Supplementary Data

Observation of high enantioselectivity for the gas phase hydrogenation of methyl pyruvate using supported Pt catalysts pre-modified with cinchonidine

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In this supplementary data we use the Kelvin equation and our reactant partial pressure to estimate the effective partial pressure for condensation as a function of pore radius.

Experimental conditions

Methyl pyruvate : $C_4 H_6 O_3$ $M_R = 102$ g mol^{-1}

In a typical experiment we lose 0.066 g h^{-1} of methyl pyruvate (at 20°C) from the vapouriser, *i.e.* 6.47 x 10^{-4} mol h^{-1}

Flow rate of diluent He is 80 ml min^{-1} or 4.8 l h^{-1} or 4.8 x 10^{-3} m^3 h^{-1}.
Molar gas volume is 0.02446 m^3 mol^{-1}. So we pass 0.196 mol h^{-1} of He.

Since pressure is proportional number of moles the relative partial pressures are:

P(pyruvate) = 6.47 x 10^{-4} = 3.3 x 10^{-3}
P(He) 0.196

Experiment is carried out at atmosphere pressure, so

P(pyruvate) + P(He) = 1 bar
P(pyruvate) = 3.3 x 10^{-3} atm or 330 Pa

Kelvin Equation:

$$\ln\left(\frac{p}{p^o}\right) = \frac{-2\gamma v_l}{rRT}$$

relates the vapour pressure, *p*, in a pore in which the meniscus radius is *r*, to the surface tension, γ, and molar volume of the liquid, v_l.

We have no method for measuring the contact angle for methyl pyruvate and so have to assume the meniscus radius is approximately the pore radius.

The density of methyl pyruvate is 1.13 g ml^{-1} (25 degrees) so the molar volume of the liquid is 90.3 ml mol^{-1} or 90.3 x 10^{-3} l mol^{-1}, or 90.3 x 10^{-6} m^3 mol^{-1}.

The surface tension of organic molecules of similar size range from around 25 mN m^{-1} (pent-3-one) to 45 mN m^{-1} (ethyl diol). Taking 35 mN m^{-1} as an estimate for methyl pyruvate at an experimental temperature of 40 °C (313 K) we can plot the expected relative partial pressure *vs.* pore radius, Figure 1.

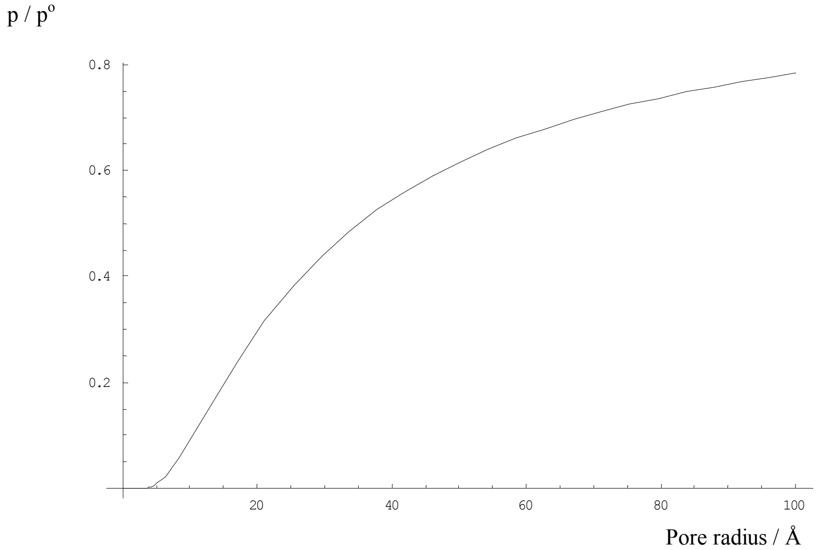

Figure 1 Kelvin equation plot.

So with an average pore radius of about 40Å the vapour pressure will be halved.

To measure the vapour pressure of methyl pyruvate a vacuum pump was used to reduce the pressure over liquid pyruvate at 0°C. After pumping for 10 minutes the vessel was sealed and allowed to stand for a further 10 minutes to establish liquid/vapour equilibrium. The pressure was then measured using a standard gauge and the temperature increased in stages to 40°C.

The results are shown in Figure 2 from which the partial pressure of methyl pyruvate at the reaction temperature of 40 ^{o}C can be estimated to be 130 Torr or 0.17 atm.

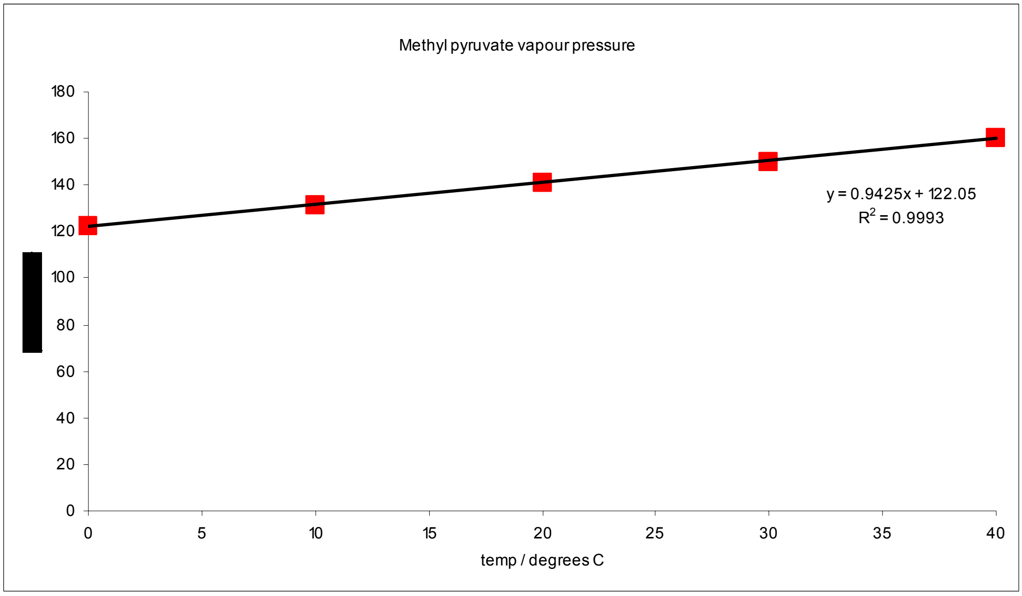

Figure 2

So under reaction conditions p/p^{o} = 0.019, i.e. the experimental partial pressure of pyruvate is around a factor of 50 below the normal vapour pressure and from the above plot shown in Figure 1, would require pores less than 5 Å radius to see condensation.
In experiments with 0 °C vaporizer we see flow rates of 0.025 g h^{-1} and so the effective partial pressure is reduced further by a factor of almost 3.

The Pt/SiO_2 catalysts used in this study have an average pore radius of 45 Å and negligible pore ≤ 5 Å.

Hence these data confirm that the reaction is occurring at the gas/solid interface.

For the catalysts, we have used Pt/γ-Al_2O_3, Pt/SiO_2, we know that the average pore radius is *ca.* 45Å and there are almost no pores in the range in which capillary condensation can occur. This is now discussed in detail in the revised paper. However, to provide compelling evidence that the reaction is genuinely occurring at the gas/solid interface, we have carried out experiments with a Pt/α-Al_2O_3 catalyst which does not contain an intra particle pore structure. We still observe an ee for this reaction which can only be occurring at the gas/solid interface.