Surface Functionalization of Nanoparticles

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ABSTRACT

Palladium nanoparticles were synthesized via photolysis of palladium tetrakistriphenylphosphine with no addition of surfactant and reducing agent. The strength of chemisorption of carbon monoxide on the surface of palladium nanoparticles was studied. The source of carbon monoxide used in this project was generated in situ by photolysis of Mn(CO)\textsubscript{5}Br and dehydration of formic acid. However, carbon monoxide did not seem to be able to chemisorb onto the surface of palladium nanoparticles. The results indicated that it was not feasible for carbon monoxide to be chemisorbed onto the surface of palladium nanoparticles at atmospheric pressure. Further studies on the research papers on kinetics of adsorption and desorption could be used to explain why carbon monoxide does not adsorb onto the surface of palladium nanoparticles.

INTRODUCTION

Palladium has been intensively studied over the recent years for its efficient catalytic properties. Palladium exhibits its capabilities in different areas such as carbonylation\textsuperscript{1}, hydrogenation, C-C coupling reactions.

Using palladium nano-catalyst over metallic palladium in a reaction has a few advantages. First, it is to heterogenize a homogeneous catalyst. Although the catalyst is in solid phase, it still exhibits catalytic properties. Next, it is the ease of recovery of the catalyst, being in a different phase, palladium nano-catalyst can be easily recovered by centrifugation. Last but not least, it is the recyclability of the nano-catalyst.

In this project, the chemisorption of carbon monoxide gas on palladium nanoparticles at room temperature and atmospheric pressure is being studied. It is also to probe how strongly is carbon monoxide bounded onto the palladium surface. The study of chemisorption of carbon monoxide on palladium surface at room temperature and atmospheric pressure has yet to be reported in literature.

IR spectroscopy, UV spectroscopy and Transmission Electron Microscopy have been used extensively in this project for the characterization of nanoparticles and in the probing of the chemisorption of carbon monoxide on the surface of palladium nanoparticles. In addition, Energy Dispersive X-ray Spectroscopy (EDX) was used to confirm the identity of the nanoparticles formed.

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MATERIALS AND METHODS

Synthesis of Palladium nanoparticles
Pd(PPh$_3$)$_4$ (12 mg, 0.01 mmol; 99% Sigma-Aldrich) was dissolve in a solvent pair of 5 mL ethanol (AR grade, Aldrich) and 5 mL N,N-dimethylformamide (DMF) (HPLC grade, Aldrich). The resultant yellow solution was stirred well and was then irradiated under long range UV lamp for 6 hours. The nanoparticles formed was centrifuged for an hour and then redispersed in tetrahydrofuran (AR grade, Aldrich). The palladium nanoparticles formed was characterized using UV spectroscopy, TEM imaging and EDX.

Chemisorption of carbon monoxide on palladium nanoparticles

Photolysis of Mn(CO)$_5$Br
Mn(CO)$_5$Br was dissolved in the palladium nanoparticles solution and stirred well. The solution was then irradiated with 355 nm pulsed YAG laser under vigorous stirring. The nanoparticles were then centrifuged and redispersed in chloroform. IR spectroscopy was then performed to check for the presence of carbonyl peaks.

Dehydration of formic acid
Carbon monoxide generated by dehydration of formic acid was bubbled into the palladium nanoparticles solution for 90 minutes on vigorous stirring. After 90 minutes, IR spectroscopy was then performed on the solution to check for the presence of carbonyl peaks.

RESULTS AND DISCUSSION

Synthesis of Palladium Nanoparticles
The synthesis of palladium nanoparticles was successful. This is supported by both the UV-vis spectra and TEM images of the nanoparticles. The proposed reaction scheme of the formation of palladium nanoparticles is as follows:
In this reaction, no addition of reducing agent was because the precursor, \( \text{Pd(PPh}_3\text{)}_4 \), already contained palladium in the zero oxidation state.

When \( \text{Pd(PPh}_3\text{)}_4 \) undergoes photolysis under UV lamp, the palladium – phosphorus bonds are dissociated. The dissociated TPP will play the role of surfactant in this reaction. The exposed metal atoms will then assemble and form nanoparticles. These nanoparticles were then capped by the TPP in the solution.

The controlled reactions that were done for generation of carbon monoxide gas showed that indeed there was carbon monoxide produced. However, these generated carbon monoxide was unable to chemisorbed on the surface of the palladium nanoparticles, at least, it is not observed.

**Analysis on the negative results**

Surface chemistry and adsorption/desorption rate measurements are often done in ultra high vacuum system (UHV) where the pressure is below 100 nanoPascal or about \( 10^{-9} \) Torr. By adopting UHV condition, molecules has very big mean free path and therefore the molecular energetic are often determined by the ambient temperature. This will affect how well information at molecular level can be related to experimental data obtained at elevated pressure.

There were many competing factors for the adsorption on the palladium nanoparticles surface. In the solution mixture, the palladium nanoparticles are exposed to various molecules such as TPP (surfactant), THF (solvent) and oxygen (air). All these would further decrease the probability of carbon monoxide adsorbing onto palladium surface, as the adsorption of carbon monoxide gas is dependent on the surface coverage on the palladium itself. The metal surface is usually clean by heating or bombardment by noble gas ions (e.g. \( \text{Ar}^+ \)) followed by annealing.
Palladium is able to catalyze the reaction between adsorbed oxygen and carbon monoxide to carbon dioxide. Both carbon monoxide and oxygen are capable of adsorbing onto palladium surface while carbon dioxide does not. This could explain why carbon monoxide absorption was not observed in the IR spectra.

V. Bertin et al. reported that due to the interaction between gas phase carbon monoxide and the adsorbed species, the activation energy for desorption is dramatically decreased. Yamada et al. mentioned that at pressure higher than µPa scale, the absorption rate would be too fast to be observable. This is in coherence to the values reported by V. Bertin et al. and P. Junell et al.

CONCLUSION

Palladium nanoparticles were successfully synthesized by photolysis of Pd(PPh₃)₄. No addition of surfactant and/or reducing agent was required in this synthesis.

Adsorption of carbon monoxide gas onto palladium nanoparticles surface is not achievable in solution phase, room temperature and atmospheric pressure. Study on carbon monoxide adsorption on palladium nanoparticles can only be done in UHV system via in situ studies.

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REFERENCE

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