

Supporting information for

Pd Nanoparticles in Dendrimers Immobilized on Silica-Polyamine Composites as Catalysts for Selective Hydrogenation

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XPS spectrum of the BP-1 dendrimer hybrid

XPS spectrum of the modified support confirmed the presence of the $(\text{CH}_2)_3\text{N}$ fragment, which are relevant for dendritic and polyallylamine areas of the support, and also the presence of Si-O and Si-C bonds^{1,2}. As compared with the BP-1 starting material, the surface content of silicon and oxygen content was observed to drop to about one half of their original values (6.0% and 16.9%, respectively, versus 14.7% and 34.6%), while the atomic concentrations of carbon and nitrogen were doubled (61.1% and 16.0 % respectively versus 40.2% and 10.5%), indicating the dendrimers were successfully bound to the BP-1 surface.

^{13}C NMR

The ^{13}C NMR spectrum of the dendrimer-modified support (Figure. S1) contained the following resonances: 13-20 ppm, assigned to the alkyl chains that are directly related to silicon; 28 ppm, assigned to the $\beta\text{-CH}_2$ groups in the poly-alkylamine fragments; 41.6 ppm assigned to the $\alpha\text{-CH}_2$ primary amino-groups of both the dendrimers and the polyallylamine phase of the initial support; 53.5 ppm assigned to the $\alpha\text{-CH}_2$ group in the secondary and tertiary nitrogen atoms in poly-alkylamine fragments of the dendrimer³⁻⁵. The signals at 71 ppm refer to the bound methylene groups in the $\text{NH-CH}_2\text{-OH}$, formed in the interaction of formaldehyde with the support surface and dendrimers.

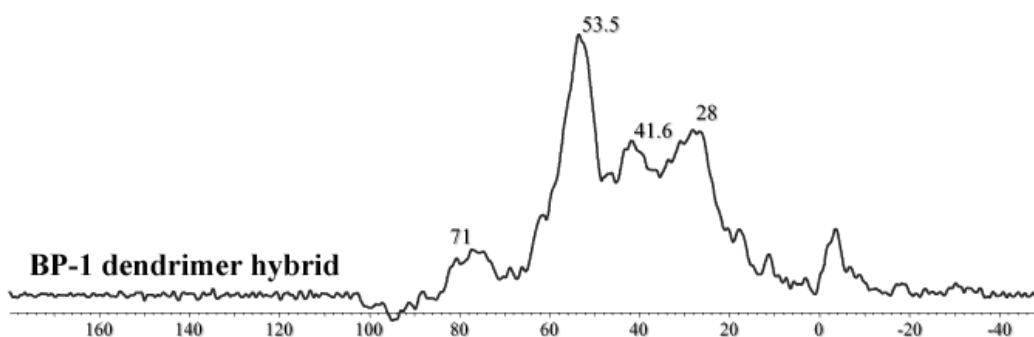


Figure S1. ^{13}C NMR spectrum of the BP-1 dendrimer hybrid.

The ^{13}C NMR spectra of **1** and **2** were recorded and confirmed the presence of dendrimers in both samples (Fig. S2). In the spectra of materials containing palladium nanoparticles the intensity of the signals corresponding to the carbon atoms located in α -position of the primary amino-groups in the range of 30-45 ppm increased significantly. The broad signals at 51.1-56.6 ppm correspond to

the carbon atoms at tertiary amines. The growth of the nanoparticles results in a decrease in the dendritic fragment mobility and appears broadened and reduced the intensity of polypropylene imine signals.

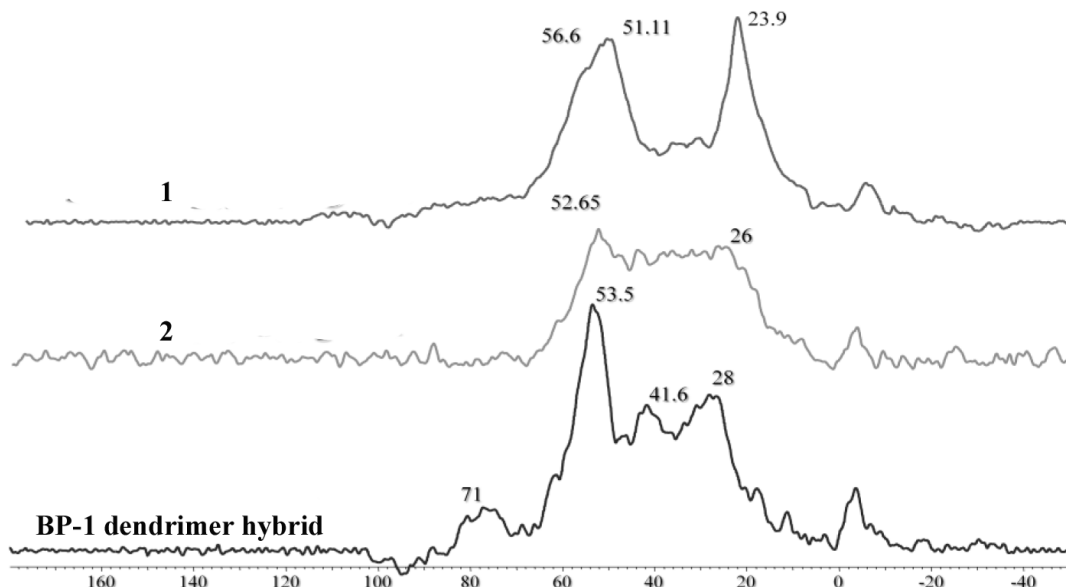
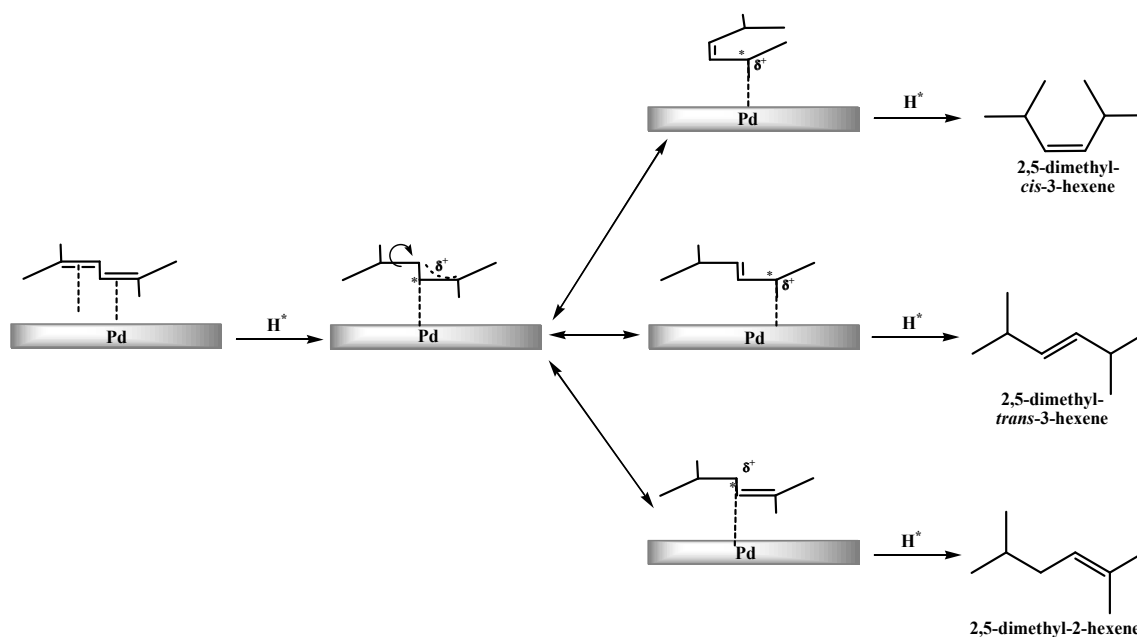


Figure S2. ^{13}C NMR spectra of materials **1** (upper trace), **2** (middle trace) and **BP-1 dendrimer hybrid** (bottom trace).



Scheme S1. A possible mechanism of 2,5-dimethyl-2,4-hexadiene hydrogenation on the dendrimer-containing Pd catalysts.

Table S1. Hydrogenation of styrene in the presence of catalyst precursor 1^a

Entry	P, atm.	t, h	Substrate/Pd, mol/mol	Conv.,%	SA, h ⁻¹
1	10	0.25	6765	74	20025
2	30	0.25	6765	89	24085
3	10	0.25	13530	62	33560
4	30	0.25	13530	82	44385
5	30	0.25	21425	77	65990
6	30	0.25	32140	62	79700
7	30	0.25	64275	43.5	111840

^a Reaction conditions: 1 ml of substrate, 1.5 ml of the solvent, for 15 min., at 70 °C.

^b SA = specific activity, mole product/mole catalyst/t

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