

## New avenues in nanocarrier system design for the delivery of enhanced methane oxidation catalysts

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Metal-organic Frameworks (MOFs) are a class of material in which bonds between metal nodes and organic linkers define a highly porous and easy tunable topology. MOFs have been widely used in gas storage and separation, catalysis and drug delivery. Meanwhile, the partial or total oxidation of methane to fuels represents a promising line of energy research and, in this context, the loading of Au and Pd nanoparticles (NPs) onto supports has yielded nanocomposites with high activity. However, agglomeration of the NPs under reaction conditions typically limits the reusability of these catalysts. This has led to interest in using MOFs as supports; their porous structures inhibiting agglomeration. Moreover, we have recently developed a new kind of MOF; monolithic MOFs ( $\text{monoMOFs}$ ) are mechanically robust, can be stable to high temperatures and pressures and retain high apparent surface areas. They have been recently used in both gas storage and catalysis.

This project involves the preparation of individually bimetallic AuPd NPs or AuPd/TiO<sub>2</sub> nanocomposites. These have been immobilized using the monolith of zeolitic imidazolate framework-8,  $\text{monoZIF-8}$ . Before moving on to methane oxidation, initial studies looked at model processes. This had the benefit of enabling the initiation of work at the Brookhaven National Laboratory (BNL), who could provide atomistic-level insights into the mechanism by which the composites AuPd/(TiO<sub>2</sub>)@ $\text{monoZIF-8}$  promote oxidation. Data obtained at Stony Brook revealed a vital role for TiO<sub>2</sub> in enhancing activity, with AuPd@ $\text{monoZIF-8}$  needing undesirably high temperatures to achieve 100% oxidation. In contrast, TiO<sub>2</sub> enabled the catalysts to operate well at 443K, with reaction completing at 573K. Having established the importance of interaction between AuPd and TiO<sub>2</sub>, further analysis took place at the BNL. Extensive *in situ* XANES, EXAFS and FT-EXAFS proved the stability of  $\text{monoZIF-8}$  incorporating AuPd or AuPd/TiO<sub>2</sub> under operational conditions. These data were reinforced by techniques such as XRD and TGA at Cambridge. Crucially, results from the BNL ruled out the possibility of the co-existence of individually

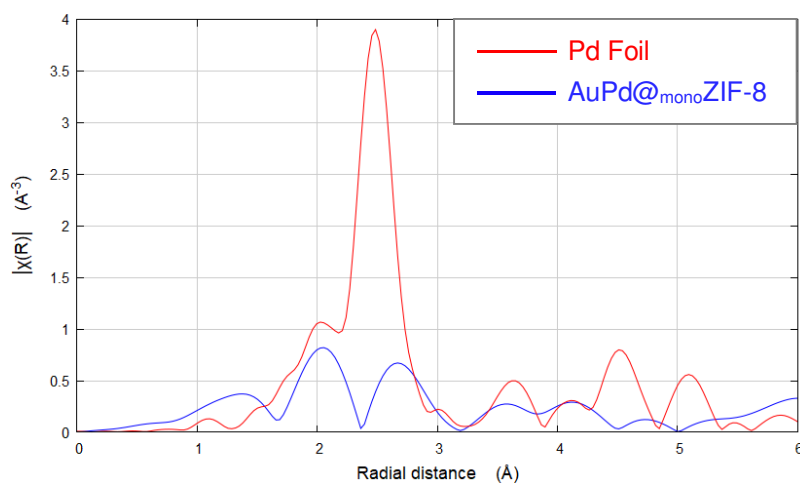


Fig. 1 Pd K-edge FT-EXAFS data from the BNL for the catalytically active composite AuPd@ $\text{monoZIF-8}$  during a model reaction, proving an Au-Pd bond  $\sim 2.5$  Å long in the catalyst.

monometallic Au and Pd NPs in this system, instead proving the existence and operational retention of individually bimetallic, intermixed AuPd NPs (Fig. 1); overall, a synergy between Au, Pd and TiO<sub>2</sub> is vital to the low temperature operation of this system.

A major aspect of the current work is expanding the availability of  $\text{monoMOFs}$  for catalyst support. In doing this, we have worked on zirconium-MOF  $\text{monoUiO-66}$ , preparing an array of samples for initial testing in liquid phase methane

oxidation under mild conditions. This has extended work at Cambridge on the use of highly stable  $\text{monoUiO-66}$  for energy sector applications. Results obtained through collaboration of the PI with researchers at Cardiff University, UK exemplify how  $\text{monoUiO-66}$  can be successfully used as a support for  $\text{AuPd/TiO}_2$  nanocomposites in the liquid phase oxidation of methane to methanol and formic acid (Fig. 2). Two issues merit comment. First, the amount of methanol and formic acid created *exceeds the state-of-the-art* for supported catalysts under the same conditions. However second, the catalyst can *rapidly* decompose  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$ . This complicates the harnessing of the decomposition intermediate for methanol formation. Based on these results we are now investigating the balance between catalyst stability and  $\text{H}_2\text{O}_2$  decomposition rate. Moreover,  $\text{AuPd}$  particle size and  $\text{TiO}_2$  distribution throughout the MOF have emerged as factors that play significant roles in defining activity. A range of systematically varied samples of  $\text{AuPd/TiO}_2@_{\text{monoUiO-66}}$  are currently undergoing detailed characterization to further our understanding of the relationship between nanocomposite size and dispersion throughout the monolith and methane oxidation efficiency.

Extension of the still young field of  $\text{monoMOFs}$  has been ongoing, with two new catalytically relevant monoliths, MIL-100 and MIL-53, being prepared. MIL-100 is interesting because it contains Lewis acidic Fe nodes, while

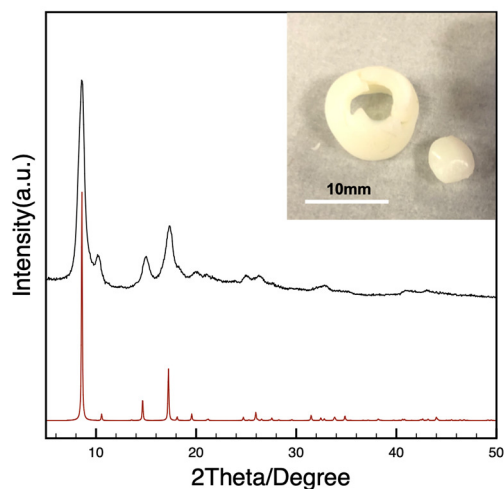


Fig. 3 XRD pattern and optical image of  $\text{monoMIL-53}$  (red: simulated, black: synthesized).

MIL-53 has special significance because of its interesting ‘breathable’ porosity. As shown by Fig. 3, after extensive variation of synthetic parameters, samples were achieved that showed the glassy characteristics of monolith formation whilst the XRD pattern matched that of the simulated material. Further characterization of these potential catalyst supports is ongoing.

To ensure project cohesion the CoI recently visited Cambridge for 6 weeks, enabling the team to analyze preliminary oxidation results and plan the extension of MOF synthesis. With arrangements now in place for liquid phase methane oxidation testing, discussion also focused on setting up gas phase oxidation at Stony Brook and the prioritization of new samples for dispatch there and to the BNL for further operando analysis.

PRF funding has had a major impact on the PI and CoI, facilitating their entry into the field of methane activation and so broadening their portfolio of research in the energy sector. The PI has now gained links with the BNL, receiving preliminary data from researchers there and planning the next round of sample submissions for operando studies. The background of the Postdoctoral Fellow has provided important new expertise in catalysis to the Cambridge group. In addition to his research, following the training from last year, the Postdoctoral Fellow has gained new experience and training in a range of techniques; TGA, GC-MS and LC-MS. This work has also supported several graduate students in the PIs group with interests in nanoparticle immobilization and monolith creation. This has been at no cost to the PRF. An undergraduate research project student also participated in the project for six months. A paper is currently being prepared on the operando study of  $\text{AuPd/TiO}_2@_{\text{monoZIF-8}}$  and further opportunities for collaborative funding are being explored.

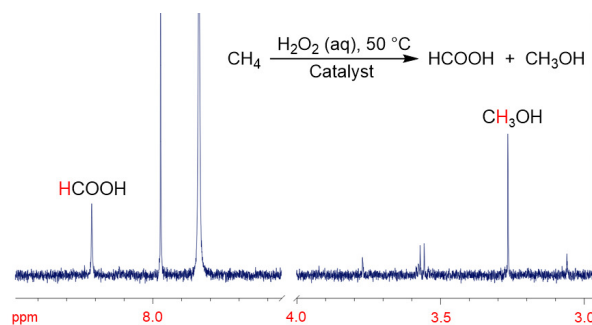


Fig. 2 Selected preliminary  $^1\text{H}$  NMR spectroscopic data showing methane oxidation by  $\text{AuPd/TiO}_2@_{\text{monoUiO-66}}$ .