

MONOMETALLIC AND BIMETALLIC CATALYSTS BASED ON Pt AND Cu FOR THE SELECTIVE TRANSFORMATION OF FURFURAL

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Abstract

The utilization of biomass for the co-production of sustainable fuels and chemicals has the power to transform global energy and materials markets. This necessitates the development of new catalytic processes capable of selectively transforming highly functionalized organic molecules into either alternative 'drop in' chemical intermediates and fuels, or entirely to products with novel properties. Here, we investigate the selective hydrogenation of furfural to furfuryl alcohol under extremely mild reaction conditions over monodisperse Pt, Cu and Pt/Cu nanoparticles supported on a variety of solid oxide supports.^[1] The results are compared with Temperature Programmed Desorption (TPD) and Scanning Tunneling Microscopy (STM) studies of furfural in the presence of H₂ on a Pt(111) extended surface.^[2] Finally, we report recent results on the reactivity of furfural on highly diluted PtCu alloy nanoparticles. Additionally, Single Atom Alloys (SAA)^[3] have been investigated for this reaction.

Introduction

The development of novel catalytic processes for the selective transformation of bioderived organic molecules into useful chemicals, chemical intermediates, and commercial products is a key requirement for the realisation of a bioresource-based chemical industry. Therefore, fundamental understanding of the mechanistic aspects governing controlling such catalytic processes is critical. Lignocellulosic and oleochemical biomass are very attractive from a commercial point of view due to their high natural abundance and the vast number of products that can be derived from them. In this respect, furfural is one of the most promising renewable platform compounds.^[1] It is obtainable via the acid-catalyzed hydrolysis of C5 sugars such as xylans and xylose and can be upgraded for a range of applications.^[4-7] The majority of furfural produced annually worldwide is hydrogenated to furfuryl alcohol for use as an adhesive, resin, or corrosion-resistant coating. Current industrial processes rely on a copper chromite catalyst, typically operated at high H₂ pressure and temperature, this catalyst will rapidly undergo decomposition to chromic oxide over time which damages both the environment and human health, disposal of this material is prohibited in landfill.^[1]

Here we investigate the selective hydrogenation of furfural to furfuryl alcohol under extremely mild reaction conditions over Pt nanoparticles supported on SiO₂, ZnO, γ -Al₂O₃, CeO₂ and MgO.^[1] The results are compared with TPD and STM studies of furfural on a Pt(111) extended surface under ultra high vacuum conditions (UHV).^[2] The results elucidate important features of furfural's adsorption and hydrogenation and correlate coverage-dependent orientation and self-assembly with selectivity toward hydrogenation versus decomposition pathways when in the presence of pre-adsorbed hydrogen. Finally, we report recent results on the reactivity of furfural on Pt/Cu bimetallic nanoparticles and ultra-dilute Pt deposited on host Cu nanoparticles, creating a SAA surface.

Experimental

Pt nanoparticles were synthesised by reducing $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ in ethylene glycol and encapsulating with polyvinylpyrrolidone, cleaning and suspending in EtOH. This was followed by addition to an oxide support such as: $\gamma\text{-Al}_2\text{O}_3$, CeO_2 , MgO , ZnO and SiO_2 . The resulting slurries were slowly dried under vacuo, and the resulting dried powders were calcined in air at 300 °C to remove the PVP stabiliser. The resulting materials were reduced at 200 °C under flowing 10% H_2/N_2 for 1 h, cooled and stored in air. Catalytic hydrogenation was performed using a 12-port Radleys Plus Reaction Station at a H_2 pressure of 1 atm. Single crystal work was conducted in an Ultra high vacuum (UHV) chamber operated at a base pressure of 3×10^{-10} Torr, equipped with an Omicron 4 grid retarding field analyzer for Low-Energy Electron Diffraction (LEED) or Auger Electron Spectroscopy (AES) and a VG 300 quadrupole mass spectrometer whose ionizer was positioned 6 mm from the front face of the sample. Measurements were performed with a linear heating ramp of 9.9 K s^{-1} .

Results and discussion

The platinum catalysed liquid phase hydrogenation of furfural was studied over five different oxide supports as a function of solvent and temperature. Furfural hydrogenation was found to be sensitive to Pt particle size, with those of approximately 4 nm being highly active and selective for the hydrogenation reaction in methanol, even at 50 °C, whereas smaller Pt nanoparticles present in the MgO and SiO_2 catalysts promote some decarbonylation to furan. Certain alcohols such as ethanol favour the formation of undesired acetal side products through reaction with furfural at 70 °C, although such competing reactions can be suppressed by lower temperature operation or through supporting Pt particles on more basic metal oxides. The results presented in Table 1 show that Pt containing $\gamma\text{-Al}_2\text{O}_3$, CeO_2 and MgO provide very high selectivities towards furfuryl alcohol and furfural conversions $\geq 70\%$. Pt/ ZnO leads to extensive decarbonylation of furfural over the ZnO support which appears to dominate Pt catalysis.

Table 1 . Furfural hydrogenation over Pt catalysts after 7 h reaction in methanol at 50 °C; 2-furaldehyde dimethyl acetal expressed as Solvent Product (SP)

Catalyst	Furfural Conversion / %	Furfuryl alcohol Selectivity / %	Furan Selectivity / %	SP Selectivity / %
Pt/ $\gamma\text{-Al}_2\text{O}_3$	80	99	1	0
Pt/ MgO	79	97	3	0
Pt/ CeO_2	77	98	1	1
Pt/ SiO_2	35	90	7	3
Pt/ ZnO	7	60	40	0

Our single crystal work demonstrates that the clean Pt(111) surface leads to the decomposition and decarbonylation of furfural to produce surface carbon and furan respectively. Pre-adsorbed hydrogen on Pt(111) minimises the decomposition furfural and the formation of furan while promotes the formation of furfuryl alcohol and methyl furan. At relatively higher temperatures the formation of methyl furan is observed, a product that was not observed in our liquid phase hydrogenation studies on Pt nanoparticles. The conversion of furfural appears to be higher at low coverages an effect associated with steric hindrance at high furfural coverages in agreement with our STM studies. Critically, furfural adsorbs relatively weaker on Pt(111) as compared to Pd(111) and Cu(111) consistent with vastly different chemistry the molecule presents on dispersed Pt and Pd catalysts. Our STM measurements found that at low furfural coverage, the molecule aligns planer to the surface, whereas at higher coverages the furfural aligns and tightly packs in an end on configuration. This is where the molecule interaction through the carbonyl group opposed to the ring system.

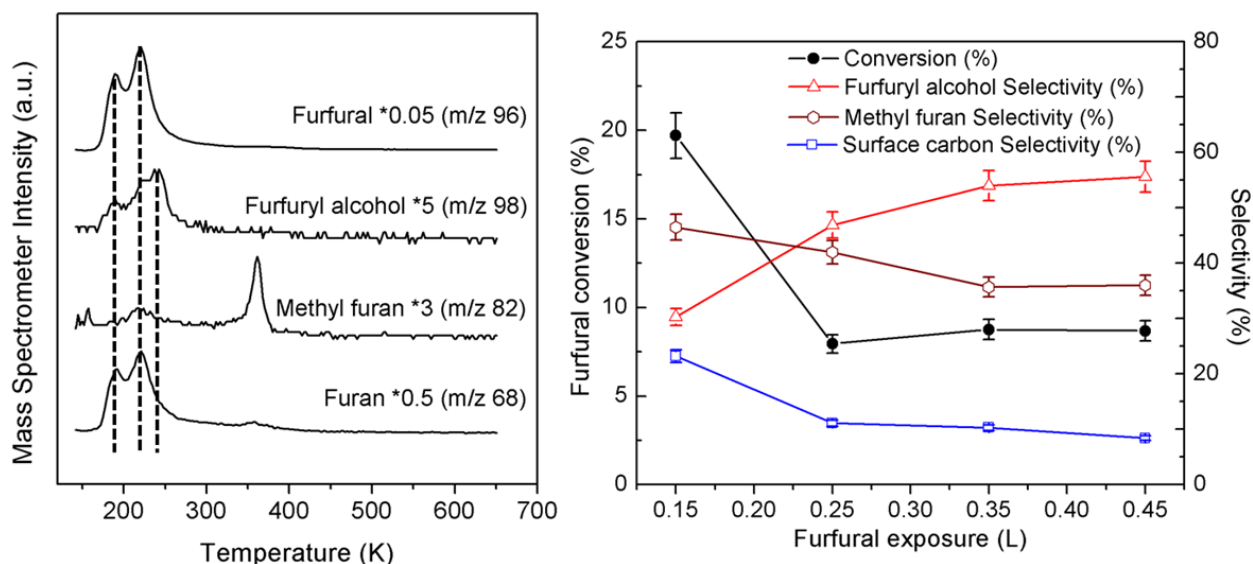


Figure 1. TPR data after exposing Pt(111) to 40 L H₂ and 0.25 L of furfural (left); conversion and selectivity results as function of furfural exposure with prior adsorption of 40 L of H₂.

The selective hydrogenation of furfural was studied over bimetallic PtCu nanoparticles to determine the effect of both noble metal dilution and if a beneficial effect is witnessed when using a PtCu₃ surface. Furfural hydrogenation was previously found to be sensitive to Pt particle size, with those of approximately 4 nm being highly active and selective for the hydrogenation reaction in methanol, even at 50 °C, whereas smaller Pt nanoparticles present in catalysts promote some decarbonylation to furan.¹ To limit decarbonylation reaction pathways and CO poisoning, the nanoparticles synthesised for this work were between 4-6 nm. Fig. 2 shows overlaid PXRD diffractograms of Pt₁₀₀, Cu₁₀₀, Pt₃₈Cu₆₇ and Pt₁₈Cu₈₂. There is a presence of the Cu(111) feature for the monometallic Cu catalyst and a PtCu₃ region for the bimetallic catalysts with no monometallic areas observable. Transmission Electron Microscopy in conjunction with Energy Dispersive X-ray Spectroscopy shows that the Pt₃₈Cu₆₇ bimetallic catalyst has nanoparticles with a random Pt and Cu dispersion, suggesting a true bimetallic structure.

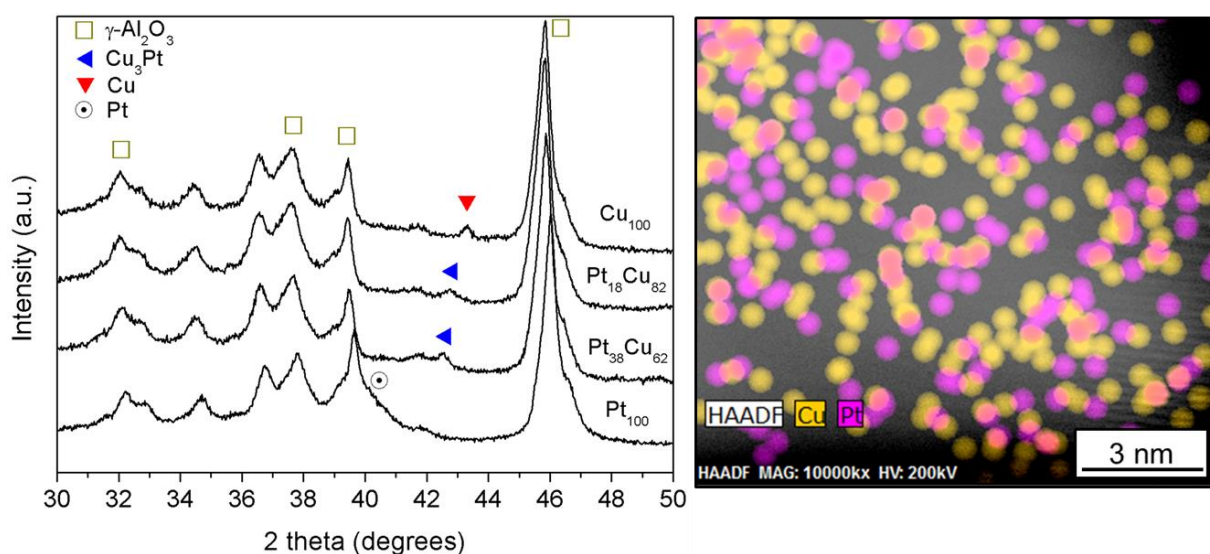


Figure 2 (left) Characterisation data of the monometallic Pt, Cu and bimetallic catalysts using PXRD and (right) Dark field HRTEM image of Pt₃₈Cu₆₂ with EDX line scan (Cu – orange, Pt – pink)

Batch catalytic measurements of the catalysts using a range of hydrogen pressures showed that the Pt₃₈Cu₆₂ bimetallic catalysts had far higher initial rates of reaction at 1.5 and 10 bar than the pure Pt/ γ -Al₂O₃ catalyst. PtCu₃ materials also had similar conversion and selectivity towards furfuryl alcohol after 7 h (Fig. 3). Pt containing catalysts were found to be superior under all conditions when compared with the monometallic Cu material. When reaction rates were normalised per gram of active metal in each reaction, the initial rates were found to be far faster for both the bimetallic PtCu than that of the monometallic Pt counterpart when at lower pressures (1.5 bar) (Fig. 3).

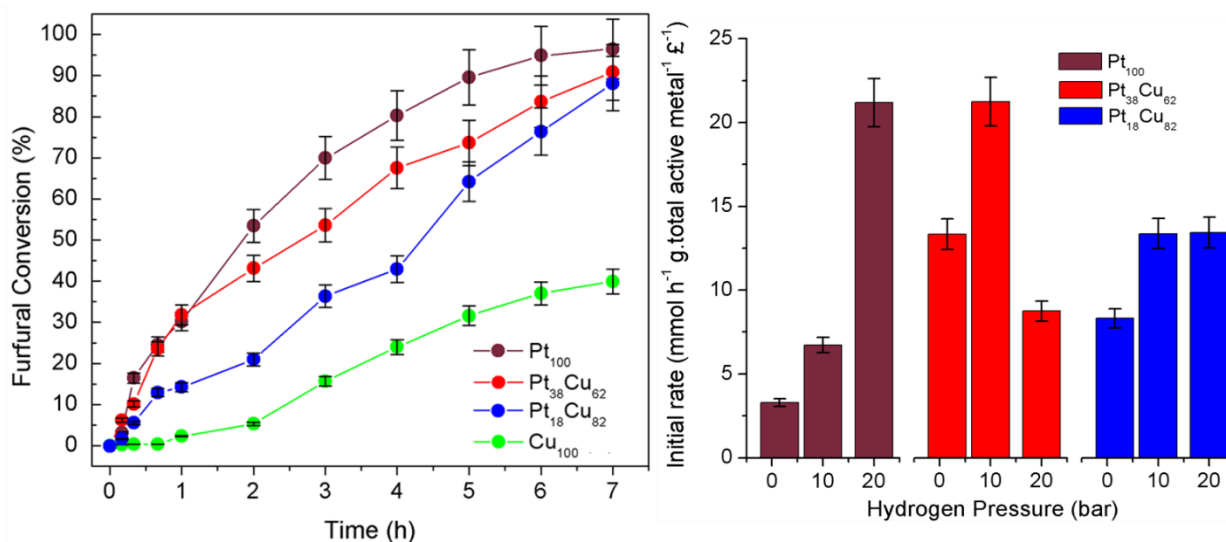


Figure 3. (left) Reactivity of the monometallic and bimetallic catalysts over 7 h and (right) the initial rate of reaction taken after the first hour, normalised for active metal content and cost (GBP).

Finally, recent work on Pt/Cu SAAs shows that relatively small amounts of Pt alloyed in the topmost layer of the Cu host particles have the ability to activate the relatively inert Cu surface at ambient pressure and low temperature for the selective hydrogenation of furfural to furfuryl alcohol. After a brief period of time where surface CuO is reduced, the activated surface is able to both adsorb hydrogen onto Pt atomic sites and react with the adsorbed furfural which preferentially interacts on Cu sites. The subsequent rates of reaction for the SAA are extremely high as compared with both monometallic and bimetallic catalysts with higher metal loadings. As a result, the SAA are a far more cost effect material due to the dilute Pt content.

Conclusions

It has been shown that furfural, an important biomass derived molecule, can be selectively hydrogenated under very mild temperature and hydrogen pressure conditions on a variety of Pt based catalysts. Although effective across a series of catalysts, 4 nm Pt nanoparticles supported on γ -Al₂O₃ were proved to be the most active and selective. The nature of the material and the mild operation conditions allow for its high recyclability. The single crystal work suggests that the presence of H₂ on the Pt surface suppresses the decarbonylation of furfural to furan and enables the hydrogenation of the molecule. The conversion of furfural appears to be higher at low furfural coverages due to steric hindrance. Finally, Pt/Cu alloys have been investigated and were found to be highly active and selective for the hydrogenation reaction. This is where a dilute Pt bimetallic alloy was found to exhibit higher rates of reaction and high furfuryl alcohol selectivity opposed to monometallic Pt benchmarks. Further Pt dilution was found to be even more beneficial after a period of inactivity due to a surface CuO layer, this is not an issue for bulk PtCu bimetallic alloys.

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References

- [1] M.J. Taylor, L. J. Durndell, M.A. Isaacs, C.M.A. Parlett, K. Wilson, A.F. Lee, G. Kyriakou. Appl. Catal. B-Environ. 180 (2016) 580-585.
- [2] M.J. Taylor, L. Jiang, J. Reichert, A.C. Papageorgiou, S.K. Beaumont, K. Wilson, A.F. Lee, J.V. Barth, G. Kyriakou. J. Phys. Chem. C 121 (2017) 8490-8497.
- [3] G. Kyriakou, M.B. Boucher, A.D. Jewell, E.A. Lewis, T.J. Lawton, A.E. Baber, H.L. Tierney, M. Flytzani-Stephanopoulos, E.C.H. Sykes. Science 335 (2012), 1209-1212.
- [4] K. Yan, G. Wu, T. Lafleur, C. Jarvis. Renewable Sustainable Energy Rev. 38 (2014) 663–676.
- [5] P. Gallezot. Chem. Soc. Rev. 2012, 41, 1538–1558.
- [6] M.J. Climent, A. Corma, S. Iborra. Green Chem. 16 (2014) 516–547.
- [7] D.C. Elliott, T.R. Hart. Energy Fuels 23 (2009) 631–637.