# Electrified Microheterogeneous Catalysis in Low Ionic Strength Media

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The ability to drive catalytic processes when dc voltages are applied to low ionic strength dispersions has been demonstrated for the selective partial oxidation of propene at 0 °C in an aqueous dispersion of $Pd^{II}$–$Cu^{II}$ supported on Y zeolite where the primary partial oxidation product can be either acetone or propylene oxide depending on the nature of the dispersed solid; in the absence of the applied electrifying force no product forms and in the absence of the molecular catalyst no selective oxidation occurs.

Electrochemical transformations of molecules are traditionally achieved in media of high ionic strength, where the high concentration of ions acts to carry the electric current in the medium and to minimize electromigration effects on the reacting molecules.[1] One of the outcomes of the advent of ultramicroelectrodes has been the exploration of electrode processes in media of low ionic strength,[2] including the use of dispersions of submicrometre-sized metal spheres[3] and nanometre-sized Pt supported on zeolite type Y[4] to yield practical amounts of electrogenerated product.

We seek to effectuate known catalytic reactions by the use of electrifying forces (potentials or currents or fields) applied to low ionic strength dispersions of catalytically active solids, but in the absence of ultramicroelectrodes. We term this process: electrified microheterogeneous catalysis. The model reaction we chose to test this premise is based on the partial oxidation of alkenes, specifically the $Pd^{II}$–$Cu^{II}$-catalysed oxidation of propene to acetone. This oxidation can be achieved homogeneously,[5] typically in a chloride-rich environment, or heterogeneously in the gas phase at elevated temperatures for oxidation of propene to acetone (or ethene to ethanal) by supporting the $Pd^{II}$ and $Cu^{II}$ on zeolite type Y.[6–8] Tominaga and coworkers observed a selectivity for acetone of 85% over other oxidation products of propene (including ethanal and propanal) when propene, water and oxygen reacted over $Pd^{II}Cu^{II}$–NaY at 403 K.[6a] They proposed a mechanism analogous to the one derived for the homogeneous catalytic Wacker reaction,[5] as shown in eqns. (1)–(4) where $Z^-$ represents a fixed anionic site in the zeolite lattice. This general mechanism has also been recently shown to be consistent for the oxidation of ethene to ethanal over $Pd^{II}Cu^{II}$–NaY at 373 K.[7]

$$[Pd^{2+}, 2Z^-] + C_3H_6 + H_2O \rightarrow MeC(O)Me + [Pd^0, 2(H^+Z^-)] \quad (1)$$

$$[Pd^0, 2(H^+Z^-)] + 2[Cu^{2+}, 2Z^-] \rightarrow [Pd^{2+}, 2Z^-] + 2\,[Cu^+Z^-, H^+Z^-] \quad (2)$$

$$2[Cu^+Z^-, H^+Z^-] + \tfrac{1}{2}O_2 \rightarrow 2[Cu^{2+}, 2Z^-] + H_2O \quad (3)$$

$$C_3H_6 + \tfrac{1}{2}O_2 \rightarrow MeC(O)Me \quad (4)$$

We run electrified microheterogeneous reactions with a dilute suspension of zeolite powder in 18 MΩ cm water; dispersion is maintained by a rapid flow of helium through a glass dispersion electrolysis cell,[3,4] see Fig. 1. The reactor is

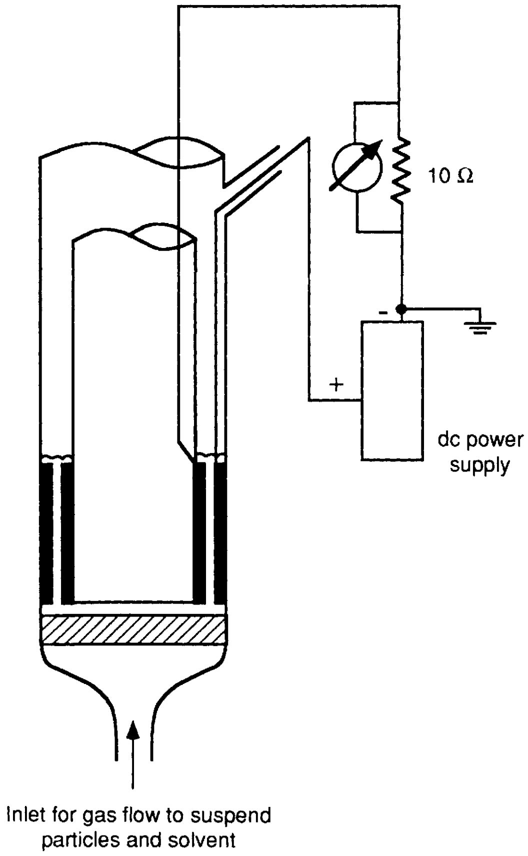

**Fig. 1** A cross-sectional schematic of the glass dispersion cell and the electronic circuit used to perform electrified microheterogeneous catalysis. The cell is equipped with a water jacket (not shown) to control the reaction temperature, which was maintained at 0 to 5 °C for all experiments described in this work. The dc voltage is applied across two concentric platinum foil cylinders (5 cm high with a 0.4 cm gap). The usual suspension density is 50 mg zeolite per 20 ml $H_2O$.

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**Table 1** Electrified microheterogeneous catalysis of propene oxidation: observed products under reaction and control conditions[a]

| $Pd^{II}Cu^{II}$–NaY: $Pd^{II}$ Source (calcined ?) | Applied dc V/V[b] | Propene : oxygen[c] | Acetone (% Sel.)[d] | Propanal (% Sel.)[d] | Propylene oxide (% Sel.)[d] | Ethanal (% Sel.)[d] | Propylene oxide : acetone/ mol/mol |
|---|---|---|---|---|---|---|---|
| $PdCl_2$ (no)[e] | 20 | 2 : 1 | 75 | 3 | 20 | 1 | 0.3 |
| $PdCl_2$ (yes) | 30 | 1 : 1 | 11 | 10 | 67 | 6 | 6 |
| $PdCl_2$ (yes) | 60 | 1 : 1 | 6 | 14 | 36 | 23 | 6 |
| $Pd(NH_3)_4Cl_2$ (yes) | 20 | 1 : 1 | 4 | 7 | 47 | 21 | 12 |
| $Pd(NH_3)_4Cl_2$ (yes) | 60 | 1 : 1 | 5 | 12 | 38 | 23 | 8 |
| Controls | | | Number of products | | | | |
| NaY | 30 | 1 : 1 | ≥12[f] | | | | 2 |
| 1 mmol $dm^{-3}$ NaOH | 20 | 1 : 1 | ≥12[f] | | | | 2 |
| $Pd^{II}Cu^{II}$–NaY + 0.1 mol $dm^{-3}$ NaOH | 10 | 1 : 1 | ≥12[f] | | | | 0.7 |
| $Pd^{II}Cu^{II}$–NaY | 0 | 1 : 1–100 : 1 | 0 | | | | — |
| $Pd^{II}Cu^{II}$–NaY + $H_2O_2$[g] | 0 | 1 : 1–100 : 1 | 0 | | | | — |

[a] Liquid-phase products were identified by gas chromatography–mass spectrometry and quantitated using gas chromatography with a flame-ionization detector and the appropriate standard solutions. [b] The $Pd^{II}Cu^{II}$–NaY (or NaY) dispersion was activated (as described in the text) before sparging with He + propene + $O_2$ and applying the stated voltage for 60 min; suspension density was 2.6 ± 0.1 mg $ml^{-1}$. [c] The propene : oxygen stoichiometry is especially critical as we have found that selectivity is diminished at high oxygen contents (*e.g.* 1 : 5 propene : oxygen).[12] [d] % Sel. is the selectivity of the reaction for the listed product relative to the total moles of obtained product; the total moles of product includes an assigned number of moles of $C_1$ product equivalent to that obtained for ethanal. The actual selectivities for propylene oxide, acetone and propanal are higher by an unknown amount owing to the generation of ethanal from an ethene impurity in our as-received propene (analysed at 0.05%). Substituting ethene for propene during electrified microheterogeneous catalysis over our catalyst generates ethanal with an apparent 100% selectivity. [e] Early experiments with a different batch of non-calcined $Pd^{II}Cu^{II}$–NaY were run with no added oxygen (oxygen was generated *in situ via* oxidation of water) and produced acetone in >85% selectivity, even at an applied voltage of +100 $V_{dc}$. [f] In addition to acetone, propanal, propylene oxide and ethanal, the following compounds were found by gas chromatography–mass spectrometry: acrolein; hydroxyacetaldehyde; propan-2-ol; propan-1-ol; allyl alcohol; 1-hydroxypropan-2-one; acetic acid; propanoic acid; and propane-1,2-diol. Due to the great number of products, selectivities were not calculated. [g] Introduction of $H_2O_2$ to the dispersion was done either at the initiation of the experiment in stoichiometric excess (0.4 to 1.2 mol $dm^{-3}$) or by titration of aliquots into the dispersion over the course of the experiment.

defined by the volume of suspension contained between the two concentric feeder electrodes. After an activation step (applying +80 $V_{dc}$ across the feeder electrodes for 20 min to achieve a steady-state current[9]‡), propene and oxygen are introduced into the helium sparging gas and +10 to 60 $V_{dc}$ is applied across the cell. A separator was not used to isolate the electrodes in these experiments; the absence of a microporous separator avoided any electroosmotic effects arising from the low ionic strength of the dispersion.[10]

Table 1 summarizes the oxidation products obtained under similar reaction conditions for $Pd^{II}Cu^{II}$–NaY,§ and includes the relevant controls for this system. As exposure of NaY to water releases $Na^+$ into solution,[4,9,11] the controls include 1 mmol $dm^{-3}$ NaOH (containing no zeolite particles) to gauge the effect of direct electrolysis of propene at the feeder electrodes in dilute electrolyte, and NaY suspended in 18 MΩ cm water to determine the effect on the reaction selectivity in the absence of the molecular catalyst ($Pd^{II}$–$Cu^{II}$) but in the presence of the zeolite support.

The prime result, as seen in Table 1, is that selective $Pd^{II}$–$Cu^{II}$-catalysed oxidation of propene can be achieved at 0 °C in a low ionic strength liquid phase when a dc voltage is applied to an aqueous dispersion of $Pd^{II}Cu^{II}$–NaY. When the catalyst is prepared with immediate sequential exchange of $Pd^{II}$ and $Cu^{II}$ (*i.e.* without a calcination step before $Cu^{II}$ exchange[12]), acetone is the major product (>70% selectivity), as was observed for the gas-phase oxidation of propene at elevated temperatures.[6a] Unlike gas-phase catalysis, we find that propylene oxide is the most significant additional oxidation product and when the catalyst preparation includes a calcination step (to release the ammine ligand coordinated to the $Pd^{II}$ centre), propylene oxide becomes the dominant product, see Table 1. This ability to synthesize propylene oxide is notable as partial oxidation of the olefin to the epoxy compound is not a typical outcome for this catalytic system.

Our present cell design conveniently combines the means to suspend the zeolite powder and the means to add reactant gases to the sparging gas stream, but it is a single-pass reactor for the reactant gases. In addition, propene experiences a minimal residence time in the dispersion (estimated at <10 s) due to the flow rate necessary to maintain suspension of the zeolite particles (~100 ml $min^{-1}$). Also, with the limited solubility of propene in $H_2O$ at 0 °C, only a fraction of the reactant becomes available at the pertinent interface (which is the gas–solid–liquid interface at the catalyst surface). As most of the propene is 'wasted' on its pass through the cell, the conversion efficiency can be artificially varied as a function of the amount of propene in the helium sparging stream. Our present propene conversion efficiency for 2% propene-in-helium is ~0.2%.

In the absence of the molecular catalyst, for either dilute NaOH or an aqueous dispersion of NaY, the selectivity for oxidation is lost. If a traditional slurry electrolysis is performed by dispersing $Pd^{II}Cu^{II}$–NaY in an electrolyte with a more usual salt concentration (in this instance, 0.1 mol $dm^{-3}$ NaOH) and then applying +10 $V_{dc}$, all selectivity is again lost.

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‡ The shifting of the equilibrium for the autoprotolysis of water in the presence of sodium-compensated aluminosilicate zeolites (leading to ion exchange of sodium ion in the zeolite for proton in the water)[11] also occurs during the dispersion electrolysis of water in the presence of zeolite and has been previously noted;[4] we have observed that the kinetics of this process are dependent on the identity of the charge-compensating cation in the zeolite and on the magnitude of the applied dc voltage.

§ The catalyst is prepared by sequential aqueous ion exchange of NaY (micrometer-sized powder with no binder) in a solution of either $PdCl_2$–$NH_4OH$ or $Pd(NH_3)_4Cl_2$ (to a weight loading of 1%) followed by exchange in a solution of $CuCl_2$ (6.5 wt%). Calcining 1 wt% $Pd^{II}$–NaY (prepared from either solution) before cupric exchange yields catalysts of comparable behavior. A complete description will follow separately.

In all three cases more than 12 oxidation products result. The ability of the supported molecular catalyst to regulate the product distribution is all the more impressive when compared to these productive but indiscriminate control experiments.

The necessity of an applied voltage to drive the oxidation was shown for a control experiment where the aqueous dispersion of $Pd^{II}Cu^{II}$–NaY was activated at +80 $V_{dc}$ and then exposed to the reactants for 60 min, but without re-applying a dc voltage: at 0 °C and in the liquid phase, no product forms, even in the presence of the molecular catalyst. Similarly, if the $Pd^{II}Cu^{II}$–NaY is activated and then exposed to the reactants for 60 min without an applied voltage, but with aliquots of a chemical oxidant ($H_2O_2$) added over the reaction period, no products form, and in particular, no propylene oxide forms. $H_2O_2$ is a chemical reagent plausibly generated *in situ* during the electrolysis of water (a process occurring concomitantly during these electrified microheterogeneous reactions), thus, this latter control shows that the presence of $H_2O_2$ cannot replicate the results obtained with the catalyst in the presence of the applied voltage.

The ability to drive catalytic processes with applied voltages in low ionic strength media, such as we have demonstrated with the $Pd^{II}$–$Cu^{II}$-catalysed oxidation of propene, should be relevant to a range of other catalysed reactions where known chemistry from the heterogeneous and homogeneous catalysis literature can be adapted to perform electrified microheterogeneous catalysis in dispersions of the appropriately prepared solid. Such solids do not need to be restricted to zeolites.[13] It should be emphasized again that our model reaction, the selective partial oxidation of propene, was driven at 0 °C and in the absence of chloride ion. The results of our exploration of this and other catalysed processes as effected in electrified microheterogeneous dispersions will be described separately.

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