Electronic Supplementary Information for the manuscript entitled:

Ammonium formate decomposition on Au/TiO$_2$: A unique case of preferential selectivity against NH$_3$ oxidation[†]

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Experimental Section:

Preparation of Au/TiO$_2$ catalysts: Au/TiO$_2$ was prepared by a modified incipient wetness impregnation technique according to a previously published method[12]: Anatase TiO$_2$ (DT51, Cristal Global; BET surface 90 m^2/g, ØD50 = 1.7 µm) was impregnated with a solution of the gold precursor, HAuCl$_4$ (Sigma), of 0.032 M in Au, calculated on the basis of the amount of gold loading desired and the volume of water equivalent to the pore volume of the support. The sample was aged for 1 h at room temperature. Washing with aqueous NH$_3$ (1M) twice followed by distilled water ensured effective removal of chloride from the samples (less than 0.07 wt% as estimated by XPS). Calcination was performed at 400 °C for 5 h in air. ICP-OES analysis indicated a 0.56% Au loading for the 0.5% Au/TiO$_2$ catalyst. A pH adjusted aqueous suspension consisting of the catalyst powder and Ludox AS-40 (Sigma) as a binder was prepared in accordance to the procedure reported previously.[13] The washcoated ceramic cordierite (400 cpsi, Corning) monoliths were dried using a hot gun and then calcined in air at 400 °C for 5 h.

In the experimental setup, 40% ammonium formate (Sigma) solution was sprayed on the catalyst-coated monolith in a flow of model exhaust gas[15]. The cylindrical monolithic catalysts were wrapped around with ceramic paper before being place inside the reactor in order to prevent bypass of the reactant gas mixture. Gaseous reaction products at the reactor outlet were quantified by FTIR spectroscopy, while aerosols and high-molecular compounds were analyzed by HPLC.

Characterization: Particle size was measured on a Horiba LA-950 laser diffraction particle analyzer, utilizing Mie-scattering to derive the particle size. Specific surface area was determined on a Quantachrome Autosorb by physisorption of nitrogen at -196 °C. The crystallographic structure was determined by powder X-ray diffraction (XRD) on a D8 Advance Bruker AXS diffractometer with Cu-Kα radiation in a 2θ range from 10°-80°. The amount of deposited gold was determined by ICP-OES anaylsis. 'XPS measurements were performed using a VG ESCALAB 220iXL spectrometer (*Thermo Fisher Scientific*) with a focused Al Kα mono-source (spot size: 500 µm, power: 150 Watt) and a magnetic lens system. The spectra were recorded in constant analyzer energy mode at pass energy of 30 eV for high resolution acquisition of core levels. The XPS system was calibrated using the Ag $3d_{5/2}$, the Cu $2p_{3/2}$ and the Au $4f_{7/2}$ peaks after Ar ion sputtering of the samples surface. The full width half maximum of the Ag $3d_{5/2}$ is 0.76 eV at pass energy of 30 eV. The data was evaluated using the Avantage software (v. 4.43, *Thermo Fisher Scientific*) and the background subtraction has been performed according to Shirley. Scanning transmission electron microscope (STEM) images were obtained on a Hitachi HD-2700 at 200 kV acceleration voltage.

Calculation of pseudo-first order rate constants

Mass based rate constants were calculated using the formula:

$$k_m = \frac{-V^*}{m} \ln(1 - X)$$

Where,

k_m is the mass based pseudo-first order rate constant in $Lg^{-1}s^{-1}$,

V^* is the gas flow under reaction conditions in Ls^{-1},

m is the catalyst mass (mass of the washcoat present of the monolith) in g, and

X is the conversion

BET Analysis

Table S1 BET surface area of fresh and hydrothermally aged 0.5 wt% Au/TiO_2 catalysts.

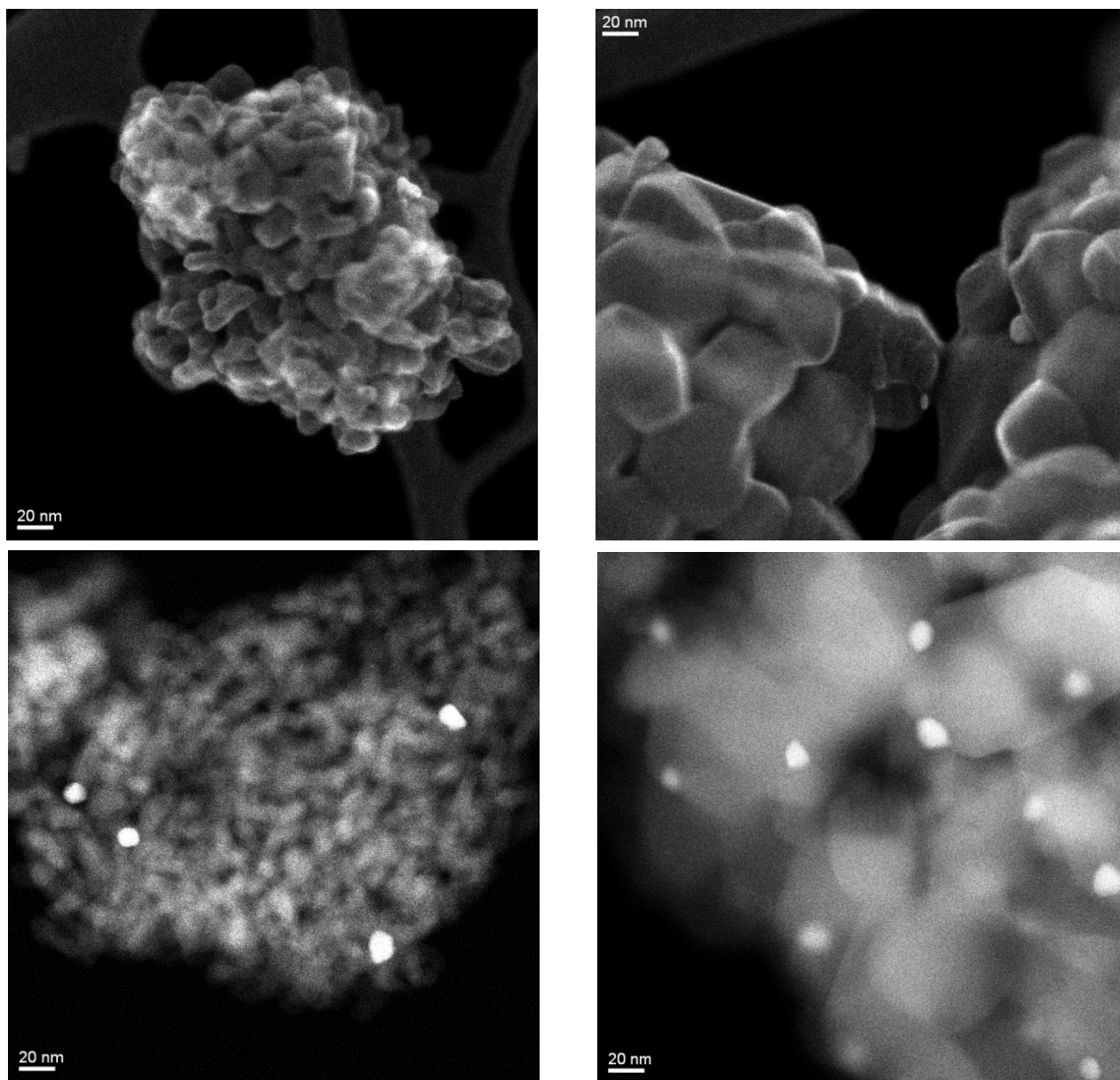| Sample	BET Surface Area (m^2/g)
Fresh	75
5 h Aged	51
10 h Aged	49

Supplementary figures

Fig. S1 SEM and HAADF-STEM images of 0.5 wt% Au/TiO_2, fresh (left column) and 10 h hydrothermally aged (right column) catalysts, showing sintering of TiO_2 particles upon aging without any significant change in Au particle size.
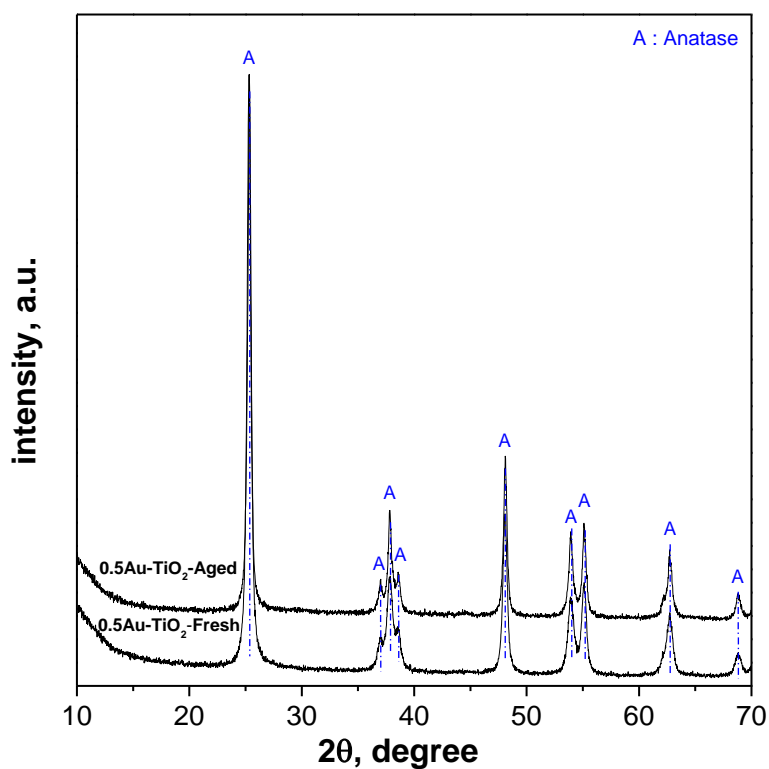
Fig. S2 XRD patterns of fresh and 10 h hydrothermally aged 0.5 wt% Au/TiO$_2$ catalysts showing the absence of any major peaks associated with the rutile phase. The TiO$_2$ crystallite sizes were determined to be 25 nm and 32 nm in the fresh and 10 h hydrothermally aged samples, respectively.
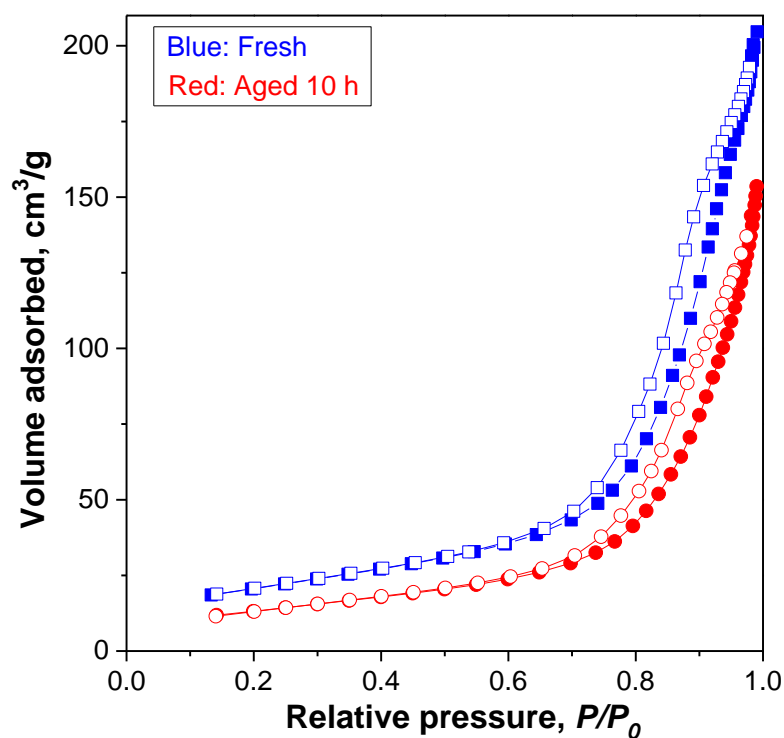

Fig. S3 N$_2$ sorption isotherms of fresh and 10 h hydrothermally aged 0.5 wt% Au/TiO$_2$ catalysts. Closed symbols indicate the adsorption branch while the open symbols represent the desorption branch.