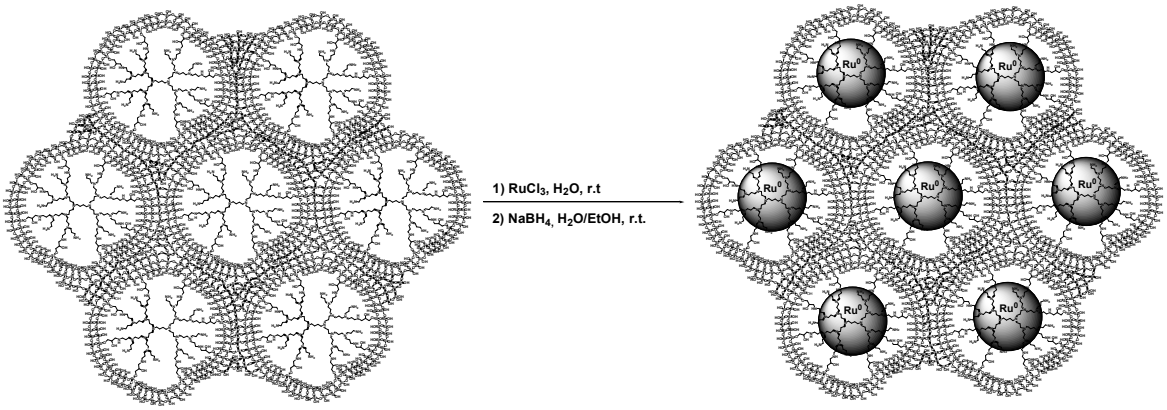
Supplementary Materials: Dendrimer-Stabilized Ru Nanoparticles Immobilized in Organo-Silica Materials for Hydrogenation of Phenols

Eduard Karakhanov, Anton Maximov, Anna Zolotukhina, Adila Mamadli, Anna Vutolkina and Andrey Ivanov

Table S1. Porosity properties of dendrimer-based hybrid materials according to nitrogen low temperature adsorption and desorption.

Porosity Properties	G2-dendr-*meso*-SiO_2	G3-dendr-SiO_2
Langmuir Surface Area, m^2/g	179.0	83.9
BET Surface Area, m^2/g	118.5	53.9
BJH Adsorption cumulative surface area (d: 17.0–30.0 Å), m^2/g	429.0	52.1
BJH Adsorption cumulative volume (d: 17.0–30.0 Å), cm^3/g	8.1	0.2
BJH Adsorption average pore width, Å	75.3	14.1
Nitrogen content, wt %	6.3	4.6



Scheme S1. Encapsulation of Ru nanoparticles into PPI dendrimers, immobilized in silica pores.

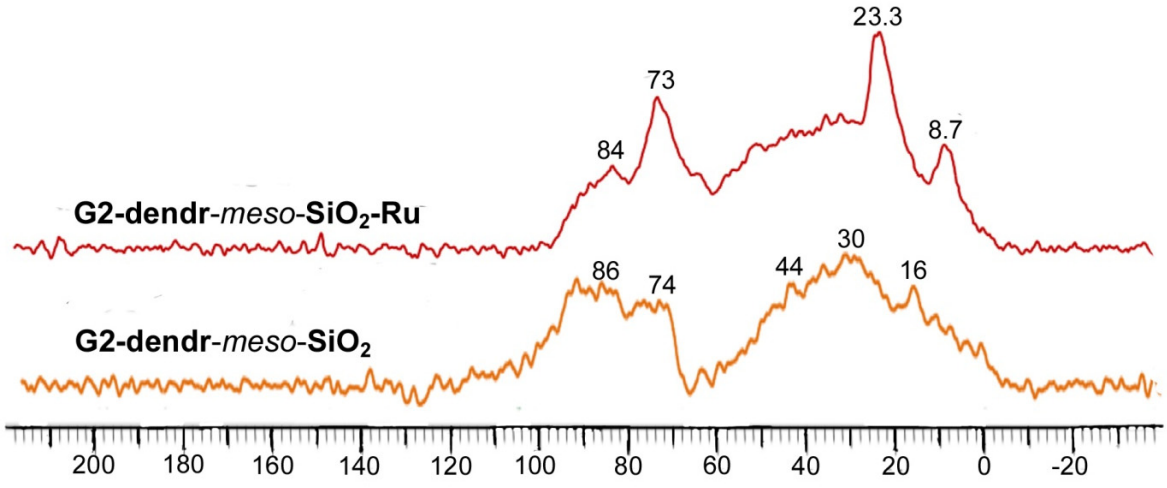


Figure S1. ^{13}C MAS NMR spectra of G2-dendr-*meso*-SiO_2-Ru catalyst and its carrier.

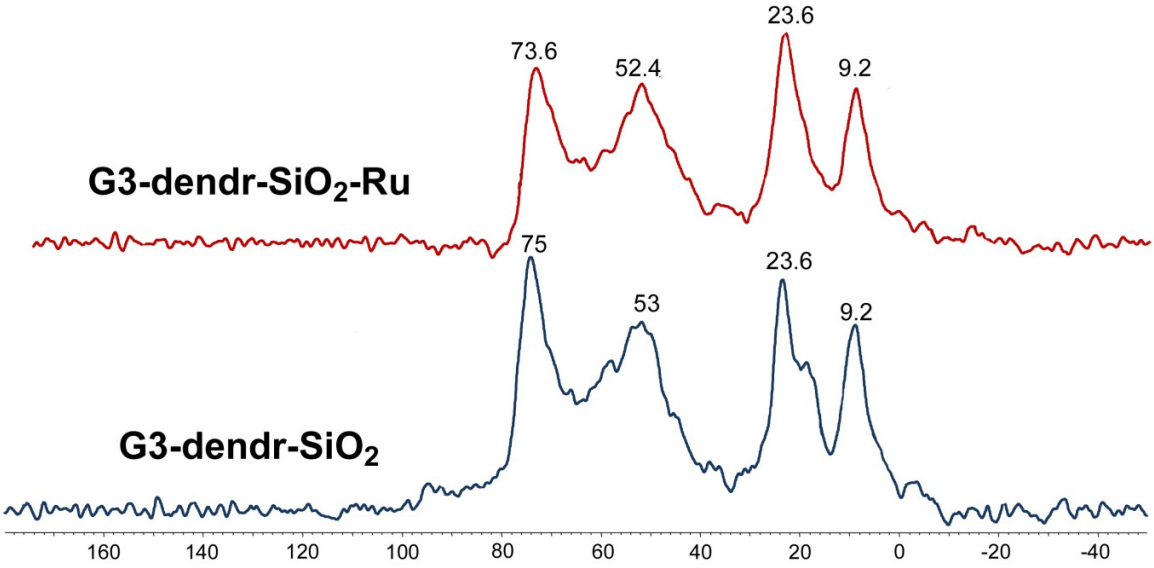


Figure S2. ^{13}C MAS NMR spectra of G3-dendr-SiO_2-Ru catalyst and its carrier.

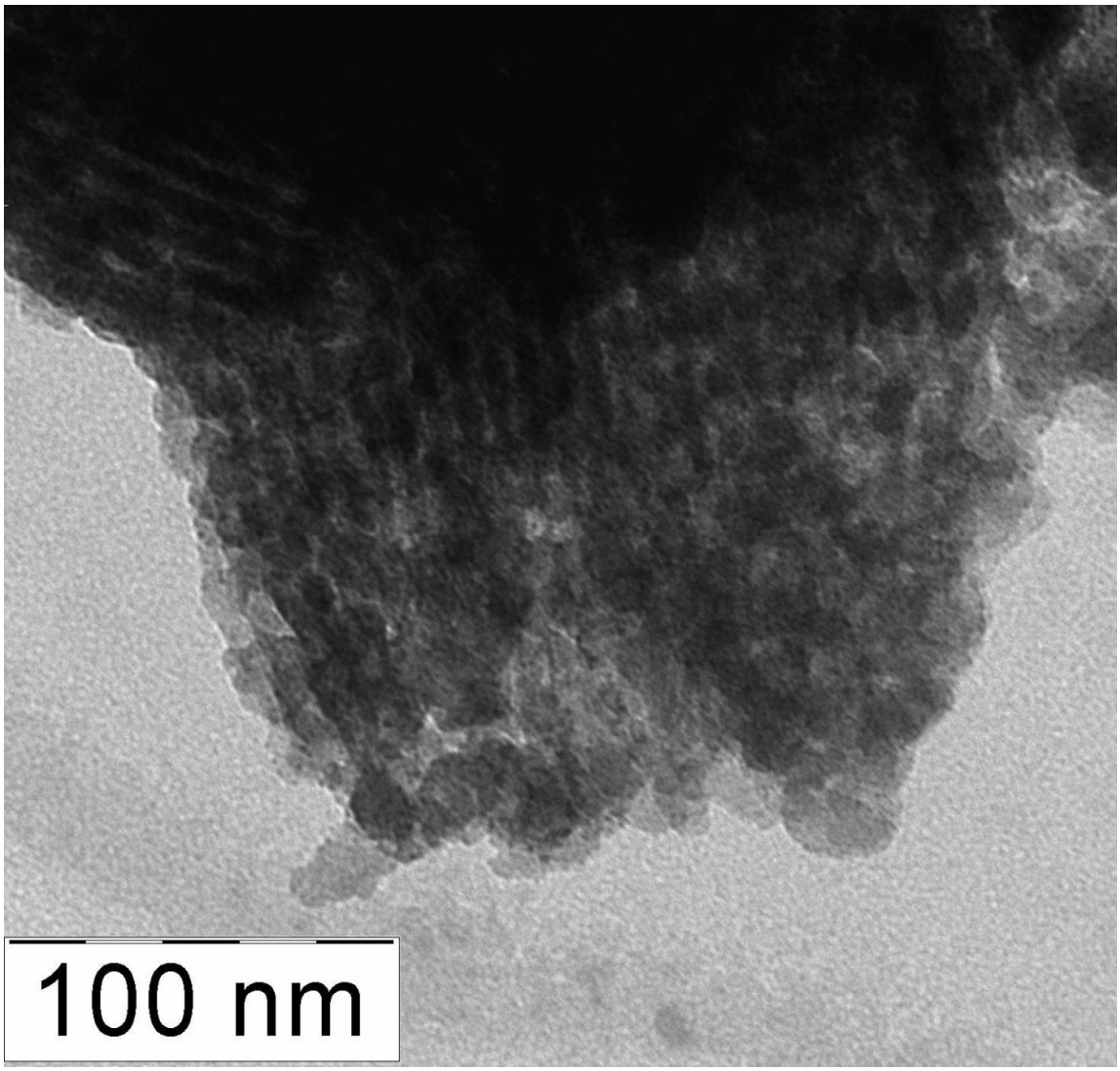


Figure S3. Maintenance of mesoporous structure in G2-dendr-*meso*-SiO_2-Ru after reduction by aqueous $NaBH_4$.

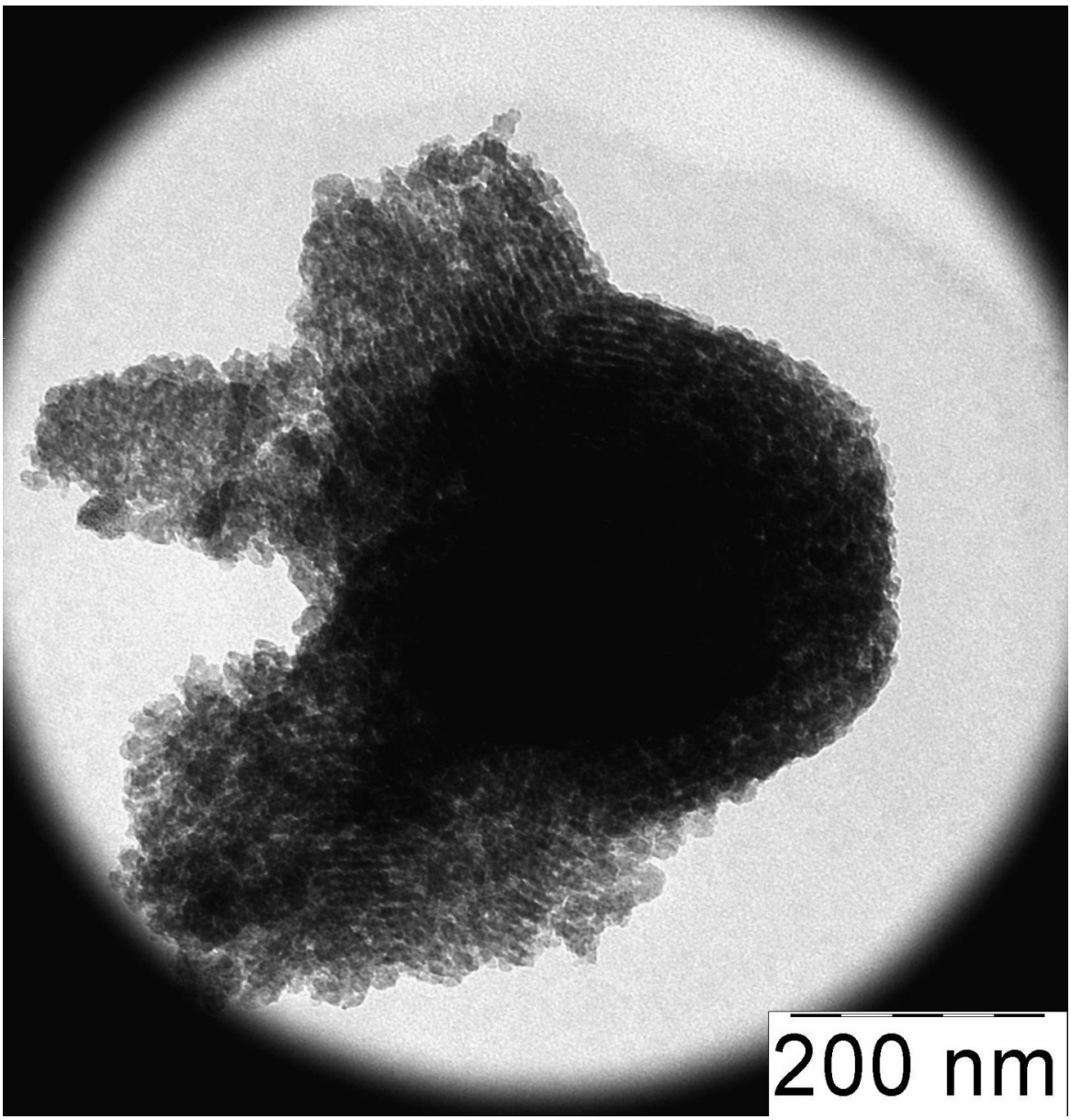


Figure S4. An overview TEM image of G2-dendr-*meso*-SiO_2-Ru

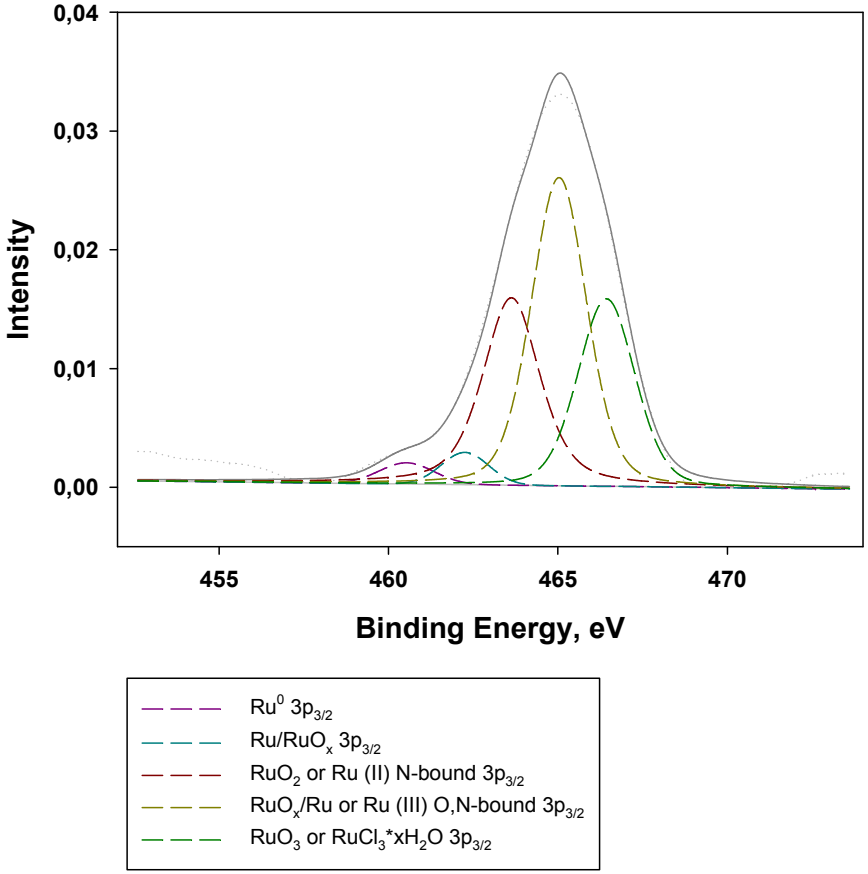


Figure S5. XPS spectrum of G2-dendr-*meso*-SiO_2-Ru, Ru 3p line.

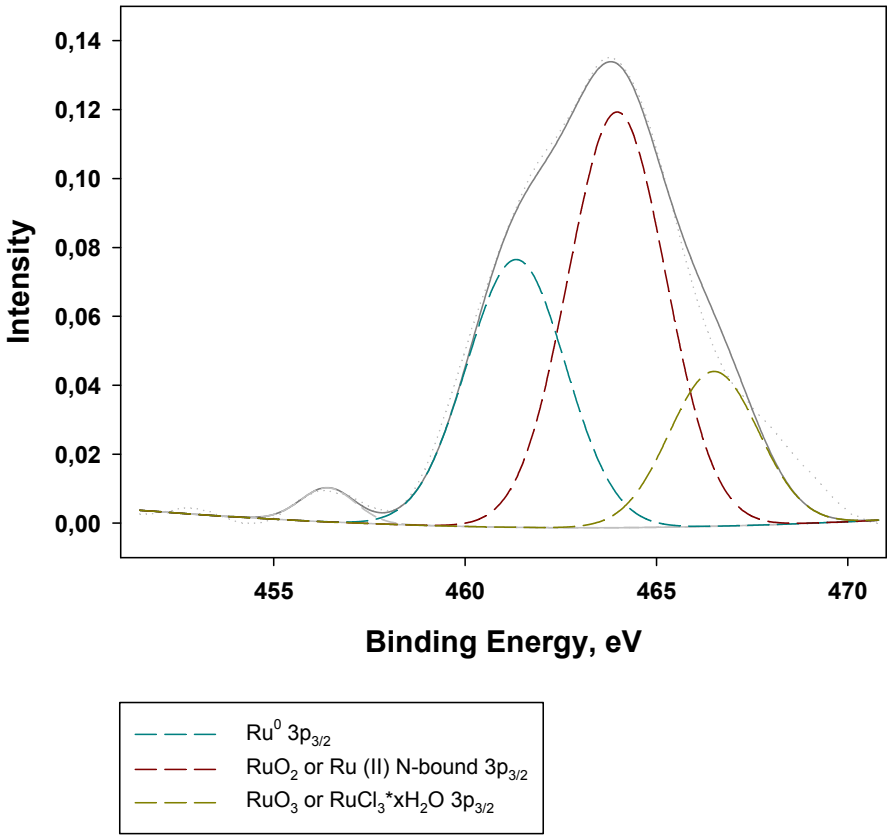


Figure S6. XPS spectrum G3-dendr-SiO_2-Ru, Ru 3p line.

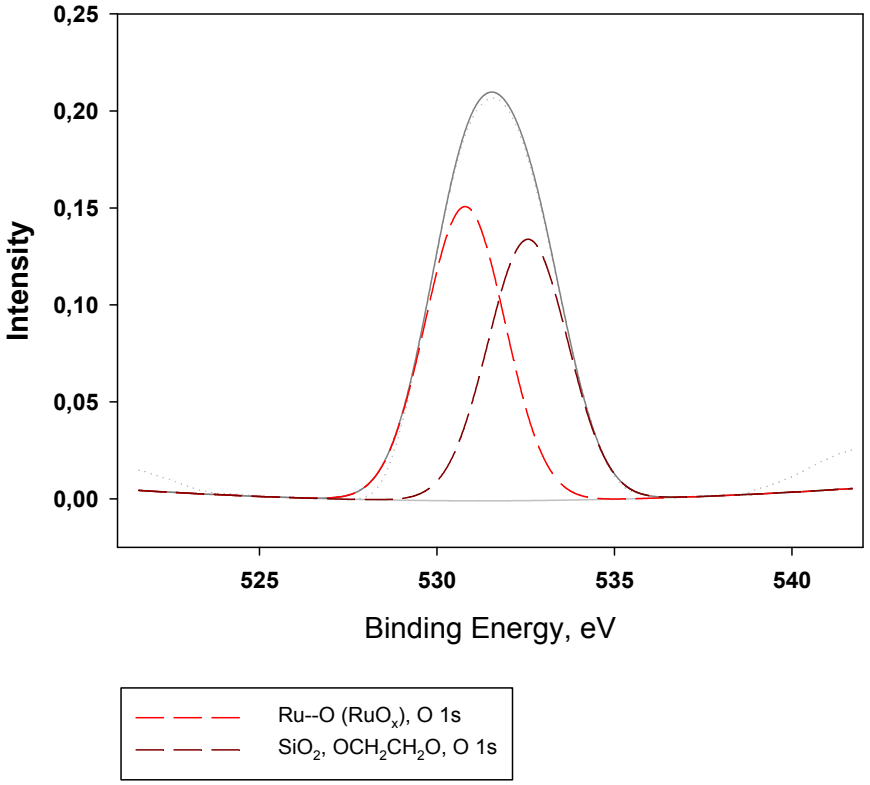


Figure S7. XPS spectrum of G2-dendr-*meso*-SiO$_2$-Ru, O 1s line.

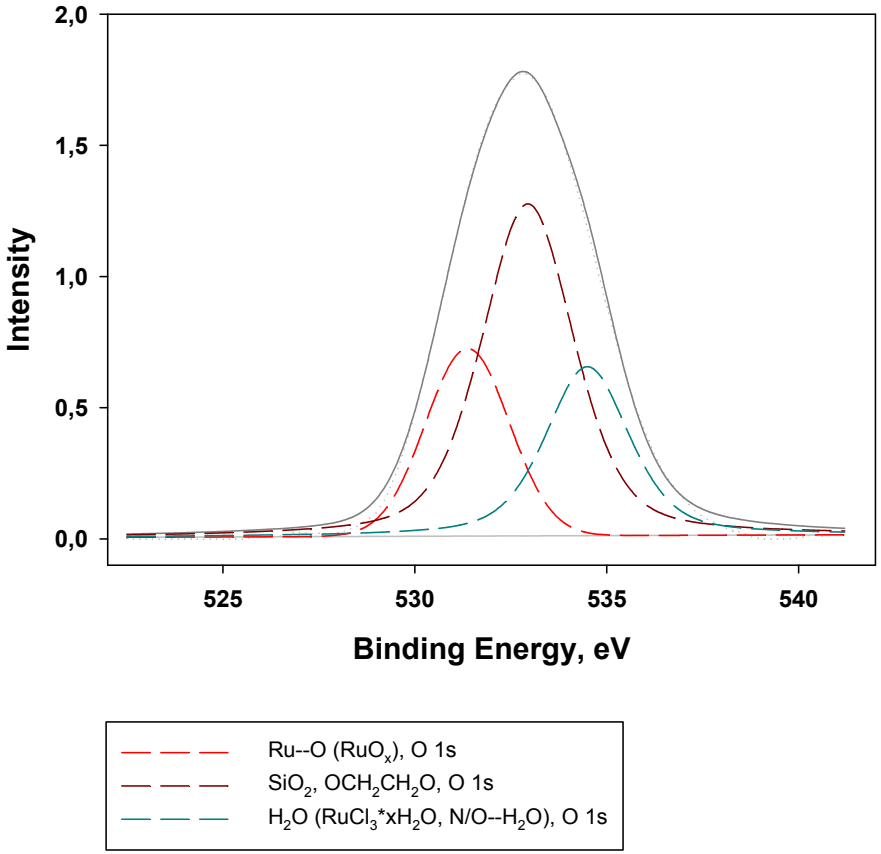


Figure S8. XPS spectrum G3-dendr-SiO$_2$-Ru, O 1s line.

Table S2. Hydrogenation of phenol in water in the presence of G3-dendr-SiO_2-Ru catalyst under various conditions at substrate/Ru of 377.

Entry	*T*, °C	*P*, MPa	*t*, h	Conv., %	TOF (H_2), h^{-1}	Products
1	85	3	6	100	1820	Cyclohexanol 100%
2			2	98		Cyclohexanol 94% Cyclohexanone 6%
3			0.5	94		Cyclohexanol 92% Cyclohexanone 8%
4			0.25	54		Cyclohexanol 85% Cyclohexanone 15%
5			0.1	20		Cyclohexanol 64% Cyclohexanone 36%
6	85	1	6	71	1172	Cyclohexanol 97% Cyclohexanone 3%
7			2	66		Cyclohexanol 91% Cyclohexanone 7% 2-cyclohexenone 2%
8			1	13		Cyclohexanol 75% Cyclohexanone 22% 2-cyclohexenone 3%
9			0.5	4		Cyclohexanol 78% Cyclohexanone 18% 2-cyclohexenone 4%
10	70	3	6	100	3100	Cyclohexanol 100%
11			2	86		Cyclohexanol 99% Cyclohexanone 1%
12			1	80		Cyclohexanol 98% Cyclohexanone 2%
13			0.75	71		Cyclohexanol 94% Cyclohexanone 5% 2-cyclohexenone 1%
14			0.6	20.5		Cyclohexanol 90% Cyclohexanone 8% 2-cyclohexenone 2%
15			0.5	1		Cyclohexanol 68% Cyclohexanone 27% 2-cyclohexenone 5%
16	70	1	6	46	225	Cyclohexanol 90% Cyclohexanone 10%
17			4	41		Cyclohexanol 87% Cyclohexanone 12% 2-cyclohexenone 1%
18			3	21		Cyclohexanol 73% Cyclohexanone 23% 2-cyclohexenone 4%
19			2	0		-

Table S3. Hydrogenation of phenol in water in the presence of G3-dendr-SiO_2-Ru catalyst under various conditions at substrate/Ru of 754–887.

Entry	Substrate/Ru, mol/mol	*T*, °C	*P*, MPa	*t*, h	Conv., %	TOF (H_2), h^{-1}	Products
1	754	85	3	6	100	1853	Cyclohexanol 98% Cyclohexanone 2%
2				2	71		Cyclohexanol 89% Cyclohexanone 10% 2-cyclohexenone 1%
3				1	45		Cyclohexanol 78% Cyclohexanone 17% 2-cyclohexenone 5%
4				0.5	0		-
5	754	85	1	6	32	212	Cyclohexanol 79% Cyclohexanone 20% 2-cyclohexenone 1%
6				2	19		Cyclohexanol 75% Cyclohexanone 25%
7				1	8		Cyclohexanol 66% Cyclohexanone 30% 2-cyclohexenone 4%
8				0.5	0		-
9	887	80	3	6	99	1841	Cyclohexanol 98.5% Cyclohexanone 1% 2-cyclohexenone 0.5%
10				2	66.5		Cyclohexanol 98% Cyclohexanone 1% 2-cyclohexenone 1%
11				1	39		Cyclohexanol 69% Cyclohexanone 28% 2-cyclohexenone 3%
12				0.5	0		-

Table S4. Hydrogenation of phenol in water in the presence of G2-dendr-*meso*-SiO_2-Ru catalyst [1].

Entry	*P*, MPa	*t*, h	Conv., %	TOF (H_2), h^{-1}	Products
1	3	6	90	6090	Cyclohexanol 100%
2		2	74		Cyclohexanol 100%
3		0.5	56		Cyclohexanol 95% Cyclohexanone 5%
4	1	6	71	3126	Cyclohexanol 97% Cyclohexanone 3%
5		2	54.5		Cyclohexanol 93% Cyclohexanone 7%
6		0.5	32		Cyclohexanol 68% Cyclohexanone 29% 2-cyclohexenone 3%

[1] Reaction conditions are: S/Ru = 1843, at 80 °C, *m*(substr.) = *V*(H_2O).

Table S5. Hydrogenation of alkyl-substituted phenols in the presence of G2-dendr-*meso*-SiO_2-Ru [1].

Entry	Substrate	Substrate/Ru, mol/mol	*t*, h	Conv., %	TOF (H_2), h^{-1}	Products
1	*o*-Cresol	1962	6	30	596	*cis*-2-methylcyclohexanol 6.5% *trans*-2-methylcyclohexanol 76.5% 2-methyl-2-cyclohexenone 2.5% phenol 7% cyclohexanol 2% cyclohexanone 1% toluene 1% methylcyclohexane 0.5%
			2	16.5		*cis*-2-methylcyclohexanol 23% *trans*-2-methylcyclohexanol 63.5% 2-methyl-2-cyclohexenone 5% phenol 6% cyclohexanol 1% cyclohexanone 0.5% toluene 1.5%
			0.5	5.5		*cis*-2-methylcyclohexanol 60% *trans*-2-methylcyclohexanol 23% 2-methylcyclohexanone 4% 2-methyl-2-cyclohexenone 9.5% phenol 3.5%
2	*p*-Cresol	1905	6	97	2886	*cis*-4-methylcyclohexanol 2.5% *trans*-4-methylcyclohexanol 80% phenol 1.5% cyclohexanol 14.5% toluene 0.5% methylcyclohexane 1%
			2	78		*cis*-4-methylcyclohexanol 33.5% *trans*-4-methylcyclohexanol 52.5% 4-methyl-2-cyclohexenone 5% phenol 6% cyclohexanol 1% toluene 1% methylcyclohexane 1%
			0.5	29		*cis*-4-methylcyclohexanol 53% *trans*-4-methylcyclohexanol 27.5% 4-methyl-2-cyclohexenone 16.5% phenol 1% toluene 2%
3	*o*-Ethylphenol	1960	6	96.5	3728	*cis*-2-ethylcyclohexanol 0.5% *trans*-2-ethylcyclohexanol 88.5% phenol 0.5% cyclohexanol 8.5% ethylbenzene 1.5% ethylcyclohexane 0.5%
			2	84		*cis*-2-ethylcyclohexanol 36.5% *trans*-2-ethylcyclohexanol 58.5% phenol 1.5% cyclohexanol 3% cyclohexanone 0.5%
			0.5	32.5		*cis*-2-ethylcyclohexanol 75% *trans*-2-ethylcyclohexanol 20.5% 2-ethyl-2-cyclohexenone 1.5% phenol 1.5% cyclohexanone 0.5% 2-cyclohexenone 1%

4	*p*-Ethylphenol	1890	6	88	2097	*cis*-4-ethylcyclohexanol 1.5% *trans*-4-ethylcyclohexanol 93.5% cyclohexanol 4% ethylcyclohexane 1%
			2	70		*cis*-4-ethylcyclohexanol 40.5% *trans*-4-ethylcyclohexanol 57.5% 4-ethylcyclohexanone 0.5% cyclohexanol 1% ethylcyclohexane 0.5%
			0.5	24		*cis*-4-ethylcyclohexanol 37.5% *trans*-4-ethylcyclohexanol 9.5% 4-ethylcyclohexanone 37% 4-ethyl-2-cyclohexenone 16%
5	*o*-Allylphenol	2480	6	76	3759	*cis*-2-propylcyclohexanol 67% *trans*-2-propylcyclohexanol 21.5% 2-propylcyclohexanone 4% 2-propyl-2-cyclohexenone 1.5% propylbenzene 3% propylcyclohexane 2.5%
			2	56		*cis*-2-propylcyclohexanol 63% *trans*-2-propylcyclohexanol 12% 2-propylcyclohexanone 15.5% 2-propyl-2-cyclohexenone 8% propylbenzene 1% propylcyclohexane 0.5%
			0.5	21		*cis*-2-propylcyclohexanol 57% 2-propylcyclohexanone 27% 2-propyl-2-cyclohexenone 16%
6	*p-tert*-butylphenol	1922	6	97	4879	*cis*-4-tert-butylcyclohexanol 41% *trans*-4-tert-butylcyclohexanol 48% 4-tert-butyl-2-cyclohexenone 4% tert-butylbenzene 4% phenol 1.5% cyclohexanol 1.5%
			2	78		*cis*-4-tert-butylcyclohexanol 55% *trans*-4-tert-butylcyclohexanol 34.5% 4-tert-butyl-2-cyclohexenone 7% tert-butylbenzene 2.5% phenol 1%
			0.5	45		*cis*-4-tert-butylcyclohexanol 64% *trans*-4-tert-butylcyclohexanol 25.5% 4-tert-butyl-2-cyclohexenone 10% tert-butylbenzene 0.5%

[1] Reaction conditions are: at 80 °C, 3 MPa of H_2, V(substrate) = $V(H_2O)$.

Table S6. Hydrogenation of alkyl-substituted phenols in the presence of G3-dendr-SiO_2-Ru [1].

Entry	Substrate	Substrate/Ru, mol/mol	*t*, h	Conv., %	TOF (H_2), h^{-1}	Products
1	*o*-Cresol	945	6	58	608	*cis*-2-methylcyclohexanol 7% *trans*-2-methylcyclohexanol 59% 2-methyl-2-cyclohexenone 4.5% phenol 15% cyclohexanol 2% cyclohexanone 6% 2-cyclohexenone 6.5%
			2	23.5		*cis*-2-methylcyclohexanol 51% *trans*-2-methylcyclohexanol 39% 2-methyl-2-cyclohexenone 8% phenol 2%
			1	1		*cis*-2-methylcyclohexanol 75% 2-methylcyclohexanone 9% 2-methyl-2-cyclohexenone 14% phenol 2%
			0.5	0		-
2	*p*-Cresol	918	6	84	580	*cis*-4-methylcyclohexanol 8% *trans*-2-methylcyclohexanol 74% 4-methyl-2-cyclohexenone 0.5% phenol 2% cyclohexanol 15.5%
			2	31.5		*cis*-4-methylcyclohexanol 14% *trans*-2-methylcyclohexanol 68% 4-methyl-2-cyclohexenone 5% phenol 5% cyclohexanol 7% cyclohexanone 1%
			1	8.5		*cis*-4-methylcyclohexanol 32% *trans*-2-methylcyclohexanol 23.5% 4-methyl-2-cyclohexenone 41% phenol 2.5% cyclohexanol 0.5% cyclohexanone 0.5%
			0.5	0		-
3	*o*-Ethylphenol	945	6	70	881	*cis*-2-ethylcyclohexanol 44% *trans*-2-ethylcyclohexanol 49.5% 2-ethyl-2-cyclohexenone 2% phenol 0.5% cyclohexanol 3% cyclohexanone 1%
			2	41		*cis*-2-ethylcyclohexanol 64% *trans*-2-ethylcyclohexanol 29% 2-ethyl-2-cyclohexenone 4% phenol 1% cyclohexanol 1% cyclohexanone 1%
			1	9.5		*cis*-2-ethylcyclohexanol 72.4% *trans*-2-ethylcyclohexanol 15% 2-ethyl-2-cyclohexenone 11% phenol 1.5%
			0.5	0		-

			6	80		*cis*-4-ethylcyclohexanol 4% *trans*-4-ethylcyclohexanol 84.5% 4-ethyl-2-cyclohexenone 0.5% ethylbenzene 1.5% ethylcyclohexane 3% phenol 4% cyclohexanol 2.5%
4	*p*-Ethylphenol	910	2	43	635	*cis*-4-ethylcyclohexanol 15% *trans*-4-ethylcyclohexanol 79.5% 4-ethyl-2-cyclohexenone 2% ethylbenzene 1.5% ethylcyclohexane 1.5% phenol 0.5%
			1	15		*cis*-4-ethylcyclohexanol 41% *trans*-4-ethylcyclohexanol 17% 4-ethyl-2-cyclohexenone 40.5% ethylbenzene 1% ethylcyclohexane 0.5%
			0.5	0		-
			6	63		*cis*-2-propylcyclohexanol 63% *trans*-2-propylcyclohexanol 21% 2-propylcyclohexanone 7% 2-propyl-2-cyclohexenone 9%
5	*o*-Allylphenol	1193	2	22	857	*cis*-2-propylcyclohexanol 56% *trans*-2-propylcyclohexanol 6.5% 2-propylcyclohexanone 5% 2-propyl-2-cyclohexenone 32.5%
			1	2.5		*cis*-2-propylcyclohexanol 13% 2-propylcyclohexanone 1.5% 2-propyl-2-cyclohexenone 85.5%
			0.5	0		-
			6	97		*cis*-4-*tert*-butylcyclohexanol 52% *trans*-4-*tert*-butylcyclohexanol 38% 4-*tert*-butyl-2-cyclohexenone 5% *tert*-butylbenzene 3% phenol 1% cyclohexanol 1%
6	*p-tert*-butylphenol	925	2	71	1162	*cis*-4-*tert*-butylcyclohexanol 52% *trans*-4-*tert*-butylcyclohexanol 29% 4-*tert*-butylcyclohexanone 0.5% 4-*tert*-butyl-2-cyclohexenone 15% *tert*-butylbenzene 2% phenol 1% cyclohexanol 0.5%
			1	26		*cis*-4-*tert*-butylcyclohexanol 46% *trans*-4-*tert*-butylcyclohexanol 20% 4-*tert*-butylcyclohexanone 3% 4-*tert*-butyl-2-cyclohexenone 27.5% *tert*-butylbenzene 1.5%
			0.5	0		-

[1] Reaction conditions are: at 80 °C, 3 MPa of H_2, V(substrate) = $V(H_2O)$.

Table S7. Comparison of activities of G3–HMDI–Ru [57] and G3-dendr-SiO_2-Ru in hydrogenation of alkyl-substituted phenols [1].

Entry	Substrate	Substrate/Ru, mol/mol (G3–HMDI/G3-dendr-SiO_2)	*t*, h (G3–HMDI/G3-dendr-SiO_2)	G3–HMDI–Ru		G3-dendr-SiO_2-Ru	
				Conv., %	TOF (H_2), h^{-1}	Conv., %	TOF (H_2), h^{-1}
1	phenol	960/887	0.5/2	57	2745	66.5	1841
2	*o*-cresol	1015/945	2/2	10.5	160	23.5	608
3	*p*-cresol	997/918	2/2	0	0	31.5	580
4	*o*-ethylphenol	1025/945	2/2	13.5	207	41	881
5	*p*-ethylphenol	990/910	2/2	55	815	43	635
6	*o*-allylphenol	1040/1193	2/2	17	265	22	857
7	*p*-tert-butylphenol	1005/925	0.5/1	22	1325	26	1162

[1] Reaction conditions are: at 85 °C G1–HMDI–Ru and for 80 °C for G2-dendr-*meso*-SiO_2-Ru, 3 MPa of H_2, V(substrate) = V(H_2O).