An experimental approach for controlling confinement effects at catalyst interfaces

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Abstract: Catalysts are conventionally designed with a focus on enthalpic effects, manipulating the Arrhenius activation energy. This approach ignores the possibility of designing materials to control the entropic factors that determine the pre-exponential factor. Here we investigate a new method of designing supported Pt catalysts with varying degrees of molecular confinement at the active site. Combining these with fast and precise online measurements, we analyse the kinetics of a model reaction, the platinum-catalysed hydrolysis of ammonia borane. We control the environment around the Pt particles by erecting organophosphonic acid barriers of different heights and at different distances. This is done by first coating the particles with organothiols, then coating the surface with organophosphonic acids, and finally removing the thiols. The result is a set of catalysts with well-defined “empty areas” surrounding the active sites. Generating Arrhenius plots with >300 points each, we then compare the effects of each confinement scenario. We show experimentally that confining the reaction influences mainly the entropy part of the enthalpy/entropy trade-off, leaving the enthalpy unchanged. Furthermore, we find this entropy contribution is only relevant at very small distances, where the “empty space” is of a similar size as the reactant molecule (<3 Å for ammonia borane). This suggests that confinement effects observed over larger distances must be enthalpic in nature.

General

All chemicals used in this study were purchased from commercial sources (>97% pure) and used as received. Ammonia borane 97% was obtained from Sigma Aldrich (682098). Reaction kinetics were studied using the homebuilt bubble counter. This system has been described in detail elsewhere.[1]

Additional data

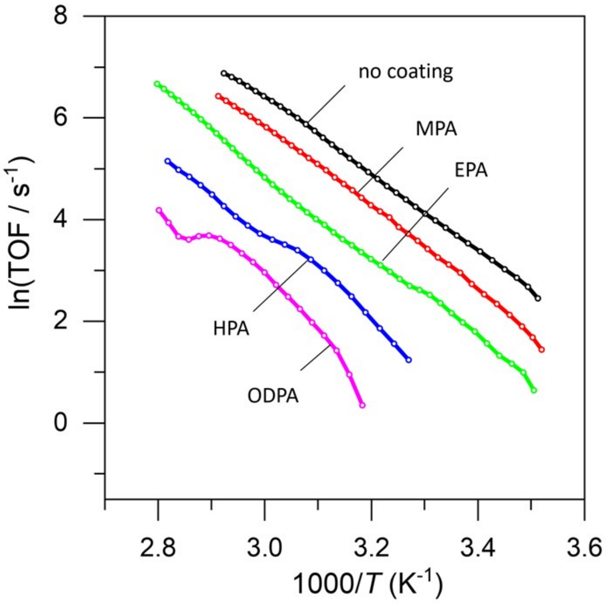

Figure S1: Ammonia borane hydrolysis using pristine 0.05 wt% Pt/γAl_2O_3, and coated with b) methyl phosphonic acid, c) ethyl phosphonic acid, d) hexyl phosphonic acid, and e) octadecyl phosphonic acid.

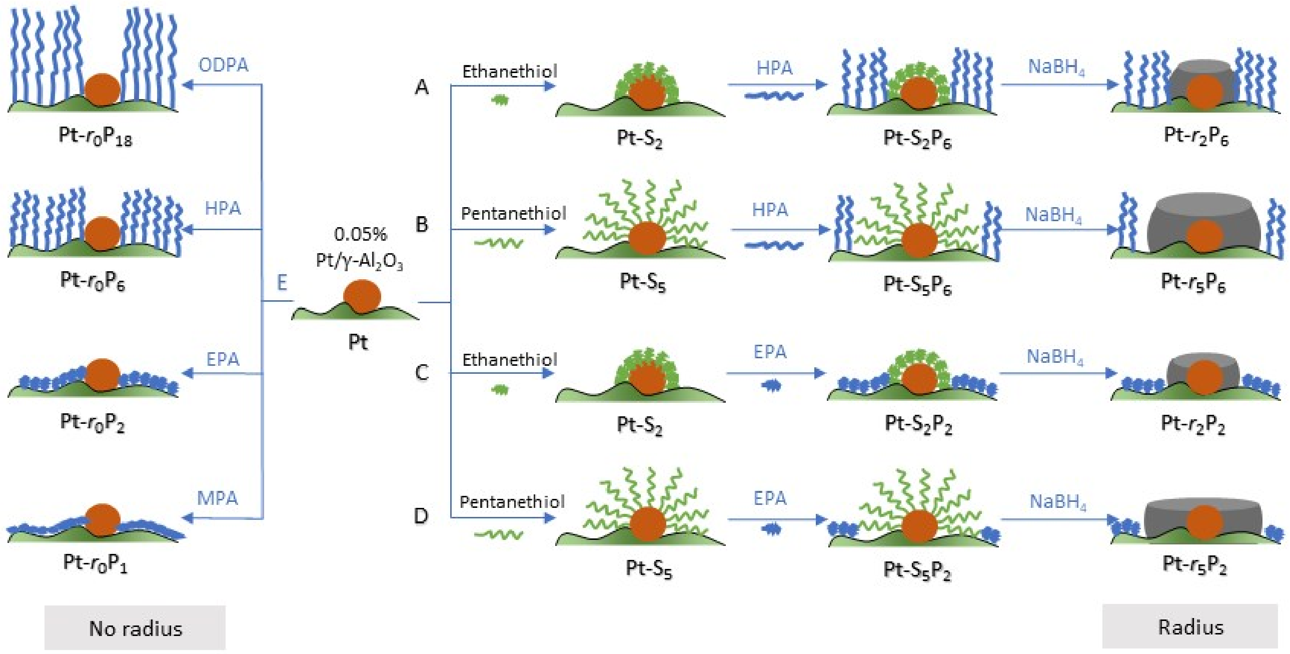

Figure S2: Scheme showing an overview of all prepared catalysts.

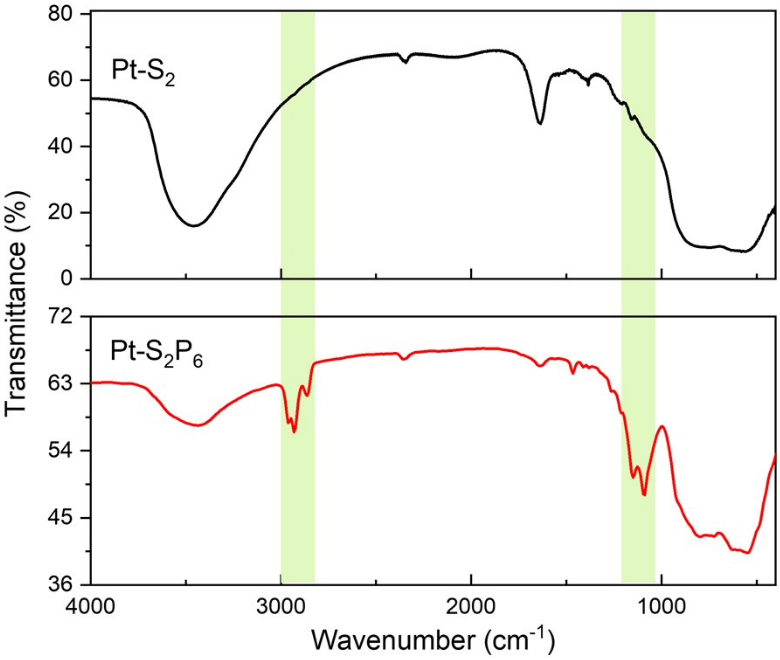

Figure S3: FTIR of Pt-S_2 (ethanethiol-coated) and Pt-S_2P_6 (ethanethiol- and HPA-coated).The signals of surface-bound hexyl phosphonic acid are indicated with green areas.

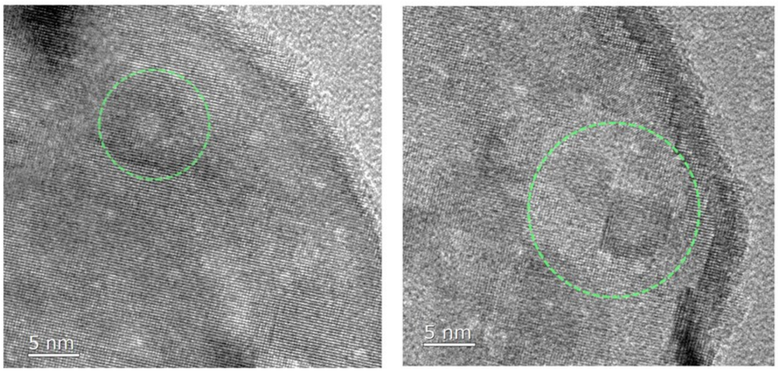

Figure S4: Additional HRTEM images of Pt-r_5P_6 (pentanethiol- and HPA-coated) catalyst.

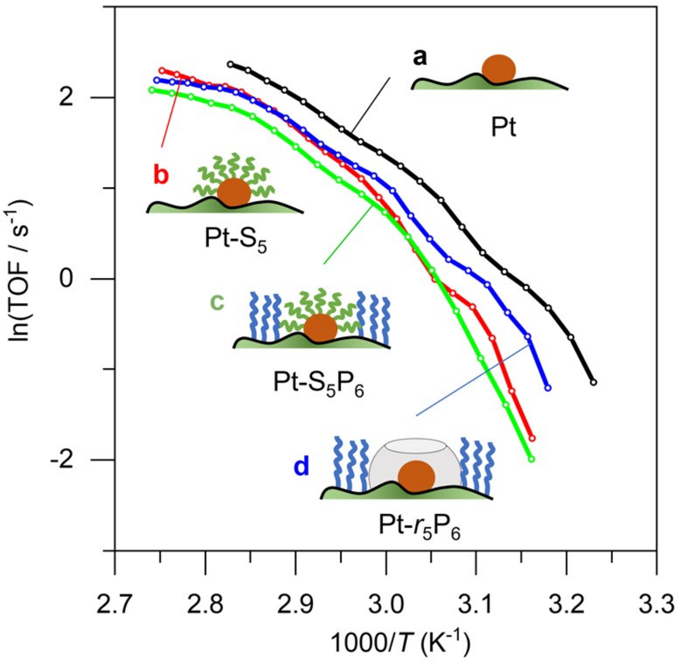

Figure S5: Catalytic data for the water-free dehydrogenation of ammonia borane in NMP with (a) 0.05% Pt/γAl_2O_3, (b) Pt/γAl_2O_3 with pentane thiol coating, (c) Pt/γAl_2O_3 with both pentane thiol coating and phosphonic acid coating, and (d) the “free space“-catalyst after removal of the thiol. Each data point represents a window average of 10–50 measurements using equal time interpolation (see below for more details).

Procedure for isothermal hydrolysis of ammonia borane

Aqueous ammonia borane (0.40 mL, 2M) was loaded into a syringe (1 mL) equipped with a glass capillary (0.32 mm, 15 cm) that reaches into the reactor below the solvent level. The catalyst (40 mg) was suspended in water (6.0 mL) and a stirring bar (8 x 3 mm) was added. The reactor was closed, and the capillary directly inserted into the liquid through one of the syringe ports. All remaining ports were closed. The reactor was then purged with nitrogen using a flowrate of 5 mL min^{-1} for 5 min. During purging, the reactor was heated to the desired temperature. After the temperature stabilized, the purging was stopped. After 5 seconds, the reactant was injected, resulting in some bubbles forming due to volume displacement. The gas production was then monitored until reaction completion.

Procedure for non-isothermal hydrolysis of ammonia borane

An aqueous solution of ammonia borane (0.40 mL, 2M) was loaded into a syringe (1 mL) equipped with a glass capillary (0.32 mm, 15 cm) that reaches into the reactor. The catalyst (40 mg) was suspended in water (6.0 mL), cooled to 10 °C and a stirring bar (8 x 3 mm) was added. The reactor was closed, and the capillary directly inserted into the liquid through one of the syringe ports. All remaining ports were closed. The reactor was then purged with nitrogen using a flowrate of 5 mL min^{-1} for 5 min. The temperature was verified to be room temperature (20-25 °C) before the reaction was started. After 5 seconds, the reactant was injected, resulting in some bubbles forming due to volume displacement. Five seconds later, a ramp of 2 °C min^{-1} was initiated. The sample was heated to 85 °C and held there for 5 min. At the end of the heating program the purge gas (nitrogen) was turned on and heating was stopped.

Procedure for non-isothermal *dehydrogenation* of ammonia borane

Anhydrous NMP solution of ammonia borane (0.40 mL, 2M) was loaded into a syringe equipped with a glass capillary (0.32 mm, 15 cm) that reaches below the liquid level. The catalyst (40 mg) was suspended in NMP (6.0 mL) and a stirring bar (8 x 3 mm) was added. The reactor was closed, and the capillary directly inserted into the liquid through one of the syringe ports. All remaining ports were closed. The reactor was then purged using a flowrate of 5 mL min^{-1} for 5 min. After 5 seconds, the reactant was injected, resulting in some bubbles forming due to volume displacement. Five seconds later, a ramp of 0.5 °C min^{-1} was initiated. The sample was heated to 140 °C and held there for 5 min. At the end of the heating program the purge gas (nitrogen) was turned on and heating was stopped. The sample was cooled down to room temperature while being purged with nitrogen.

Procedure for Pt impregnation on γ-Al_2O_3

γ-Al_2O_3 extrudate (Ketjen) was grinded and sieved to obtain particles with a diameter of 90 – 53 µm. Grinded γ-Al_2O_3 (1g) was loaded into a vial (30 mL) equipped with a vacuum port and a syringe for injecting liquid under vacuum. The goal is to fill 80% of the incipient volume with a Pt solution. An aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (2.6 mg mL^{-1}) was prepared and 3.9 mL was loaded in the syringe. The alumina powder was stirred using a magnetic stirrer (1000 rpm) and vacuum was applied for about 1 minute prior to injection of the liquid. Directly after injection, the vial was agitated manually (with help of the magnetic stirring) to obtain a homogeneous mixture of Pt on alumina. The vacuum was released, leaving a powder that is almost dry to the touch. The alumina was further homogenized using a mortar and pestle and dried overnight at 80°C in a petri dish, followed by 2h at 120 °C. The next day, the powder was loaded in the tube furnace and heat-treated under N_2 at 225 °C (5 °C/min ramp), with a 1h holding time. Next, the sample was reduced at 225°C (5 °C/min ramp) for 2h using a mixture of 10% H_2 in N_2. The catalyst was stored under argon.

Procedure for synthesis of phosphonic acid coated catalysts with no free volume (Pt-R_0P_z)

0.05% Pt/γ-Al_2O_3 (250 mg, 6 µmol Pt) was added to a solution phosphonic acid (40 mM, 40 cm^3) in THF and stirred overnight. The solution was decanted, and the catalyst annealed at 120 °C for 12 h. The catalyst was washed with THF (3 x 20 cm^3), then air-dried in a fume hood at room temperature.

Procedure for synthesis of free volume Pt-R_yP_z catalysts

Methanethiol coating (synthesis of Pt-S_1)

Methyl iodide (3.25 mL, 52 mmol) added to thiourea (3.46 g, 45 mmol) moistened in ethanol (3 cm^3) and left to reflux with stirring at room temperature. The solvent was removed *in vacuo*, isolating S-methylisothiuronium iodide as a white crystal. The white crystal dissolved in water (3.6 cm^3) and heated to 100 °C, evolving methanethiol as a gas. Methanethiol was collected in a cold finger, dissolved in ethanol (5 cm^3), then poured into a suspension of 0.05wt%Pt/Al_2O_3 (400 mg, 10 µmol Pt) in ethanol (20 cm^3) and stirred for 24 h. The solution was decanted, and the catalyst washed with ethanol (1 x 20 cm^3). The catalyst was dried in vacuum oven overnight at 40 °C. At this stage a 100 mg sample of Pt-S_1 was removed for catalytic testing.

Ethanethiol/pentanethiol coating (synthesis of Pt-S_2 and Pt-S_5)

Under a N_2 environment, 0.05% Pt/γ-Al_2O_3 (500 mg, 13 µmol Pt) was added to 10 mM ethanolic thiol solution (20 cm^3, 0.4 mmol) and stirred for 24 h. The solution was decanted, and the catalyst washed with ethanol (1 x 20 cm^3). The catalyst was dried in vacuum oven overnight at 40 °C. At this stage a 100 mg sample of Pt-S_y was removed for testing.

Phosphonic acid coating (synthesis of Pt-S_yP_z)

Under a N_2 environment, Pt-S_y (400 mg, 10 µmol Pt) to a solution phosphonic acid (40 mM, 40 cm^3) in THF and stirred overnight. The solution was decanted, and the catalyst annealed at 120 °C for 12 h. The catalyst was washed with THF (3 x 20 cm^3) and air dried in a fumehood overnight. At this stage a 100 mg sample of Pt-S_yP_z was removed for testing.

Removal of thiolate coating (synthesis of Pt-R_yP_z)

Pt-S_yP_z (300 mg, 6 µmol Pt) added to a solution of $NaBH_4$ (0.5 M, 40 cm^3) in 1:1 EtOH/H_2O and stirred for 10 minutes. The solution was decanted, and the catalyst washed with 1:1 EtOH/H_2O (3 x 20 cm^3). The catalyst was dried in a vacuum oven at 40 °C overnight.

Bubble detection algorithm

Any interruption of the laser is logged as a bubble. It does not discriminate, but outputs all the data it observes. The bubble counter calculates a constant background average of light intensity (translated into voltage by the ADC) and records any sudden reductions of light intensity. If the intensity of the light goes over a threshold, the bubble counter starts a stopwatch to record the time it takes before it falls again below the threshold. This is the beam interruption time. The moving average that is constantly being updated protects against false positive detection of gradual changes in background. Bubbles always pass quickly. If the BIT reaches above 10000 (1.106 s, based on 9044 Hz counting frequency) the algorithm automatically resets and reverts to baseline monitoring mode. This protects, for example, against sudden but persistent changes to light intensity, for example somebody switching of the light, causing the machine to wait indefinitely for the light intensity to return.

Processing of bubble counter data (by custom software)

The data obtained from the bubble counter are saved in two files: one file listing the time and size the beam-interruption time (BIT) and one file listing all the temperature control data from the PID module. From the first file, we only use the time data of when the bubbles were observed, because time between bubbles was a much better predictor of bubble volume compared to BIT.[1]

The second file lists temperature data versus time. Every second the temperature data is logged into this file, so there is more temperature data than bubble counting data. This extra data is used to calculate an average of the temperature of 5s before and after the requested time. There is some background noise in the measurements of temperature. Temperature data is observed using a NTC resistor bridge with an analog-digital converter to record the voltages. These voltages are calibrated against a reference thermocouple every half year and stored in the device. We verified that the temperature average outputted form our device over is accurate within 0.5 °C.

Data merging & windowing

The data in both files is merged using a macro. For every bubble, the macro looks up the temperature of the reaction and takes the window average of the 10s window around this time. Note that with a constant ramp rate, this will have no negative effect on the accuracy of the temperature average. Window averaging of temperature data reduces noise and hence reduces noise in the obtained Arrhenius plots.

When all bubbles have their corresponding temperature average logged, the data is screened for outliers. Outliers are for example bubbles with BIT less than 15 were previously proven to correspond to microbubbles or rare disturbances before/after a bubble. These bubbles are rejected from the dataset. The same happens for any data points with BIT larger than 500. On average, we reject less than 0.1% of the bubbles.

Flowrate correction

As described before,[1] a linear flow correction is applied to the bubble counting data. This is to account for changes in bubble volume. The volume of the bubble is calculated with the following expression:

$$V(x) = c_1 x + c_2 = 0.14314x + 7.1341$$

Here, c1 and c2 are constants and x is flow rate in bubbles per second. Volume V(x) is in microliters.

Blank experiment correction

This correction is only performed for non-isothermal experiments. The reason this is necessary is because the gas above the liquid will expand with increasing temperature and generate extra bubbles. Also the liquid contributes a vapor pressure that in total accounts for roughly 3 mL of gas over one experiment. On the total volume this is never more than 10% of the gas production of the entire experiment.

To correct for void volume expansion and vapor pressure, a blank experiment with only solvent is ran with exactly the same parameters. This is exactly the same as the normal reaction with the one difference that the catalysts and reagent are omitted. The resulting data is then subtracted from the reaction experimental data. These blanks are stored in the bubble counter software so it can be easily applied to load new measurements.

Processing of volume data into Arrhenius plots

All ‘extra’ data from bubbles caused by purging and volume displacement after reactant injection are deleted. This leaves only the gas production by the catalytic experiment.

Interpolation of data

Unless specified otherwise, processing is done as follows: First, the volume data is interpolated to reduce the number of points. This can be done in two ways, by a window average of the data points, or by interpolating evenly spaced points in time from the source data. Both methods have advantages and disadvantages. Window averaging has the advantage it averages the data, but because the data points are not evenly spaced across the temperature axis, the majority of points will end up in the high temperature region. Equal point spacing indeed gives a good spread of points, but technically averages less points in the start and more in the later part of the reaction. For us this is not a problem, since interpolation of a cumulative volume essentially sums up all points in one interval, effectively averaging out any error in individual data points. Unless specified otherwise, we used a 50 point equal-spacing algorithm.

Calculation

Then the volume-*vs.*-time data is processed with a spreadsheet to obtain the different plots. The table **S1** below gives a detailed description how the data is calculated. After interpolation, we take the derivative of the volume data versus time (col **6**/**7**). Taking the derivative vs temperature is out of the question because the ramp rate is not constant in the beginning of the experiment. Then the fractional conversion (col **10**) is calculated, based on the expected volume which in turn is based on the added amount of ammonia borane.

Table S1. Calculation parameters.

Col	**Name**	**Source / Calculation**
1	Time (min)	Raw data
2	Beam interruption time (BIT units)	Raw data
3	Volume (uL)	Raw data
4	Volume, blank subtracted (uL)	Raw data
5	Temperature (°C)	Raw data
6	Time Interpol (min)	50 point interpolation from X=**1**,Y =**4**, X data
7	Volume Interpol (uL)	50 point interpolation from X=**1**,Y =**4**, Y data
8	Temperature interpolation (°C)	Interpolation of X=**6** in (X=**1**,Y=**5**), Y data
9	Observed rate (uL/min)	Derivative of (X=**6**, Y=**7**), vs time!
10	Fractional conversion (0..1)	1 – (**7**/maximum expected volume)
11	Intrinsic rate (uL/min)	**9** / ((1-**10**)^n) n = reaction order = 0.15 for ammonia borane hydrolysis
12	Observed rate (M/min)	**9** / constant, depending on stoichiometry of the reaction and molar concentration
13	Intrinsic rate (M/min)	**11** / constant, depending on stoichiometry of the reaction and molar concentration
14	1000/T	1000/(**8** + 273.15)
15	ln (k)	ln(**13**)
16	TOF	ln(((**11**/[eq. of H_2 per eq. AB])*10^-6/[molar volume]) / ((([loading%]/100)*(0.001*[mass catalyst]))/[molar mass Pt])) = ln(((**11**/3)*10^-6/22.4) / ((([loading%]/100)*(0.001*[mass catalyst]))/195.1))

References

[1] T. K. Slot, N. R. Shiju, G. Rothenberg, *Angew. Chem. Int. Ed.* **2019**, *58*, 17273–17276.