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On the origin of high-temperature phenomena in Pt/Al_2O_3

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Supplementary information

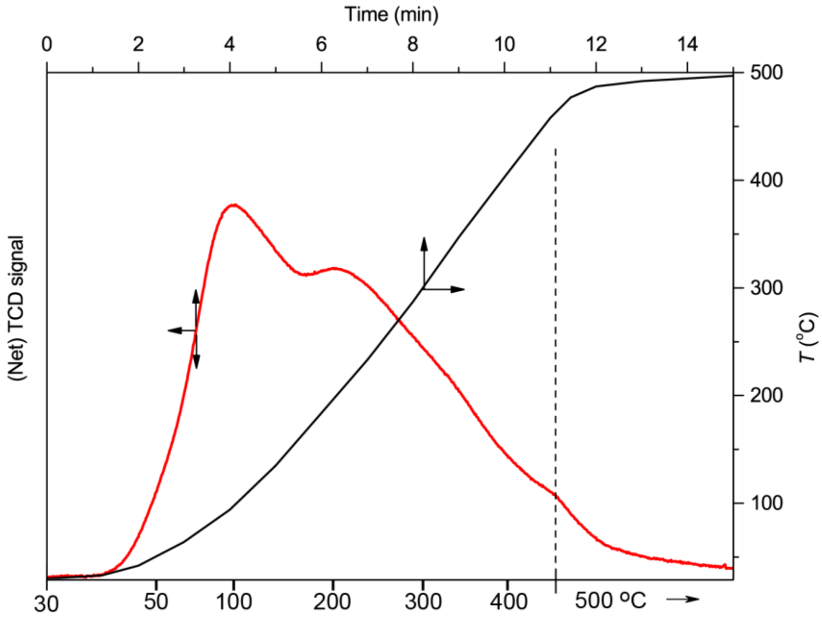
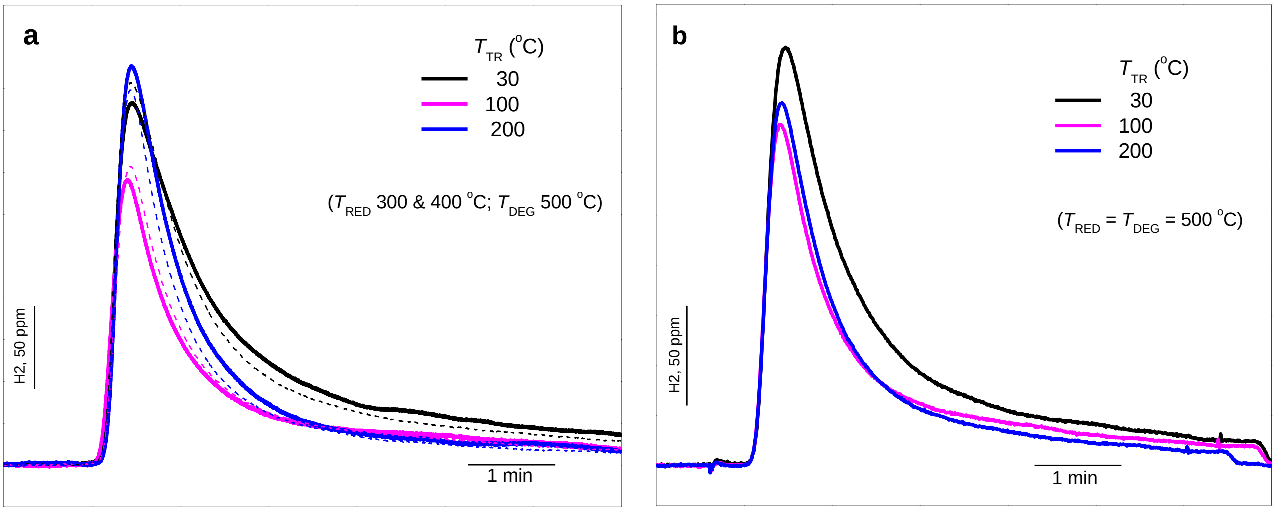


Fig. S1 An example of experimental curves recorded under standard conditions (Ar flow rate 25 cc/min, nominal heating rate 50 °/min, 30→500 °C, sample mass 400 mg). Black curve shows temperature in the middle of sample *vs*. time after start of heating, and red curve shows the detector response to evolving H_2. In the given case (a linear scale for left Y axis and upper X axis), the amount of H_2 desorbed is strictly proportional to the area under the curve or any of its segments. The expected delay with linear heating of the sample at the beginning of the run results in a non-linear scale for the lower X-axis (which shows the temperature in the middle of sample). The vertical dashed line in the figure indicates time when *furnace* temperature has reached its final value (here, 500 °C) and the run continues *quasi*-isothermally.



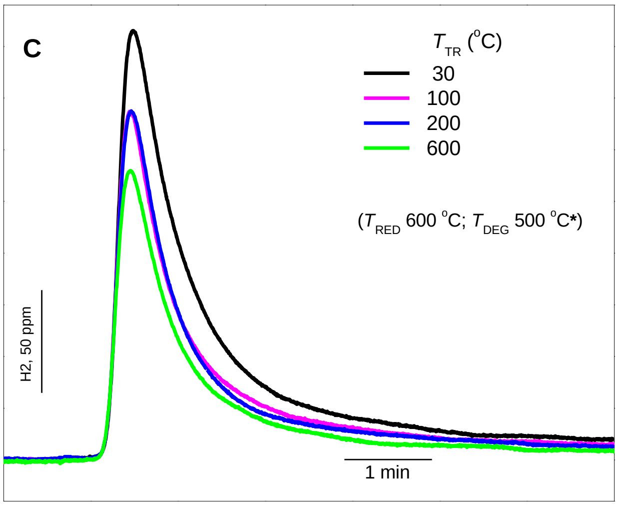


Fig. S2 Relevant results for the hydrogen adsorption/desorption at sub-ambient temperatures. Here, a degassed 1%Pt/Al_2O_3 sample (T_{DEG} = 500 °C) was treated in flowing H_2 at a temperature T_{TR} (specified in the figure), then cooled under H_2 down to -70 °C and purged at that temperature with Ar. The H_2-traces in the figure relate to hydrogen that withstood the purging with Ar at -70 °C but desorbs from the Pt surface upon heating to room temperature (details for the procedures may be found in ref. S1).

Panel (a) shows results for the sample that was initially reduced at 300 °C (solid lines) and 400 ° C (dashed lines). One can see that curves' shape and area respond significantly to T_{TR} in the given range (T_{TR} 30-200 °C), and the sample behaves similarly regardless of T_{RED} (300 or 400 °C).

Panel (b) shows corresponding curves for the sample that was reduced at T_{RED} of 500 °C. One can see a considerable difference between the black and magenta curves, but only marginal difference for the magenta and blue curves. This indicates that some of the transformations in Pt-clusters' structure, which were possible in case (a), became hindered after the reduction at T_{RED} 500 °C (which equaled to T_{DEG}).

Panel (c) shows results for the sample that was reduced at still higher temperature (T_{RED} = 600 °C) and was than degassed at 500 °C under wet conditions (as in Fig. S16). In the given case, the H_2-desorption traces are insensitive to T_{TR} in the range of T_{TR} 100-400 °C, but the increase of T_{TR} to 600 °C affects appreciably the amount of the "extra" hydrogen (green curve in the panel).

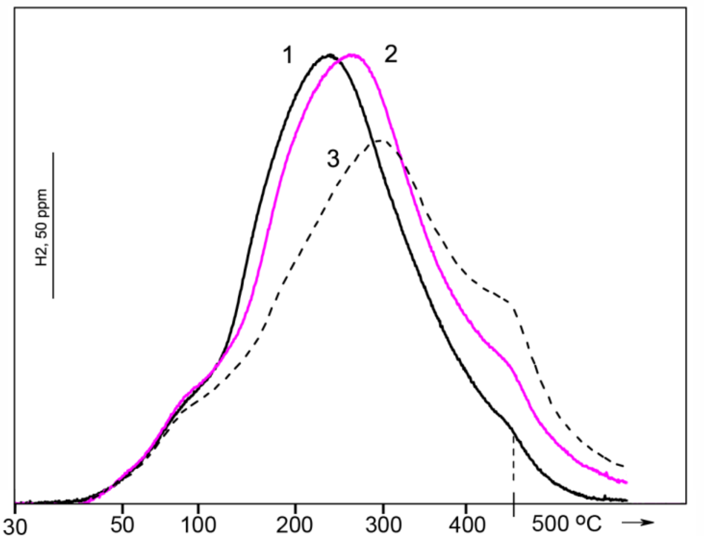


Fig. S3 H_2-TPD curves of a 0.5%Pt/γ-Al_2O_3 sample. (1) After initial reduction at 300 °C (1 h). (2) In repeated run at T_{TR} of 300 °C (15 min). (3) After subsequent reduction at 400 °C (1 h).

One can see an appreciable difference between curves (1) and (2), which is probably a consequence of the presence of H_2O (the reduction product) before run (1) and removal of the water during that run.

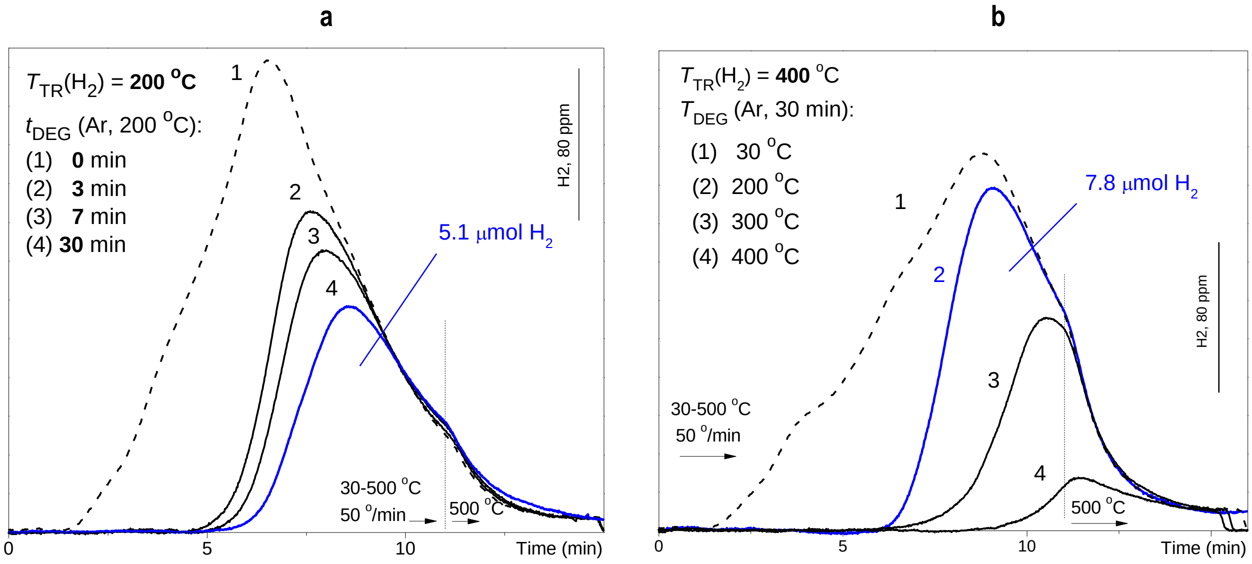


Fig. S4 Estimating the amount of residual hydrogen in 1%Pt/γ-Al_2O_3 sample after degassing for different times (a) and at different temperatures (b). Blue curves correspond to equal conditions of degassing and, so, the difference between these curves reflects the difference in H_2-treatment temperature [200 °C (a) vs 400 °C (b)].

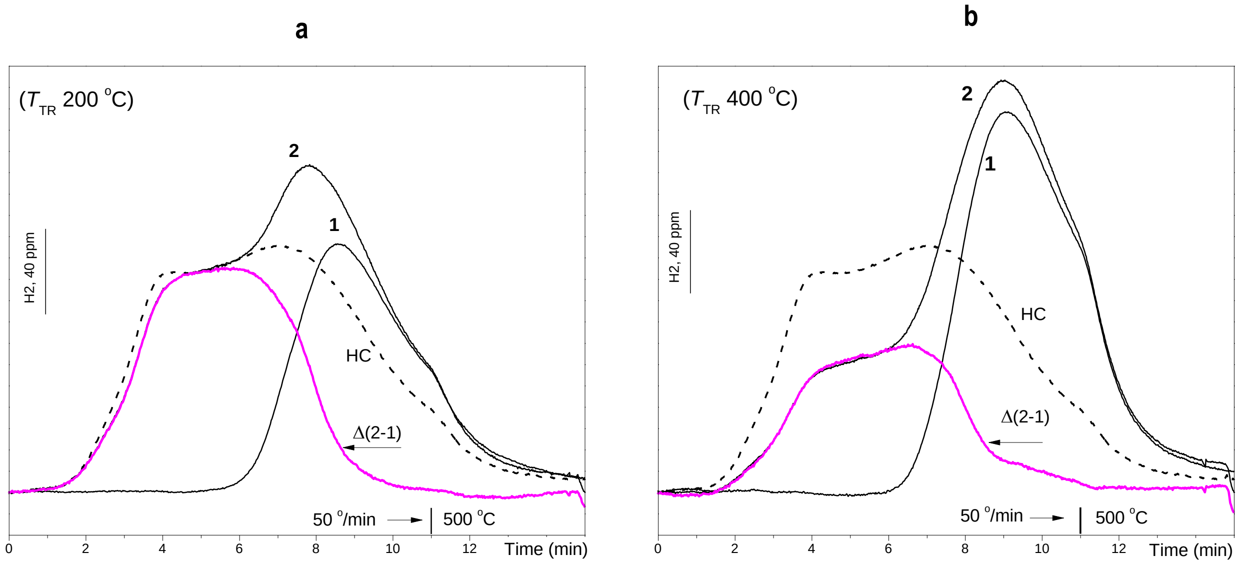


Fig. S5 H_2-TPD curves of 1%Pt/γ-Al_2O_3 after partial desorption (1) and readsorption of hydrogen (2). Initial H_2-treatment at T_{TR} of 200 °C (a) and 400 °C (b), further degassing with Ar at 200 °C for 15 min, and H_2 readsorption at 30 °C in pulse mode. Magenta lines show the difference in H_2 desorption under conditions (1) and (2), and dashed curve represents the case when the readsorption is done after standard degassing (T_{DEG} 500 °C). One can see that curve (2) in panel (a) practically coincides at the beginning with the dashed curve, but it does not take place in panel (b), where the sample was pretreated by H_2 at the higher temperature [400 °C (b) vs 200 °C (a)]. It means that mild degassing may be not sufficient to destroy the hydrogen-induced changes and return the sample to its initial state.

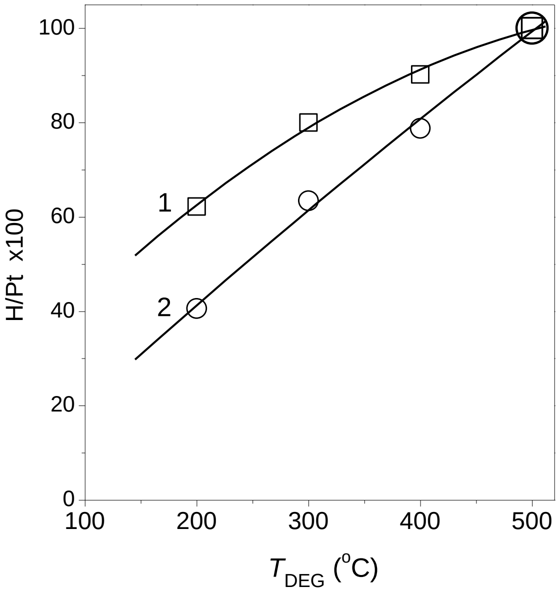


Fig. S6 H_2-adsorption capacity of 1%Pt/γ-Al_2O_3 as a function of T_{TR} and T_{DEG} (chemisorption measurements by pulse technique at 25 °C; T_{TR} 200 °C (1) and 400 ° C (2); degassing time 30 min). The sample was initially reduced at 400 °C and stabilized in a few TPD runs at T_{TR} <400 °C. According to the data, the higher is the temperature of H_2 treatment, the higher should be the degassing temperature to have consistent chemisorption data.

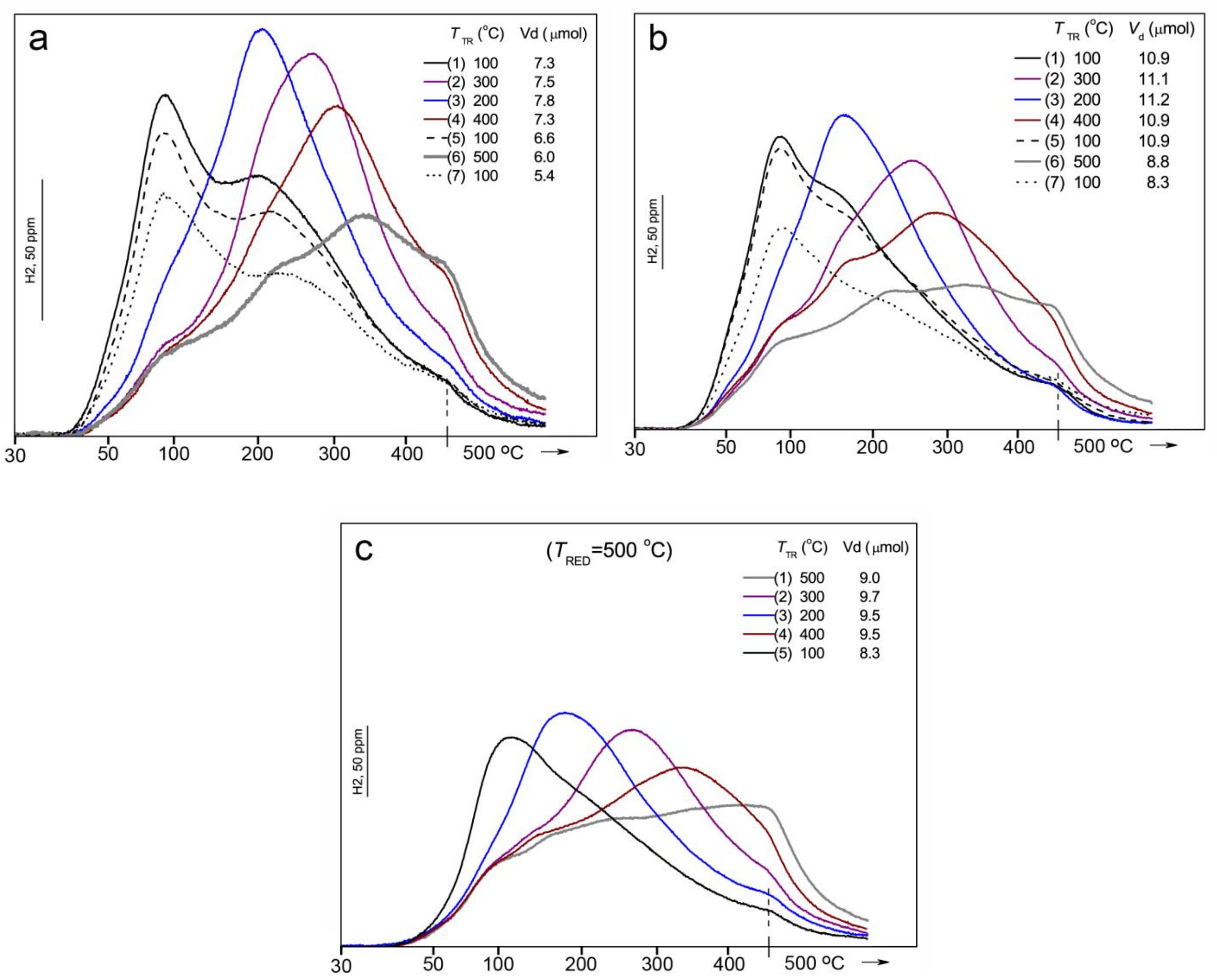


Fig. S7 H_2-TPD curves of freshly prepared 0.5%Pt/γ-Al_2O_3 (a) and 2.5%Pt/γ-Al_2O_3 (b) samples (T_{ox} 500 °C, T_{RED} 400 °C, T_{DEG} 500 °C) and an aged sample of 1%Pt/γ-Al_2O_3 (c) (the latter sample was reoxidized and rereduced at T_{ox} = T_{RED} = 500 °C). H_2-treatment temperatures (T_{TR}) and the order of treatments are shown in the figure; the dashed and dotted curves in panels (a) and (b) represent repeated runs at T_{TR} 100 °C before and, accordingly, after further reduction at 500 °C. Other conditions: H_2-treatment time 60 min at 500 °C and 15 min in the other cases; sample mass 400 mg (a, c) and 150 mg (b); for the sake of better comparison, the scale of Y-axis was normalized per mass of Pt (accounting sample mass and Pt loading).

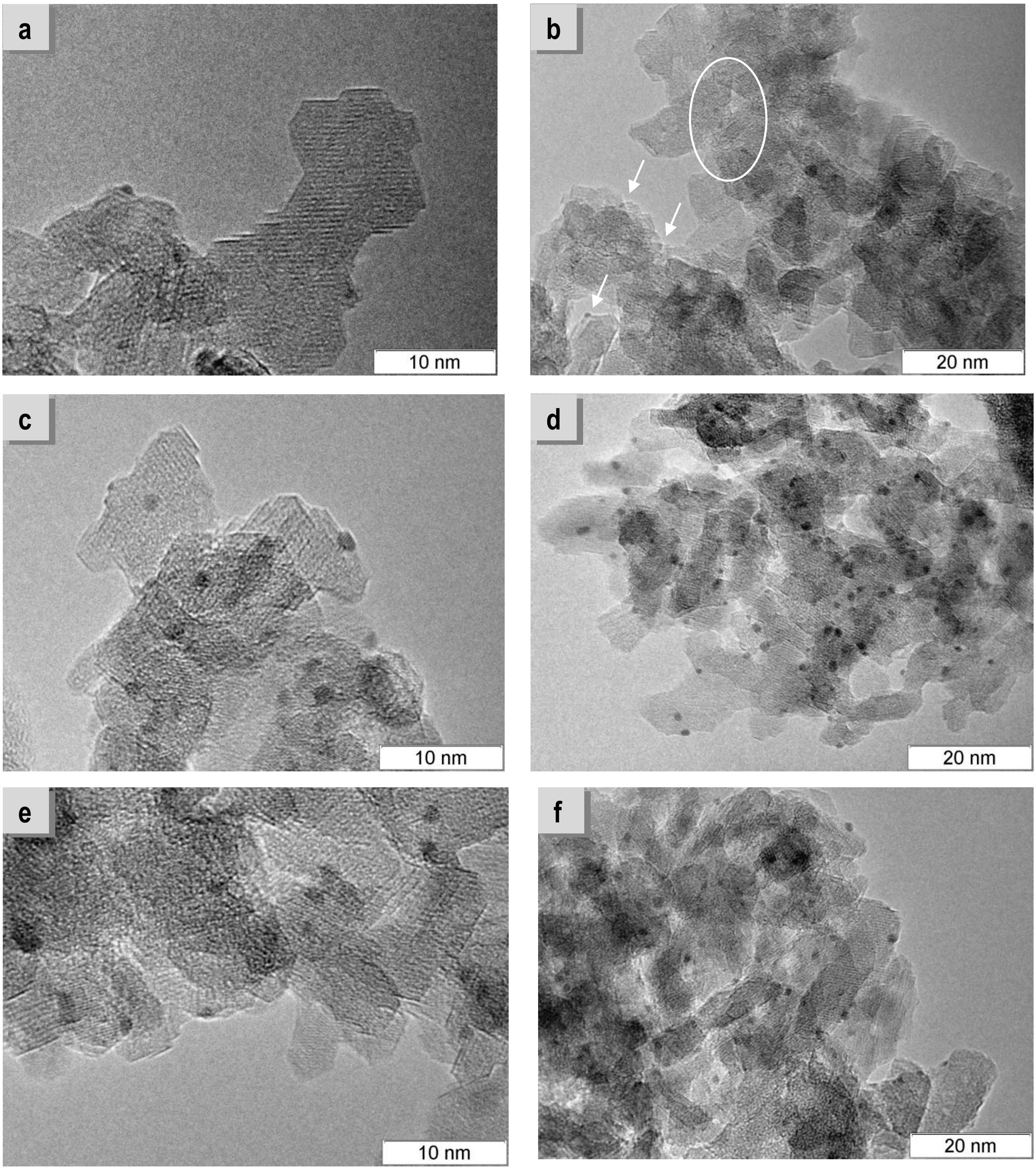


Fig. S8 Representative TEM images of 0.5%Pt/γ-Al$_2$O$_3$ (a, b), 2.5% Pt/γ-Al$_2$O$_3$ (c, d), and 1%Pt/γ-Al$_2$O$_3$ (e, f) samples in Fig. S7 (after completion of those experiments). As could be expected from previous study,[S1] the sample with Pt loading of 0.5 wt.% still contains very small Pt clusters, < 1 nm, which are barely distinguishable in the TEM images (a, b). The sample with Pt loading of 1 wt.% (e, f) was earlier used, from time to time, for comparative purposes and underwent numerous treatments in different atmospheres at temperatures up to 600 °C; this increased the cluster size from 1 nm (characteristic for the fresh sample in Fig. 2) to ~ 2 nm, characteristic for the sample with a higher Pt loading (c, d).

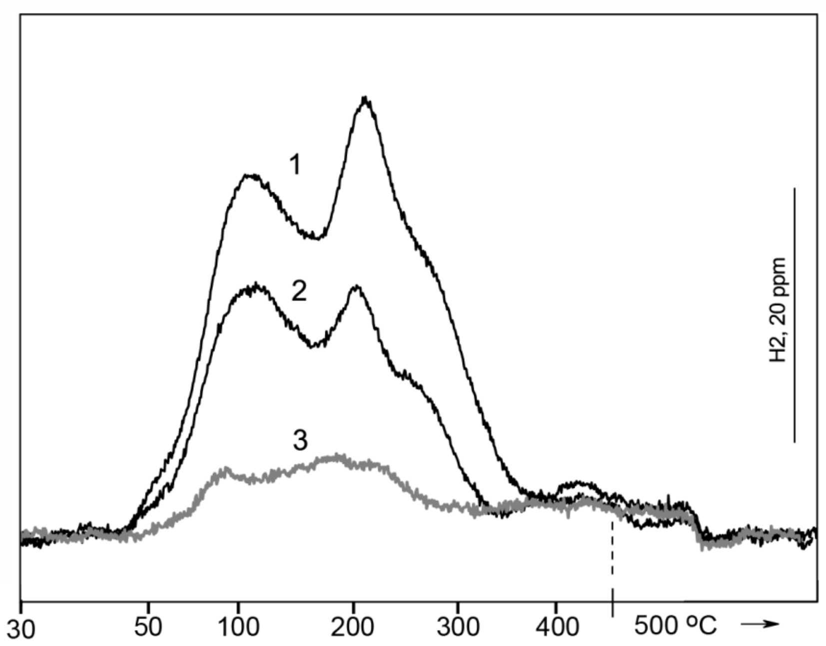


Fig. S9 Successive H_2-TPD runs (30→500 °C) with Pt-free γ-alumina. The sample was initially degassed with Ar at 600 °C (30 min) and treated in flowing H_2 at 500 °C before each of the runs (with further cooling under H_2 and purging at 30 °C with Ar); after run (2), the sample was additionally kept at room temperature for 2 h under the Ar carrier gas (prior to H_2 treatment). It can be seen from the figure that the rehydroxylation of alumina surface by water, which comes with the carrier gas (around 5 ppm H_2O under our experimental conditions)[S1], cancels the effect of initial degassing at 600 °C. In the experiments with Pt/γ-Al_2O_3 samples at $T_{TR} \leq T_{DEG} \leq 500$ °C we could therefore neglect the hydrogen adsorption/desorption on/from the support (see Fig. S10); an increment to the total desorption should only be expected at T_{TR} of 600 °C (Fig. S11).

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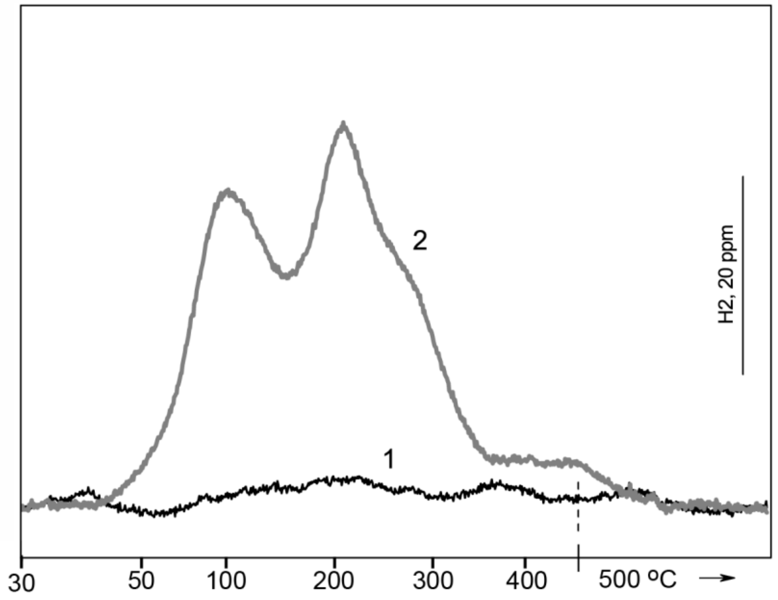

Fig. S10 H_2-TPD runs with (Pt-free) γ-Al_2O_3. The sample was initially oxidized and degassed under standard conditions (O_2, 500 °C; Ar, 500 °C). It was then treated in flowing H_2 (30 min) at 500 °C (1) and 600 °C (2), followed by cooling to 30 °C under H_2 and purging with Ar.

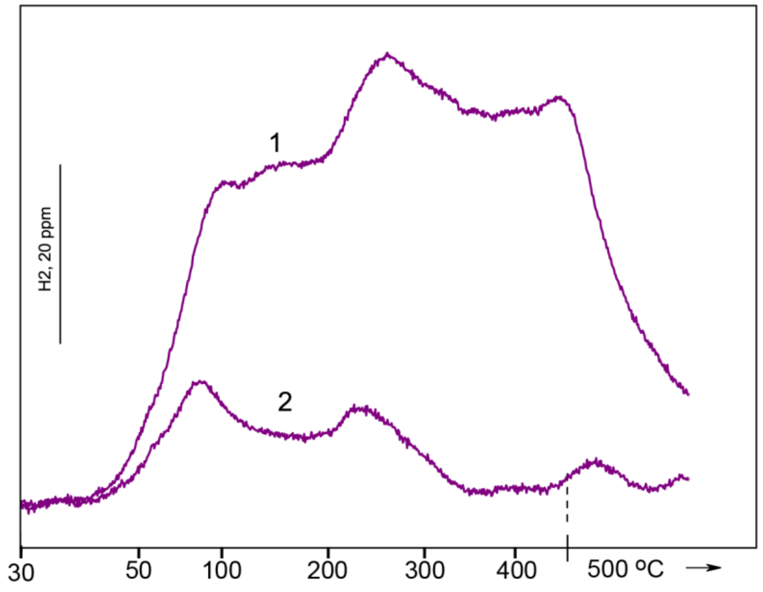

Fig. S11 H_2-TPD curves of 0.5%Pt/γ-Al_2O_3 (1) and HCl-treated γ-Al_2O_3 (2) after treatments in flowing H_2 at T_{TR} 600 °C (1 h), followed by cooing under H_2.

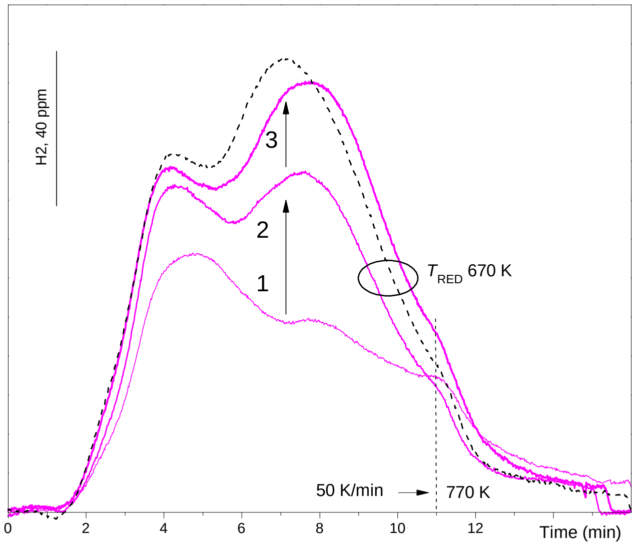

Fig. S12 An example of recovering the initial state for 1%Pt/γ-Al_2O_3 sample through calcination. Magenta curves represent H_2 TPD from the sample after HC measurements (T_{DEG} 500 °C, H_2 adsorption at 25 °C in pulse mode). Previous treatments (successively): 1) reduction at 600 °C, 1 h; 2) reoxidation at T_{OX} 500 °C, 1 h, and re-reduction at 400 °C; 3) reoxidation at T_{OX} 550 °C, 1 h, and re-reduction at 400 °C. Corresponding curve for freshly prepared sample (T_{RED} 400 °C) is shown for comparison by dashed black line.

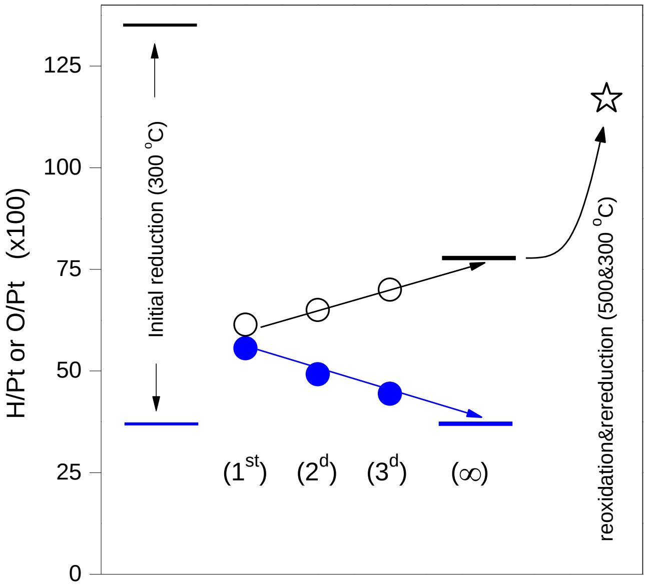

Fig. S13 Changes in HC and OC values (open and solid symbols, respectively) in repeated measurements (OC+HC) with a 0.5%Pt/γ-Al_2O_3 sample that was reduced at 600 °C. The sign (∞) indicates the level achievable by further O_2 and H_2 treatments at ambient or moderately elevated temperatures (<300 °C).

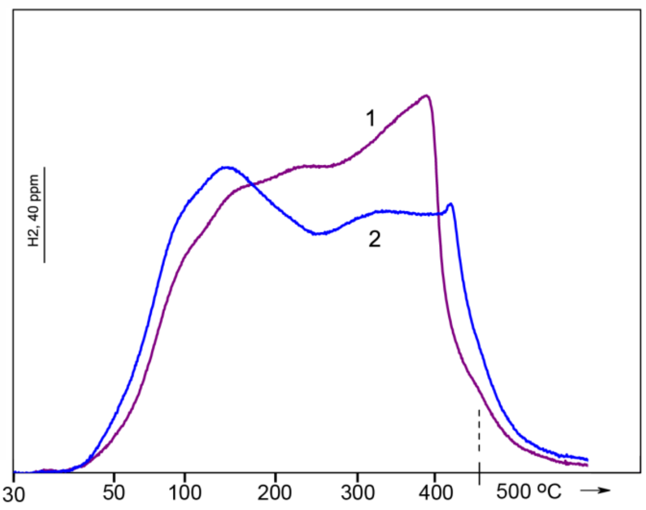

Fig. S14 H_2-TPD curves obtained for a 1%Pt/γ-Al_2O_3 sample (T_{TR} 500 °C) with *ex situ* addition of 1 µl of H_2O: (1) using standard procedures (see below); (2) injecting H_2O into the sample tube under He, followed by sample retreatment with H_2. In the latter case, the air oxygen had opportunity to adsorb uniformly on all Pt particles, and the resulting curve (2) distinctly differs from curve (1).

Standard procedures in the experiments with water addition:

In order to keep the gas lines before the sample tube dry, water was added to the samples *ex situ*. Following H_2-treatments, the sample tube was disconnected from the instrument (the sample still being under H_2), the required quantity of liquid water was injected, and the tube was sealed again to the system; all this took about half a minute. As some oxygen could (and did) penetrate into the tube during the operations in air, a slow flow of H_2 was then provided to convert O_2 into H_2O within the very first layers of the sample. The data in Fig. S14 confirm efficacy of these procedures.

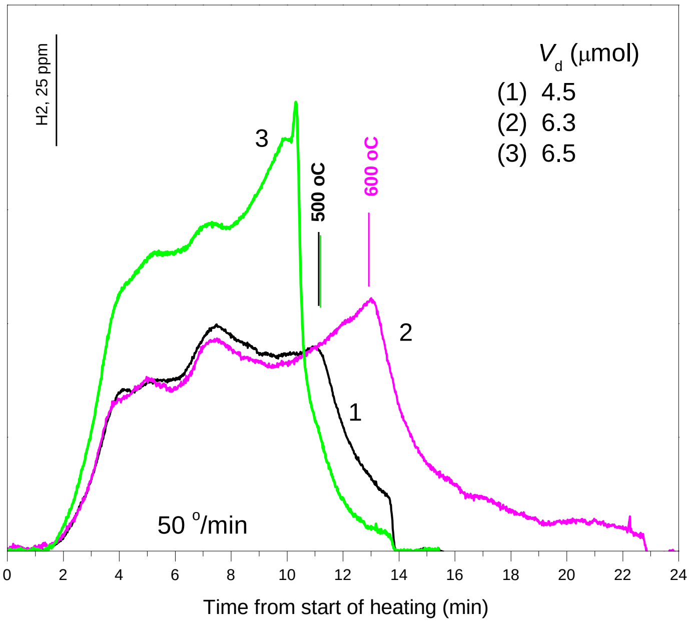

Fig. S15 H_2-TPD curves of a 0.5%Pt/γ-Al_2O_3 sample pretreated with H_2 at T_{TR} 600 °C. Runs (1) and (2) were conducted under dry conditions and run (3) with addition of 2 µl of H_2O; in case (2), the final temperature for H_2-TPD was increased to 600 °C.

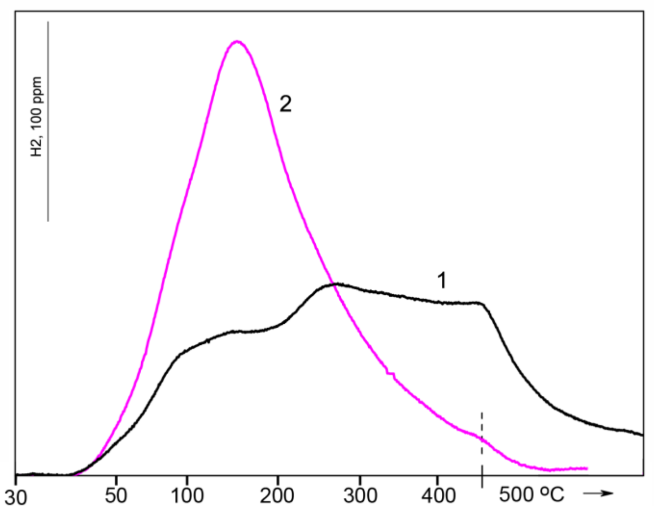

Fig. S16 H_2-TPD curves of a 1%Pt/γ-Al_2O_3 sample: (1) after H_2 treatment at T_{TR} 600 °C; (2) following the same treatment plus eighteen H_2/O_2 titrations at 30 °C. H/Pt ratio in HC measurements after run (2) equaled 0.74, as compared to H/Pt ratio of 0.56 after run (1).

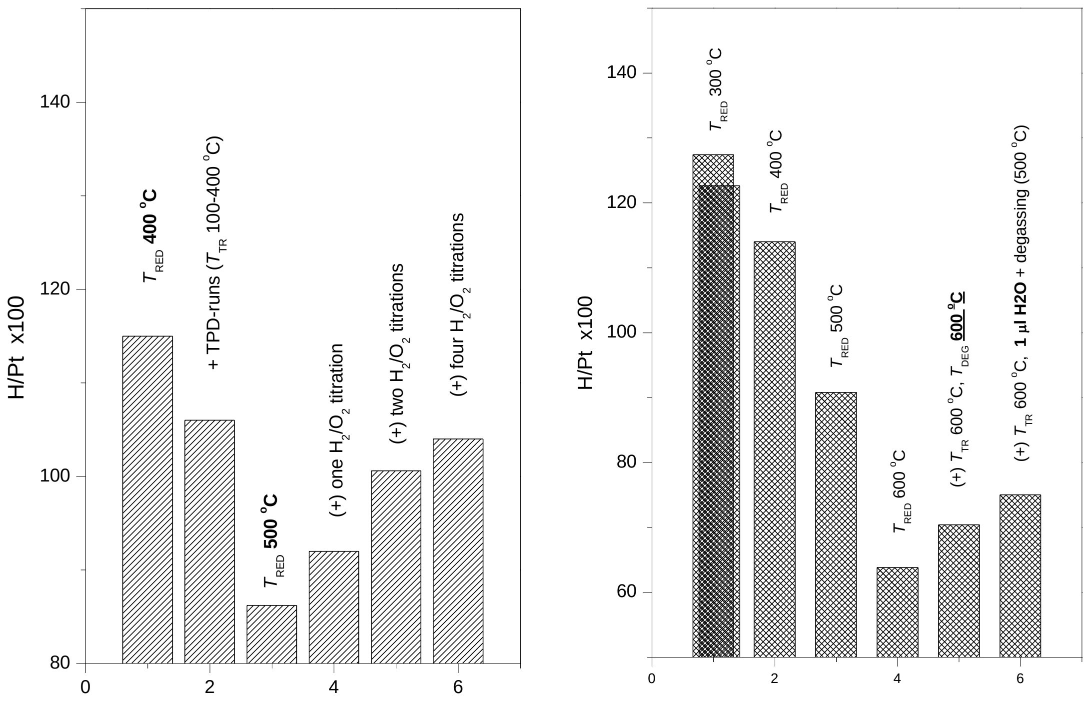

Fig. S17 Characteristic changes in HC values (H/Pt ratio) for 0.5%Pt/γ-Al_2O_3 samples in the course of successive treatments (specified in the figure).

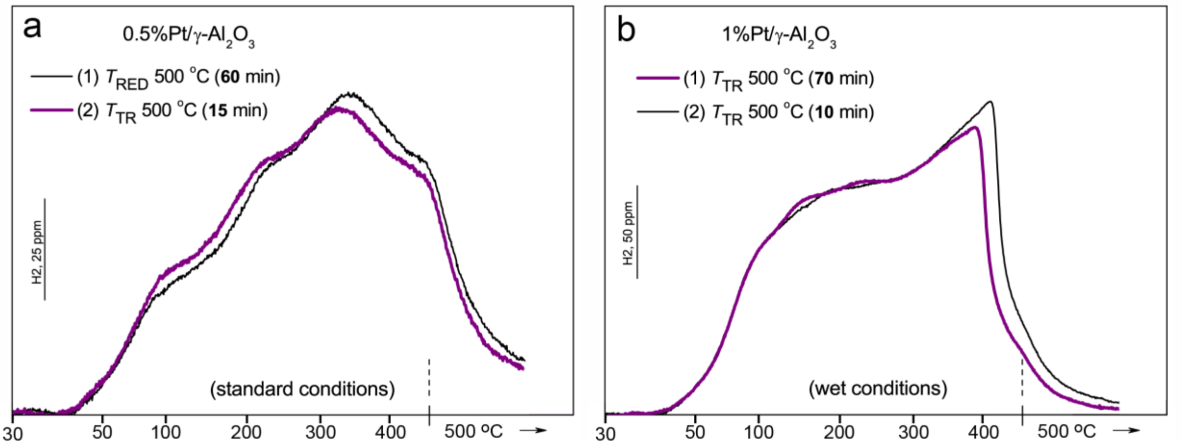

Fig. S18 An example demonstrating that the duration of H_2 treatments has only marginal influence on samples' properties. Pretreatment conditions are specified in the figure. In the panel at right, 1 μl of H_2O was added before the runs to allow all hydrogen to be evolved.

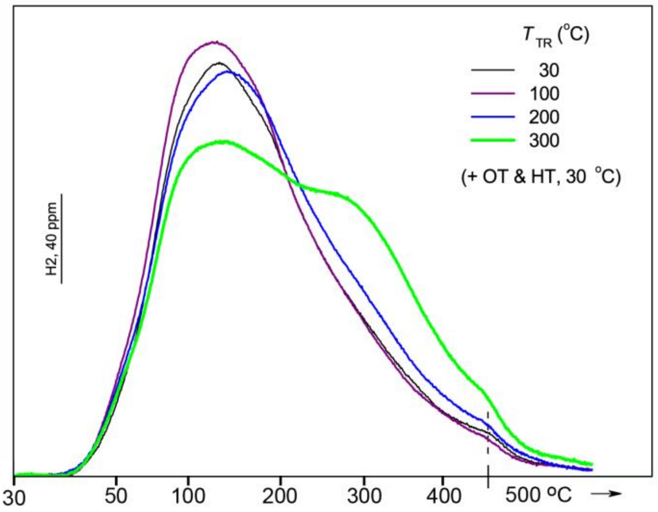

Fig. S19 H_2 TPD curves of a 1%Pt/γ-Al_2O_3 sample after H_2-treatments at different T_{TR} (specified in the figure) which were followed by O_2 titration of adsorbed hydrogen (in pulse mode) and final treatment in flowing H_2 at 30 °C for 5 min. It is seen that the curves at T_{TR} 30-200 °C are similar and, so, the titrations were able to provide an equal structure for the supported clusters (this corresponds to previous observations)[S1]. However, the curve at T_{TR} of 300 °C distinctly differs from the other curves, thereby indicating that H_2 treatment at this temperature caused stronger changes for Pt clusters and/or metal–support interface.

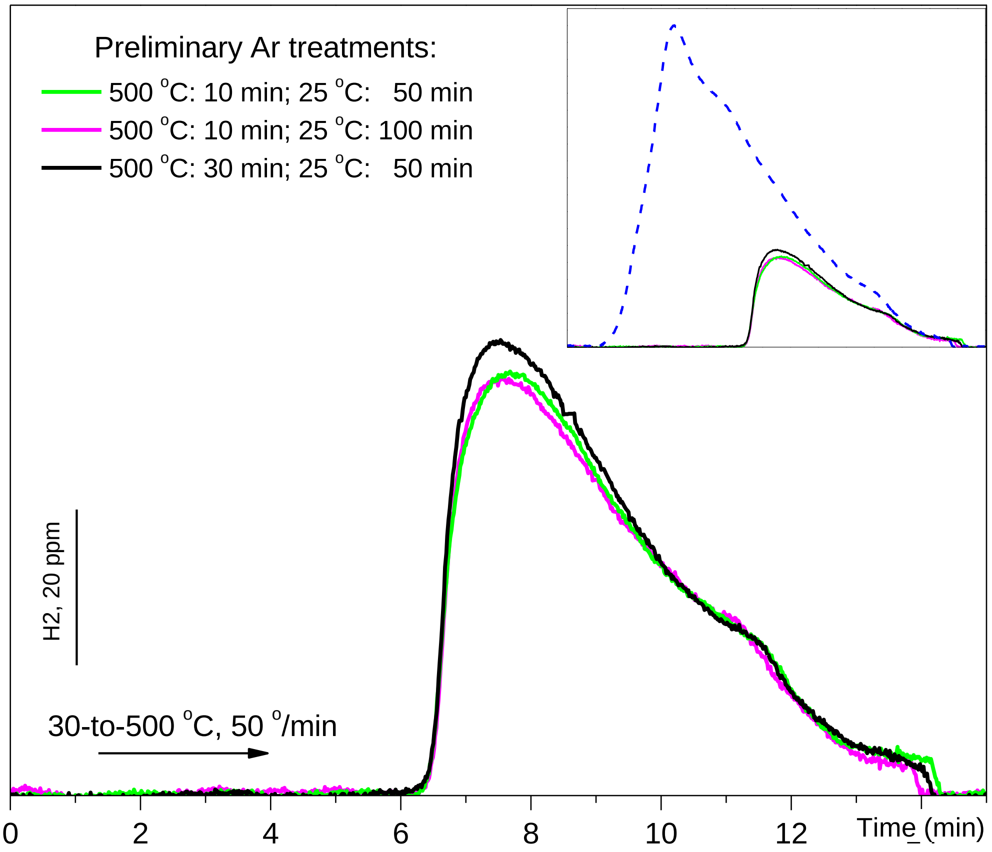

Fig. S20 Control tests on the possible effect of O_2 impurities in the Ar carrier gas. The H_2-desorption traces relate to 2.5%Pt/γ-Al_2O_3 sample (150 mg; standard preparation, preliminary stabilized) that was degassed and left in flowing Ar for different times before final treating with a 70-μl dose of H_2 (this amount is small enough for all hydrogen to adsorb). In the inset, these traces are compared with H_2-TPD curve for the same sample after H_2 treatment under standard conditions (here, at T_{TR} 100 °C, dashed line).

The first run was performed with preliminary exposure of the sample to Ar at room temperature for 50 min, which is usual for our experiments and sufficient for cooling the furnace (we used clamshell furnace, and the sample tube could be rapidly cooled with the aid of a fan). Before the second run, the exposure to Ar was increased to 100 min. Any difference in resulting TPD-curved will therefore reflect influence of accumulated (adsorbed) oxygen, which amount should have been doubled in the second case. However, the difference between the H_2 traces in these runs can be considered negligible (at the level of uncertainty in baseline), and this rules out any significant influence of O_2 impurities on the results we report. (In experiments as in the main body of Fig. S20, it required 10-20 h of treating the sample in the carrier gas for a sufficient amount of O_2 to be delivered and H_2-desorption trace to vanish; this corresponds to the results of different tests that showed that the concentration of O_2 in our gases, *when they reached the sample tube*, is within 1-2.5 p.p.m., depending on the case.[S1])

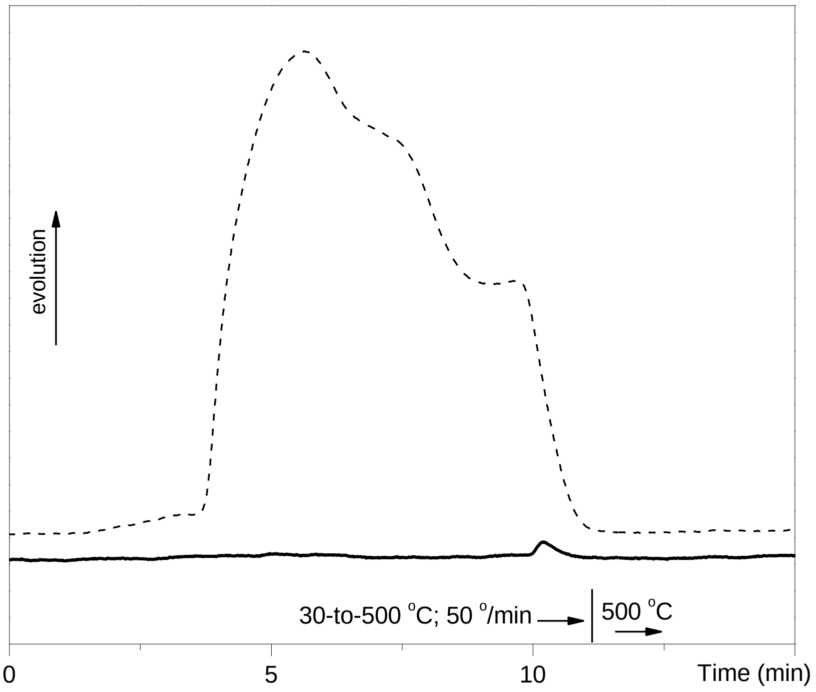

Fig. S21 A control experiment that excludes the possibility of any significant contribution from carbonaceous species and water gas-shift reaction under our conditions. The solid curve was obtained after reoxidation (T_{ox} 500 °C, 1h) and rereduction (T_{RED} 500 °C, 1 h) of air-stored 1%Pt/γ-Al_2O_3 sample, using the same TPD-conditions as in Fig. 3a (H_2O 1 µl) but with He as the carrier gas, instead of Ar. Under these conditions, TCD is (almost) insensitive to evolving H_2 but is sensitive to heavier gases, such as CO_2, which might form by the reaction: $C_xH_y + H_2O \rightarrow CO_2 + H_2$. Considering the solid curve, one can see only a very small peak at the end of heating stage, and the peak may be due to admixtures that appeared during the H_2O addition (which was done in air). Dashed curve shows the evolution of CO/CO_2 in comparative experiment after consecutive CO-O_2-CO treatments of the same sample (here, the molar amounts of carbon oxides evolved approximately correspond to the molar amount of Pt).

The results are in line with other tests, which showed that surface carbonates, carbonaceous deposits, or organic species were practically absent under our conditions (see ref. S1). The results also show that H_2O vapors were effectively trapped before the carrier gas reached TCD. (All TPD experiments were performed with a stainless steel helical trap installed in front of the detector and cooled down to -100 °C.)

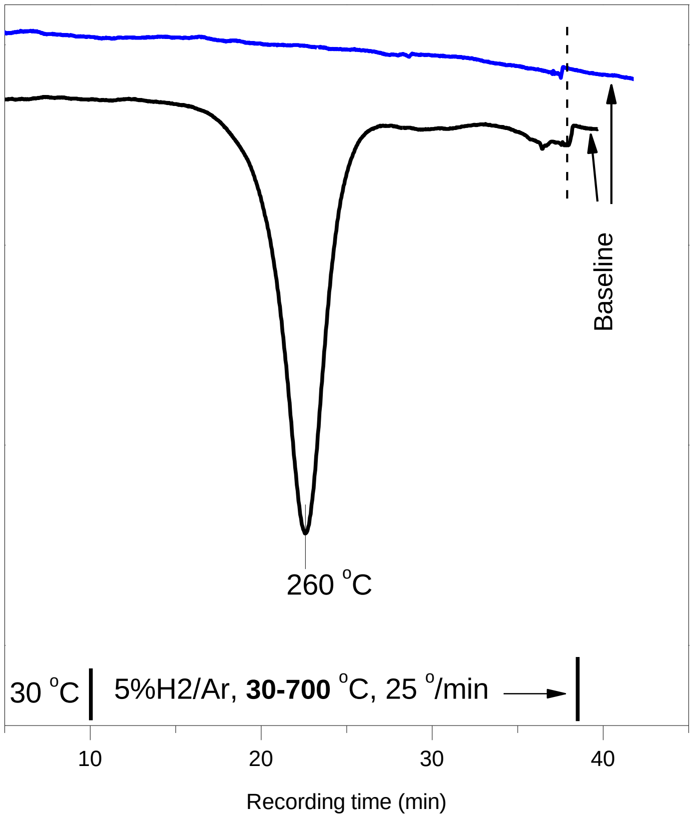

Fig. S22 H_2-TPR curves of HCl-treated γ-Al_2O_3 (blue line) and 0.5%Pt/γ-Al_2O_3 sample with the metal precursor (black line). Both samples were pretreated in situ in flowing O_2 under our standard conditions (500 °C, 1 h). The peak at 260 °C corresponds well to previous TPR studies of Pt/γ-Al_2O_3 after analogous treatments (*e.g.*, see the most detailed study by Lieske at al.[S2]), and the absence of other clear peaks in the TPR-curves confirms that the purity of the support and our pretreatment conditions were adequate to have sufficiently pure Pt/γ-Al_2O_3 samples.

Experimental details to Fig. S22 and S23: The procedures were basically the same as in TPD-experiments. At the beginning, the sample (400 mg) was kept at 30 °C in the carrier gas (here, 5%H_2/Ar, 25 cc/min) to stabilize the baseline (stage I), then heated to the final temperature at a nominal rate of 25 °C/min (stage II), and the process could continue isothermally (stage III). At the final stage (IV), the baseline signal was determined again (*via* directing the carrier gas to TCD by-passing the sample). The curves in Fig. S22 and S23 are presented as recorded, without baseline subtraction, and vertically off-set for clarity; dashed lines in Fig. S23 show the estimated baseline for the whole run.

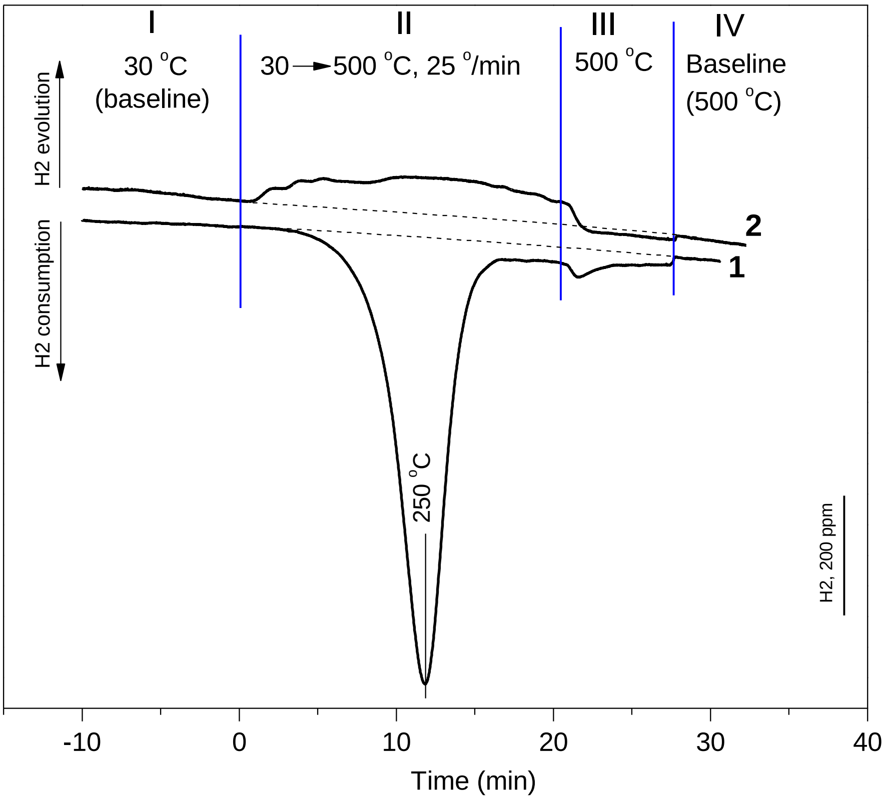

Fig. S23 (1) H_2-TPR curve of a 1%Pt/γ-Al_2O_3 sample with supported metal precursor (following standard treatment by O_2 at 500 °C, 1 h). (2) Subsequent run, after cooling the sample under the 5%H_2/Ar carrier gas to 30 °C. Considering the first run, one can see a high consumption of H_2 at the temperature characteristic of Pt^{n+}-to-Pt^0 transition but only a weak one at the higher temperatures, at which conditions the formation of oxygen vacancies on the alumina surface should take place. At first sight, this conflicts with expectations from Scheme 1. However, the progressive increase of temperature during TPR run must also stimulate hydrogen desorption from Pt surface, and this can compensate the consumption of H_2 in reduction processes. In its turn, the H_2-desorption in run (1) is masked by the H_2-consumption, but it becomes apparent in run (2), which was done with fully reduced sample. Note that the isothermal conditions at stage III decrease the desorption rate to zero in run (2) but “accelerate” the H_2 consumption in run (1). Note also that water being formed in the course of Pt^{n+} reduction will promote the autocatalytic reduction (by facilitating the access of Pt^{n+} species to Pt^0 nuclei) but will slow down the formation of the surface vacancies.

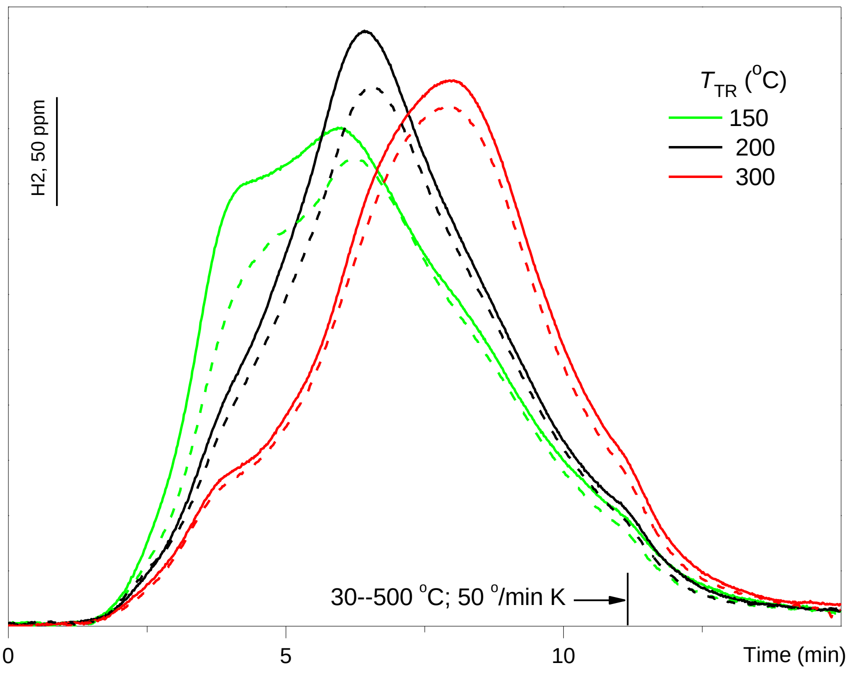

Fig. S24 An example of H_2-TPD curves for 1%Pt/γ-Al_2O_3 samples that were preliminary reduced at 300 °C (solid lines) and 400 °C (dashed lines) and then used in a series of experiments at $T_{TR} \leq T_{RED}$.

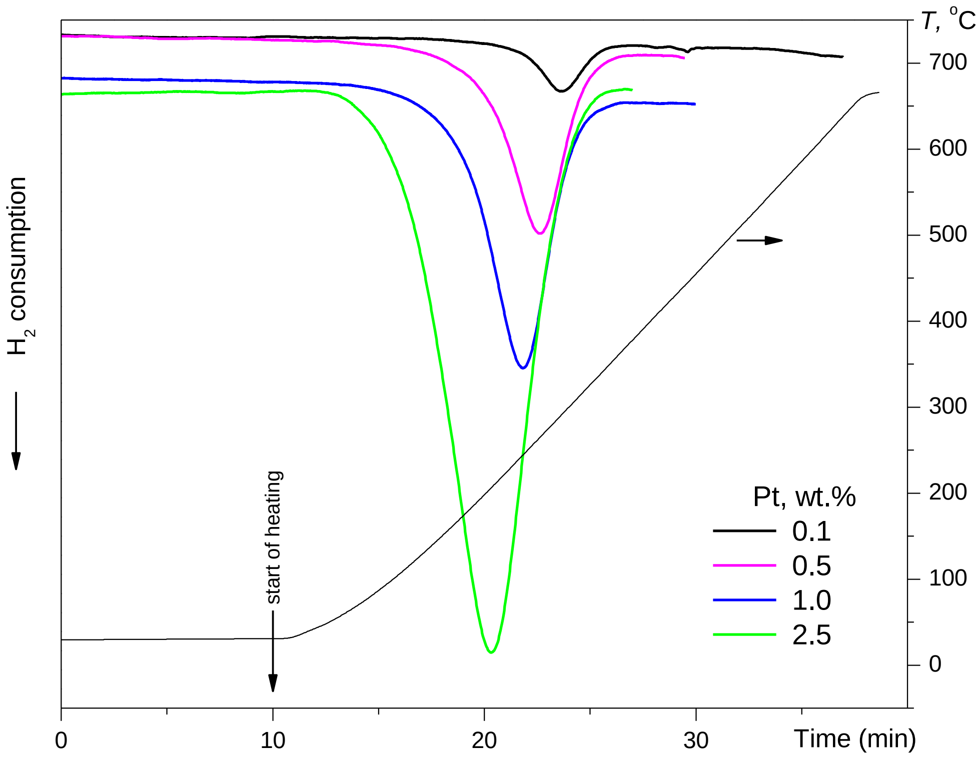

Fig. S25 Available H_2-TPR data for Pt/γ-Al_2O_3 samples with different Pt loading (following the calcination of supported metal precursor; sample mass 400-500 mg; 5%H_2/Ar as the carrier gas, heating rate 25 °C/min). The curves are presented as recorded, without subtracting the baseline, and vertically offset for clarity; H_2 consumption at heating stage is only shown.

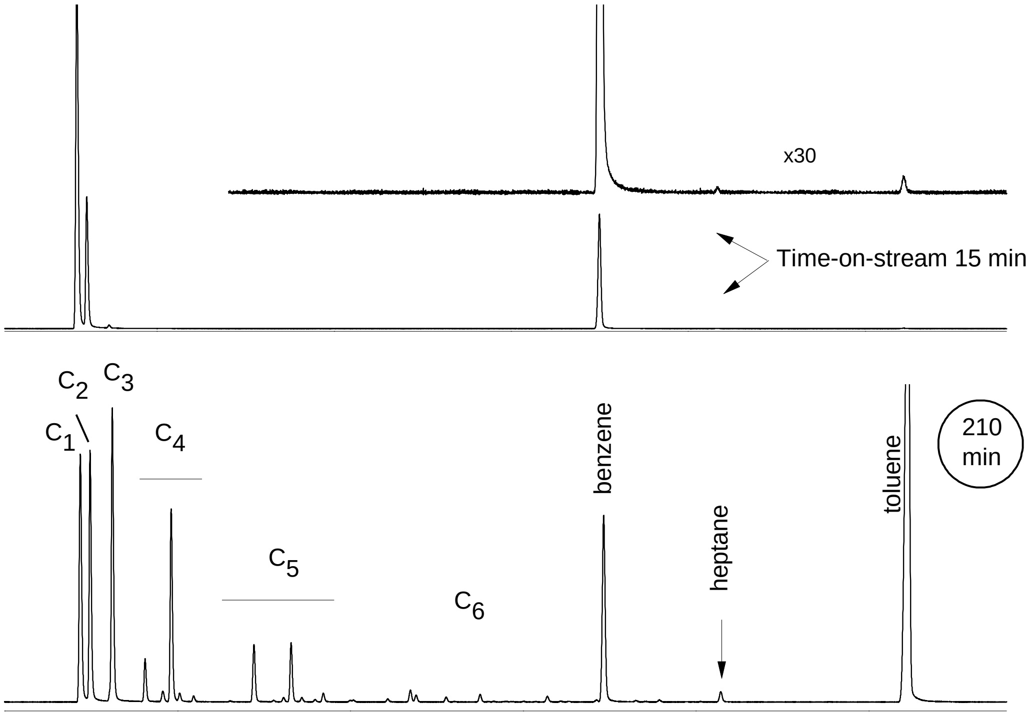

Fig. S26 Chromatograms of the reaction products at the beginning and at the end of the run in Fig. 5a (T_{RED} 450 °C). One can see that hydrogenolysis activity of fresh catalyst is so high that the substrate and all primary products are converted to benzene or C_1-C_2 hydrocarbons, and even to the end of the run the catalyst retains its ability to convert all heptane in one pass.

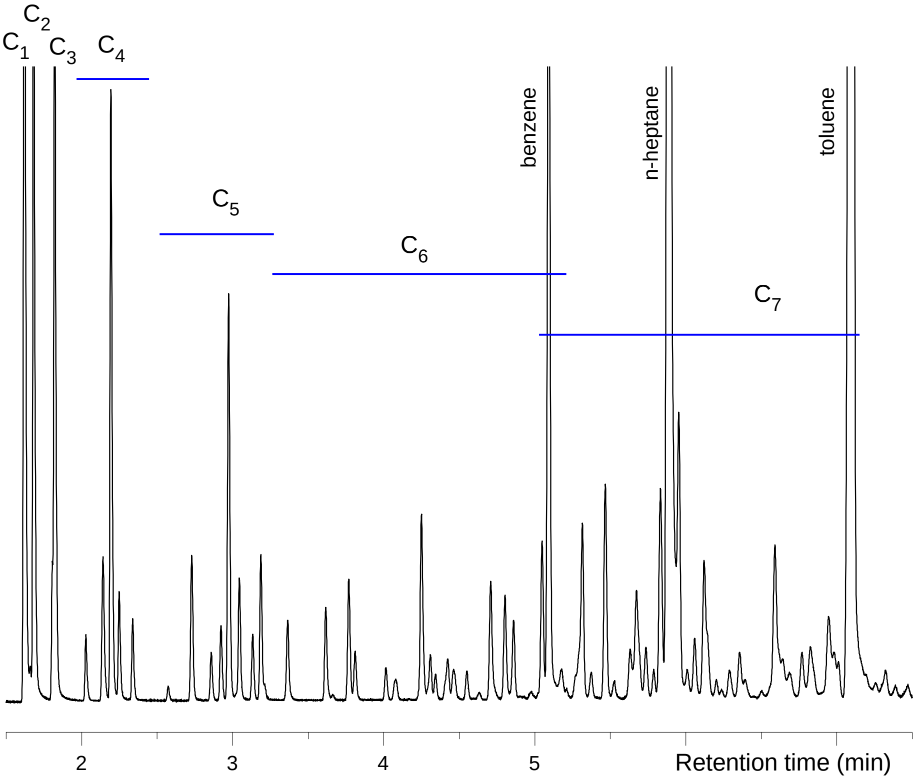

Fig. S27 A chromatogram of the reaction products at the end of the run in Fig. 5b (T_{RED} 500 °C). The catalyst produces a typical set of reforming products (alkanes, α-, cis/trans β- and γ-alkenes, various linear and cyclic isomers, as well as benzene and toluene; xylenes and heavier products of dismutation and dimerization were also detected, at longer retention times). This is in line with the observations in ref. S3 that HTHTs influence the catalytic properties of Pt/γ-Al_2O_3 in the same way as promoting by additives (e.g., Sn).

Experimental details to Fig. 5 and S26, S27

The 0.5%Pt/Al_2O_3 sample (100 mg) with supported metal precursor (H_2PtCl_6) was placed into a tubular quartz reactor (i.d. 8 mm) using a quartz wool plug to support the sample. A flow of O_2 (30 cc/min) was provided to the reactor and the sample was heated to 500 °C (15 °C/min) using a temperature-programmed furnace. The sample was at 500 °C under O_2 flow for 1 h, and the reactor was then cooled to ambient temperature. After flushing the reactor with He, a flow of H_2 (30 cc/min) was provided and the sample was reduced at 450 °C or 500 °C for 1 h (heating rate 15 °C/min).

Catalytic testing was performed immediately after the reduction. The sample temperature was set at 450 °C and H_2 flow rate at 60 cc/min. After stabilization of conditions, n-heptane was fed into the stream at H_2/C_7H_{16} mol ratio of 50. Heptane was dosed through a (very) thin stainless steel capillary placed into liquid heptane, and the dosing rate could be adjusted by varying the pressure above the liquid phase. We used a home-made device with a computer-controlled pressure unit, which assured constant C_7H_{16}/H_2 ratio in the stream (deviations less than ±2%).

The reaction products were analyzed on-line using a chromatograph with a FID detector and a DB-1 capillary column (J&W Scientific, 60 m × 0.25 mm, 1 μm; He as carrier gas, 2 bar). Sampling was made with the aid of a heated six-way valve (VICI) fitted with a 1 cm^3-loop. Product identification was done using reference compounds and literature data.

The degree of conversion was calculated by formula:

$$C = ([n\text{-}C_7]_0 - [n\text{-}C_7])/[n\text{-}C_7]_0,$$

where $[n\text{-}C_7]_0$ and $[n\text{-}C_7]$ stand for the concentration of n-heptane in the inlet and outlet feed, respectively. The product yields were calculated in terms of carbon efficiency, *i.e.*, the combined yield of products from a certain group was calculated by formula:

$$Y_P = \Sigma([C_{i,n}] \times n_i)/([C_7]_0 \times 7),$$

where $[C_{i,n}]$ stands for molar concentration of product *i* with n carbon atoms in the molecule, and $[C_7]_0$ is the concentration of the substrate in the inlet feed.

References

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