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Supporting Information

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The different reaction pathway for the reduction of aromatic nitrocompounds on gold catalysts

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Experimental Section

Catalytic experiments were done in 2 mL home-made glass reactors, following the next procedure. Firstly, 5 mgr of the 1.5 wt% Au/TiO_2 catalyst are placed into the reactor, together with the reaction mixture, i.e. 0.405 mol substrate, 9.15 mol toluene, 0.096 mol o-xylene. The system is then purged with H_2 before heating up the solution, in order to completely remove the oxygen from the system. Under atmospheric pressure of H_2, the reactor is heat at 110 ºC and the pressure is finally fixed at 9 bar of H_2 (starting point of the reaction). Aliquots at different reaction times were taken and analyzed by both GC and MS-GC measurements.

The gold catalyst used in the present work consists on 1.5 wt% gold on TiO_2, which can be supplied by the World Gold Council (reference catalysts, Type A) or, otherwise, could be prepared by depositing the gold from an aqueous solution of $HAuCl_4$ on a sample of TiO_2 (P25 Degussa). The deposition-precipitation procedure is done at 343 K and pH of 7, using NaOH to maintain this pH during 2 h. Under these conditions, a 80 % in the efficiency of gold deposition is expected. The catalyst is then recovered, filtered, washed with deionized water, and dried at 373 K overnight. Finally, the powder is calcined at 673 K in air flow for 4 h. Under this procedure, 3.5 nm gold nanoparticles (averaged size) supported on TiO2 are obtained, as shown in Figure S1.

In situ FTIR experiments have been performed with a Biorad FTS-40A spectrometer using an IR flow quartz cell connected to a vacuum line with gas dosing possibilities. Prior to adsorption experiments the samples has been evacuated at room temperature at $3*10^{-2}$ mbar. FTIR kinetic experiments have been performed in situ after co-adsorption of 0.1mbar NB and/or NOB and 6.3mbar H_2. IR spectra of pure compounds (aniline (Aldrich, 99%, A9880), nitrosobenzene (Aldrich, 97%, N24609), azoxybenzene (Riedel-de Haën, 99%, 45763) and phenyl-hydroxylamine (see [14] for synthesis procedure)), have been obtained for identification of the intermediate products. The integration procedure used to determine the surface concentration has been done by decovolution of the IR peaks using ORIGIN 7.0 software. In the decovolution procedure Gaussian peaks have been used. The FWHM of each IR band have been kept constant during decovolution , while peak position have been adjust by the decovolution iterative procedure. The same peak maxima have been obtained in all samples, while only peak areas have been changed.

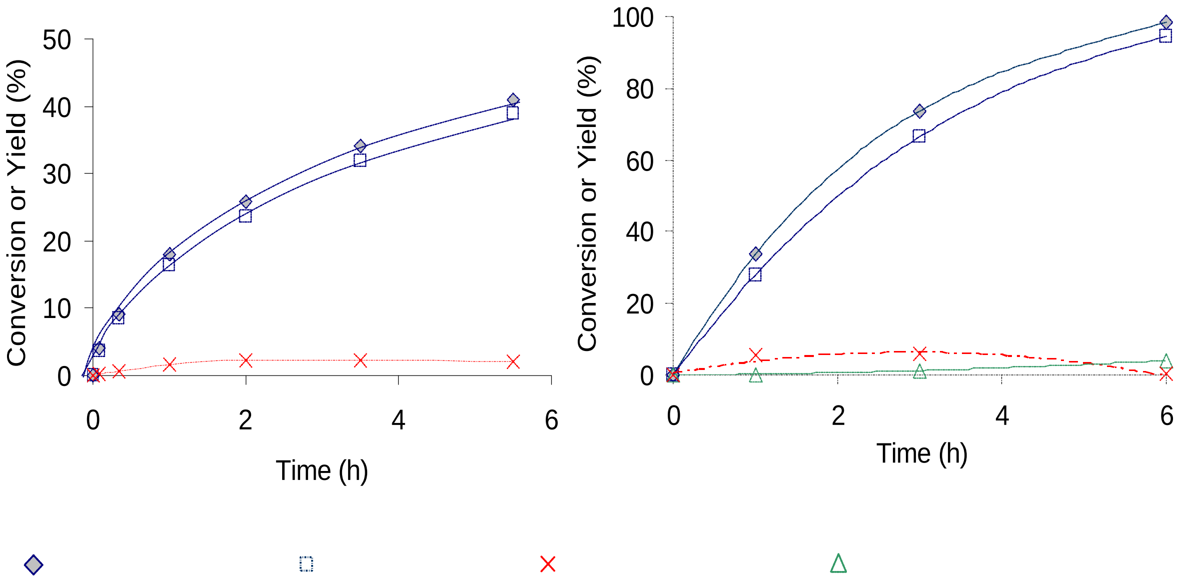

Figure S1: Evolution of species with time during the hydrogenation of nitrobenzene (a), and nitrostyrene (b).

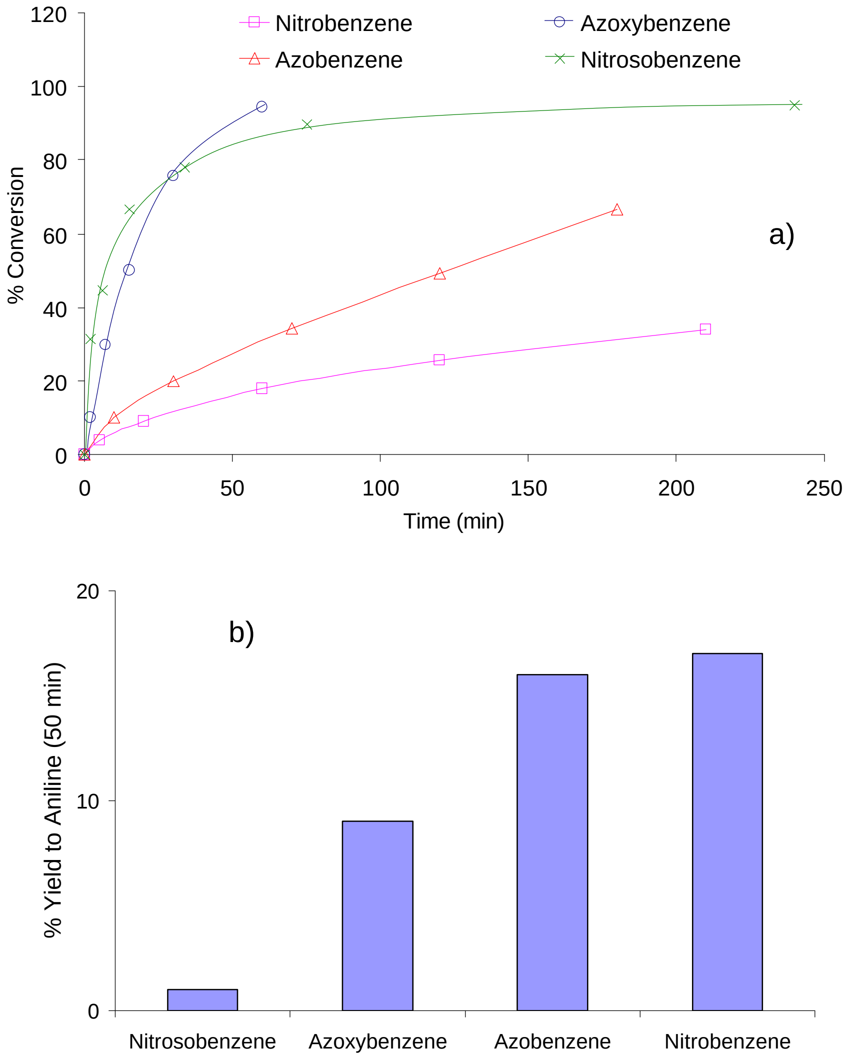

Figure S2: Evolution of conversion with time (a), and yield to aniline after 50 minutes reaction (b), when nitrobenzene, nitrosobenzene, azoxybenzene, or azobenzene are used as substrates.

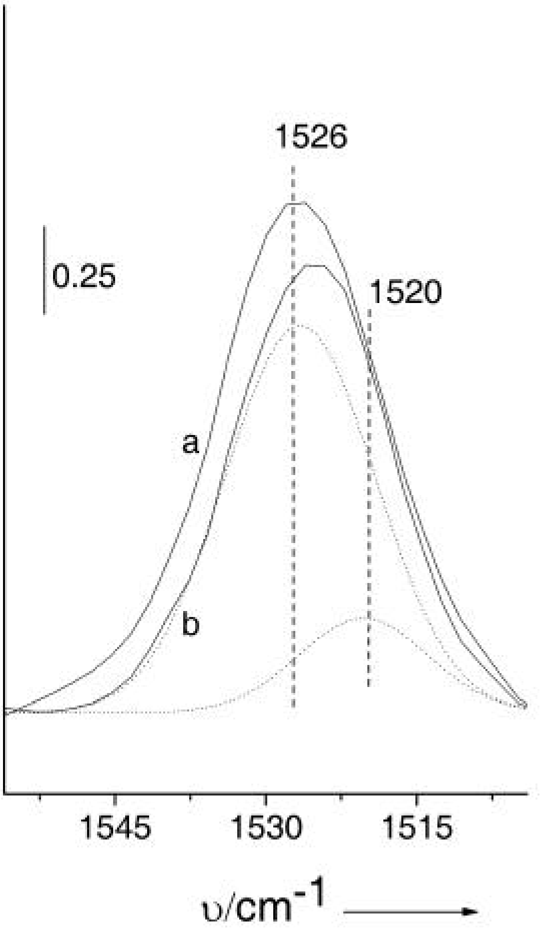

Figure S3: FTIR spectra in the asymmetric νas(NO_2)stretching IR region of nitrobenzene adsorption on a) TiO_2, (b) Au/TiO_2 samples.

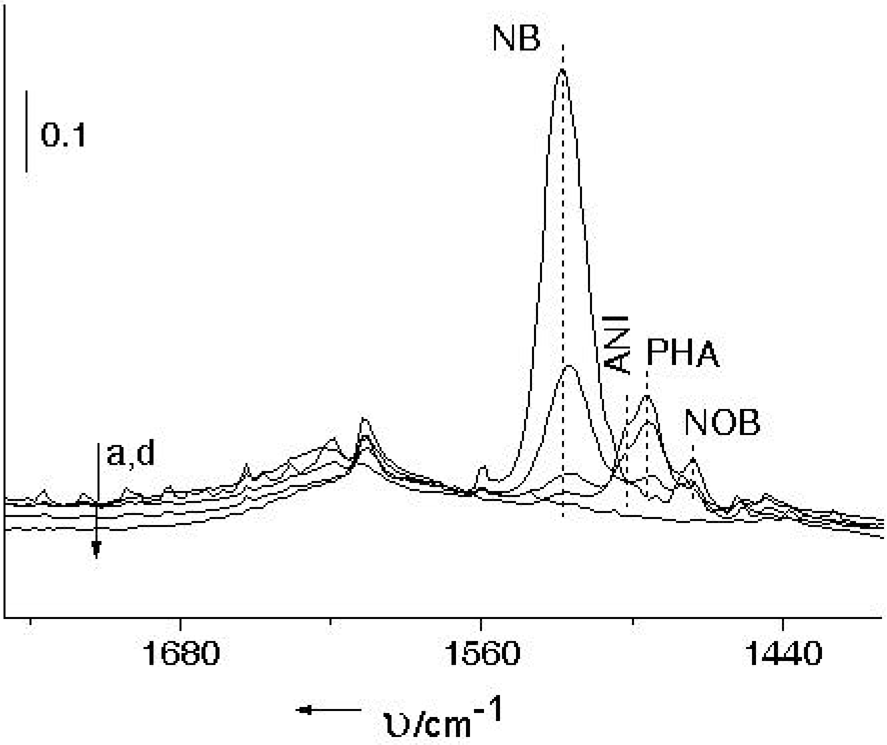

Figure S4. Time resolved FTIR spectra at 120 ºC after NB/H_2 co-adsorption on Au/TiO_2 sample. a) 0 min, b) 6 min and c) 35 min, d) 90 min. (NB nitrobenzene, ANI aniline, PHA phenylhydroxylamine, NOB nitrosobenzene)

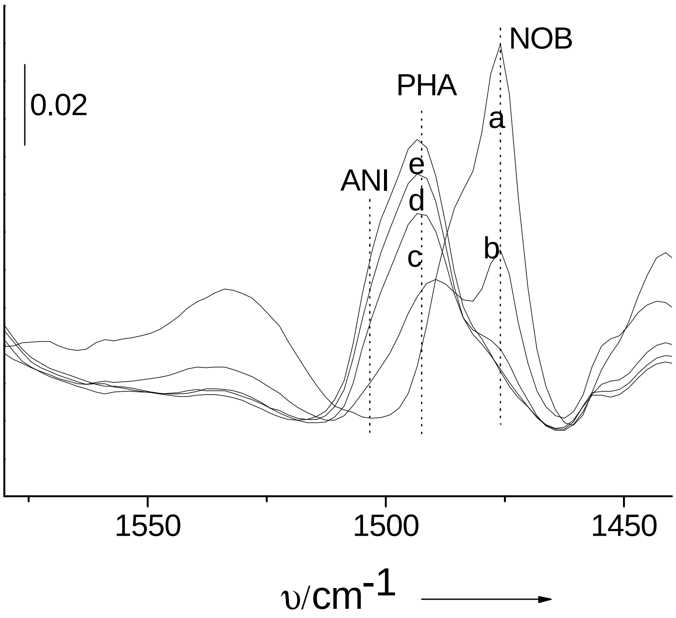

Figure S5: Time resolved FTIR spectra at 120 ºC after NOB/H_2 co-adsorption on Au/TiO_2 sample. a) 0 min, b) 11 min and c) 34 min, d) 50 min, e) 90 min.