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Utilisation of gold nanoparticles on amine-functionalised UiO-66 (NH₂-UiO-66) nanocrystals for selective tandem catalytic reactions

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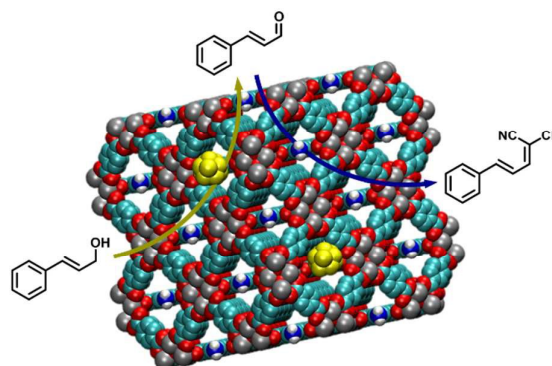
Colloidal deposition of gold nanoparticles (Au NPs) onto NH₂-UiO-66 nanocrystals has been demonstrated with the resulting hybrid catalyst proving robust and versatile for one-pot, heterogeneous conversions involving the selective oxidation of primary alcohols in tandem with Knoevenagel condensation reactions. Within these systems, structure-property correlations have been established to confirm that the active sites for the oxidation and condensation reactions are intrinsically correlated to the Au NPs and pendant amine groups respectively.

Tandem reactions utilising multifunctional catalysts have great importance in industrial processes for maximising productivity whilst minimising materials and production costs.[1] By eliminating isolation, purification and analysis of intermediate products, as well as catalyst separation and recycle, the efficiency of a process can be drastically improved. Consequently, the design of multifunctional catalysts is of significant importance for optimising processes that involve consecutive steps to acquire the target product in good yield and purity. It is known from a practical perspective that heterogeneous catalysts pose many benefits, over their homogeneous counterparts, due to the ease of recovery and re-use,[2] but they also provide more effective control of the physical and chemical environment, and the ability to isolate well-defined active sites on a surface.[3] The employment of a heterogeneous catalyst can be a useful platform for positioning two or more active sites within the same catalyst with a high degree precision and control, thereby facilitating the generation of the desired transition-state that could result in greater activity/selectivity control.[3b, 4]

In recent years, metal-organic frameworks (MOFs), a class of crystalline nanoporous materials, have become increasingly popular for application in catalytic reactions.[5] The higher degrees of chemical stability displayed by some MOFs[6] coupled with the ease of functionalisation[7] and high porosity[8] make them ideal candidates for effecting tandem catalytic reactions. For MOFs to be successfully employed in catalytic applications, they need to be stable and resistant to degradation under a variety of catalytic conditions, which can include changes in chemical and thermal environments. UiO-66 and associated structures[9] are of particular interest, due to the high stability under a range of conditions.[10] It is also stable in aqueous solutions – an essential property for catalytic reactions performed in water, or where water is a significant by-product – such as dehydrogenative oxidation reactions. UiO-66 is a zirconium based MOF containing terephthalate linkers.[9a] Functionality has been introduced to the framework using modified terephthalate linkers in the initial synthesis with no further post synthetic modification. For example, NH₂-UiO-66 can be synthesised using 2-aminoterephthalic acid,[9b, 11] which is a simple and effective way to introduce isolated active centres to UiO-66. For more complex functionality, post-synthetic modification has been demonstrated on the UiO family of MOFs by addition of organic anchors[12] or complexation with organometallic precursors.[13]

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Fig. 1 Schematic concept of tandem reaction on Au/NH₂-UiO-66 catalyst; Au NPs represented by gold spheres on the host MOF framework.

With sustainable catalysis in mind, metal nanoparticles (NPs) have also been at the forefront of recent research due to the

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quantum-size effects that result in active surface properties differing from bulk metals.[14] As such, the combination of NPs with MOFs has emerged as a method for enhancing catalytic properties through precision engineering of nanostructures and discovery of synergistic functionality (for example, Fig. 1).[15] NPs have been applied as catalysts for a variety of chemical transformations; most notably in oxidations,[16] reductions[17] and coupling reactions.[18] Moreover, noble metal NPs and their bimetallic analogues have shown exceptional proficiency for activating abundant and environmentally benign oxidants such as molecular oxygen[16c, 19] and simple peroxides,[20] that exemplify their potential in green and sustainable processes. There are some elegant examples of NP/MOF hybrid materials that have been employed for catalytic processes including the use of Au/MOFs in oxidation reactions,[21] however the MOFs are often used purely as supports and few studies report the use of the MOF host as having an active role toward the material functionality.[22] A recent report of encapsulated Pd@NH$_2$-UiO-66 has shown activity towards an oxidation–acetalisation tandem reaction that converts benzyl alcohol into 2-phenyl-1,3-dioxolane, although TONs remain modest after 22 hours of reaction,[23] and a similar PdAg@MIL-101 also showed activity toward a hydrogenation–reductive amination process to generate secondary arylamines from benzaldehyde and nitrobenzene.[24] This does, however, highlight the scope and potential of applying NP/MOF materials in consecutive processes, especially with the breadth of existing single-step catalytic applications of the separate NP and MOF entities.
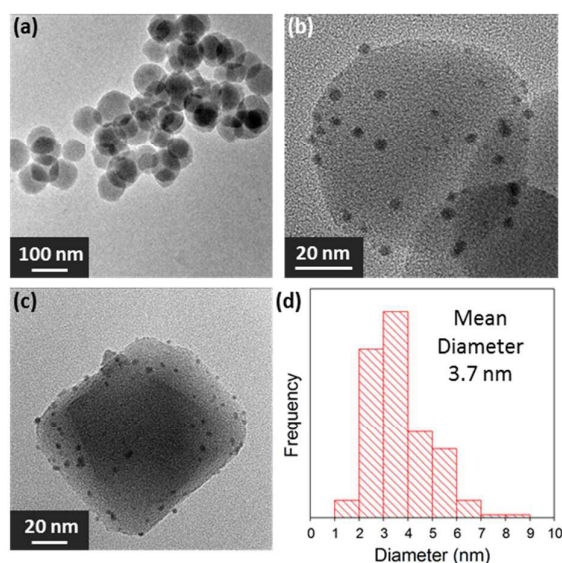

Fig. 2 TEM Images of (a) UiO-66 nanocrystals, (b) Au/UiO-66, (c) Au/NH$_2$-UiO-66 and (d) NP size distribution of Au/NH$_2$-UiO-66.

Herein, we present the facile preparation of highly active and selective nanoscale Au/NH$_2$-UiO-66 catalysts for one-pot, tandem reactions; firstly involving selective oxidation of cinnamyl alcohol, a primary alcohol, and the subsequent Knoevenagel condensation of the resulting aldehyde product with malononitrile. The Au NP surfaces are the active site for the selective oxidation of alcohols to aldehydes, while the

pendant amine groups on the MOF linkers provide a nucleophilic or basic site to catalyse the condensation step.

UiO-66 and related materials were opportunistically selected for this process due to their noteworthy structural integrity in the presence of water,[25] a significant by-product from the catalytic oxidation process. Spherical nanocrystals of UiO-66 and angular nanocrystals of NH$_2$-UiO-66 were prepared by a benzoic acid modulated synthesis[11] (See ESI for detailed synthetic conditions). Au NPs were subsequently prepared by a colloidal dispersion using PVP as a stabilising agent, with subsequent deposition to the surface of the MOF nanocrystals. Characterisation of the materials by TEM (Fig. 2) and FESEM (Fig. 3) identify the uniform morphology of the nanocrystals as well as the adhesion and well dispersed nature of the Au NPs on the MOF surface. It was noted that the UiO-66 nanocrystals were spherical in shape; in contrast, the NH$_2$-UiO-66 nanocrystals were more angular, revealing increased definition of facets and vertices that are common in larger crystals of these MOFs,[11] indicating that the presence of the NH$_2$ group on the organic linker affects the growth mechanism of the framework. The benefits of using UiO-66 type MOF nanocrystals as opposed to polycrystalline versions, is that a much higher external surface area is available for deposition of metal NPs, enhancing the ability to form isolated and well dispersed NP active sites and reducing potential for migration and sintering.
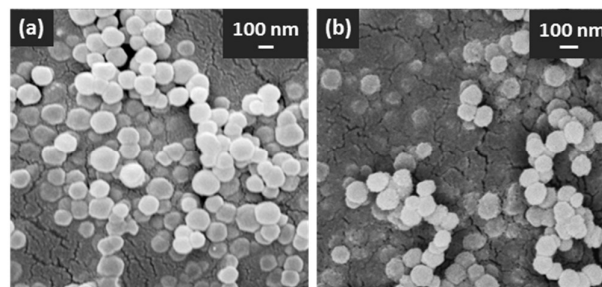

Fig. 3 FESEM images of (a) nano Au/UiO-66 and (b) nano Au/NH$_2$-UiO-66

In addition, TGA and BET data confirm the integrity of the MOF host before and after deposition of the NPs (Figs. S1-S4, ESI†), with porosity and thermal stability above 350 °C maintained throughout the synthetic and functionalisation procedures. In fact, the total surface area of the material increases from 764 m^2/g to 801 m^2/g, likely due to the NP deposition step acting as an auxiliary solvent wash. The lower surface areas, compared with reported literature, are due to the nanocrystalline nature of the material, with reduced ratios of internal to external surfaces as reflected by the steep slope in the N$_2$ adsorption isotherms between P/P$_o$ values of 0.3-0.8 (Figs. S3-S4, ESI†). It has been suggested that some benzoic acid could be trapped in the cavities of the UiO-66 type frameworks, as outlined in one study.[11] However, TGA experiments carried out in the presence of O$_2$ indicated weight losses expected for the decomposition of the framework (Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_6$) to ZrO$_2$ as shown in Fig. S1 (ESI†). If a significant quantity of benzoic acid was entrapped within the framework (Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_6$·(C$_7$H$_6$O$_2$)$_x$), a greater weight loss would be expected due to the combustion of additional organic moieties to CO$_2$. This was not observed in our studies and so we can conclude that if any free benzoic acid is

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trapped within the framework, it will be in negligible fractions. This trend was also observed for NH_2-UiO-66 MOF materials (Fig. S4, ESI†). PXRD data before and after deposition conclusively reveal that the framework structure and crystallinity are preserved in the deposition process (Fig. S5, ESI†). Incorporation of the amine functionality to the NH_2-UiO-66 analogue was confirmed by FT-IR spectroscopy. Primary N-H stretches at 3505 and 3391 cm^{-1}, as well as a C-N stretch at 1256 cm^{-1} were observed and comparable to the free ligand, 2-aminoterephthalic acid (Fig. S6 and S7, ESI†).

In order to probe the viability of the catalyst active sites toward their respective reactions, Au/UiO-66 and NH_2-UiO-66 were separately examined for the oxidation (Scheme 1A) and condensation (Scheme 1B) reactions respectively. The oxidation of cinnamyl alcohol on Au/UiO-66 presented good activity (Fig S8A, ESI†) with a significant increase in TON with substrate concentration. This indicates that the reaction is not limited by surface reactions, but more likely by diffusion and/or adsorption rates. Interestingly, when the oxidant/substrate stoichiometry was varied (Fig S8B, ESI†), a significant rise in TON was observed between 0.5-1.2 TBHP equivalents with only minor improvements up to 3 equivalents. Hence, as the oxidant concentration is not limiting in high excess, equal molar ratios are required to secure optimum oxidant efficiencies (Fig. S9, ESI†).
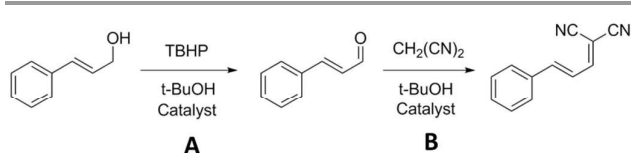
Scheme 1 Oxidation of cinnamyl alcohol to cinnamaldehyde (A) and subsequent Knoevenagel condensation with malononitrile to form cinnamylidene malononitrile (B).

The condensation reaction using NH_2-UiO-66, under similar reaction conditions as employed for the oxidation reaction, required longer periods to achieve high yields. The choices of solvent and reaction conditions for the condensation reaction were limited to those utilised in the oxidation step. This allowed for integration of the processes into a one-pot system.

Table 1 Catalytic data for the tandem oxidation-condensation reaction using Au/NH₂-UiO-66 as a bifunctional catalyst.

#	Catalyst	Time (hrs)	Conversion (%)ᵃ	Selectivity (%)ᵇ	Yield (%)
1	Blank	34	11	83	9
2	Au/NH₂-UiO-66ᶜ	24	1	> 99	1
3	Au/NH₂-UiO-66ᵈ	34	79	> 99	77

See Fig. 4 for detailed reaction conditions. ᵃ Conversion of cinnamyl alcohol. ᵇ Selectivity to cinnamylidene malononitrile. ᶜ Malononitrile added at start of reaction. ᵈ Malononitrile added after 10 hours.

The tandem process (Scheme 1) with the hybrid catalyst was attempted initially by combining all reactants at the start of the reaction (entry 2); however, as can be seen from Table 1, no reaction was observed. This was highly unanticipated given that both the Au NPs and NH_2-UiO-66 were shown to be active catalysts for the separate oxidation and condensation

reactions respectively, as shown earlier (Fig. S8 and Tables S1-S2, ESI†).
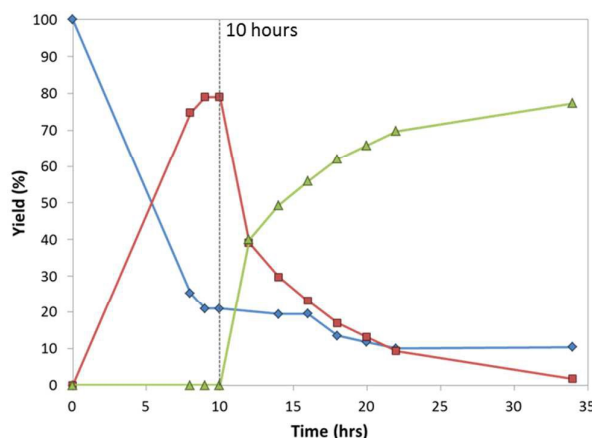
Fig. 4 Reaction profile of the tandem process with addition of malononitrile after 10 hours of reaction. Key: Blue diamonds – cinnamyl alcohol, red squares – cinnamaldehyde, green triangles – cinnamylidene malononitrile. Reaction conditions: Cinnamyl alcohol (0.1 g), Au/NH₂-UiO-66 catalyst (40 mg; 1 wt % metal), chlorobenzene as internal standard (0.2 g), TBHP (70 wt% in H₂O; 0.245 mL), *tert*-butanol (7 mL), stirred for 10 hours at 70 °C. After 10 hours - malononitrile (0.1 g)

A more thorough scrutiny of the reaction process revealed that the malononitrile was inhibiting the oxidation step on the Au NPs, possibly due to unfavourable interactions between the malononitrile and the Au NPs. The sequential addition of malononitrile at a later stage in the reaction (allowing for the oxidation step to proceed initially (see entry 3 and Fig. 4)) was sufficient to allow significant yields of cinnamylidene malononitrile to be produced via this tandem one-pot method. With the oxidation showing negligible background activity (entry 1) and the condensation revealing significant increases in conversions and selectivities (Tables S1 and S2, ESI†), it is clear that these site-isolated Au NPs and pendant amine sites are highly active and selective catalysts for their respective transformations in this bifunctional NP/MOF hybrid catalyst.

For Au NPs, the surface adsorption of the aromatic alcohols along with the formation of surface superoxo-species,[14a] promote the catalytic dehydrogenative oxidation of alcohols to aldehydes.[16c] As with homogeneous organocatalysts[26] and studies utilising NH_2-MOFs[27] in Knoevenagel condensation reactions with benzaldehyde, the amine groups provide a basic active site with the necessary properties to catalyse the reaction; firstly, the amine groups facilitate abstraction of the methylene hydrogens from the malononitrile, forming a carbanion species that can react with the aldehyde, with the ejection of water resulting in the formation of the final *α,β*-unsaturated dicyano-product (Fig. S10, ESI†).[27] It is highly likely that an analogous mechanism operates in the case of cinnamaldehyde as well.

In conclusion, we have expanded the rational design and scope of NP/MOF materials toward tandem catalytic applications. Specifically, by demonstrating that colloidal Au NPs can be deposited on the surface of NH_2-UiO-66 nanocrystals through a facile colloidal immobilisation method, we have developed a hybrid catalyst, where both the Au NPs and amine-groups on the MOF serve as active sites for sequential oxidation and condensation of cinnamyl alcohol to cinnamaldehyde and further to cinnamylidene malononitrile.

This method also opens up the opportunity to perform versatile couplings of α,β-unsaturated alcohols with reactive methylene compounds to form extended conjugated systems. With the abundance of catalytic applications for metal NPs as well as functionalised MOF materials, there is considerable scope for further development of NP/MOF materials targeted towards other cascade processes. These hybrid catalysts could have a significant impact on catalytic transformations employed in the fine-chemical or pharmaceutical industries, where multi-step reactions are commonplace.

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