Electronic Supplementary Material (ESI) for Faraday Discussions.

SUPPORTING INFORMATION

Mechanistic in situ investigation of heterogeneous hydrogenation over Rh/TiO$_2$ catalysts: selectivity, pairwise route, catalysts nature

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Catalyst preparation procedure

In total, two series of the Rh/TiO_2 catalysts were prepared with the variation of several different preparation parameters. Titanium dioxide (Hombifine N, S_{BET}=103 m^2/g) was used as the support. The TiO_2 samples were calcined at 550 °C for 2 h prior to use and then dried at 120 °C for 6 h. Rhodium (III) nitrate (or acetate) solution was prepared by the dissolution of rhodium (III) hydroxide in the necessary amount of nitric (or acetic) acid. For the preparation of rhodium (III) hydroxide, 20 mL of 8.4M sodium hydroxide solution was added to 20 mL of 1.2M rhodium (III) chloride solution. The obtained mixture was heated while stirring until the complete change of solution color from red to light yellow, and then the reaction mixture was acidified to pH of 11. The formed precipitate of rhodium (III) hydroxide was washed to complete removal of Cl^- ions and then dissolved in the required amount of nitric or acetic acid. Precise rhodium content in the prepared catalysts was determined by X-ray fluorescence (XRF); the found values are presented in Table S1.

In the first set, the precursor solution was varied. Two catalysts were prepared by incipient impregnation (0.8 mL/g) of dry TiO_2 by the calculated amount of rhodium nitrate or acetate solution. The reactants were mixed thoroughly till wetted state and were left in air for 24 h. The materials were then dried in air at 120 °C for 3 h, and calcination of the impregnated support in the air at 600 °C for 2 h followed by the reduction in H_2 flow at 330 °C for 3 h finalized the preparation procedure. For the third catalyst, binuclear acetic rhodium (II) complex $[Rh_2(OAc)_4]$ (preparation procedure is described in ref.[1]) was used as the precursor. The catalyst was prepared by incipient impregnation of dry TiO_2 with $[Rh_2(OAc)_4]$ solution in ethanol, then the solvent excess was evaporated at 40 °C at reduced pressure. The subsequent calcination/reduction treatment was the same as described above.

In the second series, the temperature of calcination was varied. The general preparation procedure is identical to the procedure described above for the catalyst prepared from $Rh(NO_3)_3$, except for the final calcination stage – samples were either dried in an argon flow at 120 °C for 3 h (referred to as the catalyst prepared without calcination) or calcined in air at 400 °C for 4 h or at 500 °C for 3 h or at 600 °C for 2 h.

Table S1. Rh content in the prepared catalysts determined by X-ray fluorescence analysis

Varied parameter	**Parameter**	**Rh content, %**
Precursor solution	$Rh(NO_3)_3$*	1.01%*
	$Rh(OAc)_3$	0.97%
	$[Rh_2(OAc)_4]$	1.03%
Calcination temperature	No calcination	1.01%
	400 °C	1.01%
	500 °C	1.01%
	600 °C*	1.01%*

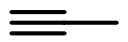
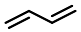
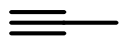
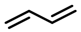
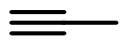
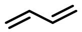
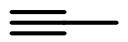
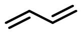
* denote the same catalysts

Additional tables

Table S2. Correction coefficients *C* used for calculation of the 'true' intensity of the signals at high gas flow rates.

Substrate	***C***
1,3-butadiene and butane	2.59
propylene, CH-group	2.67
propylene, CH_2-group	2.65
propylene, CH_3-group	1.83
propane, CH_2-group	1.92
propane, CH_3-group	2.07

Table S3. Weight amount of rhodium and atomic ratio of elements calculated from XPS data

Varied parameter	Parameter	Rh, wt. %				Rh/Ti				C/Ti				O/Ti			
		before				before				before				before			
Precursor	$Rh(NO_3)_3$*	1.72	2.12	2.03	2.13	0.025	0.023	0.023	0.023	1.096	1.576	2.058	1.389	2.395	2.770	2.703	2.739
	$Rh(OAc)_3$	0.94	1.46	1.30	1.30	0.009	0.016	0.014	0.014	1.287	1.854	1.768	1.446	2.350	2.620	2.615	2.598
	$[Rh_2(OAc)_4]$	1.37	–	0.90	0.90	0.016	–	0.010	0.009	2.116	–	1.847	1.404	2.703	–	2.625	2.578
Calcination temperature, °C	without	2.18	–	2.12	–	0.022	–	0.025	–	1.313	–	2.240	–	2.412	–	2.722	–
	400	2.44	–	2.36	–	0.025	–	0.027	–	1.478	–	1.782	–	2.410	–	2.766	–
	500	1.81	–	2.19	–	0.018	–	0.025	–	1.260	–	2.196	–	2.416	–	2.655	–
	600*	1.72	2.12	2.03	2.13	0.017	0.023	0.023	0.023	1.096	1.576	2.058	1.389	2.395	2.770	2.703	2.739

* denotes the same catalysts

References

(1) Drago, R. S.; Cosmano, R.; Telser, J. EPR Spectra and Bonding in the 2:1 Base Adducts of Rh2(Carboxylate)4+. *Inorg. Chem.* **1984**, *23*, 3120–3124.