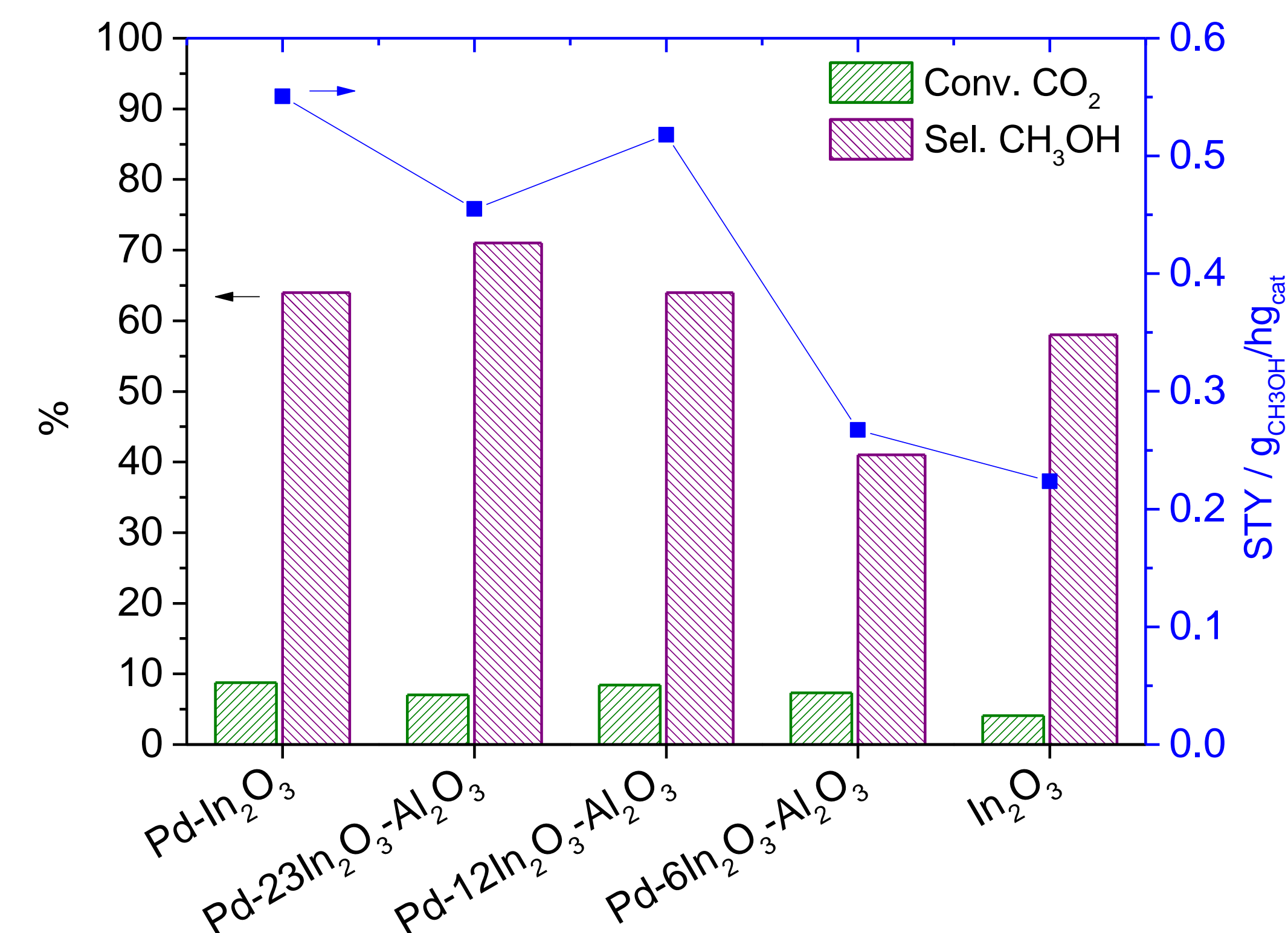


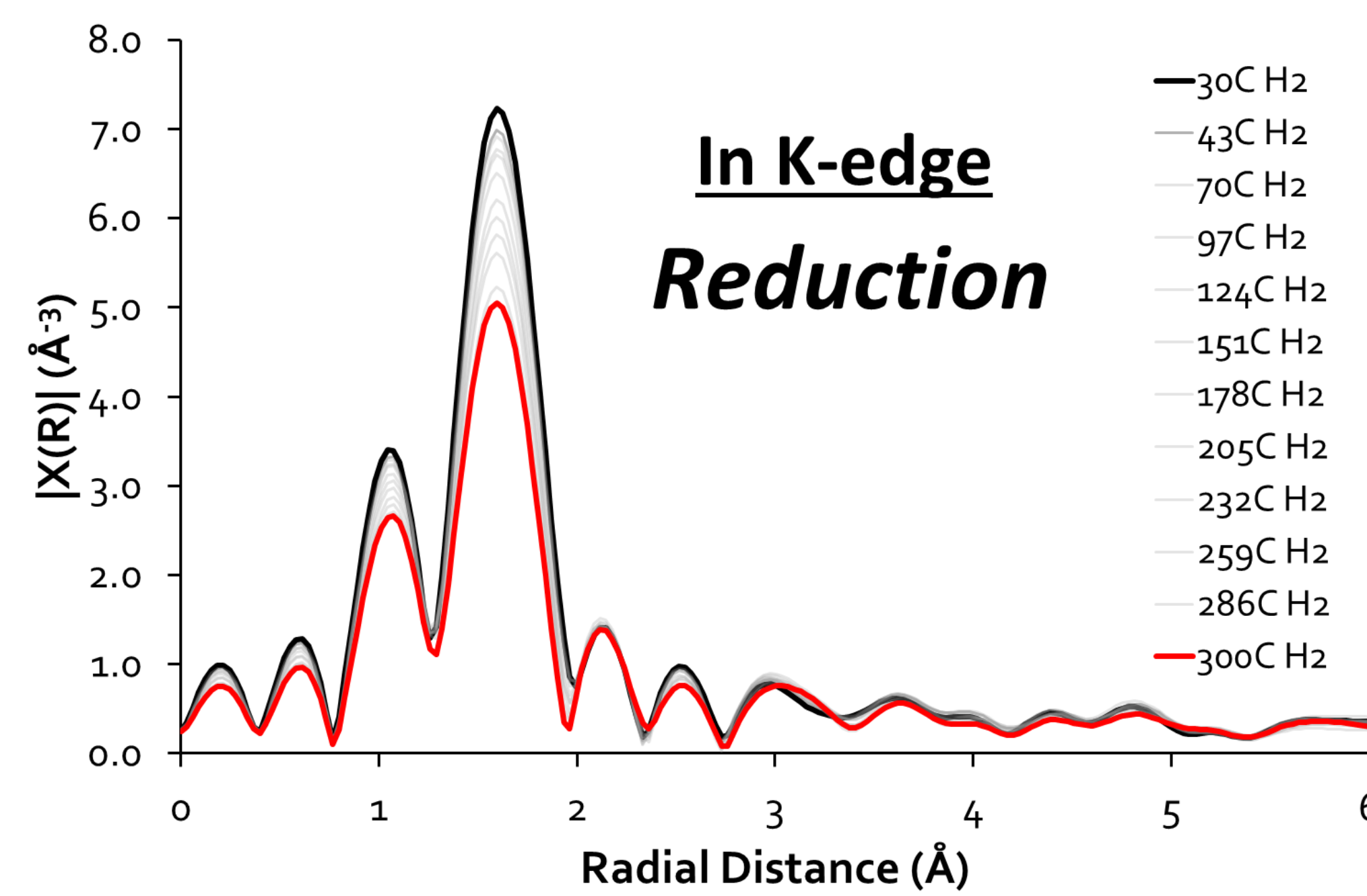
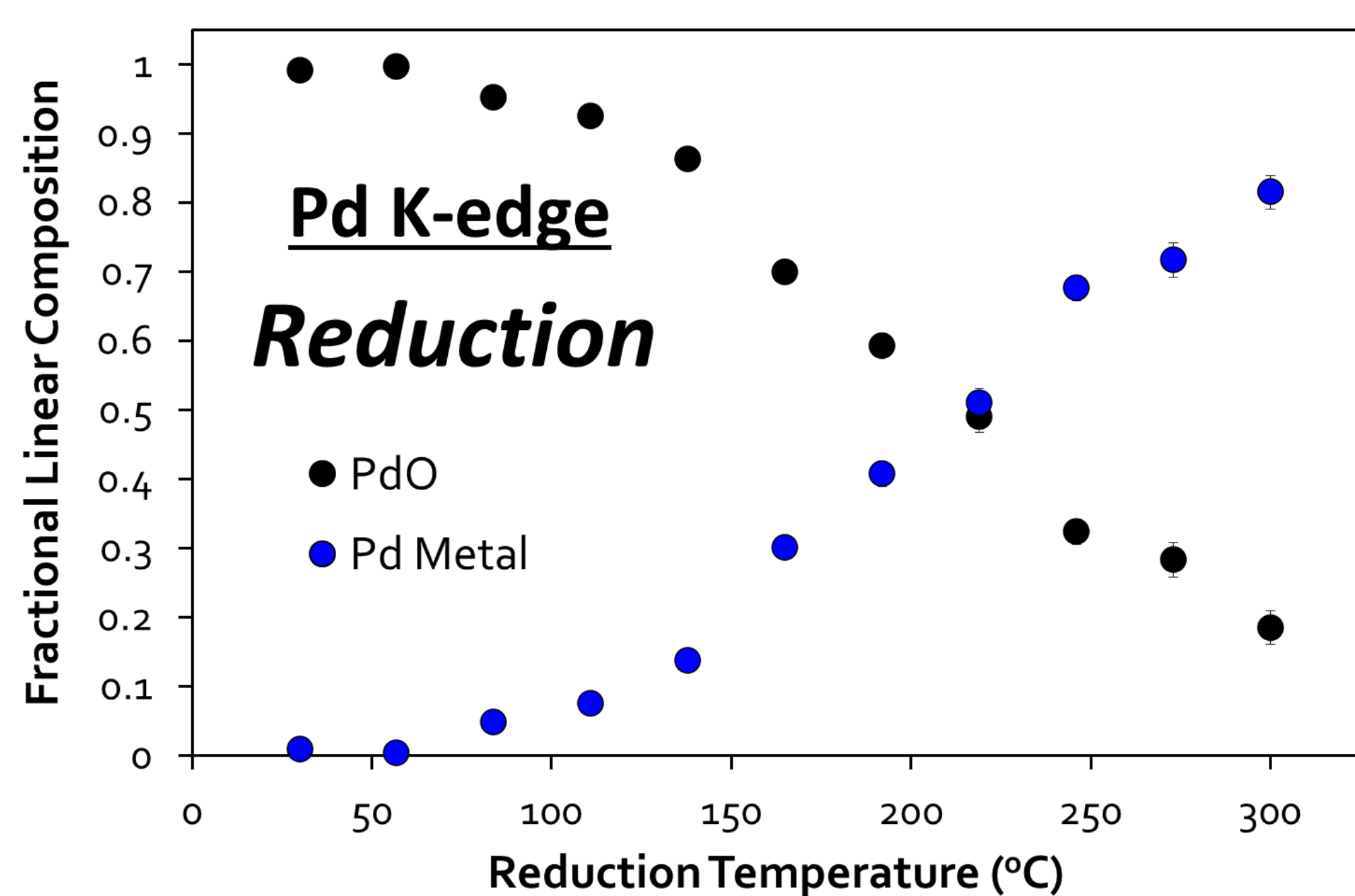
CO₂ Hydrogenation to Methanol

Converting CO₂ to methanol offers a sustainable pathway to many bulk chemicals, but this process is challenging, as high temperatures are needed to activate CO₂, but excessively high temperatures will form CO, not methanol.

Indium oxide is a selective CO₂ to methanol catalyst,^[1] as surface oxygen vacancies limit CO formation. Recent work has shown that **combining Palladium and Indium oxide** leads to a highly effective catalyst,^[2] though the interactions between the two species are not well understood.^[3]



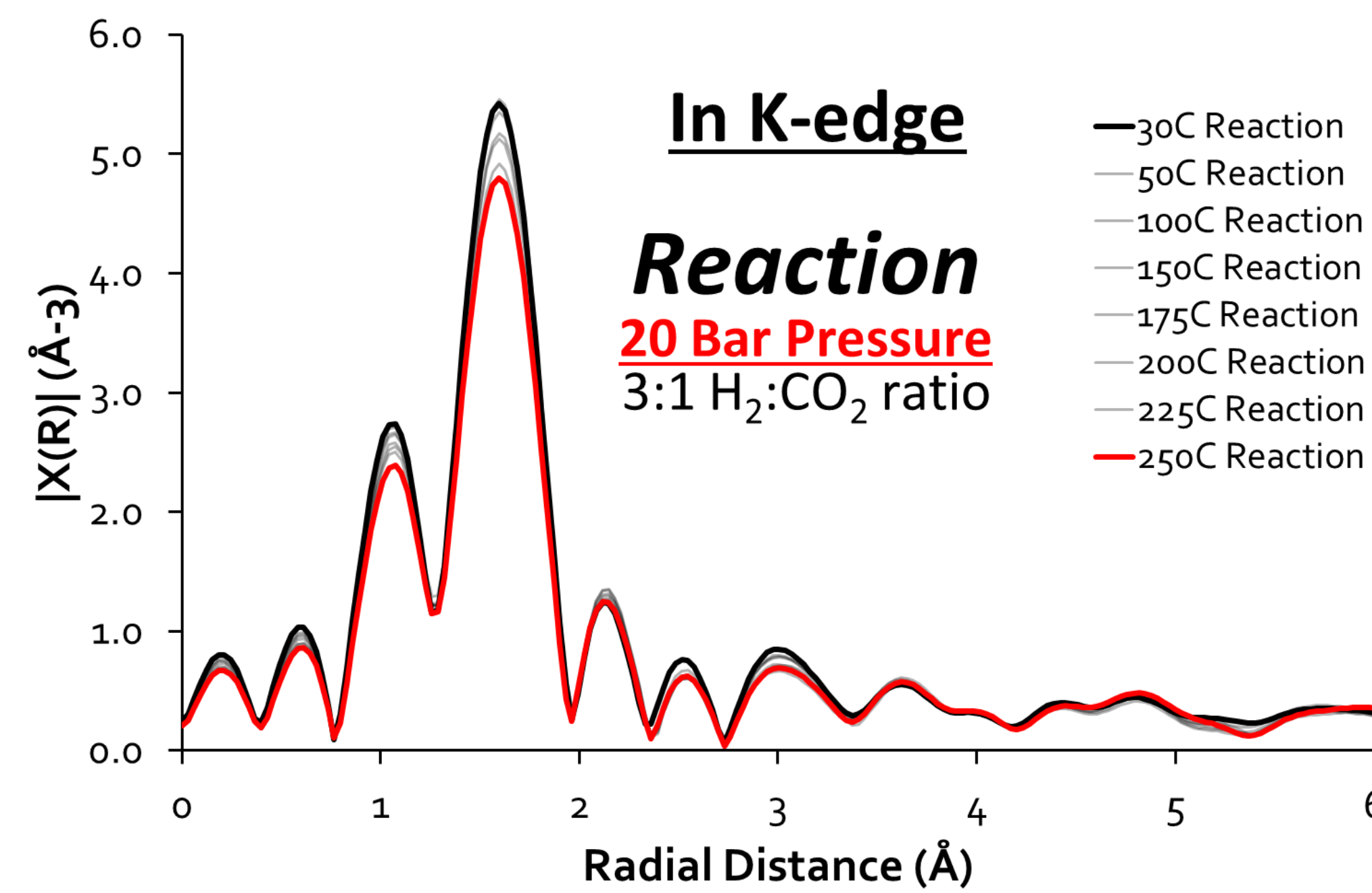
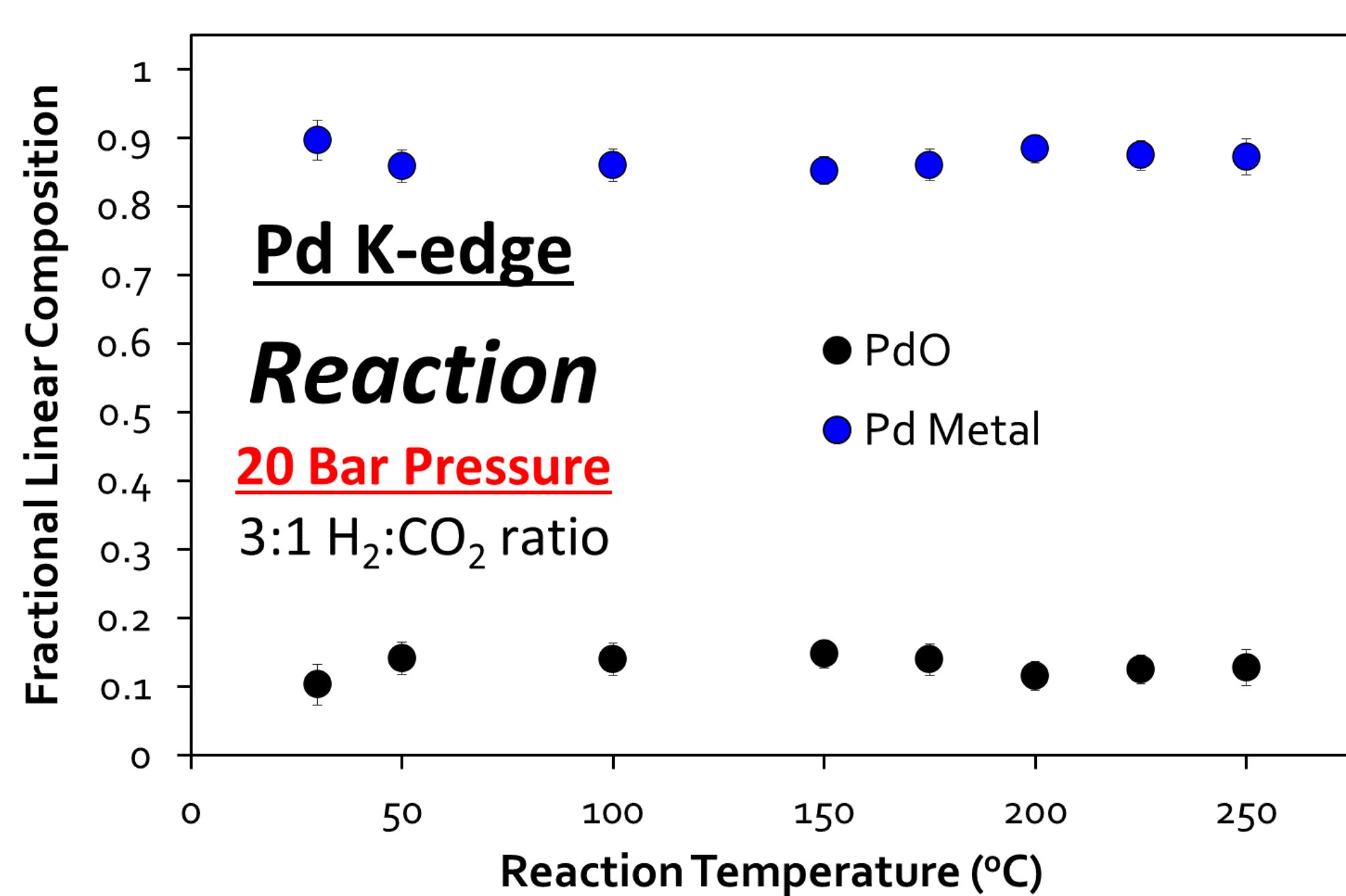
Operando X-ray Absorption Studies at Diamond B18 of Pd-12In₂O₃Al₂O₃



PdO reduces to Pd Metal, with some PdO remaining

In shows a small decrease in In-O character, which stays on cooling, showing oxygen vacancies formed

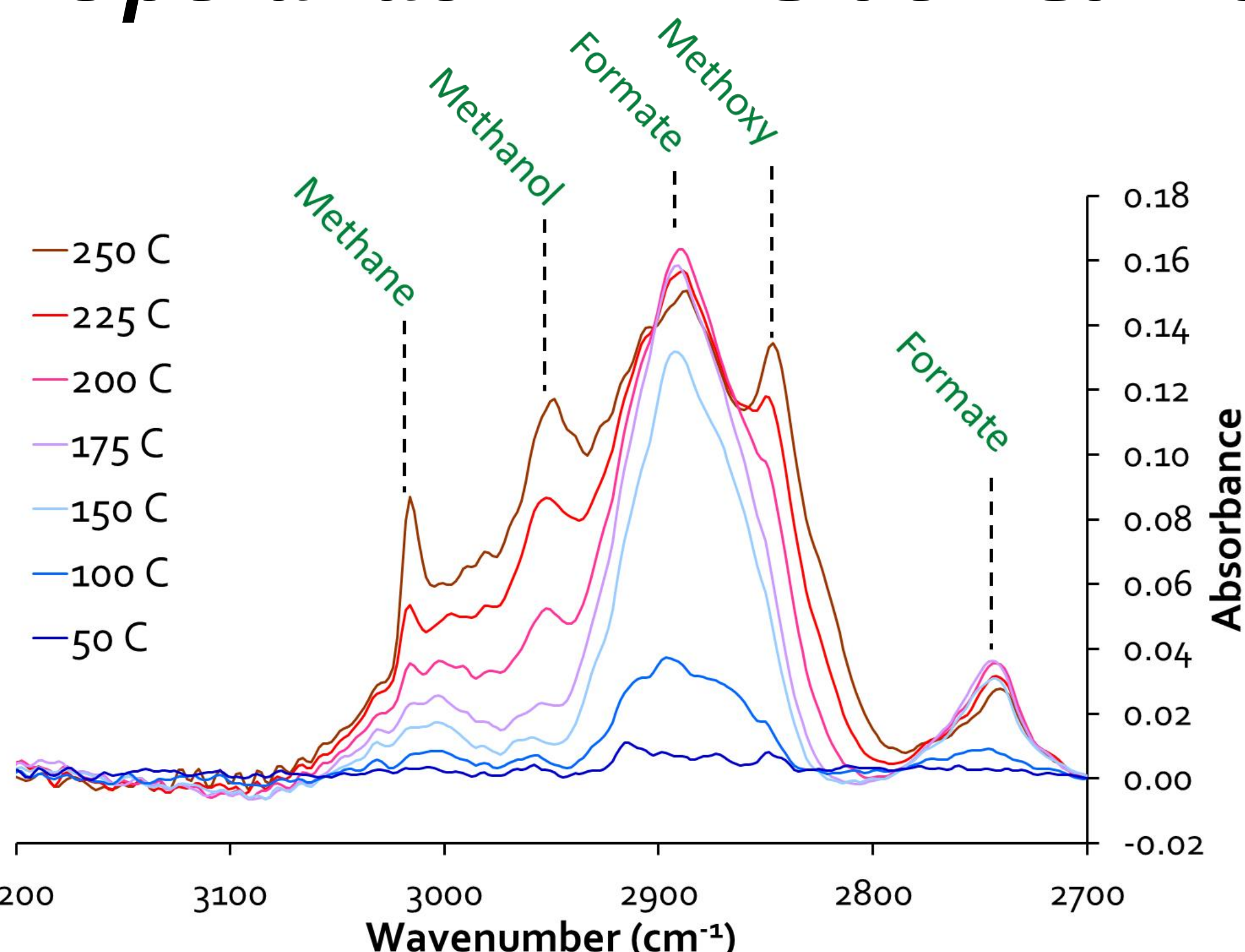
Pd and In change at different rates, **suggests distinct sites?**



Under reaction conditions no real change in Pd or In environments.

Shows the active sites are **pre-formed during reduction**, but little change under reaction conditions

Operando DRIFTS at RCaH of Pd-6In₂O₃-Al₂O₃



At 20 bar of pressure

Formate species form at low temperatures (150 °C)

These are then converted to methoxy and methanol, as seen by GC-MS

Above 225 °C methane begins to form, in agreement with catalytic data

Conclusions

No evidence of alloying seen

Pd splits H₂, while In₂O₃ vacancies activates CO₂

Species need to be in close proximity for this to occur

Further *operando* XRD measurements required to probe possible alloyed phases

References

- [1] O. Martin *et al*, *Angew. Chem. Int. Ed.*, **2016**, *55*, 6261.
 [2] M. S. Frei *et al*, *Nature Commun.*, **2019**, *10*, 3377.
 [3] Schiaroli *et al*, *Appl. Catal. B*, Under review.

Acknowledgements

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