Polymer Supported Iridium Catalysts for the Capture and Conversion of CO₂ to Formic Acid

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Introduction
Carbon dioxide (CO₂) is a promising candidate as renewable resource for the production of useful materials because it is abundant, non-toxic, and economical [1]. One such example of this is the direct hydrogenation of CO₂ which leads to the production of formic acid. Formic acid is a beneficial product that could be used as a preservative, an insecticide, a reducing agent of metallic ions, a precursor for further upgrade to esters, allyl alcohols, and oxalic acid, and others [2]. The objective of this work was to design a new catalyst capable of both capturing CO₂ and converting it to formic acid once captured. To that end, a highly-branched polyethyleneimine (PEI) polymer was modified at the primary amines to form a bidentate imine-triphenylphosphate functionality and then coordinated with an Ir metal center (Scheme 1). The resulting material was then referred to as PEI-PN-Ir. The PEI backbone of the catalyst contains multiple types of amine functionalities capable of capturing CO₂ in an aqueous environment [3], potentially bringing it in close proximity to the PN-Ir functionality which is capable of acting as a hydrogenation catalyst [4]. Additionally, several other similar catalysts with different ligand P and N type functionality were synthesized. These materials were then tested for catalytic activity in the hydrogenation of CO₂ to formic acid.

![Scheme 1. Synthesis sequence for PEI-PN-Ir.](image)

Materials and Methods
To synthesize PEI-PN-Ir, PEI and 2-(diphenylphosphino)benzaldehyde were reacted in toluene. The resultant product was then refluxed in ethanol with IrCl₃. In a typical reaction, a 50 mL stainless steel batch reactor rated to 300 °C and 3000 psig was charged with a 27 mL mixture of water, triethylamine (base), 1,4-dioxane (internal standard), and PEI-PN-Ir in varying quantities. The reactor was then purged three times with H₂ and then charged with 40 bar H₂ and stirred for 30 minutes to activate the catalyst. The headspace in the reactor was then evacuated and the reactor was charged with 20 bar CO₂ and 20 bar H₂ at room temperature. The mixture was heated to the appropriate temperature and allowed to react. The reaction results were analyzed by ¹H NMR using dioxane as an internal standard.

Results and Discussion
The synthesized materials were subjected to a series of techniques to identify the structure and properties including FTIR, XPS, and NMR. PEI-PN-Ir was tested for catalytic activity in the hydrogenation of CO₂ to formic acid. In the first study, the total system volume (water + base) was kept constant but the relative ratio of water to base was altered (Table 1). When the system contained no water, no formic acid was produced indicating water was a necessary component in the reaction. Successively doping in more water lead to higher reaction rates until a maximum at 5% base was reached. At 0% added base, the TOF value while low was non-zero indicating the PEI-PN-Ir material was capable of capturing CO₂ and subsequently converting it to formic acid. The PEI-PN-Ir material was tested for recyclability which showed an initial decrease in activity after the first cycle but then reaction rates remained stable for subsequent reactions. Additionally, similar catalysts with different P and N-type functionalities were synthesized. It was determined that the combination of imine and triphenylphosphine functionality in PEI-PN-Ir yielded the highest reaction rates.

<table>
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<tr>
<th>Base Vol. %</th>
<th>Activity (mol FA mol Ir⁻¹ h⁻¹)</th>
<th>Base Vol. %</th>
<th>Activity (mol FA mol Ir⁻¹ h⁻¹)</th>
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Significance
This work exhibits a newly-synthesized, multi-functional catalyst capable of both capturing CO₂ from the gas phase, bringing it into the aqueous phase, and catalyzing its hydrogenation to formic acid.

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References
5. McNamara, N.D., Xu, Z., Hicks, J.C. manuscript in progress
6. Xu, Z., McNamara, N.D., Hicks, J.C. Submitted