Supplementary information

Nanoconfinement of Mg_6Pd particles in porous carbon: size effects on structural and hydrogenation properties

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As described by Samson [1] and illustrated in Figure S1, the Mg_6Pd structure comprises 3 sites (10, 11, 13) exclusively occupied by Pd atoms and one shared with Mg (12). The distribution of Pd-Mg interatomic distances and number of Mg atoms around each Pd-site are gathered in Table S1. All together, these 4 independent sites provide 14 different Pd-Mg interatomic distances in the 2.5-3.5 Å range. Taking into account the multiplicity and occupancy of each site, the average coordination number in the first Pd sphere contains 10.8 Mg atoms (approximated to 11 for EXAFS fits). To ensure convergence of EXAFS fits, the 14 different Pd-Mg interatomic distances have been reduced to three (3R-model) and four (4R-model) averaged distances.

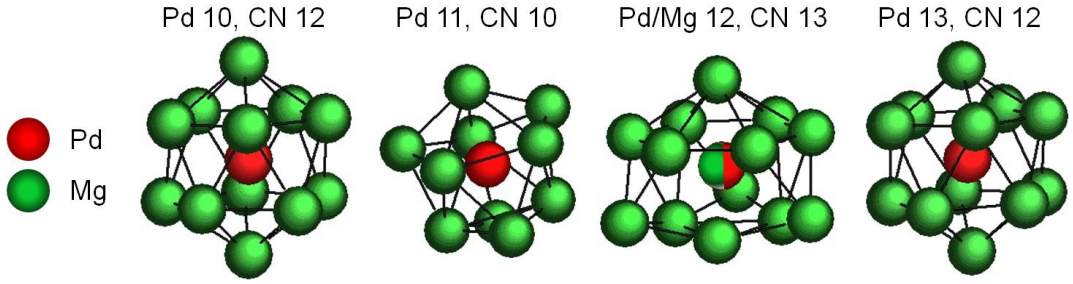

Figure S1. Representation of the first coordination sphere around each Pd site in the Mg_6Pd structure.

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Table S1. Distribution of the Pd-Mg distances in Mg_6Pd bulk (a = 20.108 Å, site occupancy factors for Pd and Mg atoms on site 12 both taken as 0.5).

Pd10	Pd11	Pd12	Pd13	Average	4R-model	3R-model
	3Mg 2.669Å			0.86Mg 2.669Å	1.71Mg 2.69Å	
	3Mg 2.708Å			0.86Mg 2.708Å		
3Mg 2.783Å				0.86Mg 2.783Å		
		1Mg 2.835Å		0.14Mg 2.835Å		5.71Mg 2.79Å
3Mg 2.837Å				0.86Mg 2.837Å	4.00Mg 2.84Å	
			3Mg 2.840Å	0.86Mg 2.840Å		
			3Mg 2.865Å	0.86Mg 2.865Å		
		3Mg 2.874Å		0.43Mg 2.874Å		
			3Mg 2.940Å	0.86Mg 2.940Å		
	3Mg 2.944Å			0.86Mg 2.994Å	3.43Mg 2.96Å	3.43Mg 2.96Å
			3Mg 2.965Å	0.86Mg 2.965Å		
3Mg 2.997Å				0.86Mg 2.997Å		
		6Mg 3.115Å		0.86Mg 3.115Å	1.71Mg 3.12Å	1.71Mg 3.12Å
3Mg 3.125Å				0.86Mg 3.125Å		
Following atoms are not included in the 1st coordination EXAFS fit:						
	1Mg 3.626Å			*0.29Mg 3.626Å*	*0.71Mg 3.71Å*	*0.71Mg 3.71Å*
		3Mg 3.762Å		*0.43Mg 3.732Å*		

Figure S2 shows theoretical EXAFS spectra and FT moduli of bulk Mg_6Pd for each of the four different Pd sites as well as their average contribution. Variations in amplitude and phase between contributions lead to a dumped FT average signal, especially for the first coordination sphere.

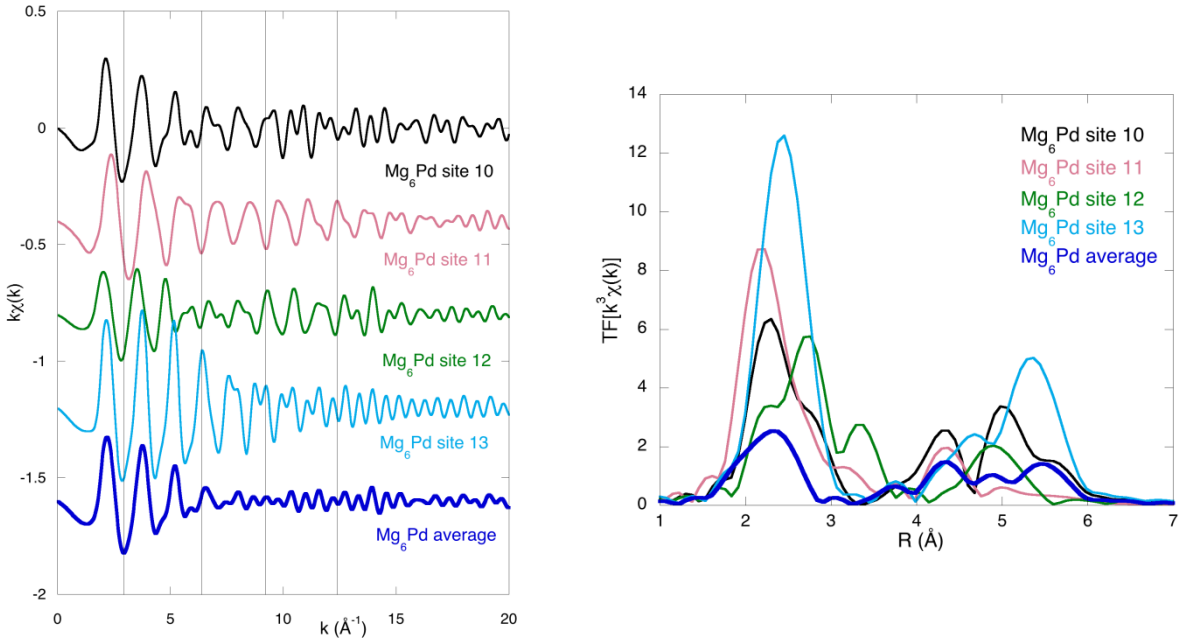

Figure S2. Comparison of EXAFS theoretical signals (left) and FT moduli (right) for the four Pd sites in Mg_6Pd and their averaged contribution to the overall spectrum. The vertical lines emphasize the phase shifts between the signals of the different sites.

References

[1] Samson S. Complex Cubic A_6B Compounds. II. The crystal structure of Mg_6Pd. Acta Crystallogr 1972;B28:936.