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In situ EPR study of chemoselective hydrogenation of nitroarenes on Au/Al_2O_3 catalyst

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1. Reagents.

Aqueous hydrogen tetrachloroaurate H[$AuCl_4$]. (49.47 wt.% Au) from Aurat (Russia) was used for catalyst preparation. Nitrobenzene (99%), 3-nitrostyrene (97%), 4-nitroacetophenone (97%), benzaldehyde (98+%) and *n*-decane (99+%) from Acros Organics were used as supplied. Toluene (99.5%) from ECOS (Russia) was employed as solvent.

2. Catalyst characterization.

The gold content was measured by atomic absorption spectroscopy on a Hitachi Z-8000 instrument. Transmission electron microscopy (TEM) studies were carried out with a JEM-2010 electron microscope (JEOL). Textural characteristics were determined from nitrogen adsorption–desorption isotherms (77 K) recorded using a Micromeritics ASAP 2400 instrument.

3. Catalysts performance.

The investigation of the catalytic properties was performed using a H-Cube Pro™ (Thalesnano) continuous flow device equipped with CatCart®30 stainless-steel packed-bed reactors of 30 mm in length and 4.0 mm in inner diameter.[1–3] Before catalytic run, the reactor containing the catalyst (0.200 g, grain size of 0.25–0.50 mm) was installed in the setup, and the mixture of toluene with hydrogen was fed to the reactor until the required reaction parameters were reached. Afterwards, the inlet was switched to the flask filled with a 0.025 M solution of substrate in toluene. This moment was assigned as the starting point of the reaction. The catalytic tests were performed at the temperature range of 50–65 °C under hydrogen pressure of 10 bar, while liquid and hydrogen feed rates were set to 0.5 and 60 ml min^{-1}, respectively. The performance of catalyst was evaluated by the analysis of samples taken 30–34 min after the start of the experiment. The reaction products were analyzed by GC (Agilent 6890N instrument with a flame-ionization detector and a HP 5-MS capillary column 60m×0.32mm, 0.25 μm) using *n*-

decane as the internal standard. Identification of the products was done by GC-MS (Shimadzu GCMS-2010SE System).

4. TEM data.

Figure S1 contains the TEM image of the Au/Al_2O_3 catalyst. The small black dots represent the metal gold particles with diameter up to 3.5 nm. The particle size distribution has a maximum at approximately 1.8 nm with a standard deviation (SD) equal to 0.3.

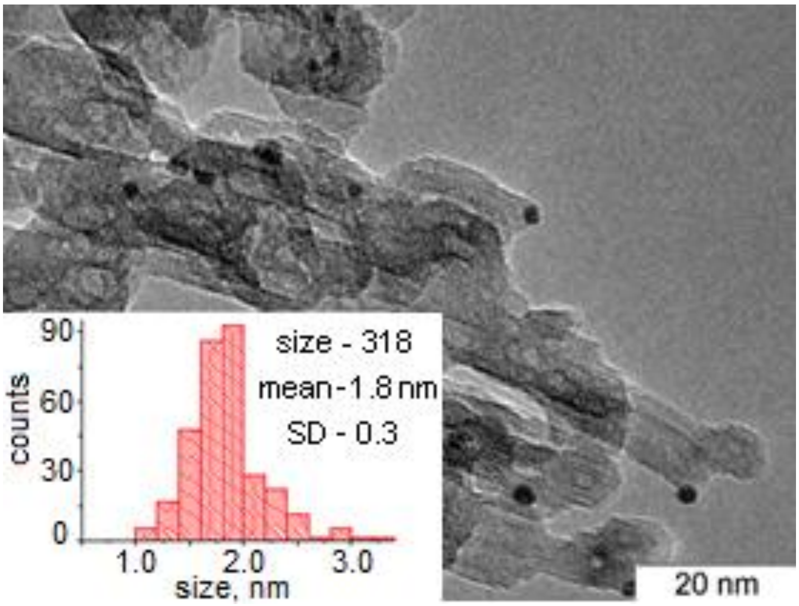

Figure S1 TEM images of the 2.0% Au/Al_2O_3 catalyst.

5. Chemoselective hydrogenation of nitroaromatic compounds on the Au/Al_2O_3 catalyst.

The Au/Al_2O_3 catalyst containing 2.0 wt% Au (BET surface area: 143 m^2 g^{-1}, total pore volume: 0.64 ml g^{-1}) with the mean Au particle diameter equal to 1.8 nm (Figure S1) demonstrated a highly chemoselective hydrogenation of nitroarenes to the corresponding anilines in the flow reactor (Table S1). Nitrobenzene hydrogenation gives exclusively aniline. Hydrogenation of 3-nitrostyrene and 4-nitroacetophenone leads to the formation of 3-vinylaniline and 4-aminoacetophenone with selectivity of 96 and 97% at the substrate conversions of 99 and 100 %, respectively (see Table S1, entries *2* and *3*). These results are in agreement with the known data on hydrogenation of nitroarenes on Au/Al_2O_3 catalysts.[1,2] The comparison of characteristics of the fresh and spent Au/Al_2O_3 catalyst allows concluding that leaching or redistribution of gold atoms between the particles does not occurs during the reaction.[2,3]

To explain the very high chemoselectivity towards the hydrogenation of nitro group on Au/Al_2O_3 catalyst we have studied the hydrogenation of nitrobenzene in the presence of benzaldehyde. In addition to aniline and benzyl alcohol, *N*-benzylideneaniline and *N*-benzylaniline were observed among the reaction products.[3] The results given in Table S1 indicate that the hydrogenation of benzaldehyde was strongly inhibited by the addition of nitrobenzene. At the same time, the hydrogenation of nitrobenzene is almost not affected by the presence of benzaldehyde (see Table S1, entries *6* and *7*). Figure S2 shows the evolution of selectivity towards *N*-benzylideneaniline, *N*-benzylaniline, and benzyl alcohol as a function of nitrobenzene conversion at the different contact times. It was found that benzyl alcohol was not formed until the almost complete consumption of nitrobenzene. When the nitrobenzene conversion reaches ~97%, the majority of nitro groups have already been reduced to amino groups and desorbed in the form of aniline. At this moment, the active sites of Au/Al_2O_3 become available to the carbonyl group of benzaldehyde that is hydrogenated yielding benzyl alcohol. Therefore, the high chemoselectivity observed over Au/Al_2O_3 catalysts is the result of preferential adsorption of nitroarene *via* the nitro groups on the catalyst active sites.

Table S1 Hydrogenation of organic molecules on Au/Al_2O_3 catalyst in the flow reactor.[a]

Entry	Substrate	T/°C	Conversion (%)	Selectivity (%)
1	nitrobenzene	60	100	100
2	4-nitroacetophenone	65	100	97
3	3-nitrostyrene	60	99	96
4	benzaldehyde	60	70	100
5[b]	benzaldehyde	60	64	2[c]
6	nitrobenzene	50	99	–
7[d]	nitrobenzene	50	95	–

[a] Reaction conditions: Au/Al_2O_3 catalyst (200 mg), substrate (0.025 M), toluene, H_2 (10 bar), reaction time of 30–34 min, liquid and hydrogen feed rates of 0.5 and 60 ml min^{-1}, respectively. [b] Nitrobenzene (0.025 M) was added. [c] Selectivity towards benzyl alcohol. [d] Benzaldehyde (0.025 M) was added.

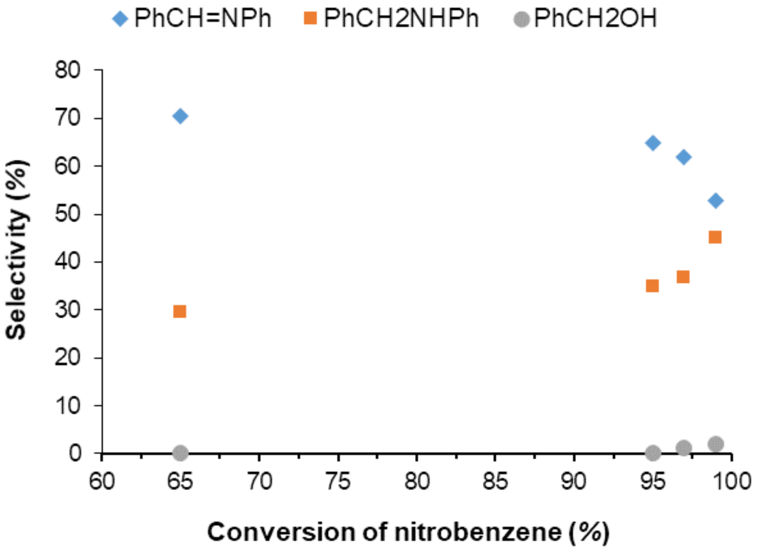

Figure S2 Evolution of the selectivity towards *N*-benzylideneaniline, *N*-benzylaniline, and benzyl alcohol on Au/Al_2O_3 during the conversion of nitrobenzene in the flow reactor at the different contact times. Reaction conditions: nitrobenzene (0.025 M), benzaldehyde (0.025 M), 60 °C, H_2 (10 bar).

References

1 A. L. Nuzhdin, B. L. Moroz, G. A. Bukhtiyarova, S. I. Reshetnikov, P. A. Pyrjaev, P. V. Aleksandrov and V. I. Bukhtiyarov, *ChemPlusChem*, 2015, **80**, 1741.

2 A. L. Nuzhdin, S. I. Reshetnikov, G. A. Bukhtiyarova, B. L. Moroz, E. Yu. Gerasimov, P. A. Pyrjaev and V. I. Bukhtiyarov, *Catal. Lett.*, 2017, **147**, 572.

3 A. L. Nuzhdin, E. A. Artiukha, G. A. Bukhtiyarova, S. Yu. Zaytsev, P. E. Plyusnin, Yu. V. Shubin and V. I. Bukhtiyarov, *RSC Adv.*, 2016, **6**, 88366.