

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

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Using methane to produce methanol through partial/total oxidation represents a very promising avenue of energy research. Au and Pd nanoparticles (NPs) have already shown high activity for methane oxidation on inorganic supports. However, the thermal agglomeration of NPs can (both here and generally) reduce catalytic activity. Metal-organic frameworks (MOFs) represent exciting porous materials with high surface areas and flexible structures. In a nanoparticulate form, they have already been widely used as catalyst supports to prevent NP agglomeration. However, only recently have the first generation of monolithic MOFs (monoMOFs) been prepared without recourse to chemical binders and/or high pressures. This has avoided previous problems of pore blockage/collapse and also offers an appealing solution to the problem of catalyst recyclability in liquid phase reactions. This new type of monoMOF therefore represents a robust, porous material that exhibits superior properties to traditional, powdered MOFs. Based on the PIs research into monoMOFs and NP@monoMOF composites, $\text{SnO}_2\text{@monoZIF-8}$ has been shown to be trivially recyclable following catalytic applications.

The first part of this project focused on making Au, Pd and individually bimetallic AuPd NPs. Since nanoscopic TiO_2 has been shown to promote PdO reduction and electron transfer (enabling even lower temperature methane oxidation), AuPd- TiO_2 NPs have also been prepared. The best samples were immobilized using the monolithic MOF monoZIF-8 . So far, 22 NP and NP@MOF samples have been prepared and characterized.

Of most interest (as they work at lower temperature) are individually bimetallic AuPd NPs. AuPd@monoZIF-8 has been prepared by adding preformed (according to STEM) AuPd NPs or their metal salt precursors to the precursor sol for or to preformed monoZIF-8 . The best results came from adding AuPd NPs before monoZIF-8 formation. Having established this, the synthesis temperature, time and reagent concentrations were optimized.

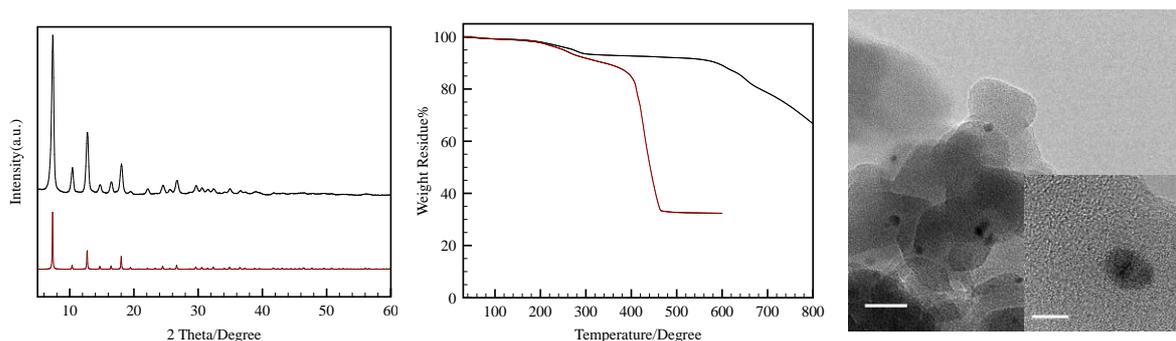


Fig. 1 left to right: XRD patterns (AuPd@monoZIF-8 (black) and simulated ZIF-8 (red)), TGA data (under N_2 (black) or air (red)) and representative TEM images of AuPd@monoZIF-8 . Scale bars: 20 nm and 5 nm (inset).

Samples were extensively characterized (XRD, TGA, (S)TEM, ICP-AES). Comparison of XRD data with simulations and analysis of high-resolution TEM data point to the successful fabrication of AuPd@monoZIF-8 . FIB-SEM has established the nature of the distribution of the AuPd NPs throughout the monolith. Based on the TGA results, the loaded monoZIF-8 is stable to 600°C under nitrogen and 400°C under air. This suggests the composite is stable at temperatures at which it becomes a contender for promoting gas phase methane oxidation. High

resolution microscopy (Fig. 1) has shown that within the monolith, mean NP size is 4.36 ± 0.92 nm i.e. agglomeration is prevented.

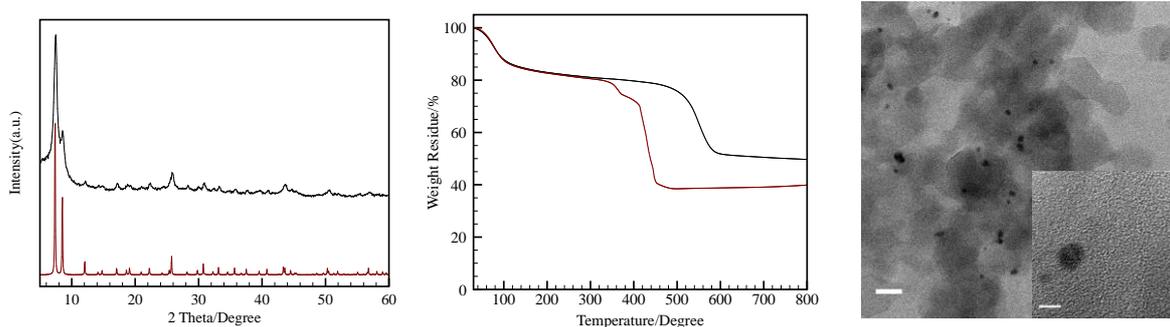


Fig. 2 left to right: XRD patterns ($\text{AuPd}@_{\text{mono}}\text{UiO-66}$ (black) and simulated UiO-66 (red)), TGA data (under N_2 (black) or air (red)) and representative TEM images of $\text{AuPd}@_{\text{mono}}\text{UiO-66}$. Scale bars: 20 nm and 5 nm (inset).

Preliminary tests suggest that for liquid phase methane oxidation, $_{\text{mono}}\text{ZIF-8}$ is insufficiently stable in water. We have therefore sought new and more water stable $_{\text{mono}}\text{MOFs}$ and identified the Zr based UiO MOFs as good candidates. The synthesis conditions for $_{\text{mono}}\text{UiO-66}$ and $\text{AuPd}@_{\text{mono}}\text{UiO-66}$ have been studied and we have now obtained and characterized the latter composite in which we have evidenced $_{\text{mono}}\text{UiO-66}$ incorporating highly dispersed AuPd NPs. Thermal stability has been shown under nitrogen and air up to 400°C , so the composite easily fulfills the requirements for liquid phase catalysis. The successful extension of $_{\text{mono}}\text{MOF}$ syntheses to incorporate 12-coordinate Zr systems has allowed the water stability issue to be addressed; we have proved that $(\text{AuPd}@)_{\text{mono}}\text{UiO-66}$ is stable in boiling water for 7 days. According to microscopy, the AuPd NPs loaded into $_{\text{mono}}\text{UiO-66}$ are 5.28 ± 1.56 nm, which are a little larger than those on ZIF-8 due to the higher preparation temperature for UiO-66, but still plausible for applications. With this in mind, Zr MOFs that can be prepared at different temperatures have been investigated. We have recently verified the preparation of $_{\text{mono}}\text{MOF-808}$.

The project CoI visited Cambridge for 6 weeks over the summer and plans were finalized for catalyst testing in the US and the submission of the most interesting composites to the Brookhaven National Laboratory (BNL). Samples of $\text{AuPd}(-\text{TiO}_2)@_{\text{mono}}\text{ZIF-8}$ and $\text{AuPd}(-\text{TiO}_2)@_{\text{mono}}\text{UiO-66}$ are now in the US for preliminary gas phase catalytic tests at Stony Brook. Initial data recently obtained points to the superior performance of titania-containing systems. A Parr reactor setup for conducting liquid phase methane partial oxidation is being set up at Cambridge. Samples due for liquid phase testing have been divided, with half of each sample sent to Stony Brook to facilitate transfer of the most catalytically promising samples to the BNL for reaction mechanism studies.

The PRF funding is already having a significant impact, allowing the PI and CoI to enter the field of methane activation for the first time. Some funding already existed in the PIs group for the study of $_{\text{mono}}\text{MOF}$ and $\text{NP}@_{\text{MOF}}$ materials, but not for $\text{NP}@_{\text{mono}}\text{MOF}$ energy materials, so the activity of the PI in this wider area has been encouraged. The background of the funded Postdoctoral Fellow in catalysis has also brought new expertise into the Cambridge group and this has been instrumental in enabling us to set up a catalytic rig for liquid phase partial methane oxidation in house. Links between PI and CoI have been strengthened with the exchange of samples, and previous discussions with scientists at the BNL have now developed into definite collaboration, with plans for analyzing selected samples at the BNL taking definite shape for the near future based on the results of initial catalysis testing in the UK and US. In addition to his research, the Postdoctoral Fellow completed chemical and X-ray safety training upon arrival in Cambridge as well as training courses in FIB-SEM and (S)TEM. This project is supporting several graduate students in the PIs group at no cost to the PRF through collaboration with the funded Postdoctoral Fellow in the areas of NP synthesis and characterization. Arrangements are also in place for the Postdoctoral Fellow to supervise an undergraduate research project student, starting October.