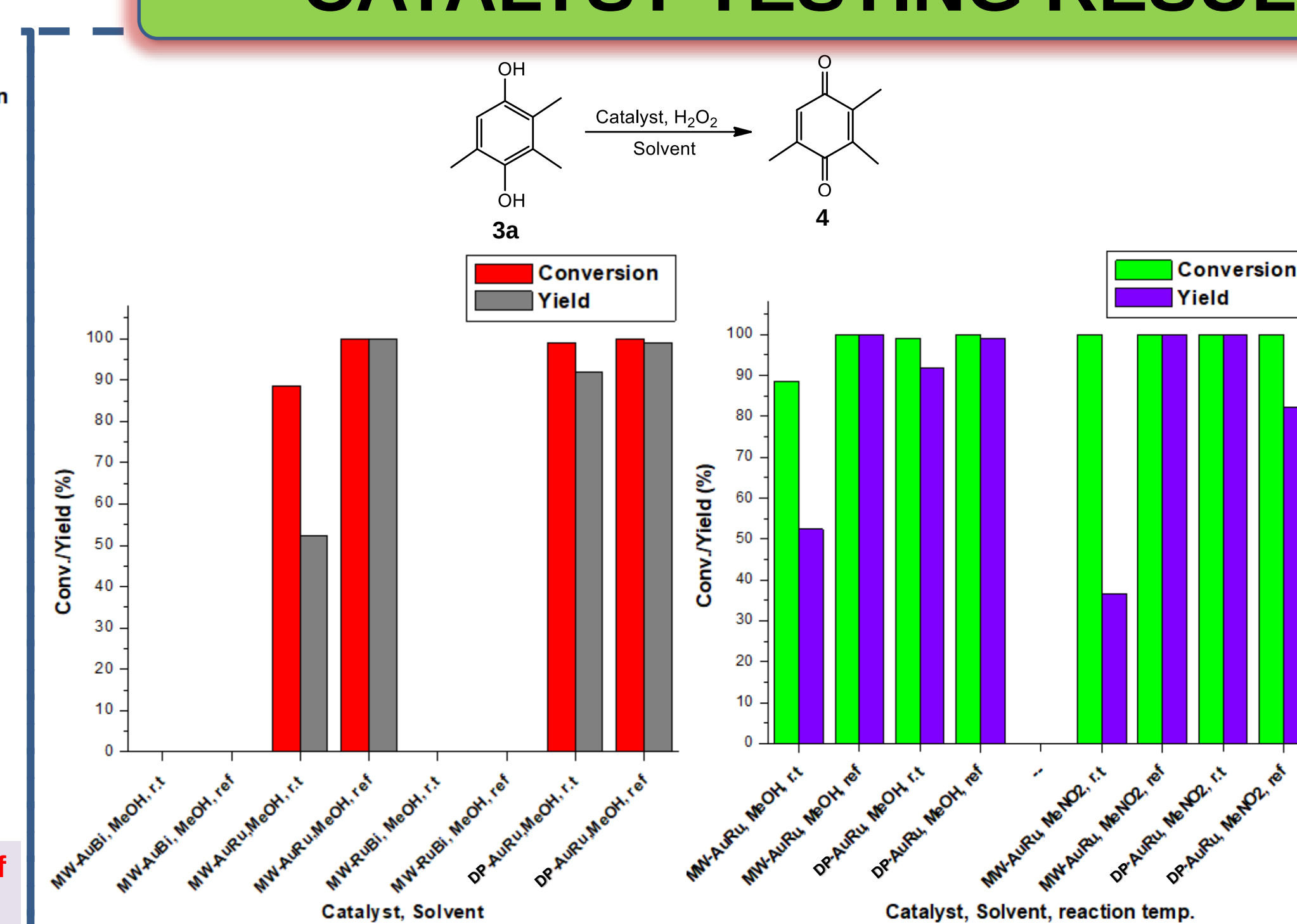


Figure 7: Reaction of 3a at different temperatures using various SiO₂ supported catalysts and solvents. (The loading is 5% for each metal)

- ✓ Bi-containing catalysts are not active towards the 3a oxidation, regardless of temperature conditions.
- ✓ Au-Ru catalysts are very active in catalyzing the substrate, up to 100% conversion & yield in MeOH for both IM and MW.

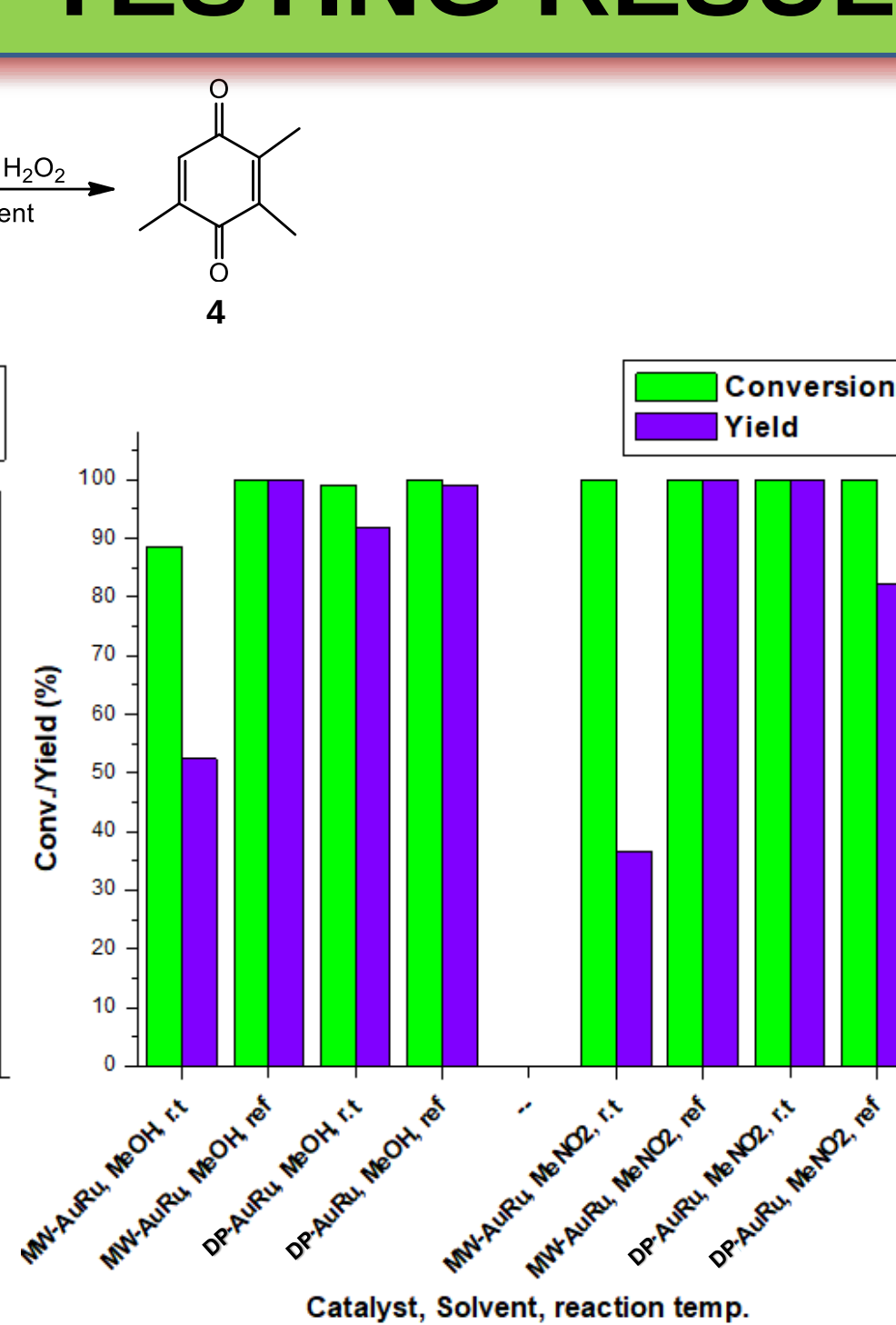


Figure 8: Activities observed for 3a at different temperatures using different SiO₂ catalysts and solvents. (ref: solvent reflux T. The loading is 5% for each metal)

- ✓ Complete conversion of 1a is always achieved in Nitromethane.
- ✓ High conversions are also observed in MeOH, 88-100%.
- ✓ 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-AuRu catalyst which shows low to moderate yields in both solvents (35-52%).

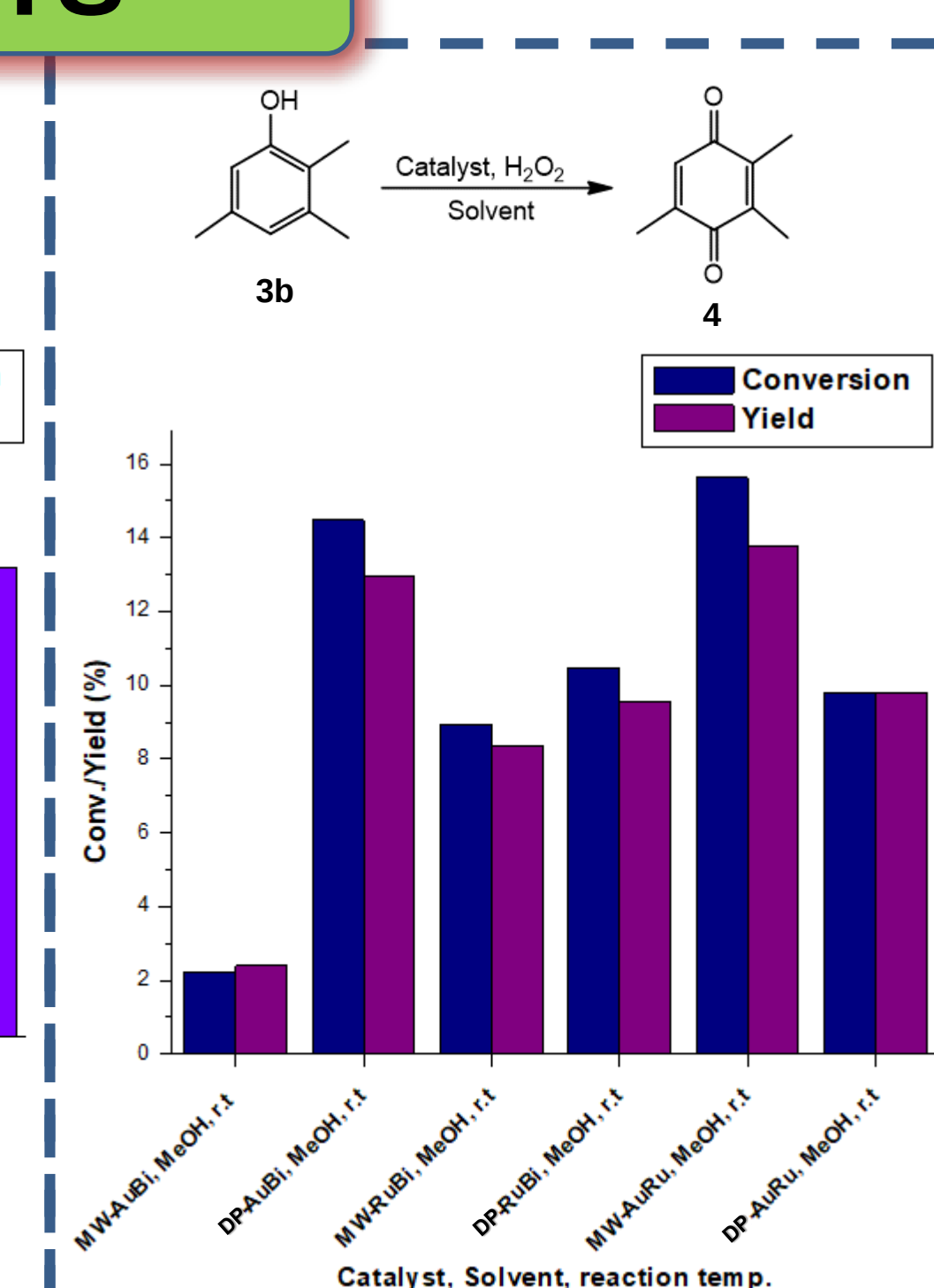


Figure 9: Oxidation of 3b at different temperatures on various catalysts. (The loading is 1% for each metal)

- ✓ Catalysts show relatively low activity in 3b oxidation using MeOH, 2-14% conversion.
- ✓ The catalyst preparation method as well as the composition does not seem to greatly influence the outcome of the reaction

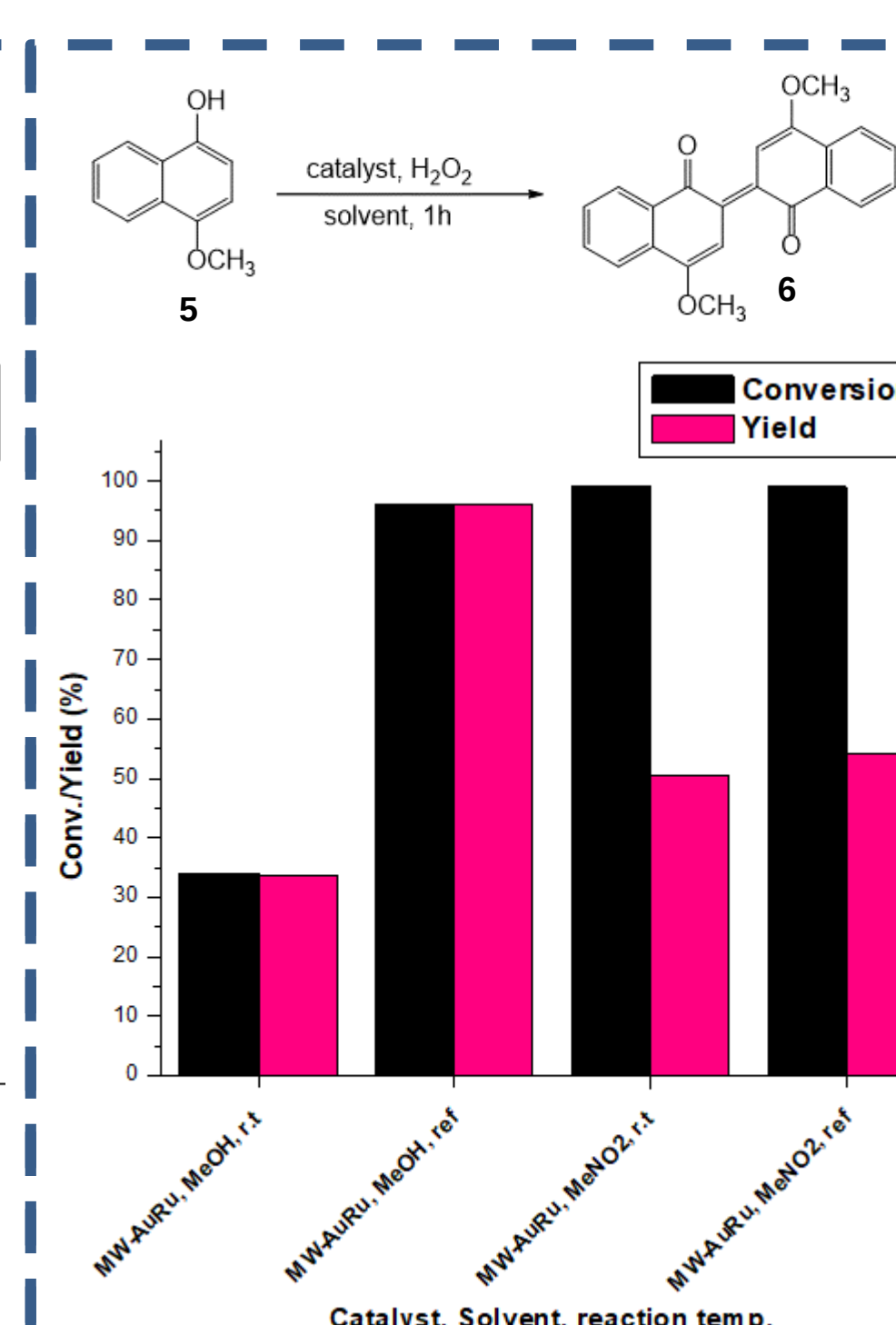


Figure 10: Oxidation of 5 on SiO₂ based catalysts at r.t. and under reflux. (The loading is 5% for each metal)

- ✓ High conversions are always observed in MeNO₂, 99-100%.
- ✓ Moderate yields are observed in MeNO₂.
- ✓ 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%.
- ✓ Moderate yields are observed at lower temperatures, 34-50%.

CONCLUSIONS

- ✓ Ru-Pd/TiO₂ showed excellent catalytic activity as compared to other catalysts tested on substrate 1.
- ✓ The presence of Au nanoparticles on TiO₂ supported Ru catalyst lowered its activity in the oxidation of 1.
- ✓ The order of the activity in the solvents for oxidation of 1 is: MeOH>MeNO₂>MeCN.
- ✓ The increase in temperature promoted the reaction proceedings giving high yields and selectivities of the phenoxazinones 2.
- ✓ Au-Ru/SiO₂ catalysts are more active compared to Ru-Bi/SiO₂ and Au-Bi/SiO₂ catalysts for substrates 3 and 5.
- ✓ Bi promoted catalysts are have low activity due to the blockage of active sites of active metal.
- ✓ MeOH and MeNO₂ promote high conversion for 3a, yield and selectivity of 4 is favored at higher temp, regardless of catalyst composition or prep method.
- ✓ MeNO₂ promotes high conversions in 5 oxidation compared to MeOH and the reaction is favored at higher temperatures

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ACKNOWLEDGEMENTS

