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Heterogenisation of a Carbonylation Catalyst on Dispersible Microporous Polymer Nanoparticles

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Abstract

The methanol carbonylation catalyst, cis-[Rh(CO)2I2], has been heterogenised within a dispersible microporous polymer support bearing cationic functionality. The microporous polymer has a core-shell structure in which the porous and insoluble core (a co-polymer of divinylbenzene and 4-vinylpyridine) is suspended in solution by long hydrophilic poly(ethylene glycol) chains, allowing a stable suspension of the nanoparticles to form. Incorporation of 4-vinylpyridine as a co-monomer allows post-synthetic modification to generate N-methylpyridinium sites for electrostatic attachment of the anionic rhodium(I) complex. The dispersibility of the polymer-supported
catalyst material facilitates the use of *in situ* transmission IR spectroscopy to obtain kinetic data for the oxidative addition of iodomethane to immobilised *cis*-([Rh(CO)₂I₂]⁻ (the rate-limiting step of the carbylation cycle). Remarkably, the oxidative addition proceeds faster than for the homogeneous system (Bu₄N⁺ counter-ion, CH₂Cl₂, 25 °C). The polymer-supported catalyst was found to be active for methanol carbylation, with a turnover frequency similar to that of the homogeneous analogue under the same conditions (10 bar CO, MeI/MeOH/CHCl₃, 120 °C). The supported catalyst is easily recovered and is shown to maintain comparable activity upon recycling.

**Introduction**

Homogeneous transition metal catalysts are widely used for organic transformations on laboratory and bulk scales.¹ They typically benefit from high activity and selectivity under relatively mild conditions, and can be tuned by choice of metal, ligand, solvent and reaction conditions. Compared with heterogeneous catalysts, however, they suffer from the need to separate product from a solution phase containing the dissolved catalyst. Typically, a distillation is required under conditions that can lead to catalyst degradation and incur significant costs.² In order to combine the benefits of both homogeneous and heterogeneous catalysis, a common approach is to immobilise a soluble metal complex on an insoluble support such as an inorganic oxide, zeolite, metal-organic framework or organic polymer.³

One of the most significant commercial bulk processes that uses homogeneous transition metal catalysis is the carbylation of methanol to produce acetic acid (global demand ~20 million tonnes p.a.⁴), employing rhodium- or iridium-based catalysts.⁵⁻⁹ The Monsanto process, developed in the 1960s, employs a rhodium catalyst and an iodide promoter, achieving very high selectivity
(> 99% based on MeOH). The active rhodium complex is a square-planar Rh(I) species, cis-[Rh(CO)₂I₂]⁻, which undergoes oxidative addition of methyl iodide, derived from the methanol feedstock (Scheme 1).

![Scheme 1](image_url)

**Scheme 1.** Cycle for rhodium/iodide catalysed methanol carbonylation.

To maintain high activity and catalyst stability, as well as to improve solubility, a relatively high concentration of water (~10% wt.) is used in the reaction medium. At lower water concentrations, an inactive Rh(III) species, [Rh(CO)₂I₄]⁻, can accumulate as an intermediate in a competing water gas shift (WGS) reaction. This species can dissociate CO and lead to precipitation of RhI₃ in parts of the plant that have lower CO partial pressure. Although high water concentration alleviates this, it increases the cost of product purification, by distillation, to produce dry acetic acid. Variations of the Monsanto process have been introduced that allow operation at lower water concentration. For example, the Celanese Acid Optimisation (AO Plus) technology employs lithium iodide as an additive that stabilises the Rh catalyst and maintains high carbonylation activity at significantly lower water concentration. Related Rh-catalysed processes for carbonylation of methyl acetate...
to acetic anhydride under anhydrous conditions use lithium iodide (Eastman)\textsuperscript{15} or quaternary ammonium iodide salts (BP Chemicals).\textsuperscript{16} BP Chemicals’ Cativa™ process uses a promoted iridium/iodide homogeneous catalyst system that achieves high activity and selectivity for methanol carbonylation at low water concentration.\textsuperscript{17,18}

Another approach to minimise problems with solubility at low water concentration is to heterogenise the catalyst by immobilisation on a solid support.\textsuperscript{5,16,19} A range of support materials that bind the Rh catalyst directly through a covalent interaction have been investigated, including inorganic oxides,\textsuperscript{20,21} zeolites,\textsuperscript{22-25} polymers,\textsuperscript{26-31} carbon\textsuperscript{32} and covalent triazine frameworks.\textsuperscript{33} Many of these systems exhibit reaction rates slower than that of the homogeneous process, likely due (in part) to the covalent tethering of the catalyst, which modifies the first coordination sphere of the Rh complex. Leaching of catalyst due to lability of the Rh–support interaction can also be problematic.

An alternative strategy for heterogenisation, which preserves the first coordination sphere of the catalyst, is immobilisation of the anionic Rh complex on a cationic support by electrostatic interactions.\textsuperscript{34-37} This approach has been observed to result in less catalyst leaching compared with covalent tethering. In 1981, Drago \textit{et al.} described the effective immobilisation of $\text{cis}$$\cdot$$\text{[Rh(CO)$_2$I$_2$]}^-$ on polymer supports based on $N$-methylated polyvinylpyridines.\textsuperscript{38} The carbonylation activity was equal to the homogeneous system at 120 °C with minimal leaching of the supported catalyst. This ionic attachment approach was adopted in the Acetica™ process developed by Chiyoda and UOP which employs a polyvinylpyridine resin tolerant of catalytic reaction conditions.\textsuperscript{39} The pyridyl groups are quaternised in the presence of iodomethane, and the anionic catalyst, $\text{cis}$$\cdot$$\text{[Rh(CO)$_2$I$_2$]}^-$ is bound electrostatically to the support. The supported catalyst showed no deactivation after continuous operation for 7,000 hours and its activity is competitive with the homogeneous process,
with decreased by-product formation via the WGS reaction due to the lower water concentration employed.

The catalytic mechanism for this type of supported system was investigated by Haynes et al. using cross-linked poly(4-vinylpyridine-co-styrene-co-divinylbenzene) in the form of thin films suitable for in situ transmission IR spectroscopy.\textsuperscript{40} N-methylation with methyl iodide and subsequent reaction with [Rh(CO)\textsubscript{2}I\textsubscript{2}]\textsuperscript{2-} generated the electrostatically bound complex cis-[Rh(CO)\textsubscript{2}I\textsubscript{2}]\textsuperscript{2-} (Scheme 2). EXAFS measurements indicated that the structure of supported cis-[Rh(CO)\textsubscript{2}I\textsubscript{2}]\textsuperscript{2-} is essentially the same as determined crystallographically for the N-methylpyridinium salt and IR spectroscopic monitoring showed that the same organometallic steps occur for the supported complex as in solution, with kinetics of MeI oxidative addition comparable to the solution phase.

\begin{center}
\begin{tikzpicture}
  \tikzstyle{every node}=[draw]
  \node (pol) at (0,0) {\text{pol}};
  \node (N) at (0.5,0) {\text{N}};
  \node (Me) at (1.5,0) {\text{Me}};
  \node (Rh) at (2.5,0) {\text{Rh}};
  \node (CO) at (3,0) {\text{CO}};
  \node (I) at (4,0) {\text{I}};
  \node (pol2) at (5.5,0) {\text{pol}};
  \node (N-Me) at (6,0) {\text{N-Me}};
  \node (Rh2) at (7,0) {\text{Rh}};
  \node (CO2) at (7.5,0) {\text{CO}};
  \node (I2) at (8.5,0) {\text{I}};
  \draw[->] (pol) -- (N);\draw[->] (N) -- (Me);\draw[->] (Me) -- (Rh);\draw[->] (Rh) -- (CO);\draw[->] (I) -- (pol2);\draw[->] (pol2) -- (N-Me);\draw[->] (N-Me) -- (Rh2);\draw[->] (Rh2) -- (CO2);\draw[->] (CO2) -- (I2);
\end{tikzpicture}
\end{center}

\textbf{Scheme 2.} Route to ionically attached \textit{cis}-[Rh(CO)\textsubscript{2}I\textsubscript{2}]\textsuperscript{2-}.

Microporous polymers have also been widely investigated for heterogeneous catalysis,\textsuperscript{41-43} including their use to encapsulate metal catalysts electrostatically.\textsuperscript{44-46} Recently, a new class of dispersible porous polymer has been reported, synthesised using Reversible Addition-Fragmentation chain Transfer-mediated Polymerisation-Induced Self-Assembly (RAFT-mediated PISA).\textsuperscript{47} Co-polymerisation of divinylbenzene (DVB) and fumaronitrile (FN) was mediated using a hydrophilic macromolecular chain transfer agent (macro-CTA) in an anti-solvent for the growing polymer chain. This resulted in the formation of polymer nanoparticles with a core-shell morphology. The high degree of crosslinking within the core of the sample means that the material
is microporous in nature. However, unlike most other porous polymers, these materials can form stable dispersions in a variety of organic solvents for long periods of time, permitting them to be processed and utilised for applications in the solution phase. Furthermore, their recovery from solution can be achieved either via addition of an antisolvent or centrifugation. The combination of inexpensive synthesis, high surface area, microporosity, robust chemical stability and dispersibility make them an ideal candidate for catalyst immobilisation. Ferguson et al. recently utilised this approach to synthesise dispersible porous polymer photocatalytic nanoparticles, which were found to be active for a range of photocatalytic reactions to produce pharmaceutically relevant compounds. The versatility of these porous materials for encapsulation of molecular species has also recently been demonstrated in the formation of organic white-light emitting dispersions.

Here we report the synthesis of a new dispersible porous material by co-polymerisation of 4-vinylpyridine (4VP) with DVB in the presence of a PEG-based macro-CTA. The 4VP functionality allows the material to be post-synthetically modified using iodomethane to generate a cationic support which is used to bind cis-[Rh(CO)₂I₂]⁻ electrostatically. The organometallic steps of the methanol carbonylation cycle can be followed by in situ IR spectroscopy for the supported catalyst and kinetic measurements show, surprisingly, that the rate of oxidative addition of MeI to cis-[Rh(CO)₂I₂]⁻ exceeds that in homogeneous solution. Catalytic turnover and recyclability are demonstrated, showing that this class of material has considerable potential for the development of supported catalysts.
Results and Discussion

Synthesis and characterisation of supported catalyst

Synthesis of the dispersible porous polymeric material 1 employed a RAFT-mediated PISA approach analogous to that reported by James et al.\textsuperscript{47} whereby DVB and 4VP monomers were co-polymerised in a 1:1 (w/w) ethanol:water solvent mixture using a PEG-based macro-CTA (Scheme 3). Post-synthetic modification (PSM) of 1 was accomplished by treatment with MeI to give the N-methylated polymer, 2, followed by addition of the rhodium dimer, [Rh(CO)\textsubscript{2}I\textsubscript{2}] to generate the supported catalyst material 3.

Scheme 3. Synthesis of pyridine-containing dispersible microporous polymer (1), post-synthetic N-methylation to form 2 and subsequent reaction with [Rh(CO)\textsubscript{2}I\textsubscript{2}] to form 3; (a) MeI in CHCl\textsubscript{3}, 70 °C, 72 h; (b) [Rh(CO)\textsubscript{2}I\textsubscript{2}] in CHCl\textsubscript{3}, RT, 16 h.
Materials 1-3 were characterised using IR and solid-state NMR spectroscopy, together with elemental and ICP-MS analysis. Product 1 was obtained as a white solid after extraction of unreacted monomer and drying *in vacuo*. The nitrogen content of 1 indicates incomplete incorporation of the 4VP monomer and an approximate average composition of the polymer is estimated to be PEG$_{113}$DVB$_{300}$4VP$_{60}$. After reaction with iodomethane, giving 2 as a yellow powder, the iodide content is consistent with approximately 80% of the 4VP units having been N-methylated (Table S1).

![Figure 1.](image)

**Figure 1.** (a) FTIR spectra highlighting the absorptions due to $\nu$(C-N) (green), $\nu$(C-O) (red) and $\nu$(C=O) (blue); (b) solid state $^{13}$C{$^1$H} CP/MAS NMR of materials 1 (black), 2 (red) and 3 (blue).

The IR spectra of all three materials (Figure 1(a)) show bands at 994 cm$^{-1}$ assigned to $\nu$(C-O) of the ether linkages of the solubilising PEG chains. Absorptions at 3030 and 1195 cm$^{-1}$ are characteristic of aromatic $\nu$(C-H) and $\nu$(C-N) modes of the DVB and 4VP units respectively and bands centred at 2930 and 1450 cm$^{-1}$ represent the aliphatic C-H stretching and bending modes respectively. The solid state $^{13}$C{$^1$H} CP/MAS NMR spectra of 1-3 (Figure 1(b)) each show a broad resonance at $\delta$ 40 corresponding to the aliphatic carbons of the polymer backbone. This
broad signal presumably obscures the expected peak due to the \( N \)-methyl groups of quaternised 4VP units in 2 and 3 (reported to occur at \( \delta \) 49.8 for \( N \)-methylpyridinium iodide in ethanol solution\(^{50} \)). All the materials also show a small resonance at \( \delta \) 70 due to the solubilising PEG chains, consistent with polymerisation being mediated through the RAFT macro-CTA. Peaks between \( \delta \) 120 and 160 correspond to the aromatic carbons of the two monomer units for material 1. The resonance centred at \( \delta \) 150 is lost in 2 and 3, accompanied by the appearance of a new signal at \( \delta \) 165, assigned to the \textit{para} carbon of the pyridine moiety, by analogy to the downfield shift that occurs in solution on \( N \)-methylation of pyridine.\(^{50} \) A resonance at 113 ppm, in the spectra of all three materials, is attributed to the presence of some unreacted vinyl moieties of the DVB monomer units.

On addition of a chloroform solution of \([\text{Rh(CO)}_2\text{I}]_2\) to 2, uptake of Rh complex by the polymer was indicated by the supernatant phase becoming colourless. Removal of solvent gave 3 as a brown powder. ICP-MS analysis showed 3 to contain 4.5% Rh by weight, consistent with most of the added metal complex being incorporated by the polymeric support. The IR spectrum of 3 shows two strong \( \nu(\text{CO}) \) absorptions at 2062 and 1990 cm\(^{-1} \) which are very close to those reported for the anionic rhodium complex, \textit{cis}-\([\text{Rh(CO)}_2\text{I}]^-\), in solution.\(^{51,52} \) In a control experiment, reaction of the non-quaternised material 1 with \([\text{Rh(CO)}_2\text{I}]_2\) gave a product with \( \nu(\text{CO}) \) bands 2080 and 2010 cm\(^{-1} \), the higher frequencies being consistent with coordination of a pyridyl moiety in 1 to form a covalently attached neutral complex \([\text{Rh(CO)}_2\text{I(\text{py-1})}]\).
Figure 2. (a) Nitrogen adsorption (filled) and desorption (open) isotherms at 77 K (offset successively by 25 cm$^3$ g$^{-1}$), inset shows the low relative pressure region (with no offset); (b) differential pore size distribution (offset successively by 0.1 cm$^3$ g$^{-1}$, micropore region highlighted) of 1 (black), 2 (red) and 3 (blue).

Table 1. Surface areas and pore volumes of polymer nanoparticle samples.

| Sample | $S_{\text{BET}}$ a / m$^2$ g$^{-1}$ | $V_{\text{tot}}$ b / cm$^3$ g$^{-1}$ | $V_{0.1}$ c / cm$^3$ g$^{-1}$ | ($V_{0.1}/V_{\text{tot}}$) |
|--------|-------------------------------|---------------------------------|---------------------|---------------------------|
| 1      | 366                           | 0.53                            | 0.15                | 0.28                      |
| 2      | 166                           | 0.37                            | 0.06                | 0.16                      |
| 3      | 114                           | 0.25                            | 0.04                | 0.16                      |

*Calculated over the pressure range 0.01-0.15 $p/p_0$.
*Calculated at 0.99 $p/p_0$.
*Calculated at 0.1 $p/p_0$.

To assess the porosity and surface area of 1-3, volumetric gas sorption studies using nitrogen gas at 77 K were performed on each material (Figure 2 and S1). Resulting parameters for 1-3 are given in Table 1. The specific BET surface area ($S_{\text{BET}}$) of 1 was determined to be 366 m$^2$ g$^{-1}$, with both micropores and mesopores present in the material. After quaternisation of 1 with MeI, the surface area of 2 is lower (166 m$^2$ g$^{-1}$) and the micropores are lost. A further reduction in surface
area (to 114 m$^2$ g$^{-1}$) is observed upon incorporation of the Rh catalyst in 3. Pore size analysis of 2 suggests that PSM of 1 results in a loss of the micropores of the material. Initially, the micropore volume ($V_{0.1}$) of 1 is 0.15 cm$^3$ g$^{-1}$ but this falls to 0.06 cm$^3$ g$^{-1}$ upon quaternisation of the material to yield 2. A further and more minimal decrease of micropore volume to 0.04 cm$^3$ g$^{-1}$ is observed upon incorporation of the Rh complex to yield 3. However, the mesopores are completely lost in 3 which suggests occupation by the Rh complex. The ratio of micropore: total pore volume ($V_{0.1}/V_{tot}$) is unchanged upon transformation of 2 to 3, further suggesting that the Rh complex is situated in the mesopores rather than the micropores. This correlates with the loss of hysteresis at $\sim$ 0.8 P/P$_0$ initially present on the desorption branch of the isotherm of sample 1 indicating a further loss in mesoporosity. Finally, the large uptake of gas at high relative pressure (> 0.9 p/p$_0$) is attributed to the aggregated morphology of the material and shows that even after two PSM steps the morphology of the material remains intact, as further evidenced by transmission electron microscopy (TEM, see below).

The materials are able to form stable dispersions in a wide variety of solvents as previously reported for the PEG-DVB/FN system.$^{47}$ This is attributed to the presence of the long solubilising PEG chains which allow the insoluble porous DVB/4VP core network to be dispersed in solution. The stability of an undisturbed dispersion of 1 in CHCl$_3$ was monitored by UV-Vis spectroscopy for 72 h (Figure S2). Any change in signal intensity is attributed to the material settling out of solution so correlates directly to loss of stability of the dispersion. After 72 h it was found that only $\sim$15 % of the sample had settled out of solution and the majority of the polymer was still present as a stable dispersion, indicating suitability for use in a catalytic system as proposed.

Small-angle X-ray scattering (SAXS) studies were performed on 5% w/w dispersions of samples 1-3 in MeOH (Figure 3a) to gain insight into the size and morphology of nanoparticles in each
sample. The data were successfully fitted using the same two-population model as used previously for PEG-FN/DVB dispersible porous polymers,\textsuperscript{47} which suggests the presence of aggregates of smaller primary assemblies, presumably due to both inter- and intra-particle covalent crosslinking (Figure S3). Fitting these data indicated that mean diameters for the primary particles ($D_1$) ranged from 25 nm to 34 nm, with very broad size distributions in each case (standard deviation $\geq$ 60%). Remarkably, the mean diameter of the overall aggregates ($D_2$) remained relatively constant for each sample, with values of 101-104 nm being determined (Table 2). Additionally, the standard deviation in the $D_2$ values in all cases was significantly lower ($\leq$ 20%) than that observed for $D_1$. Importantly, this proposed hierarchical structure is supported by TEM images (Figure 3b-d).

![Figure 3.](image_url)

**Figure 3.** (a) Small angle X-ray scattering of sample 1 (black), 2 (red), and 3 (blue) along with two-population fitting (dashed lines). Datasets are offset successively by a factor of 100. TEM images of sample 1 (b), 2 (c), and 3 (d) are also shown.
Table 2. SAXS particle analysis for samples 1-3 where $D_1$ is the mean diameter of the primary particles and $D_2$ is the mean diameter of the aggregates.

| Sample | $D_1$ / nm | $D_2$ / nm |
|--------|------------|------------|
| 1      | 25.2 ± 27.1 | 101.3 ± 15.7 |
| 2      | 31.6 ± 19.8 | 103.1 ± 20.6 |
| 3      | 34.2 ± 20.3 | 104.8 ± 19.2 |

Reaction of supported catalyst 3 with iodomethane

After soaking a sample of 3 in neat MeI overnight, the IR spectrum of the resulting material displays only one ν(CO) absorption in the terminal metal carbonyl region, at 2058 cm$^{-1}$, as well as a broad band at ~1700 cm$^{-1}$ (Figure 4a). This is consistent with formation of a Rh(III) acetyl complex, $[\text{Rh(CO)(COMe)I}_3]^-$, resulting from oxidative addition of MeI to cis-$[\text{Rh(CO)}_2I_2]^-$, followed by spontaneous migratory CO insertion (Scheme 4), analogous to the corresponding reactions observed in solution and in previously investigated polymer-supported systems. Upon exposure of the MeI addition product to CO (1 atm), the IR spectrum gradually changes to resemble that of pristine 3 (Figure 4a). This could arise either by reversal of the steps described above, with loss of MeI to reform cis-$[\text{Rh(CO)}_2I_2]^-$, or by coordination of CO to give $[\text{Rh(CO)}_2(\text{COMe})I_3]^-$ and subsequent reductive elimination of acetyl iodide. Since no corresponding change in the IR spectrum occurs under N$_2$, our observations suggest the latter, hence completing the sequence of steps for a single turnover of the catalytic carbonylation cycle (Scheme 1).
Figure 4. (a) IR spectra (KBr disc, ν(CO) region) of pristine 3 (blue), after soaking in MeI (orange) and after exposure to CO (green), (b) series of IR spectra (ν(CO) region) during reaction of 3 with 1 M MeI in CH₂Cl₂ (25 °C) and decay of IR absorption at 1987 cm⁻¹ during this reaction with (c) single exponential curve fit, and (d) double exponential curve fit.

Scheme 4. Reactions of polymer-supported cis-[Rh(CO)₂I₂]⁻ with MeI observed by IR spectroscopy.

The stability of dispersions of the polymer-supported complex mean that the organometallic reaction steps can be monitored in situ using transmission IR spectroscopy. Figure 4b shows the terminal ν(CO) region of a series of spectra obtained over the course of the reaction of MeI with 3 dispersed in CH₂Cl₂. The smooth decay of bands due to cis-[Rh(CO)₂I₂]⁻ is apparent, with the
terminal ν(CO) band of [Rh(CO)₂(COMe)I₃]⁻ appearing close to the high frequency band of the reactant such that these bands are not resolved from each other.

Kinetic data was extracted by monitoring the decay of the low frequency ν(CO) band of cis-[Rh(CO)₂I₂]⁻ at 1987 cm⁻¹ over time. Pseudo first-order conditions were ensured by using a large excess of MeI. Figure 4c shows a typical absorbance vs. time plot generated from one of these experiments with the data fitted to a first-order decay curve. It is apparent from this plot that the data are not perfectly fitted by a single exponential decay function. There appear to be two phases during the reaction with an initial faster decay followed by a slower downward drift. Empirically it was found that the kinetic data are better described using a double exponential decay, with contributions from two different pseudo first-order rate constants (k₁ and k₂) as illustrated in Figure 4d. Analogous experiments were repeated across a range of MeI concentrations (Figures S4-S8), giving the pseudo first-order rate constants listed in Table S2.

![Figure 5](image)

**Figure 5.** Plot of k₁ (blue, R² = 0.92) and k₂ (red, R² = 0.87) vs. MeI concentration for reaction of MeI with 3 in CH₂Cl₂ (25 °C).
Plots of $k_{\text{obs}1}$ and $k_{\text{obs}2}$ vs. [MeI] (Figure 5) are approximately linear, with slopes $k_{21} = 2.7 \times 10^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $k_{22} = 5.0 \times 10^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$, but exhibit non-zero intercepts. The slow-phase component, $k_{22}$, is similar in magnitude to the second order rate constant for the homogeneous system ($2.7 \times 10^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$ for Bu$_4$N[Rh(CO)$_2$I$_2$] at 25 °C in CH$_2$Cl$_2$) whereas the fast-phase component, $k_{21}$, is significantly larger. Mechanistic interpretation of these observations is made difficult by the inhomogeneity of dispersions of the polymer supported complex which means the rate law is likely less simple than for a homogeneous reaction. It can be speculated that the data may correspond to reactions of complexes situated at different sites within the polymer. The effective concentration of MeI within the pores of the dispersed polymer may also differ from that of the bulk solution.

Despite the deviation from simple kinetic behaviour, it is notable that the reaction of MeI with immobilised cis-[Rh(CO)$_2$I$_2$] in 3 is substantially faster than for the homogeneous analogue under the same conditions. The rate constant for the homogeneous reaction translates to a half-life of ~25000 s under the conditions of the kinetic experiment illustrated in Figure 4. Hence the initial phase of the reaction of 3 is an order of magnitude faster than that of the homogeneous complex. This behaviour differs from that of an insoluble polymer-supported system studied previously, which gave a rate constant very similar to that measured in the solution phase (2.6 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^{3} \text{ s}^{-1})$.\) Hence the dispersibility of the polymer support in 3 appears to have a significant effect on the oxidative addition rate.

**Catalytic methanol carbonylation**

To demonstrate catalytic turnover for methanol carbonylation, *in situ* high-pressure IR (HPIR) spectroscopy was used to monitor a dispersion of supported catalyst 3 in chloroform containing methanol and iodomethane at 120 °C under 10 bar CO pressure. IR spectra collected over the
course of four hours showed the growth of an absorption at 1741 cm\(^{-1}\) due to the \(\nu(\text{C}=\text{O})\) of methyl acetate, formed by esterification of the carbonylation product, acetic acid, in the presence of excess methanol (overall 2MeOH + CO → MeCO\(_2\)Me + H\(_2\)O, Scheme 5). A plot of absorbance \(\text{vs.}\) time for this band (Figure 6a) is approximately linear and a value of the catalytic turnover frequency (TOF) of 11.4 h\(^{-1}\) can be determined from the slope. Data from an experiment using Bu\(_4\)N[Rh(CO)\(_2\)I\(_2\)] under the same conditions, also plotted in Figure 6a, give a TOF of 21.8 h\(^{-1}\). The catalytic rate is lower for the polymer-supported system, despite the faster oxidative addition of MeI reported above, but the different temperature and solvent system in the model and catalytic reactions may be significant. The polymer-supported catalyst was recovered after the reaction by centrifugation and a subsequent experiment using the recovered catalyst showed that it retained activity comparable with the initial run (Figure 6b), thus demonstrating its recyclability.

**Figure 6.** (a) Plots of absorbance \(\text{vs.}\) time for \(\nu(\text{C}=\text{O})\) of MeOAc during methanol carbonylation experiments using 3 (blue) or Bu\(_4\)N[Rh(CO)\(_2\)I\(_2\)] (grey); (b) comparison of absorbance \(\text{vs.}\) time plots using 3 (blue) and a subsequent experiment with the recovered catalyst (orange). All experiments monitored at 120 °C (10 bar CO, 0.8 M MeI, 2.5 M MeOH in CHCl\(_3\)).
Scheme 5. Catalytic carbonylation of methanol to form methyl acetate.

Conclusions

A dispersible microporous polymer material based on the co-polymerisation of DVB and 4VP and mediated by a PEG-based macro-CTA has been synthesised. Post-synthetic modification of this material was achieved via N-methylation of the pyridine moieties with MeI to generate cationic sites on the support, allowing heterogenisation of the anionic carbonylation catalyst, cis-[Rh(CO)\textsubscript{2}I\textsubscript{2}]\textsuperscript{-}, via electrostatic interactions. Oxidative addition of MeI to the Rh(I) complex (the rate limiting step in rhodium/iodide catalysed methanol carbonylation) was probed \textit{in situ} using transmission IR spectroscopy. Remarkably, rate measurements showed the initial phase of the reaction to be faster by an order of magnitude than for the homogeneous analogue, Bu\textsubscript{4}N[Rh(CO)\textsubscript{2}I\textsubscript{2}], at 25 °C in CH\textsubscript{2}Cl\textsubscript{2}. Reaction of immobilised cis-[Rh(CO)\textsubscript{2}I\textsubscript{2}]\textsuperscript{-} followed a double-exponential decay, possibly indicating modulation of reactivity by different environments within the microporous polymer. Catalytic methanol carbonylation has been demonstrated for the polymer-supported catalyst, with activity about 50% that of the homogeneous catalyst under the same conditions. Recovery of the supported catalyst was achieved in a straightforward manner and the recycled material retained comparable catalytic activity in a subsequent carbonylation experiment.

Polymer-supported catalysts of this type present the opportunity to simplify product/catalyst separation and remove catalyst solubility constraints, thereby enhancing process productivity and
efficiency. More generally, we anticipate that these support materials will be applicable in the
design of a range of hybrid homogeneous/heterogeneous processes that combine the benefits of
each approach. The efficient mixing in solution and ability to incorporate molecular catalysts
should ensure high catalytic activity, while the ease of recovery removes the need for more costly
recycling procedures that can lead to catalyst degradation.

**Experimental**

**Synthesis of PEG$_{113}$-Br**

PEG$_{113}$-Br was prepared in a method similar to that reported previously.$^{53}$ Poly(ethylene glycol)
monomethyl ether (8 g, 1.6 mmol, 1 eq.) was dissolved in anhydrous toluene (100 mL). Triethylamine (0.32 mL, 2.3 mmol, 1.4 eq.) was added and the solution was cooled to 0 °C. 2-
bromoisobutyryl bromide (0.26 mL, 2.1 mmol, 1.3 eq.) was added dropwise over the course of 1
h before being left to stir overnight at room temperature. The solvent was reduced before being
precipitated into cold diethyl ether (200 mL). The crude product was dried under vacuum and
dissolved in water before being extracted with CH$_2$Cl$_2$. The organic layers were collected,
combined and dried over MgSO$_4$ before the solvent was removed under reduced pressure to afford
the PEG$_{113}$-Br product, which was stored at 5 °C (87%), (Anal. found: C, 53.8; H, 9.1. Expected
C, 54.0; H, 9.0%).

**Synthesis of PEG-based macromolecular chain transfer agent (macro-CTA)**

The PEG-based macro-CTA was synthesised in an identical procedure to that previously
reported.$^{47}$ Dodecane thiol (0.60 mL, 2.5 mmol, 1 eq.) was added to a stirred suspension of K$_3$PO$_4$
(0.53 g, 2.5 mmol, 1 eq.) in acetone (50 mL) and stirred for 10 min. Carbon disulfide (0.36 mL, 6
mmol, 2.5 eq.) was added to the suspension and left to stir for a further 10 min. PEG$_{113}$-Br (10 g,
2 mmol, 0.8 eq.) in acetone (30 mL) was added to the suspension, which was left to stir overnight at room temperature. The solution was concentrated in vacuo and the crude product was precipitated by addition of n-hexane (100 mL). This was isolated by filtration, dissolved in acetone and the precipitation procedure repeated once more using n-hexane and then once using diethyl ether. The sample was dried in vacuo at 40 °C for 16 h to afford the RAFT macro-CTA (88%), (Anal. found: C, 54.5; H, 9.1; S, 1.8. Expected: C, 54.5; H, 9.1; S, 1.8%).

**Synthesis of 1**

The PEG-based macro-CTA (0.26 g, 0.05 mmol, 1 eq.) was added to a 1:1 (w/w) mixture of water (228 mL) and ethanol (289 mL) under N₂. DVB (2.13 mL, 15 mmol, 300 eq.) and 4VP (1.65 mL, 15 mmol, 300 eq.) were added to create a 1% wt. solution. The solution was bubbled with nitrogen gas to remove any oxygen before heating to 70 °C. Polymerisation was initiated through the addition of potassium persulfate (KPS, 2.7 mg, 0.01 mmol, 0.2 eq.) and the mixture was held at 70 °C for 24 h. The product was collected by centrifugation at 4500 rpm for 1 hour before being stirred with diethyl ether to remove any unreacted monomer. Finally, the white solid was isolated through vacuum filtration and dried in vacuo at 40 °C for 16 h (0.914 g, 30%), (Anal. found: C, 87.1; H, 7.7; N, 1.7. Expected for PEG₁₁３DVB₃₀₀₄VP₃₀₀: C, 84.5; H, 7.4; N, 5.5. Expected for PEG₁₁３DVB₃₀₀₄VP₆₆: C, 86.8; H, 7.8; N, 1.7%).

**Post-synthetic modification of 1 to form 2**

A suspension of 1 (596 mg) in a mixture of CHCl₃ (60 mL) and MeI (6 mL) was generated by sonication of the mixture for 30 min. This suspension was then stirred at 75 °C under reflux for 72 h. The resulting yellow suspension was centrifuged at 4500 rpm for 1 h before decanting the supernatant and washing the solid in Et₂O (20 mL × 2). The product was dried under dynamic
vacuum at 80 °C for 16 h to give 2 as a yellow powder (564 mg). (Anal. found: C, 76.9; H, 6.9; N, 1.7; I, 10.5. Expected for product with 80% 4VP sites quaternised: C, 77.5; H, 7.1; N, 1.5; I 10.6%).

Post-synthetic modification of 2 to form 3

Dry CHCl₃ (40 mL) was added to a mixture of 2 (487 mg) and [Rh(CO)₂I]₂ (100 mg, 0.17 mmol) under N₂ gas. The mixture was sonicated for 30 minutes to suspend the nanoparticles and then stirred at room temperature for 16 h. The solvent was removed \textit{in vacuo} and the solid residue was stirred in dry \textit{n}-hexane (50 mL) for 30 min. The solid was collected by filtration and washed with dry \textit{n}-hexane (25 mL × 2). The product was dried under high vacuum for 16 h and then stored at 4 °C under CO. Product 3 was obtained as a brown powder (440 mg) (Anal. found: C, 59.0; H, 5.1; N, 1.9; I, 22.0; Rh, 4.5. ν(C≡O)/cm⁻¹ (KBr disc) 2062, 1990).

Kinetic measurements on reaction of 3 with MeI

A dispersion of 3 (~10 mg) in CH₂Cl₂ (3 mL) was generated by sonication of the mixture for 30 min. The required amount of MeI was added to a 2 mL volumetric flask and this was made up to the mark with the suspension of 3 in CH₂Cl₂ and shaken. A sample of the reaction mixture was injected into an IR liquid cell (CaF₂ windows, 0.5 mm path length) fitted with a thermostatted jacket (25 °C). IR spectra in the region 2200-1500 cm⁻¹ were recorded at regular intervals, using a spectrum of the appropriate solvent mixture as the background reference. Absorbance vs. time data for the frequencies of interest were analysed using Origin software.

Catalytic carbonylation experiments

Reactions were monitored \textit{in situ} by high-pressure IR spectroscopy using a cylindrical internal reflectance (CIR)\textsuperscript{54} cell comprising an autoclave (Parr) modified to accommodate a crystalline silicon CIR rod, as described previously.\textsuperscript{18, 55, 56} Spectra were recorded using a Perkin-Elmer Spectrum GX FTIR spectrometer fitted with an MCT detector. The cell was placed directly in the
spectrometer sample compartment and aligned to maximise IR energy throughput using a tilt table.

A background spectrum was recorded using the appropriate solvent mixture at 120 °C. In a typical procedure, a dispersion of the supported catalyst 3 was generated by addition of dry CHCl₃ (5 mL) to 2 (100 mg) and [Rh(CO)₂I₂]₂ (10 mg, 0.017 mmol) under CO. The mixture was sonicated for 30 min and stirred for 16 h at room temperature. Separately, MeI (0.5 mL) and dry MeOH (1 mL) were added to a 5 mL volumetric flask which was made up to the mark with dry CHCl₃. This solution and the catalyst suspension were added to the CIR cell and was flushed five times with CO. The cell was then pressurised with CO (10 bar) and heated to 120 °C. IR spectra were recorded at 5 min intervals over the course of 4 h in the region of 2200-1500 cm⁻¹. At the end of the experiment, the solid was recovered by centrifugation. This sample was used in a subsequent catalytic experiment with fresh CHCl₃ (8.5 mL), MeI (0.5 mL) and MeOH (1 mL) added to the cell. For comparison with a homogeneous system, an experiment was carried out under identical conditions using [Rh(CO)₂I₂]₂ (10 mg, 0.017 mmol) with Bu₄NI (13 mg, 0.035 mmol) in place of polymer support 2.

**Author contributions**

S.A.I. and A.M.J. performed the synthesis, characterisation, kinetic and catalytic experiments. M.J.D. performed the SAXS studies. R.D. and A.H. supervised the project. S.A.I., A.M.J., M.J.D., R.D. and A.H. co-wrote the manuscript.

**Conflicts of interest**

The authors declare no conflicts of interest.
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Electronic Supporting Information (ESI) available: Details of materials and synthetic methods, instrumentation, analytical, gas sorption, dispersibility and kinetic data, determination of TOF values (PDF).

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A rhodium carbonylation catalyst is immobilised on dispersible microporous polymer nanoparticles, facilitating recyclability and *in situ* kinetic measurements for a key step of the catalytic cycle.
Heterogenisation of a Carbonylation Catalyst on Dispersible Microporous Polymer Nanoparticles

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Supporting Information

S1 Materials and synthetic methods
S2 Instrumentation
S3 Elemental and ICP-MS analysis data (Table S1)
S4 Volumetric gas sorption data (Figure S1)
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S8 Catalytic carbonylation reactions – determination of TOF values
S1. Materials and synthetic methods

Dry CH₂Cl₂, CHCl₃, toluene and n-hexane were obtained from a Grubbs solvent purification system in which the solvents were degassed prior to being passed through activated alumina and a supported copper catalyst to remove protic contaminants and trace oxygen respectively.¹ These solvents were stored under N₂ and used within 24 h of collection from the dry solvent system. Other solvents were purchased from either Fisher Scientific or Sigma-Aldrich (HPLC grade unless otherwise stated) and were used without further purification. Monomers divinylbenzene (DVB, technical grade 80%, Sigma Aldrich) and 4-vinyl pyridine (4VP, 95%, Sigma Aldrich) were passed through alumina to remove the inhibitor prior to polymerisation. Other reagents were purchased from either Fisher Scientific or Sigma-Aldrich and used without further purification. Rhodium trichloride hydrate (RhCl₃·xH₂O) was purchased from Precious Metals Online and rhodium precursors [Rh(CO)₂Cl]₂ and [Rh(CO)₂I]₂ were synthesised according to literature procedures.²⁻³ Standard Schlenk techniques and glassware were used for preparative reactions.

S2. Instrumentation

Infra-red spectra of polymeric materials and supported catalyst were collected using a Perkin-Elmer 100 FTIR spectrometer. Samples were prepared by grinding with a 20× excess of pure KBr pre-dried overnight in a vacuum oven at 80 °C. The sample was pelletised at high pressure (10 tons) and analysed as a thin transparent disc.

Nitrogen gas sorption isotherms were collected at 77 K using approximately 100 mg of sample on an ASAP 2020 Micromeritics volumetric adsorption analyser. Prior to analysis all samples except 3 were degassed for at least 16 h at 120 °C under a vacuum of at least 10⁻⁵ bar. 3 was degassed under the same vacuum level but without heating to avoid any decomposition of the supported Rh complex. BET surface areas were calculated over a relative pressure range
of 0.01 – 0.15 $p/p_0$. Pore size distributions and pore volumes were calculated from the adsorption isotherms and modelled using the nonlocal density functional theory model (NL-DFT) for N$_2$ on carbon slit pores found within the micromeritics ASAP software.

Solid-state NMR samples were packed into 4 mm zirconia rotors and transferred to a Bruker Avance III HD spectrometer. 1D $^1$H-$^{13}$C cross-polarisation magic angle spinning (CP/MAS) NMR experiments were measured at 125.76 MHz (500.13 MHz 1H) at a MAS rate of 10.0 kHz. The $^1$H $\pi/2$ pulse was 3.4 $\mu$s, and two-pulse phase modulation (TPPM) decoupling was used during the acquisition. The Hartmann-Hahn condition was set using hexamethylbenzene. The spectra were measured using a contact time of 2.0 ms. The relaxation delay, $D_1$, for each sample was individually determined from the proton T$_1$ measurement ($D_1 = 5 \times T_1$). Scans were collected until a sufficient signal to noise ratio was obtained, typically greater than 1094 scans. The values of the chemical shifts are referred to that of TMS.

Carbon, hydrogen, nitrogen and sulphur elemental analysis was performed by combustion of an amount of sample in a stream of pure oxygen. The sample was placed in a tin capsule and introduced into the combustion tube of the Elementar Vario MICRO Cube CHN/S analyser via a stream of helium. Combustion products were analysed through after being passed through a copper tube to remove excess oxygen and reduce any NO$_x$ to N$_2$. Gases were separated using a Thermal Programmed Desorption column and detected using a Thermal Conductivity Detector.

Iodide analysis was performed using the Schöninger flask combustion method in which an amount of sample is combusted in an oxygen-enriched environment, the resultant gases are absorbed and a titration is conducted to determine the iodide concentration.

Transmission electron microscopy (TEM) studies were conducted using a Philips CM 100 instrument operating at 100 kV and equipped with a Gatan 1 k CCD camera. A diluted solution of the polymer material (0.10% w/w) was placed on carbon-coated copper grids, allowed to dry and then exposed to ruthenium(VIII) oxide vapor for 7 min at 20 °C prior to analysis. The
ruthenium(VIII) oxide was prepared as follows: Ruthenium(IV) oxide (0.30 g) was added to water (50 g) to form a black slurry; addition of sodium periodate (2.0 g) with stirring produced a yellow solution of ruthenium(VIII) oxide within 1 min.⁴

SAXS patterns were recorded at a synchrotron source (Diamond Light Source, station I22, Didcot, UK; Experiment ID SM23501) using monochromatic X-ray radiation (X-ray wavelength $\lambda = 0.999$ Å, with scattering vector $q$ ranging from 0.0027 to 0.25 Å⁻¹, where $q = 4\pi \sin \theta / \lambda$ and $\theta$ is one-half of the scattering angle) and a 2D Pilatus 2M pixel detector (Dectris, Switzerland). Scattering data were reduced and normalised, with glassy carbon being used for the absolute intensity calibration utilising standard routines available at the beamline⁵ and further analysed (background subtraction and data modelling) using Irena SAS macros for Igor Pro.⁶
S3. Elemental and ICP-MS analysis data

Elemental analysis data for 1 (Table S1) demonstrate that both DVB and 4VP monomers and the RAFT agent are incorporated into the polymeric material. The nitrogen content is significantly lower than that calculated on the basis of the 1:1 ratio of DVB and 4VP monomers used in the polymerisation reaction. The N content is consistent with an approximate composition for 1 of PEG_{113}DVB_{300}4VP_{60} (i.e. 5:1 DVB:4VP ratio). The iodide content of post-synthetically modified polymer 2 is consistent with quaternisation of ~80% of the pyridine sites in 1. ICP-MS analysis of 3 indicates a Rh content of 4.5% by mass. Incorporation of a [Rh(CO)I_2]^- for each methyl pyridinium site in 2 is calculated to give a Rh content of ~6.9%. Complete incorporation of all Rh added in the synthesis of 3 would give a Rh content of ~6.1%.

Table S1. Elemental analysis data for material 1, post-synthetically modified polymer 2 and supported Rh catalyst 3, along with calculated values for different compositions of polymer.

|                | %C | %H | %N | %S | %I | %Rh |
|----------------|----|----|----|----|----|-----|
| Observed for 1 | 87.1 | 7.7 | 1.7 | 0.6 |    |     |
| Calc. for PEG_{113}DVB_{300}4VP_{60} | 84.5 | 7.41 | 5.53 | 0.13 |    |     |
| Calc. for PEG_{113}DVB_{300}4VP_{12} | 86.8 | 7.76 | 1.66 | 0.19 |    |     |
| Observed for 2 | 76.9 | 6.9 | 1.7 | 0.7 | 10.5 |     |
| Calc. for PEG_{113}DVB_{300}(4VPMe^+I^-)_{60} (full quaternisation) | 75.5 | 6.95 | 1.42 | 0.16 | 12.9 |     |
| Calc. for PEG_{113}DVB_{300}4VP_{12}(4VPMe^+I^-)_{48} (80% quaternisation) | 77.5 | 7.09 | 1.46 | 0.17 | 10.6 |     |
| Observed for 3 | 59.0 | 5.1 | 1.9 | 22.0 | 4.5* |     |
| Calc. for PEG_{113}DVB_{300}4VP_{12}(4VPMe^+[Rh(CO)I_2]^-)_{48} | 64.2 | 5.73 | 1.18 | 0.14 | 17.1 | 6.93 |

*Rh content of 3 determined by ICP-MS
S4. Volumetric gas sorption data

Figure S1. Cumulative surface area vs. pore volume for 1 (black), 2 (red) and 3 (blue).

S5. Dispersibility

A sample of 1 was suspended in CH₂Cl₂ and UV-vis spectra of the dispersion were recorded over 72 h (Figure S). Over 80% of 1 remains in suspension after 72 h. Note: in contrast, the insoluble analogue to 1 (synthesised via simple radical polymerisation between 1,4-divinylbenzene and 4-vinylpyridine) could not be suspended for a single UV-vis spectrum to be recorded.

Figure S2. Series of UV-vis spectra of a suspension of 1 in CH₂Cl₂ over 72 h.
S6. Particle morphology

Figure S3. Schematic of particle aggregate morphology.
S7. Kinetic data for reaction of MeI with 3

Table S2. Pseudo first-order rate constants derived from single and double exponential decay fits and their R² values for reaction of 3 with MeI in CH₂Cl₂ (25 °C).

| [MeI] / mol dm⁻³ | 10⁴ × k_{obs}¹ / s⁻¹ | R²   | 10⁴ × k_{obs}² / s⁻¹ | 10⁴ × k_{obs}² / s⁻¹ | R²   |
|------------------|-----------------------|------|----------------------|----------------------|------|
| 1.0              | 4.44                  | 0.9791 | 11.30               | 2.06               | 0.9997 |
| 2.1              | 6.25                  | 0.9822 | 13.34               | 3.44               | 0.9998 |
| 4.2              | 10.01                 | 0.9890 | 17.46               | 5.15               | 0.9997 |
| 6.2              | 13.00                 | 0.9862 | 29.02               | 5.05               | 1.0000 |
| 8.3              | 16.52                 | 0.9953 | 28.88               | 6.09               | 1.0000 |

Fits to a double exponential decay used equation S1 to give values of k_{obs}¹ and k_{obs}².  

\[ A_t = A_\infty + A_1 e^{-k_{obs}^1 \times t} + A_2 e^{-k_{obs}^2 \times t} \]  

Figure S4. Plot of IR absorbance vs. time for band at 1987 cm⁻¹ during reaction of 3 with MeI (1.0 M) in CH₂Cl₂ (25 °C). The data are fitted by equation S1.
Figure S5. Plot of IR absorbance vs. time for band at 1987 cm$^{-1}$ during reaction of 3 with MeI (2.1 M) in CH$_2$Cl$_2$ (25 °C). The data are fitted by equation S1.

Figure S6. Plot of IR absorbance vs. time for band at 1987 cm$^{-1}$ during reaction of 3 with MeI (4.2 M) in CH$_2$Cl$_2$ (25 °C). The data are fitted by equation S1.
Figure S7. Plot of IR absorbance vs. time for band at 1987 cm\(^{-1}\) during reaction of 3 with MeI (6.2 M) in CH\(_2\)Cl\(_2\) (25 °C). The data are fitted by equation S1.

Figure S8. Plot of IR absorbance vs. time for band at 1987 cm\(^{-1}\) during reaction of 3 with MeI (8.3 M) in CH\(_2\)Cl\(_2\) (25 °C). The data are fitted by equation S1.
S8. Catalytic carbonylation reactions – determination of TOF values

For each experiment, the rate of formation of methyl acetate was determined from the slope of a plot of $\text{Abs}(1741 \text{ cm}^{-1})$ vs. time, calibrated by IR spectra of standard solutions of methyl acetate in the CIR cell under the conditions of the catalytic reaction, to give an effective extinction coefficient, $\varepsilon_{\text{eff}(1741)} = 19.3 \text{ mol}^{-1}$.  

Example calculation (supported catalyst 3, 10 % MeOH, 5 % MeI in CHCl$_3$, 120 °C, 10 bar CO, $3.5 \times 10^{-5} \text{ mol Rh}$):

Slope $\text{Abs}(1741 \text{ cm}^{-1})$ vs time = 0.0077 h$^{-1}$  
$d[\text{MeOAc}]/dt = 0.0077 \text{ h}^{-1}/19.3 \text{ mol}^{-1} = 4.0 \times 10^{-4} \text{ mol h}^{-1}$

TOF = $4.0 \times 10^{-4} \text{ mol h}^{-1} / 3.5 \times 10^{-5} \text{ mol} = 11.4 \text{ h}^{-1}$

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