

Introduction

Research on new approaches toward generation and utilization of renewable energy sources have attracted much attention. This is due to growing concern over the challenges faced with the utilization of fossil fuels. Lignin based biomass has great potential in producing biofuels and other useful bulk chemicals upon being depolymerized. There are difficulties faced with the direct utilization of the depolymerized products both as fuel and bulk chemicals due to high oxygen contents.¹ Hence, the need to selectively deoxygenate the oxygenated molecule. Selective HDO of lignin derived monomers is expected to yield products with no ring hydrogenation which results in higher value chemicals and greater H₂ usage efficiency.¹ However, this is not easily achieved as ring hydrogenation commonly occurs with heterogeneous nanoparticle catalysts.² Homogenous approach has given high selectivity but with instability limitation.³

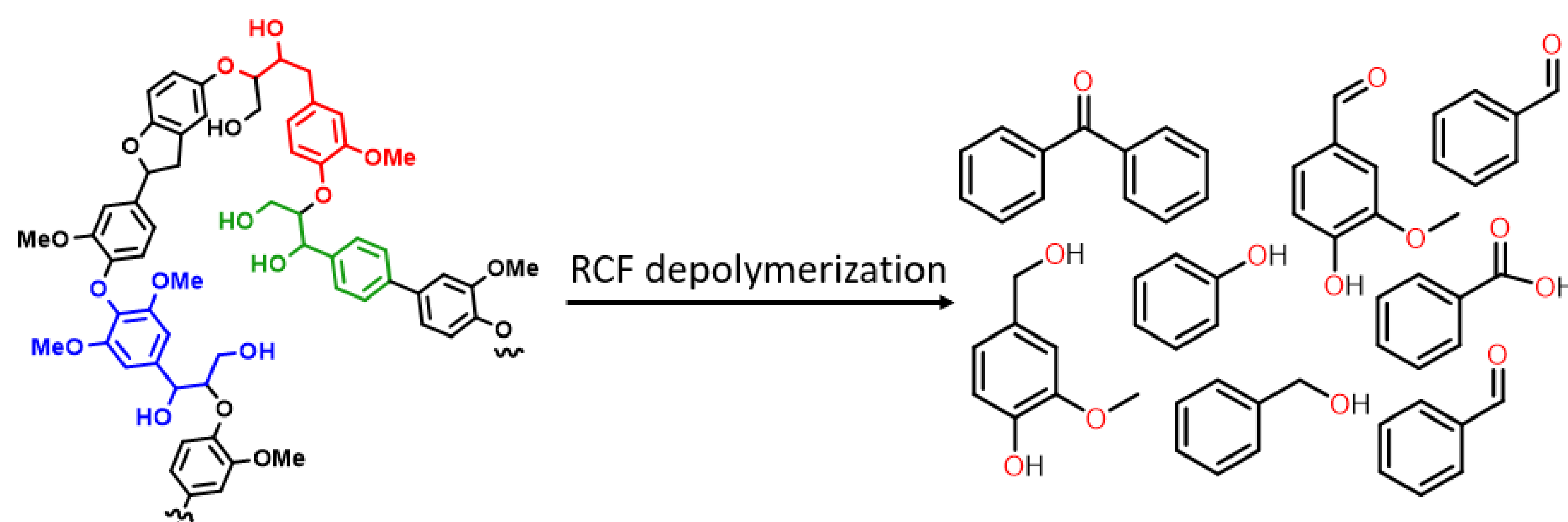


Figure 1: Reductive Catalytic Fractionation (RCF) of lignin polymer to generate oxygenated molecule.

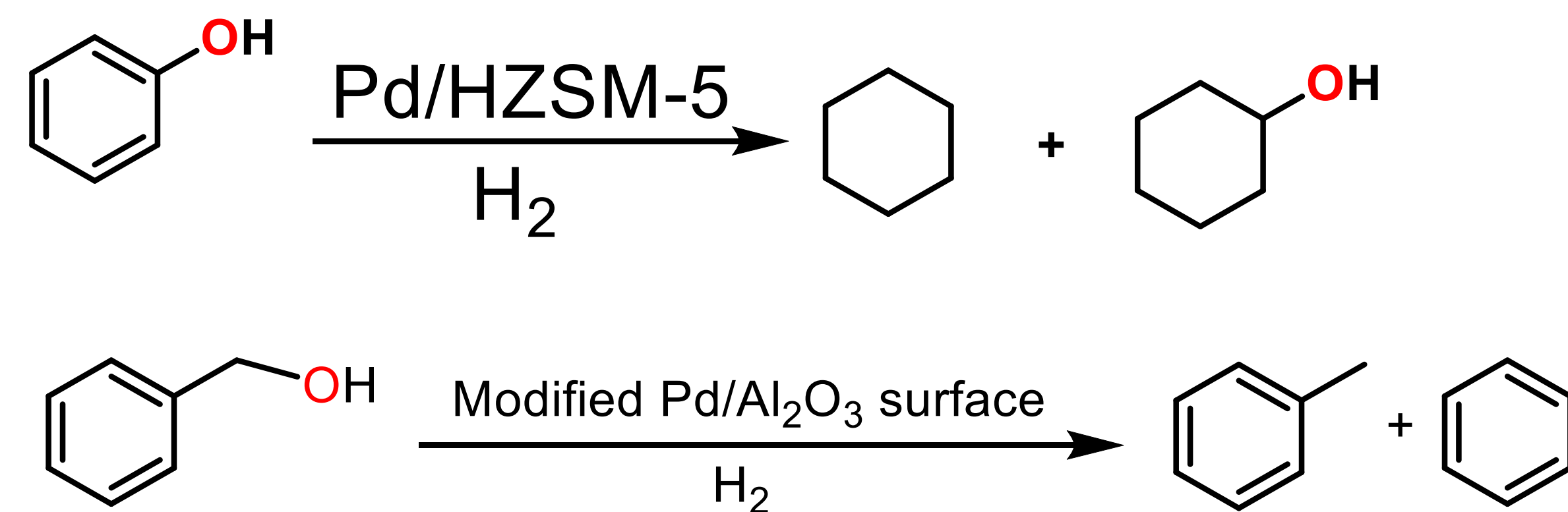
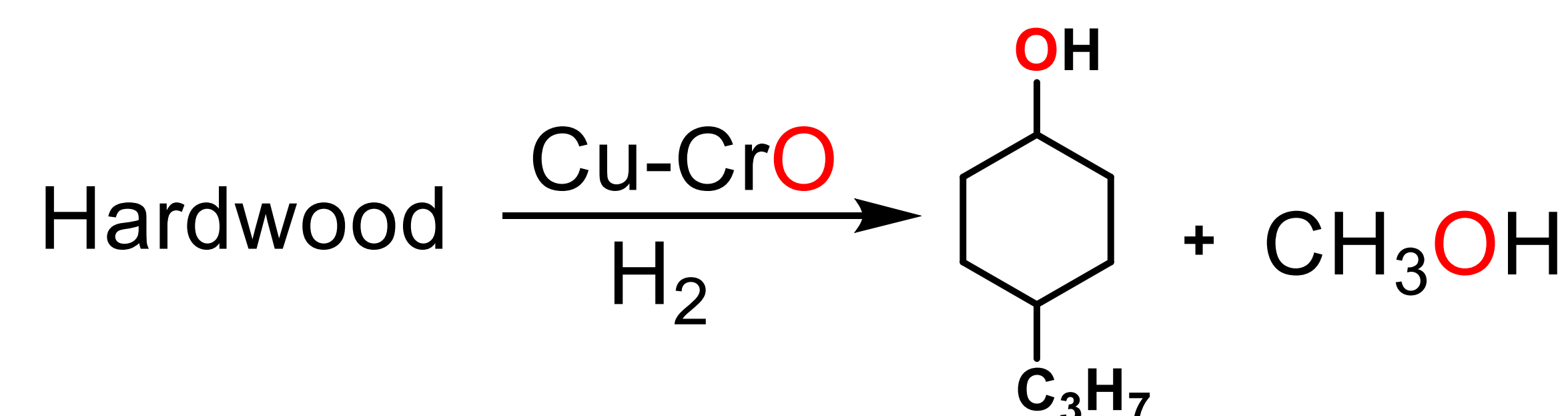


Figure 2: Former works on HDO^{1,2}

Most of the heterogenous approaches towards HDO are nonselective, producing ring hydrogenated or decarbonylated products with low energy value thereby limiting the use of lignin biomass in biofuel production^{1,2}.

Catalysts syntheses

The catalysts were synthesized using incipient wetness (IW) method or base treatment of support followed by solvent switching and reduced at 170°C and 400 SCCM (20 % H₂ balanced with N₂).

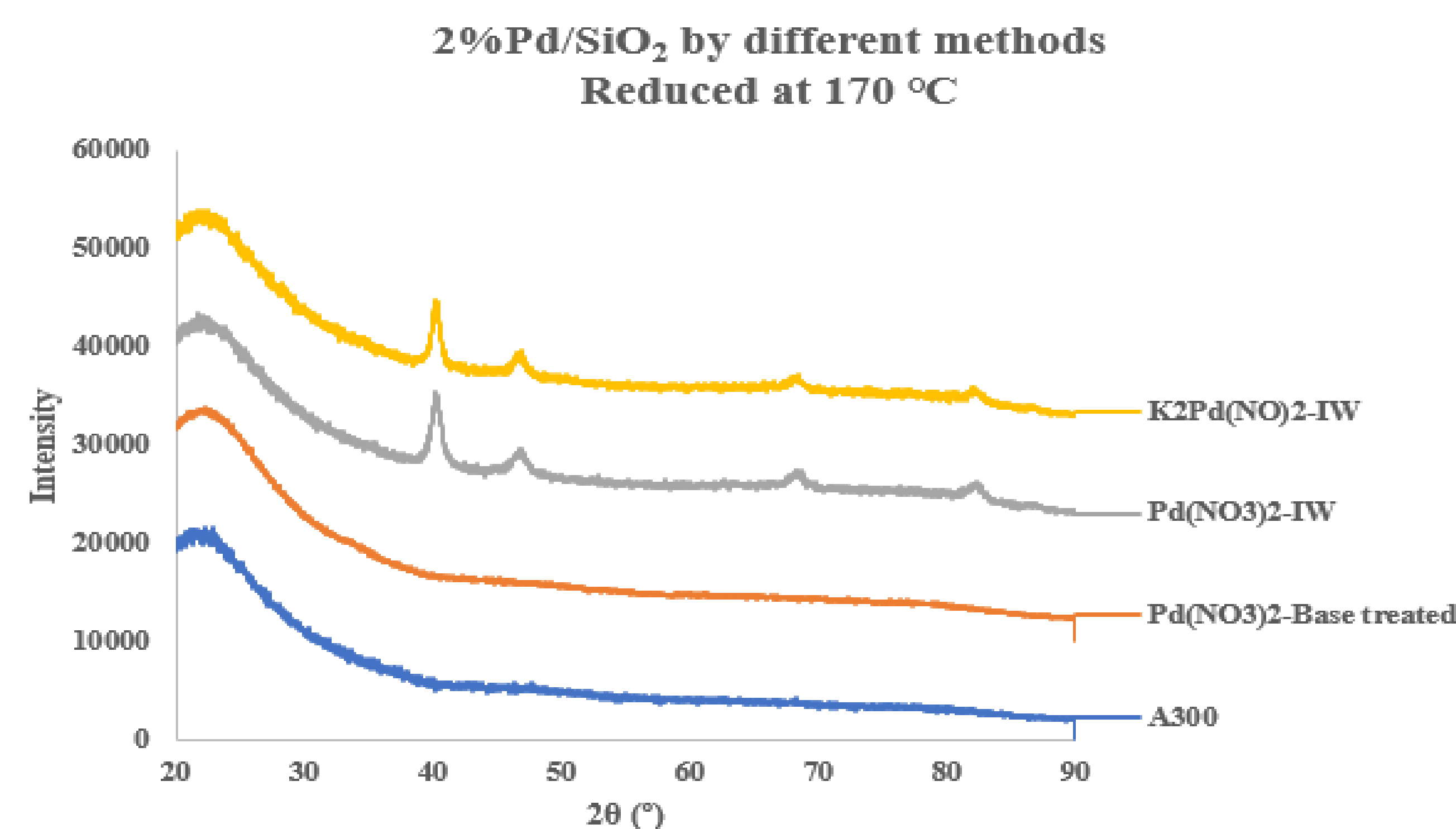


Figure 3: XRD of the synthesized catalysts

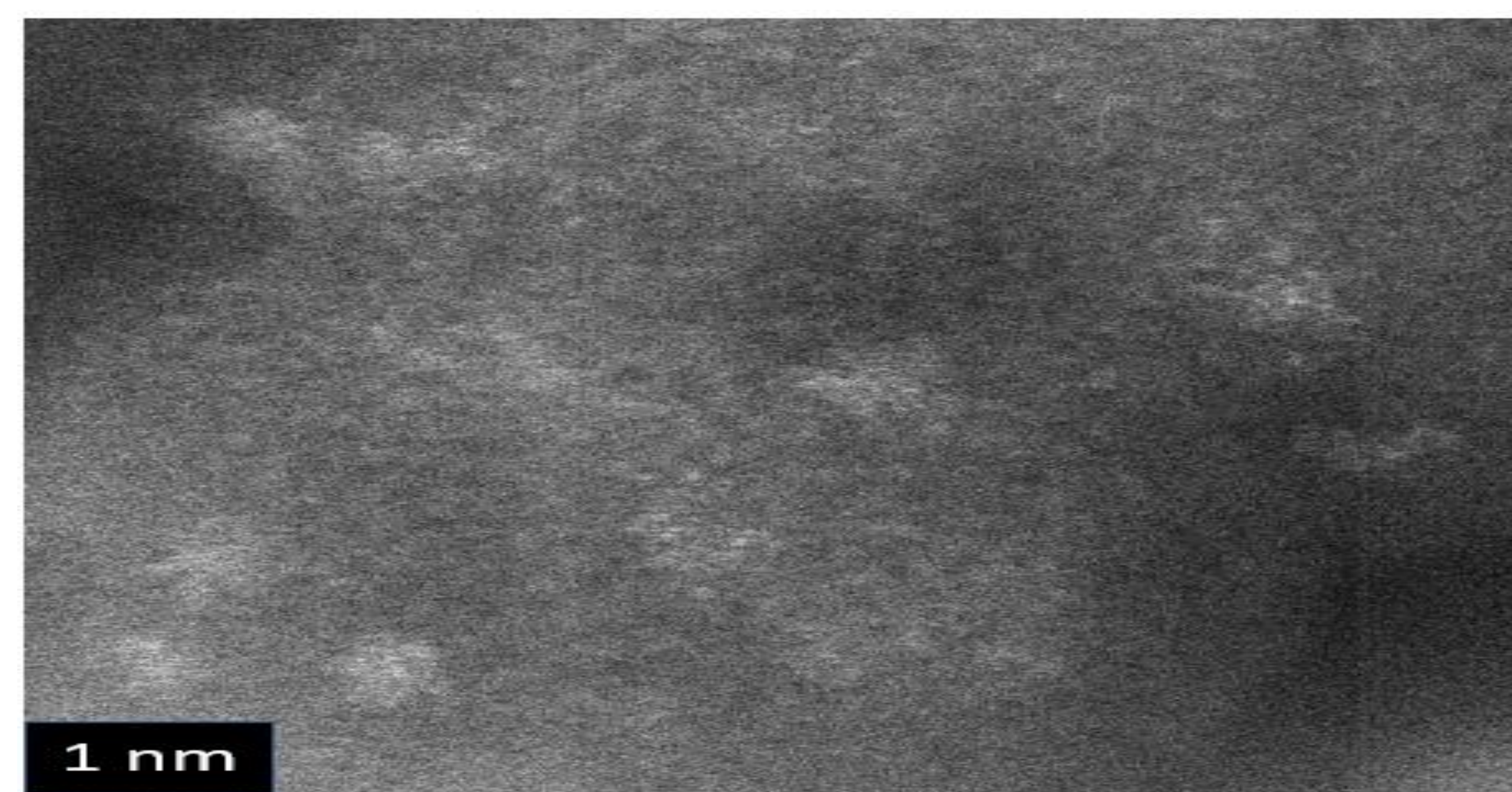


Figure 4: STEM image of Pd(NO₃)₂-Base treated

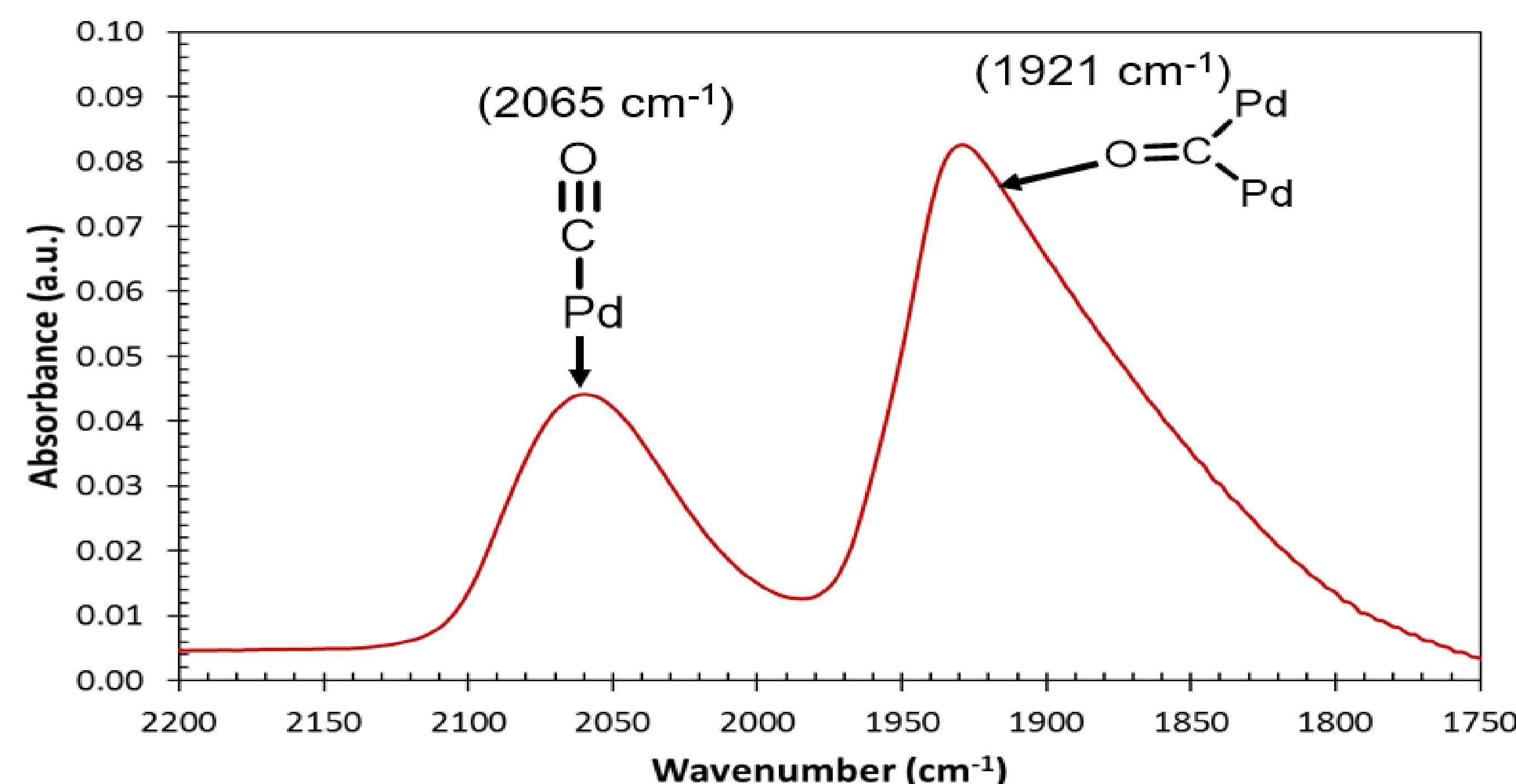


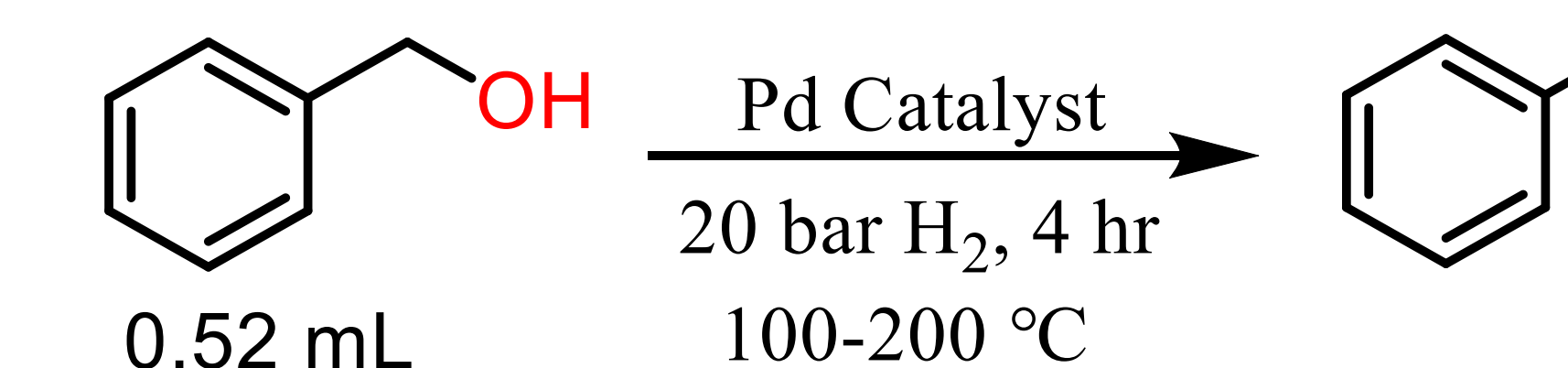
Figure 5: FTIR studies of Pd(NO₃)₂-Base treated

Catalytic Activity

Selective HDO on benzyl alcohol was carried out using the synthesized catalysts in a batch reactor employing 20 bar H₂ pressure and 100 or 200 °C for 4 hr. GCMS was used in the analysis of the HDO products. Maximum conversion and selectivity are observed at 200 °C and 20 bar H₂ pressure when Pd(NO₃)₂ based catalyst was used. In the case of K₂Pd(NO₂)₄ catalyst, maximum selectivity was achieved but conversion was low.

Catalyst	Temp. (°C)	H ₂ Pres. (bar)	Conv. (%)	Toluene Sel. (%)
(a) Pd/SiO ₂ [Pd(NO ₃) ₂]	100	20	36	>99
(b) Pd/SiO ₂ [Pd(NO ₃) ₂]	200	20	>99	>99
(c) Pd/SiO ₂ [K ₂ Pd(NO ₂) ₄]	200	20	33	>99

Table 1: Catalysts activities on benzyl alcohol



Scheme 1: Selective HDO of benzyl alcohol

Conclusion

Clusters were observed in the analysis of Pd(NO₃)₂-Base treated catalyst while nanoparticles are formed when on incipient wetness is employed. Method of catalyst preparation did not affect their performance, instead changing Pd salts used during catalyst synthesis resulted in the change in activities of the catalyst.

References

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