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An Investigation into the Use of Polymer-Supported Organometallic Catalysts in Organic Synthesis

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Abstract – The utilize of polymer-supported organometallic reagents in solid-phase synthesis is discussed, as solid-state organometallic complexes for synthesis & catalysis is a subject that is relatively unexplored. The use of well-defined organometallic complexes are not included into a platform material for solid-state catalysis is a relatively new subject. In the field of organic synthesis, particularly in the pharmaceutical business, polymer supported reagents is a widespread & powerful technique. Heterogeneous catalysis on metal surfaces or ionic platform materials is a well-studied field of chemistry with numerous industrial applications.

Keywords – Polymer Supported; Organometallic; Solid Phase Synthesis; Hydrogenation;

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INTRODUCTION

The expression “organic catalyst” has recently been introduced to define an organic compound (of relatively low molecular weight and simple structure) capable of promoting a given transformation in sub stoichiometric quantity. In this context, organic means metal-free, and it is used to differentiate this class of catalysts from that of metal-based catalytic species. A utilize of polymer supported reagents is a common and powerful approach in the field of organic synthesis, especially in the pharmaceutical industry. The majority of discoveries in the area have been performed in the solution phase, with studies in the solid state generally often reserved only for structural analysis; for example, single-crystal X-ray crystallography and, to a significantly lesser extent, solid-state nuclear magnetic resonance spectroscopy. By contrast to the solution phase, studies on the synthesis of, and catalysis using, organometallic developments in the solid phase have attracted significantly less attention, uniformly there are potential benefits to this approach, such as: improved selectivities in synthesis that comes from spatially confined environments, improved isolated produces of products & diminution of decomposition pathways permitting for products which is kinetically unsteady in solution to be detected in the solid state.

Heterogeneous catalysis on metal surfaces or ionic platform materials is a well-studied field of chemistry with numerous practical applications.

CATALYSIS IN SOLID STATE

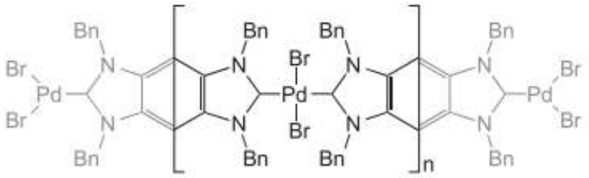
(a) Heterogeneous organometallic catalysts

The heterogenization of single-site catalysts brings together the benefits of heterogeneous catalysis (i.e. recyclability and ease of removal from the reaction mixture) with the potential for intimate control over transformations that occur at the metal center that is provided by the local ligand environment in a homogeneous system. Surface-supported organometallic chemistry, in which a platform material like silica, zeolites, or metal oxides supports the organometallic complex directly or indirectly via linker groups, is one strategy for facilitating the heterogenization with well organometallic catalyst complexes. Metal organic frameworks (MOFs) are also particularly attractive as one-, two- and three-dimensional assemblies can be created in which the metal atoms often act as the geometry-enforcing linkage points, but could be predicted as potential active sites for catalysis. A MOF could also serve as a reaction cavity, with organometallic species acting as a host/guest material. Because these materials are frequently not well characterised at the metal centre of interest, they are not included in this study, which focuses on the reactivity from well organometallic complexes in the solid state.

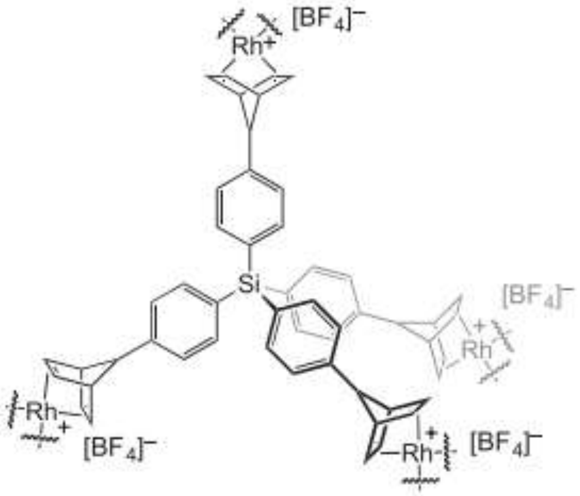
(b) Self-supported organometallic catalysis

Self-supported catalysts employ an active metal centre wherein the ligand environment also serves as a microporous substrate. When compared to heterogeneous organometallic catalysts, many of these complexes have a well-defined metal–center, making them more amenable to structural & spectroscopic research. The linkage polymers of [RhCl(CO)(1,4-(CN)2C6H4)]n, that can hydrogenate & isomerize 1-hexene with no leaching of complexes into solution, were among the first self-supported catalysts reported. Photolytic breakdown of the CO ligand produced the active rhodium site. A comparable system was created using two bridging ligands per metal, which allowed for the formation of a well-defined three-dimensional stacked layer structure. The surface & corner positions of this structure are believed to include catalytically active unsaturated metal centres, whereas the interior sites are thought to be completely inactive.

For usage in Suzuki–Miyaura C–C coupling processes, multidentate oxime, thiourea, phosphine, & NHC ligands were employed to build frameworks with Pd-centres. Karimi & Akhavan, for example, developed a palladium coordination polymer with an insoluble in water connecting bidentate NHC ligand, resulting in C-C coupling catalysis using water as the substrate and product solvent. (scheme 1). Although the authors used the mercury test, which probes for nanoparticle formation, which showed no loss in activity, it is problematic to unequivocally prove that nanoparticles are in no way involved for such systems.



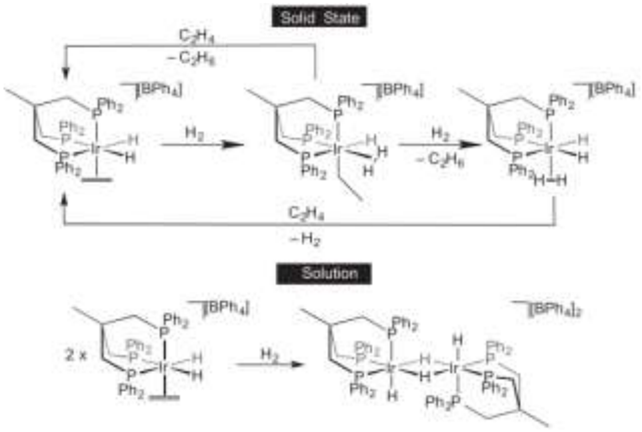
Scheme 1. A coordination polymer with Pd capable of catalysing heterogeneous Suzuki–Miyaura cross coupling in water



Scheme 2. A microporous organometallic framework based upon rhodium alkene coordination.

metal–centre and thus more amenable to structural and spectroscopic investigation. The linkage polymers of [RhCl(CO)(1,4-(CN)2C6H4)]n, that could hydrogenate & isomerize 1-hexene with no leaching of complexes into solution, were among the first self-supported catalysts reported. Photolytic breakdown of the CO ligand produced the active rhodium site. A comparable system was created using two bridging ligands per metal, which allowed for the formation of a well-defined three-dimensional stacked layer structure. The surface & corner positions of this structure are believed to include catalytically active unsaturated metal centres, whereas the interior sites are thought to be completely inert. For usage in Suzuki–Miyaura C–C coupling processes, multidentate oxime, thiourea, phosphine, & NHC ligands were employed to build frameworks with Pd-centres.

Kaskel and co-workers [110] have recently reported the formation of a microporous organometallic network based upon a rhodium alkene fragment linked to a rigid tetraphenylsilane backbone (scheme 2). While an accurate structural determination has proved difficult, the framework appeared to be air-stable unlike its homogeneous analogue [Rh(NBD)2][BF4]. This material catalysed transfer hydrogenation reactions.**15**



Scheme 3. Catalytic ethene hydrogenation in the solid state versus solution

(c) Solid-state organometallic catalysis without support

The use of well-defined organometallic complexes that are not incorporated into a platform material for solid-state catalysis is a relatively new subject. Bianchini et al. demonstrated the concept utilizing [(triphos)Ir(H)2(C2H4)] & simple ethene hydrogenation processes. At 343 K, [BPh4] (scheme 3). The catalyst was active in the solid state, in a mechanism proposed to operate via hydride migration to form an Ir−(C2H5) species, which can react with further H2 surveyed by reductive rejection of ethane. In solution, the same species was not catalytically active, because a coordinatively saturated dimeric bridging hydride species rapidly forms in the existence of H2 which was inactive for further reactions. Although some of the inactive dimeric species is also formed in the solid-state reaction, it appears to form at a slower rate than in solution. This highlights the ability of the solid state to maintain the integrity of the reactive species by playing a role in protecting them from deactivation pathways that require structural reorganization. The [BPh4] anions are considered to develop a hydrophobic lattice structure that allows tiny hydrocarbon gases to pass through. Bianchini & co-workers looked into the catalytic trimerization of ethyne to create benzene, finding that a 4-benzene complex (derived from a solid–gas reaction) is an active pre-catalyst active at 373 K in the solid state (scheme 20) (c) Without a support, solid-state organometallic catalysis The use of well-defined organometallic complexes that are not included into a platform material for solid-state catalysis is a comparatively recent subject. Bianchini et al. referred to the concept using [(triphos)Ir(H)2(C2H4)][BPh4] at 343 K in simple ethene hydrogenation processes (scheme 3).

The catalyst was active in the solid state, in a mechanism proposed to operate via hydride migration to form an Ir−(C2H5) species, which can react with further H2 follow by reductive eradication of ethane. In solution, the same species was not catalytically active, because a coordinatively saturated dimeric bridging hydride species rapidly forms in the existence of H2 which was inactive for further reactions. Although some of the inactive dimeric species is also formed in the solid-state reaction, it appears to form at a slower rate than in solution. This highlights the ability of the solid state to maintain the integrity of the reactive species by playing a role in protecting them from deactivation pathways that require structural reorganization. The [BPh4] anions are thought to form a hydrophobic lattice structure that allows minor hydrocarbon gases to pass through. Bianchini & co-workers looked into the catalytic trimerization of ethyne to create benzene, finding that a 4-benzene complex (derived from a solid–gas reaction) is an effective pre-catalyst active at 373 K in the solid state (scheme 4)

Siedle & Newmark reported the room temperature catalytic activity of iridium phosphine cations partnered with Keggin-type trianions, [Ir(H)2(PPh3)2]3[PW12O40] (scheme 4), with the hydrogenation of ethene, propene and 1-hexene demonstrated. It was also shown that 1-hexene can be isomerized to a combination of cis- & trans-2-hexenes, as well as 3-hexenes, likely by reversible CH activation via an allyl-iridium–hydride intermediate. The writers make no mention of reaction times. Excess ethyne creates benzene in catalytic quantities, comparable to Bianchini's findings, with an iridium–benzene complex acting as the precatalyst, albeit the reaction is said to be sluggish. It was also shown that CF2=CFCl can be catalytically dimerized to form cis- & trans-1,2-dichlorohexafluorocyclobutane complexes. Limbach & co-workers has stated on the solid-state catalysed hydrogenation of ethene utilizing Vaska's complex, Ir(CO)Cl(PPh3)2, by following the reaction products by gas-phase 1H NMR spectroscopy. In solution, the product of H2 addition (which presumably related to the Siedle & Newmark reported the room temperature catalytic activity of iridium phosphine cations partnered with Keggin-type trianions, [Ir(H)2(PPh3)2]3[PW12O40] (scheme 4), with the hydrogenation of ethene, propene and 1-hexene demonstrated.

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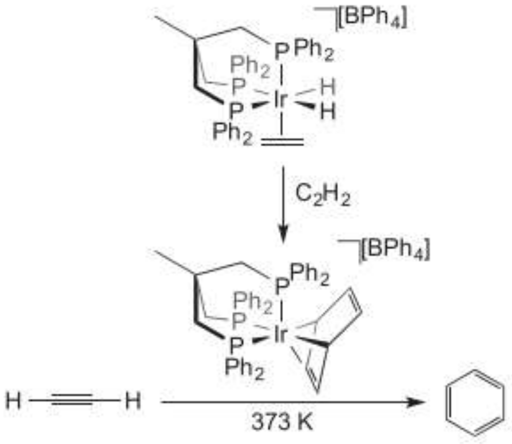
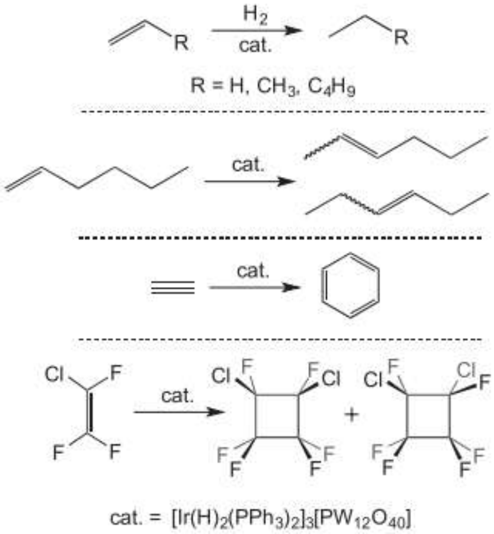
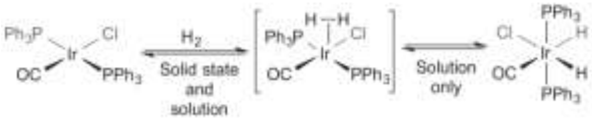


Scheme 3. Trimerization of ethyne using a solid-state catalyst

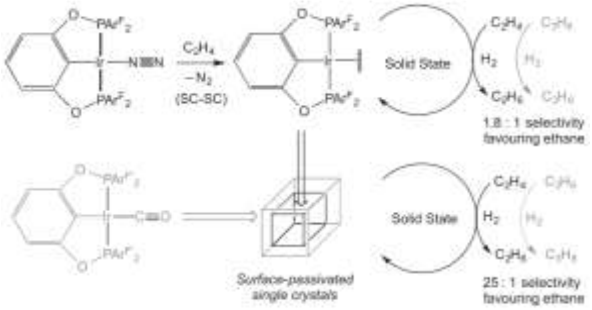


Scheme 4 Catalytic reactions using [Ir(H)2(PPh3)2]3[PW12O40]



Scheme 5. Reaction of Vaska's complex with H2 in the solid state & solution

Brookhart et al. used single crystals of (POCOP)Ir(N2) to hydrogenate ethene, which was tracked via gas-phase NMR spectroscopy. At 298 degrees Fahrenheit, the reaction necessitates At 298 K, the reaction takes 5 hours to reach 95 percent conversion, whereas at 348 K, it takes only 30 minutes. The loss of lattice-incorporated toluene at this higher temperature is thought to be the cause of the increased activity. The predicted resting state is (POCOP)Ir(C2H4). There was also a demonstration of remarkable selective catalytic hydrogenation inside single crystals. By passivating the surface sites of crystals of (POCOP)Ir(N2) with a layer of (POCOP)Ir(CO), an incomplete crystal-to-crystal transition occurs. At 348 K, the resultant material had a 25:1 preference for hydrogenating ethene in the presence of propene (scheme 6). The porous crystals are thought to provide smaller ethene & hydrogen molecules exposure to the active inner metal sites, while bigger propene molecules are unable to penetrate the surface. Only a slight selectivity in favour of hydrogenation of ethene is observed in the absence of surface passivation (1.8: 1 ratio of ethane to propane generated at 298 K), which is similar with this.



Scheme 6. Hydrogenation of ethene utilizing single crystals, & selective hydrogenation of ethene in the existence of propene utilizing surface-passivated single crystals.

CONCLUSION

We hope that this review has shown that solid-state organometallic chemistry can offer significant advantages over the solution phase, especially when kinetic stability, or overall reaction selectivity, are different in the solid state compared with solution. Another important aspect is that of green chemistry, *i.e.* developing efficient and environmentally benign methods for organic synthesis, where the fact that many supported catalysts can be recycled a number of times without loss of efficiency constitutes an important contribution in this area.

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