Heterogeneous Hydrogenation Catalysts for Parahydrogen Enhanced NMR

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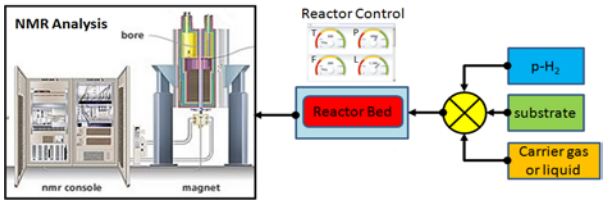
Introduction

Parahydrogen (p-H_2) induced nuclear polarization (PHIP) [1,2] is a promising technique for sensitivity enhanced NMR spectroscopy and imaging, with key advantages over DNP. In PHIP, the pure spin state of p-H_2, which itself is invisible to NMR, is transformed into a massively enhanced NMR detectable spin order by chemical hydrogenation reaction. PHIP's potential to obtain rapid assays and images of metabolism in living tissues has recently been demonstrated. However, a major impediment to biomedical applications had been the high toxicity of the homogeneous catalysts used in PHIP. The use of heterogeneous hydrogenation catalysts circumvents this problem [2]. In this new project, we report dramatic NMR signal enhancement using a supported metal catalyst. We are optimizing these catalysts for PHIP signal enhancement, and in the process, understanding the kinetics and mechanistic factors governing pair-wise H_2 transfer.

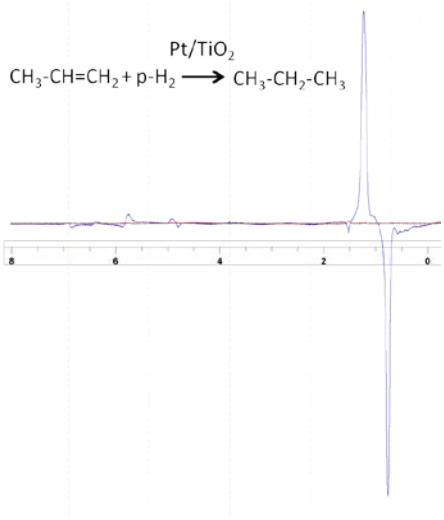
Experimental

Pt and Pd catalysts were prepared and tested for PHIP. Metal particles of varying size were dispersed onto titania and alumina. A gas stream consisting of a mixture of 50% p-H_2 and propylene substrate was passed through a temperature controlled hydrogenation reactor bed installed a few cm above the bore of a 9.4 T NMR magnet. The hyperpolarized hydrogenation products were continuously transported down the magnet bore to the NMR probe for proton detection. Temperature, flow rate, and H_2:propylene ratio were varied to optimize PHIP enhancement.



Results and Discussion

A representative proton PHIP-ALTADENA enhanced spectrum of hyperpolarized propane, formed by p-H_2 addition to propylene over a Pt/TiO_2 catalyst, is shown below. Strong net alignment is observed, consistent with the ALTADENA effect. The thermally polarized spectrum (in red) exhibits negligible signal.



Conclusions

These promising preliminary results represent a new capability for producing hyperpolarized gases and liquids in an NHMFL-affiliated lab, without having consumed any NHMFL resources up to now. The heterogeneous PHIP method beats DNP hands down in terms of low cost, simplicity, absence of toxic polarizing agents, and rate of hyperpolarized gas or liquid production. Moreover, the generality of PHIP appears to be much greater than initially anticipated. PHIP also provides a powerful new technique for investigating the kinetics and mechanisms of heterogeneous catalysis.

Acknowledgements

This project is currently supported by the ACS-PRF #52258-ND5.

References

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[3] Koptyug, I.V. *et al.,* J. Am. Chem. Soc. 5580-5586 **129** (2007).