The hydrogenation of CO_2 to methanol over PdZn catalysts

Hasliza Bahruji[a], Robert D. Armstrong[a]*, Jonathan Ruiz Esquius[a], Michael Bowker[b], Graham Hutchings[a], Wilm Jones[b] and David Morgan[a]

[a] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff, UK, CF10 3AT*
[b]*Research Complex at Harwell, The UK Catalysis Hub, Didcot, Oxfordshire, UK, OX11 0FA*
**Corresponding author: ArmstrongR4@Cardiff.ac.uk*

Abstract: Eschewing the common trend towards use of catalysts comprising of Cu, it is reported that PdZn alloys are active catalysts for CO_2 hydrogenation. Deposition of Pd (5wt.%) onto ZnO via sol immobilisation affords a catalyst with appreciable activity and methanol selectivity (χ = 11 %, SMeOH = 60 %, 2.4 mol_{MeoH} kg_{cat}^{-1} h^{-1}, GHSV= 3,333 h^{-1}) at 250 °C/ 20 bar. Catalytic activity was assigned to a PdZn(1: 1) alloy formed when the catalyst is pre-reduced *in situ* (H_2, 400 °C, 1 h). Zn is implicated in passivating Pd, which would normally be expected to decompose the reaction's formate intermediates.

Keywords: CO_2 hydrogenation, methanol, PdZn

1. Introduction

Methanol is ubiquitous within the chemical industry, with global demand exceeding 57 Mt/annum. The majority of this is met through a two- step process whereby synthesis gas is produced via methane steam reforming (i) and then reacted over a $Cu/ZnO/Al_2O_3$ catalyst to prepare methanol (ii). The energy consumption of this process is estimated to exceed 1 exajoule (1×10^{18} J)/ annum globally, with a significant carbon footprint (*ca.* 88 Mt GHG eq.). In line with political and social pressure to decrease society's dependence on fossil fuels, there is growing interest in producing methanol through more sustainable routes. One promising route is catalytic CO_2 hydrogenation. Indeed, it is feasible that methanol be prepared kinetically with CO_2 as the carbon source, provided that H_2 is produced in a renewable/ sustainable manner.

2. Experimental

5 wt. % Pd was supported on ZnO via both incipient wetness impregnation (IWI) and sol-immobilisation (SIM). For IWI, an acidic solution of $PdCl_2$ was added to ZnO (Sigma Aldrich) with vigorous mixing. The paste was then dried in static air (120 °C, 2 h) and reduced in H_2 (400 °C, 3 h, 30 ml min^{-1}). For SIM, $PdCl_2$ was added to H_2O (800 ml). Polyvinylalcohol (PVA) was then added (PVA/Pd = 1.2 wt/wt). $NaBH_4$ (0.1 M, $NaBH_4$/Pd=5 mol/mol) was then added. After 30 min of sol generation, the colloid was immobilised by adding ZnO under vigorous stirring. After 2h the slurry was filtered and washed with deionised water before drying in air (120°C, 16 h). The general procedure for preparation of supported Pd catalysts by chemical vapour impregnation (CVI) is as follows; the support was dried (2 h, 150 °C) under vacuum. Once dried, the required mass of support was added to a Schlenk flask and Pd $(acac)_2$ + where applicable Zn $(acac)_2$ (Sigma Aldrich, 99.9% purity) added. Following physical mixing, the dry mixture was heated to 140 °C under vacuum (ca. 10^{-3} mbar) for 1 h. The sample was then calcined (550 °C, 20 °C min^{-1}, 16h) in static air.

Catalyst assessments were carried out in a fixed-bed continuous-flow reactor. Catalyst (0.5 g, 300-425 μm) was pre-reduced in a flow of H_2 (30 ml min^{-1}, 1 h, 400 °C, 1 bar). Reactions were then carried out at 250 °C (typically), 20 bar using a feed comprising H_2: CO_2: N_2 (3: 1: 1)(30 ml min^{-1}). Products and conversion were quantified via GC- FID and GC- TCD.

3. Results and discussion

A series of 5 wt. % supported Pd catalysts were prepared by sol immobilisation. It is clear from the conversion vs. selectivity plot in Fig.1 that 5 wt.% Pd/ZnO afforded relatively high CO_2 conversion (10 %) and methanol selectivity (53 %). This catalyst also showed low CH_4 selectivity of *ca.* 0.01 %. This is a key consideration as commercial applications favour re-feeding of unreacted CO_2. Owing to the expense associated with gas separation, low methane productivities are preferable. A significant decrease in χCO_2 to 1.7 % was observed upon decreasing Pd loading to 1 wt.%/ ZnO SIM– with S(MeOH) increasing to 76 %.

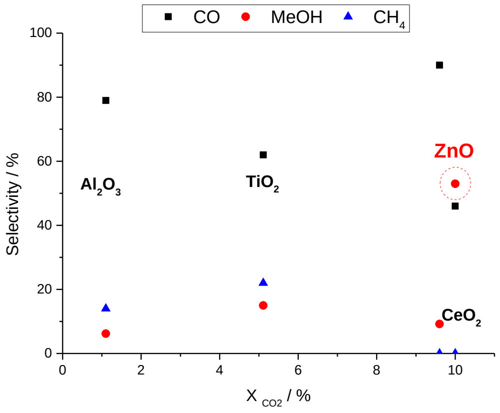

Figure 1 Conversion selectivity plots for 5 wt.% Pd catalysts prepared by SIM, Pretreatment conditions; 1 h, 400 °C in H_2 (30 ml min^{-1}). Test conditions; 250 °C, 30 ml min^{-1} of CO_2 : N_2 : H_2 (1:1:3)(approximate GHSV = 3333 h^{-1}), P(total) = 20 bar.

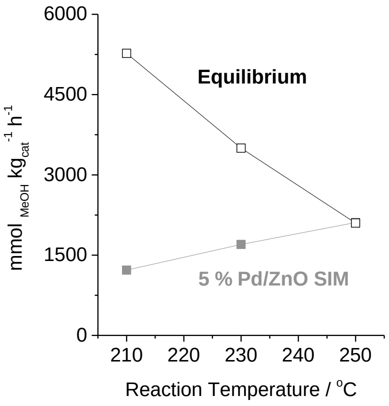

Figure 2 Methanol productivities as a function of reaction temperature; 5 wt.% Pd/ZnO SIM versus thermodynamic equilibrium.

At a reaction temperature of 250 °C, methanol productivity over 5 wt.% Pd/ZnO SIM reached that dictated by the thermodynamic equilibrium, with lower MeOH rates observed at temperatures of < 250 °C (Fig. 2). XPS and XAFS analyses of 5 wt.% Pd/ZnO showed that following pre-reduction at 400 °C, the catalyst presents a Pd-Zn scattering path at 2.60 Å in addition to a Pd-Pd scattering path at 2.85 Å, indicating the presence of both PdZn and Pd- only species. Meanwhile, pre-reduction at 150 °C yields an inactive catalyst which presents a primary co-ordination environment modelled by a single Pd-Pd scattering path at 2.74 Å. When prepared by IWI, which lacks a washing step, 5% Pd/ZnO showed remarkably low MeOH synthesis rates (20 mmol kg_{cat}^{-1} h^{-1})(Table 1). XPS analysis of this catalyst showed significant residual chlorine in this sample. TEM studies showed that this promoted aggregation of PdZn nanoparticles in the IWI sample, whilst surface Cl has also been reported to inhibit methanol synthesis through preventing formation of the formate intermediate. This was not observed for the SIM sample, which is washed during the synthesis[1].

Table 1 Catalytic activity and physical properties of 5 % Pd/ ZnO catalyst; SIM vs IMP vs CVI

Prep.	Pd Precursor	PdZn diameter/ nm	χ CO_2/ %	S(CO) / %	S(MeOH) / %	MeOH / mmol $kg_{cat}^{-1}h^{-1}$
SIM	$PdCl_2$	4.8	10.6	39	60	2400
IWI	$PdCl_2$	8.8	8.4	98	1.6	20
CVI	$Pd(acac)_2$	5.5	10.3	58	41	1600

Pretreatment; 1 h, 400 °C in H_2 (30 ml min^{-1}). Assessment; 250 °C, 30 ml min^{-1} of CO_2: N_2 : H_2 (1:1:3), P(Total)= 20 bar.

Owing to a strong dependence of reaction rate on PdZn particle size and role of chloride ions in NP aggregation, a chloride- free preparation methodology was employed. Deposition of Pd (5 wt.%) and Zn (15 w. %) onto TiO_2 via CVI yielded an active catalyst (χ = 10 %, *S*MeOH = 40 %, 1.7 mol_{MeOH} kg_{cat}^{-1} h^{-1}, mean particle size 3.9 nm), highlighting the importance of the PdZn alloy phase in catalysing this reaction.

4. Conclusions

PdZn nanoparticles are active catalysts for hydrogenation of CO_2 to methanol. Reaction rates show a strong size dependence and Cl^- sensitivity. NPs supported by CVI, a halide- free synthesis method, circumvent this.

References

1. H Bahruji, M. Bowker, G. J. Hutchings, N. Dimitratos, P. Wells, E. Gibson, W. Jones, C. Brookes, D. Morgan, G. Lalev. *J. Cat*. 2016, 343, 133-146