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Hydrogen spillover through a gas phase

Irina A. Razzhivina,[a] Gennadii A. Badun,*[a] Maria G. Chernysheva,[a] Alexey V. Garshev,[a,b,c] Valerii P. Shevchenko,[d] Konstantin V. Shevchenko,[d] Igor Yu. Nagaev[d] and Nadezhda E. Shchepina[e]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 932 8846; e-mail: badunga@yandex.ru*
[b] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *A. A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[d] *Institute of Molecular Genetics, Russian Academy of Sciences, 123182 Moscow, Russian Federation*
[e] *Natural Sciences Institute, Perm State University, 614990 Perm, Russian Federation*

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Hydrogen spillover through a gas phase in the 5% Pd/C catalyst–sodium 4-phenylbenzoate system was observed using tritium as a tracer.

Spillover is the transport of a species adsorbed or formed on a surface to another surface, which does not adsorb or form this species under the same conditions.[1] In particular, Boudart *et al.*[2] described hydrogen spillover as the migration of H atoms from metal particles to the support, from a hydrogen-rich to a hydrogen-poor surface. Baumgarten *et al.*[3,4] observed the gas phase transport of hydrogen atoms. Previously,[5] we reported the long-distance (over 10 cm) migration of activated hydrogen as the result of tritium interactions with the mesoporous silica MCM-41 with the use of a bimetallic Ru_5Pt catalyst. The experiment was carried out under a low gas pressure (1.3 Pa) at 300 to 470 K. Absence of the non-labile positions for tritium binding in the MCM-41 enforced us to measure the radioactivity of water after MCM-41 sample was suspended in it. In this case, we could not exclude the transfer of hydrogen as H^3HO that forms by the reduction of impurity oxides.

In this work, we attempted to prove the possibility of the long-distance transport of activated hydrogen atoms, which can react with the support by isotopic exchange reaction and though hydrogenate the benzene ring. For this purpose, sodium 4-phenylbenzoate (PBNa) was used as a hydrogen acceptor. To prevent the isotopic exchange reactions initiated by water, the experiments were conducted at 335 K. To activate the reaction, we used Pd applied on activated carbon [5% Pd/C catalyst (Fluka cat. #75992)].[6]

The catalyst was characterized by BET (an ASAP-2010 analyzer) and TEM (a Zeiss Libra 200 electron microscope). The analysis revealed the specific area of 0.768 $m^2\ mg^{-1}$ and the irregular distribution of Pd species of 2–22 nm in diameter. The TEM image and Pd species size distribution are shown in Figure 1.

The experiments were performed in a cylindrical glass reaction vessel (diameter, 7 cm; height, 12 cm). An additional vessel was connected to the reaction vessel with a U-tube and its bottom was cooled with liquid nitrogen to trap the volatile products including tritium water.[6] PBNa (0.5 mg, experiments 1 and 2) was distributed on the reactor walls by the evaporation of its methanol solution. In experiment 1, 5±0.5 mg of the 5% Pd/C catalyst was located in a glass cup at the bottom of the vessel. In experiment 2, the same glass cup contained 6±0.5 mg of a PBNa–5% Pd/C mixture (1:5 by weight). In experiment 3, 6±0.5 mg of a PBNa–5% Pd/C mixture (1:5 by weight) was suspended in 1 ml of hexane and then distributed on the reactor walls. The system was evacuated at 0.01 Pa and then filled with a hydrogen–tritium mixture (9:1) to 4 Pa. The catalyst was activated by heating the reactor to 335±2 K. During the experiment, the gas pressure was decreased by a half. The experiments were carried out until a constant pressure was achieved (for about 25 min). Then, the residual gas was pumped out and the system was cooled down to room temperature.

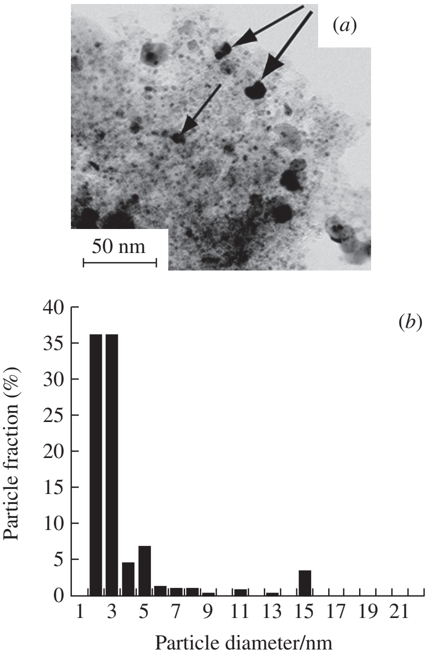

Figure 1 (*a*) TEM image of the 5% Pd/C catalyst. Pd species are shown by arrows. (*b*) Pd particle size distribution in the 5% Pd/C catalyst.

PBNa was washed off from the glass walls and the catalyst with methanol, followed by purification and chromatography analysis as described previously.[6] Each stage was controlled by radioactivity measurements (Table 1).

The decrease in the gas pressure shows the interaction of molecular hydrogen with the catalyst. The initial radioactivity of PBNa varied from 23 MBq (the sample in the cup) to 440 MBq (the sample on the walls). Most of tritium radioactivity was

Table 1 Radioactivity of the PBNa samples.

Experiment	Radioactivity/MBq		
	Initial	[^{3}H]PBNa	Hydrogenated products
1	440	0.05	0.07
2 (walls)	200	0.16	0.09
2 (cup)	23	7.0	0
3	360	6.7	0

removed during the evaporation of the solutions, while tritium chemically bound to PBNa was also found. Moreover, in the cases when PBNa was located on the walls of the reactor and spatially separated from the catalyst, both isotopic exchange and benzene ring hydrogenation were observed. If the PBNa sample was deposited directly on the 5% Pd/C, only isotopic exchange occurred.

Although the initial radioactivity of PBNa in experiments 2 (the experiment provided in the cup) and 3 were strongly different, the radioactivity of [^{3}H]PBNa was almost the same. We believe that the reaction vessel glass (experiment 3) is the main acceptor of activated tritium, but it can bind tritium in the labile form only. This result is similar to the data obtained for MCM-41.[5] Note that the sample of PBNa deposited on 5% Pd/C did not contain hydrogenation reaction products. It is probably due to the electrophilic mechanism (S_EAr) of reaction, when catalytically activated hydrogen migrates over the support in the form of cations stabilized by hydroxy and epoxy groups on the carbon matrix. Such a stabilization was confirmed by calculations and experiments.[6–11]

In experiments 1 and 2, where PBNa was located on the walls of the reaction vessel, the radioactivity of [^{3}H]PBNa was lower than that detected in experiments 2 and 3, where PBNa was in contact with the catalyst. This fact confirmed that catalytically activated hydrogen migrates over long distances with the preservation of its reactivity. Note that we also observed the formation of hydrogenation products in this case. Simultaneous reactions of isotopic exchange and hydrogenation occur when tritium reacts in the form of atoms.[6] The desorption of the activated hydrogen species from 5% Pd/C can proceed in the form of H_3 radical.[12]

Our results show that gaseous hydrogen (tritium) interacts with 5% Pd/C at 335 K followed by the migration of activated tritium over the support and its reaction with PBNa by the S_EAr mechanism. Such tritium species can also migrate over several centimeters through the gas phase and react with PBNa by both isotopic exchange and benzene ring hydrogenation.

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References

1 R. Prins, *Chem. Rev.*, 2012, **112**, 2714.

2 M. Boudart, M. A. Vannice and J. E. Benson, *Z. Phys. Chem.*, 1969, **64**, 171.

3 E. Baumgarten and G. Meyer, *React. Kinet. Catal. Lett.*, 2000, **71**, 325.

4 E. Baumgarten and L. Maschke, *Appl. Catal., A*, 2000, **202**, 171.

5 G. A. Badun, B. F. G. Johnson and N. E. Shchepina, *Mendeleev Commun.*, 2009, **19**, 235.

6 V. P. Shevchenko, I. A. Razzhivina, M. G. Chernysheva, G. A. Badun, I. Yu. Nagaev, K. V. Shevchenko and N. F. Myasoedov, *Radiochemistry*, 2015, **57**, 312 (*Radiokhimiya*, 2015, **57**, 264).

7 G. M. Psofogiannakis and G. E. Froudakis, *J. Am. Chem. Soc.*, 2009, **131**, 15133.

8 Y. Zhao and T. Gennett, *Phys. Rev. Lett.*, 2014, **112**, 076101.

9 L. Chen, A. C. Cooper, G. P. Pez and H. Cheng, *J. Phys. Chem. C*, 2007, **111**, 18995.

10 T. Chung, C. Tsao, H. Tseng, C. Chen and M. Yu, *J. Colloid Interface Sci.*, 2015, **441**, 98.

11 A. V. Arsatov, L. S. Leonova, A. E. Ukshe, Y. A. Dobrovolsky and E. A. Astaf'ev, *Mendeleev Commun.*, 2009, **19**, 292.

12 D. Bianchi, M. Lacroix, G. M. Pajonk and S. J. Teichner, *J. Catal.*, 1981, **68**, 411.

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