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

Stanislav S. Yakushkin,[a] Alexey L. Nuzhdin,*[a] Ekaterina A. Artiukha,[a] Pavel E. Plyusnin,[b] Galina A. Bukhtiyarova[a] and Oleg N. Martyanov[a]

[a] *G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 8056; e-mail: anuzhdin@catalysis.ru*

[b] *A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: plus@niic.nsc.ru*

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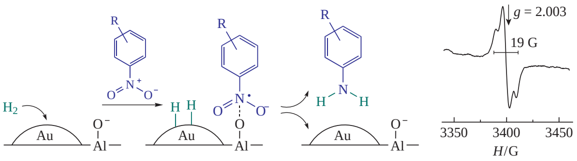
Detected by the *in situ* EPR spectroscopy immobilized nitro radical anions generated in the course of Au/Al_2O_3-catalyzed nitrobenzene hydrogenation demonstrate the abnormal hyperfine splitting and serve as intermediates of the reaction.



The chemoselective catalytic hydrogenation of functionalized nitroarenes to the corresponding anilines, which are valuable substances to manufacture a diversity of agrichemicals and pharmaceuticals, is a subject of topical interest.[1,2] It was already reported that supported Au/Al_2O_3 catalysts demonstrate one among the highest selectivities towards hydrogenation of the nitro group in a molecule containing also the C=C or C=O bond.[3–5] K. Shimizu *et al*. have proposed that the high chemoselectivity of Au/Al_2O_3 is attributed to cooperation between the acid–base pair site on γ-Al_2O_3 and the Au atoms at the metal support interface to dissociate H_2 into an H^+/H^- pair which is transferred selectively to the polar bonds in the nitro group.[3] On the other hand, M. A. Keane *et al*. have suggested that the exceptional production of *p*-chloroaniline in the *p*-chloronitrobenzene hydrogenation over Au/Al_2O_3 catalyst can be explained by selective activation of NO_2 group at Al_2O_3 Lewis acid sites and reaction with chemisorbed and spillover hydrogen.[6,7] Thus, the exact mechanism of chemoselective hydrogenation of nitroarenes to anilines on Au/Al_2O_3 catalyst remains unclear.

Hitherto, *in situ* IR spectroscopy was the only physical method used to detect the intermediates formed during hydrogenation of nitroarenes on supported gold catalysts.[8,9] Meanwhile, the interaction of nitroaromatic compounds with alumina surface is well known as leading to the formation of nitro radical anions which can be observed by EPR spectroscopy.[10–12] Herein, we report on the results of the study of nitrobenzene (NB) hydrogenation reaction on Au/γ-Al_2O_3 catalyst by the *in situ* EPR method.

The use of an Au/Al_2O_3 catalyst[†] containing 2.0 wt% Au (BET surface area, 143 $m^2\,g^{-1}$; total pore volume, 0.64 $cm^3\,g^{-1}$) with the mean Au particle diameter of 1.8 nm provided a highly chemoselective hydrogenation of 3-nitrostyrene and 4-nitroacetophenone to the corresponding anilines in a flow reactor (see Online Supplementary Materials).[4,5] To explain this result, we have investigated the hydrogenation of nitrobenzene in the presence of benzaldehyde at the different contact times. It was found that benzyl alcohol is not obtained until the almost complete consumption of nitrobenzene (see Online Supplementary Materials). Thus, the high selectivity towards the nitro group hydrogenation observed on Au/Al_2O_3 catalyst is a result of the preferential adsorption of nitroarene *via* the nitro groups on the catalyst active sites.[2,8]

To determine the nature of catalyst active sites, the EPR spectroscopy was employed for the detection of radical anions formed in the systems containing γ-alumina or Au/Al_2O_3 catalyst upon a contact with the solution of nitrobenzene in toluene.[‡] Figure 1(*a*) shows the EPR spectrum of adsorbed nitrobenzene on γ-Al_2O_3 surface calcinated at 400 °C. An intense anisotropic signal at $g = 2.003$ in the spectrum is known[10–12] and corresponds to the generation of the NB radical anions on the surface defect sites of alumina containing oxide ions, which serve as electron donors.[10,12] The formation of nitro radical anions on other metal oxides, such as MgO, ZnO, and TiO_2, was also observed.[11] A predominant feature of this spectrum is the hyperfine splitting on a nitrogen atom. The spectra simulation gives the best fit for the following values of *g* and hyperfine interaction (HFI) tensor components: $g_x = 2.003$, $g_y = 2.003$, $g_z = 2.001$, $A_x = 2.0\pm0.2$ G, $A_y = 2.0\pm0.2$ G, and $A_z = 33.5\pm0.2$ G ($1\text{ G} = 10^{-4}$ T). A low intense and easily saturated signal at $g = 1.98$ can be assigned to the delocalized electrons in the carbonaceous π-system.[13] Note that there is no resonance absorption observed for the γ-alumina calcinated at temperature lower than 400 °C.

In contrast with the case of γ-Al_2O_3, the EPR signal of nitro radical anions was observed for Au/Al_2O_3 catalyst after calcination at the lower temperature of 150 °C [Figure 1(*b*)]. In both

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[†] The Au/Al_2O_3 catalyst was prepared *via* so-called deposition–precipitation technique according to the known procedure.[16]

[‡] The EPR spectra were recorded on a Bruker X-band EleXsys 500 spectrometer equipped with an ER4102ST cavity and ER4131VT temperature control system. The preliminary treatment of samples included the calcination procedure at 150 or 400 °C for 4 h. After fast cooling, the sample was placed into the quartz tube filled with nitrobenzene (1 vol%) in toluene at room temperature. The EPR spectra were recorded at 30 min after the addition of NB solution. The simulation of EPR spectra was performed using EasySpin EPR toolbox.[17] The *in situ* EPR experiments were carried out in the quartz reactor directly in the microwave cavity at the temperature range from 25 to 90 °C. The reaction mixture contained Au/Al_2O_3 catalyst in the NB solution (1 vol%) in toluene. Gaseous hydrogen was supplied into the reactor by flow mass controller with the rate of 0.1 $dm^3\,h^{-1}$ under the atmospheric pressure. The products obtained during the *in situ* EPR experiments were analyzed by GC-MS.

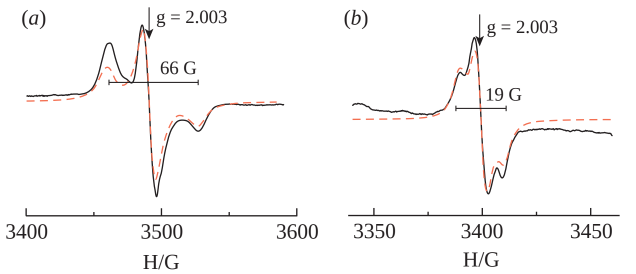

Figure 1 EPR spectra of the nitro radical anions adsorbed on (*a*) γ-Al_2O_3 after calcination at 400 °C and (*b*) Au/Al_2O_3 catalyst after calcination at 150 °C, recorded at room temperature. Dashed line shows the simulated spectra.

spectra, the signals can be assigned to the immobilized radical anions since no EPR signals were detected for the solution filtered off from solid samples. The NB radical anions generated in the presence of γ-Al_2O_3 and Au/Al_2O_3 manifest significantly different hyperfine splitting. The simulation of the spectra for Au/Al_2O_3 system looks reasonable with $g_x = 2.003$, $g_y = 2.003$, $g_z = 2.003$, $A_x = 1.5\pm0.2$ G, $A_y = 1.5\pm0.2$ G, and $A_z = 10.5\pm0.2$ G, which means the three times lower characteristic HFI constant for Au/Al_2O_3 system in comparison with that for the pure alumina surface. It should be underlined that such abnormal hyperfine splitting is observed for nitroaromatic radical anions on the alumina surface for the first time in spite of very long history of electron transfer studies *via* EPR.[10,11] Since the variation of calcination temperature demonstrated only a little effect on the value of HFI constant of nitro radical anions adsorbed on alumina,[10] we believe that this phenomenon indicates the influence of neighboring gold nanoparticles on the distribution of electron spin density within the nitro radical anions formed on the catalyst surface and, probably, means that the NB radicals observed in the Au/Al_2O_3 system are formed near to the edge of gold nanoparticles.

Figure 2 shows the EPR spectra of Au/Al_2O_3 sample recorded *in situ* in the NB solution. Injection of H_2 into the reaction mixture containing Au/Al_2O_3 catalyst leads to the severe drop of the EPR absorption intensity [see Figure 2(*c*),(*d*)]. The reaction products obtained during the *in situ* EPR experiments were analyzed by GC-MS method. Aniline, azobenzene, and azoxybenzene were detected in the solution, indicating the occurrence of NB hydrogenation.[1,14] The postreaction solution demonstrated no detectable EPR spectra proving the fact that the paramagnetic signal was specific one only for the radical species formed on the catalyst surface. Consequently, the concentration of nitro radical anions decreases once the reaction was started, which means the participation of detected radical species in the NB hydrogenation occurring on the catalyst surface.

Similar to the case of pure alumina, the paramagnetic species stabilized on Au/Al_2O_3 are probably generated *via* the interaction of nitro group of NB and oxide ions on the alumina surface. According to published data,[15] the spillover process of H atoms from metal nanoparticles to the non-reducible supports, such as alumina, is nearly impossible, which allows us to suggest that the hydrogenation of nitroarenes occurs at the border between the gold nanoparticles and alumina.

In summary, the application of EPR method has revealed the radical anions generated due to interaction between nitrobenzene in liquid phase and the active sites of Au/Al_2O_3 catalyst. The immobilized NB radical anions demonstrating the abnormal hyperfine splitting act as the active intermediates in the course of hydrogenation.

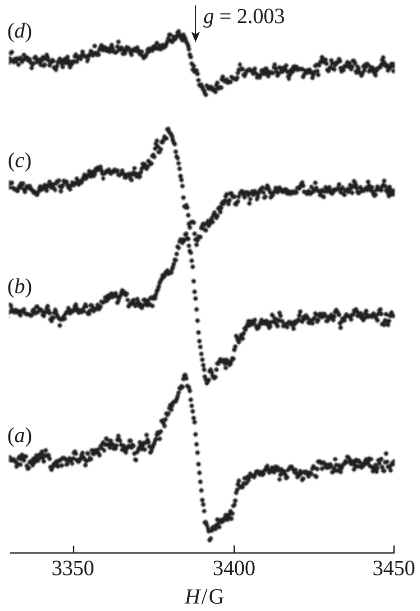

Figure 2 The EPR spectra of the nitro radical anions localized on Au/Al_2O_3 catalyst surface after the addition of NB solution recorded *in situ* under different conditions: (*a*) 25 °C; (*b*) 82 °C; (*c*) injection of H_2 (1 bar), 82 °C; and (*d*) injection of H_2 (1 bar), 90 °C.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.029.

References

1 H.-U. Blaser, H. Steiner and M. Studer, *ChemCatChem*, 2009, **1**, 210.
2 P. Serna, M. Boronat and A. Corma, *Top. Catal*., 2011, **54**, 439.
3 K. Shimizu, Y. Miyamoto, T. Kawasaki, T. Tanji, Y. Tai and A. Satsuma, *J. Phys. Chem. C*, 2009, **113**, 17803.
4 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.
5 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.
6 X. Wang, N. Perret and M. A. Keane, *Chem. Eng. J*., 2012, **210**, 103.
7 X. Wang, N. Perret, J. J. Delgado, G. Blanco, X. Chen, C. M. Olmos, S. Bernal and M. A. Keane, *J. Phys. Chem. C*, 2013, **117**, 994.
8 M. Boronat, P. Concepción, A. Corma, S. González, F. Illas and P. Serna, *J. Am. Chem. Soc*., 2007, **129**, 16230.
9 G. Richner, J. A. van Bokhoven, Y.-M. Neuhold, M. Makosch and K. Hungerbühler, *Phys. Chem. Chem. Phys*., 2011, **13**, 12463.
10 B. D. Flockhart, I. R. Leith and R. C. Pink, *J. Chem. Soc., Faraday Trans*., 1970, **66**, 469.
11 R. B. Clarkson, K. Mattson, W. Shi, W. Wang and R. L. Belford, *Mol. Eng*., 1994, **4**, 89.
12 D. A. Medvedev, A. A. Rybinskaya, R. M. Kenzhin, A. M. Volodin and A. F. Bedilo, *Phys. Chem. Chem. Phys*., 2012, **14**, 2587.
13 G. Wagoner, *Phys. Rev*., 1960, **118**, 647.
14 E. V. Shuvalova, O. A. Kirichenko and L. M. Kustov, *Russ. Chem. Bull., Int. Ed*., 2017, **66**, 34 (*Izv. Akad. Nauk, Ser. Khim*., 2017, 34).
15 R. Prins, *Chem. Rev*., 2012, **112**, 2714.
16 A. L. Nuzhdin, E. A. Artiukha, G. A. Bukhtiyarova, S. Y. Zaytsev, P. E. Plyusnin, Y. V. Shubin and V. I. Bukhtiyarov, *RSC Adv*., 2016, **6**, 88366.
17 S. Stoll and A. Schweiger, *J. Magn. Reson*., 2006, **178**, 42.

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