Supporting Information for:

Resolving Interparticle Heterogeneities in Composition and Hydrogenation Performance between Individual Supported Silver on Silica Catalysts

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Determination of Red Color Index

Step by step procedure used to calculate red color index, steps 3-5 are displayed in Figure S1:

1) Color images of several catalyst granules (20-40) at once were obtained via the eyepieces of an Olympus upright microscope using an adapter from Micro-Tech-Lab (Austria) to connect a Canon EOS5D color camera.

2) Color images were processed in ImageJ

3) Manual selection of particles was done via ‘polygon selection’

4) Via the histogram of this selected area/particle, the mean 8-bit value in the red channel was determined. Theoretically values range from 0 for intense red particles to 255 for completely transparent particles.

5) Additionally, the mean 8-bit value of the surrounding background was measured. This value is obviously equal to or larger than the values obtained for the different particles, except for the very bright transparent ones.

6) The mean red channel value of the selected particle (see step 4) was divided by the mean value of the background (see step 5)

7) The obtained ratio (values between 0 and 1) is subtracted from 1. Hence we get an increasing index for increasing ‘redness’

Figure S1. Illustration of steps 3-5 in the used procedure to calculate red color index.
Nitrogen Physisorption

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics 3Flex 3500 physisorption instrument. The sample was degassed before measurement at 423 K for 6 h under vacuum (10⁻² mbar). The pore size distribution was calculated using the BJH method (Harkins and Jura thickness curve and Faas correction, 3Flex 3.00 software).

![Pore size distribution](image)

**Figure S2.** Pore size distribution of the used silica gel with an average pore width of 60 Å.

Physicochemical properties of Silica Gel (60752 Fluka, Sigma-Aldrich) from nitrogen physisorption measurements:

- BET Surface Area = 408.6 m²/g
- BJH Desorption cumulative pore volume = 0.789 cm³/g
- BJH Desorption average pore width = 60 Å
High Resolution Scanning Electron Microscopy (HR-SEM)

On average 6 nm pore confined AgNPs are detected after crushing the sample (a), micrographs b-d were obtained without any modification of the sample in order to relate nanoparticle size on the outer surface of the granule to its color. On transparent granules with a red color index in the range of 0-0.5 (f.e. Figure S3 b) none or only a few 20-30 nm sized nanoparticles were present, markedly more of these 20-50 nm sized particles were detected on yellow granules with a red color index in the range of 0.12-20 (Figure S3 c-d). Schematic representation of Ag nanoparticle size distribution for three optically different granules is depicted in Figure S3 e.

FigureS3. HR-SEM micrographs of self-synthesized (a) and commercial (b-d) Ag/SiO₂, e) Ag NP size distribution of the outer surface of three granules with a Red Color Index (R.C.I.) of 0.07, 0.16 and 0.77 corresponding to respectively 2.9 wt %, 6.2 wt % and 15 wt % total silver loading per granule.
Focused ion beam (FIB) milling combined with SEM-EDX

Cross-section FIB slicing and milling combined with SEM and EDX were performed using an Scios Dual Beam system (FEI, The Netherlands). Before FIB cutting, a 2 μm protective layer applied to the crystal surface through ion-beam-assisted deposition (30 kV, 1 nA) to minimize the curtaining effect. Ga⁺ ion beams of 30 kV/15 nA and 1 nA were used for trench milling and sample slicing respectively; slice thickness was 3 nm. Conventional SEM (1 kV, 13-25 pA, WD = 2.2 mm) was used to observe crystal morphology after FIB milling and slicing, combined with EDX analysis. Image acquisition was performed using the lower (T1) in-lens BSE detector and using NG Microscope User Interface software (FEI); further image analysis and processing were performed with AutoSlice And View software (FEI).

**Figure S4.** Left: Weight percentage silver versus distance of a commercial Ag/SiO₂ particle, EDX analysis after FIB milling and slicing; Right: SEM micrograph of a sliced granule.
Catalytic performance testing at the single support particle level.

To test cross contamination of the 21 reaction wells via distillation of product or reagent from one well into another, solutions filled with 4-NSt (0.1 M), 4-VAn (0.1 M) and internal standard (n-tetradecane, 0.18M) in EtOH were placed in a reactor next to a pure EtOH solution, after 1h under 20 bar of H₂ heated to 100 °C, no 4-NSt or 4-VAn was detected and only minute amounts of internal standard (< 2 µM).

Prior to the catalytic reaction, single support particles are carefully placed one by one in the different wells via a stereomicroscope (Leica M165FC). After this, the multiwell can be filled with the reaction solution using a micropipette and placed in the reactor. Since thermal hydrogenation of 4-nitrostyrene results in the formation of the unwanted 4-ethynitrobenzene and little 4-vinylaniline, in each run several wells are not filled with a catalyst particle to account for this blank conversion and some wells are only filled with solvent to assure that no cross contamination has occurred. To lower solvent evaporation as much as possible the high boiling N,N-dimethylacetamide (DMA) was used as a solvent and n-hexadecane as internal standard for quantitative GC-analysis. Optimization of reaction conditions led to the use of 18 µL of a 33 mM 4-NSt solution in each microwell, performing hydrogenation under 20 bar of H₂ heated to 110 °C for 2.5 h in a Parr reactor filled with 3 mL of DMA. Analysis of the samples was carried out via gas chromatography after rinsing the wells two times with pure DMA.

Figure S5 depicts the results for 47 individual silver supported silica particles, in Figure S5 c 4-VAn yield is corrected for support granule size and normalized to the silver content. Calculation was done as follows: Every reaction well contained one support granule of which the red color index was determined according to the earlier described method. By including the size of the particle in combination with the silver loading determined by linking the red color index to EDX and ICP data, the observed catalytic conversion in a specific well could be normalized on basis of the silver content of that specific supported silver catalyst granule. The red color index–EDX relation was extensively studied and is shown in the main article in Figure 2. FIB-SEM however revealed that EDX data recorded solely from the first few micrometers below the outer surface resulted in an overestimation of Ag-loading as a consequence of a silver loading gradient. Therefore, ICP-AES measurements were performed. In order to allow correct determination of the catalyst sample’s weight, a sufficient amount of sample was required. That is why we have sorted the sample in different batches based on their optical color (see Supporting Figure S7). These data allow to correct the silver content determined from EDX measurements to give a more accurate value.
Figure S5. Single Particle experiment results (2.5 h, 20 bar H₂, 110 °C). (A) Blank-corrected absolute conversion and (B) 4-Vinylaniline (4-VAn) selectivity versus Ag-loading, based on SEM-EDX relation, (C) Normalized 4-VAn yield versus silver loading for 47 individual silver supported silica granules, estimation of silver loading based on red color index, SEM-EDX and ICP-AES measurements.

In addition some important notes on the validity of the test method: (1) there was no detectable amount of reagent or product in the wells filled only with solvent, nor in the reactor and (2) 4-vinylaniline yield in the blank reactions was consistent in the different between the different wells: 0.26±0.03 % (run 1); 0.18±0.07 % (run 2); 0.21±0.02 % (run 3); 0.23±0.04 % (run 4).

Specifications of microwell slide (Hamamatsu A10657-01):

| Material       | Slide glass       | Soda-lime glass |
|----------------|-------------------|-----------------|
| Cover glass    | Borosilicate glass|
| Number of wells| 21 (3×7)          |
| Working volume | 25 µL             |
| Dimensions     | 38 mm x 25 mm x 3.4 mm |
| Well diameter  | 4 mm (top), 3 mm (bottom) |
| Well depth     | 3.1 mm            |
Calculation of Estimated Theoretical Normalized Yield

Figure S6. Optical microscopy study on catalyst powders. Interparticle heterogeneity (n = 250-600) illustrated with pie diagram, colors represent red color index of individual Ag/SiO\textsubscript{2} granules.

The calculation of the estimated theoretical normalized yield for the commercial 6 wt% Ag/SiO\textsubscript{2} catalyst is given as an example:

1) Based on a granules’ red color index, it is classified in a specific red color index subunit (Table S1, column A)
2) Every subunit corresponds to an average Ag loading (Table S1, column B)
3) Every subunit also corresponds to an average normalized 4-Vinylaniline (4-VAn) yield, obtained from the single particle catalysis experiments (Table S1, column C)
4) Optical microscopic analysis of 250-600 granules in every sample results in a pie diagram that illustrates the interparticle heterogeneity within this sample and the abundance of every subunit (Table S1, column D)
5) Since the 4-VAn yield is normalized to nmole Ag, the mole percentage of every subunit is calculated based on columns B & D (Table S1, column E)
6) The mole percentage of each subunit is multiplied with the corresponding normalized yield, adding up these products gives us the estimated theoretical yield for every catalyst batch:

Commercial 6.0 wt% Ag/SiO\textsubscript{2}: (0.55*0.018) + (0.20*0.056) + (0.08*0.16) + (0.11*0.061) + (0.05*0.02) + 0.015*0.007 = 0.042 \text{ µmol*(nmol Ag)}^{-1}
Table S1: Calculation of Estimated Theoretical Normalized Yield for the commercial 6 wt% Ag/SiO$_2$ catalyst.

| Red Color Index | Wt% Ag | $\text{Yield}_{4\text{-VAn}}$ [$\mu\text{mol}^{*}(\text{nmol Ag})^{-1}$] | Pie Diagram | Mole% Ag |
|-----------------|--------|-------------------------------------------------|-------------|----------|
| 0.00 – 0.05     | 3.5    | 0.018                                           | 70          | 55       |
| 0.05 – 0.12     | 5      | 0.056                                           | 17          | 20       |
| 0.12 – 0.20     | 6      | 0.160                                           | 6           | 8        |
| 0.20 – 0.40     | 9      | 0.061                                           | 5           | 11       |
| 0.40 – 0.70     | 12     | 0.020                                           | 2           | 5        |
| 0.70 – 1.00     | 15     | 0.007                                           | 0           | 1.5      |

$^1$Based on red color index, SEM-EDX and ICP-AES $^2$Based on single particle experiments, 4-VAn = 4-vinylaniline.

The yellow, orange and red colors originate both from the amount of 6nm Ag NPs as well as from the large NPs at the outer surface. Hence, a yellow catalyst granule taken from an on average 13 wt% Ag containing powder has a higher silver loading than a similar colored particle in the 6 wt% commercial sample. To calculate the VAn yield normalized to the silver content per granule in the different samples, we thus included this and adjusted column B of Table S1 for every sample relative to its bulk Ag loading (as determined via ICP-AES).

Bulk catalytic performance testing of powdered catalyst.

Table S2: Bulk hydrogenation of 4-nitrostyrene with different catalyst samples (2 h, 110 $^\circ$C, 20 bar H$_2$, 0.35 mole% Ag, 70 mM 4-nitrostyrene in DMA, 500 rpm).

| Sample | Wt.% Ag$^1$ | X (%) | $\text{S}_{4\text{-VAn}}$ (%) | $\text{Yield}_{4\text{-VAn}}$ [$\mu\text{mol}^{*}(\text{nmol Ag})^{-1}$] | Est. Yield$^d$ |
|--------|-------------|-------|-----------------------------|------------------------------------------------------------------|--------------|
| 1      | 3.58 ± 0.07 | 15    | 93                          | 0.040 ± 0.003                                                    | 0.022        |
| 2      | 9.53 ± 0.37 | 29    | 93                          | 0.077 ± 0.044                                                    | 0.039        |
| 3      | 13.36 ± 0.04| 39    | 85                          | 0.094 ± 0.001                                                    | 0.064        |
| 4      | 18.97 ± 0.15| 25    | 91                          | 0.066 ± 0.017                                                    | 0.053        |
| 5$^2$  | 6.00 ± 0.40 | 25    | 93                          | 0.068                                                           | 0.042        |

$^1$Determined via ICP-AES $^2$Commercial sample $^d$Estimated Theoretical Yield based on optical screening. 4-VAn = 4-vinylaniline
Sorting
Calcined commercial silver nitrate on silica gel was manually sorted using an eyelash micromanipulator in three different fractions (Figure S7, B-D) on a stereomicroscope (Leica M165FC). A Mettler Toledo AT20 balance was used to determine the weight of the catalyst transferred into the reaction vial (unsorted sample, reaction carried out in duplo). The reaction vials were placed in a 100 mL Parr reactor and bulk catalytic experiments were performed in parallel (Table S3).

![Sorting images](image)

**Figure S7. Sorting of commercial AgNO₃ sample into 3 fractions.** (A) Scale bar 2mm, (B-D) Scale bar 1mm. Images were obtained via a Leica M165FC stereomicroscope equipped with a Leica DFC 450C camera.

| Catalyst | Wt. %¹ | M (mg) | X (%) | S₄-VAn ² (%) | S₃-ENB ³ (%) | Normalized Y₄-VAn [µmol*(nmol Ag)⁻¹] |
|----------|--------|--------|-------|--------------|--------------|-------------------------------------|
| Unsorted | 6.00 ± 0.40 | 0.085 ± 0.004 | 22 | 95 | 3 | 0.06 |
| B        | 3.52 ± 0.50 | 0.119 ± 0.002 | 10 | 94 | 4 | 0.04 |
| C        | 5.33 ± 0.70 | 0.087 ± 0.004 | 36 | 95 | 2 | 0.20 |
| D        | 8.71 ± 1.00 | 0.033 ± 0.002 | 19 | 93 | 3 | 0.13 |

¹Determined via ICP-AES; ²4-VAn = 4-vinylaniline; ³ENB=ethylnitrobenzene.
Figure S8. Pt/SiO₂ synthesis (A,B) similar to Ag/SiO₂ (D), optical microscopy reveals color heterogeneity not visible on macroscopic scale (C). Images were obtained via the eyepieces using an adapter from Micro-Tech-Lab (Austria) to connect a Canon EOS5D color camera to a Olympus BX51 Upright microscope with a standard mercury lamp, equipped with infinity corrected air objectives 4x (0.16 numerical aperture (N.A.)) and 20x (0.40 N.A.).

Synthesis conditions:
(a) aqueous Pt(NH₃)₄(NO₃)₂ (31 µmol) solution equals pore volume of 120 mg dried silica gel, drop wise added under stirring, 2 h equilibrated at 60 °C, overnight dried in oven at 120 °C, calcined under O₂ flow (0.5 °C/min 350 °C, 2 h).
(b)&(d) aqueous Pt(NH₃)₄(NO₃)₂ (49 µmol) and AgNO₃ (50 µmol) solution equals pore volume of 70 mg dried silica gel, drop wise added under stirring, 0.5 h equilibrated at R.T., overnight dried in oven at 120 °C, calcined under static air (1 °C/min 500 °C, 2 h).