Supporting Information

The Atomic Structural Dynamics of γ-Al_2O_3 Supported Ir-Pt Nanocluster Catalysts Prepared From a Bimetallic Molecular Precursor: A Study Using Aberration-Corrected Electron Microscopy and X-ray Absorption Spectroscopy

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Contents:

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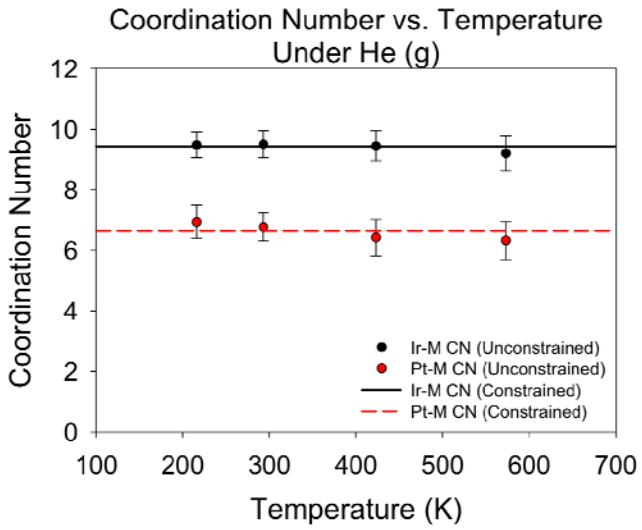
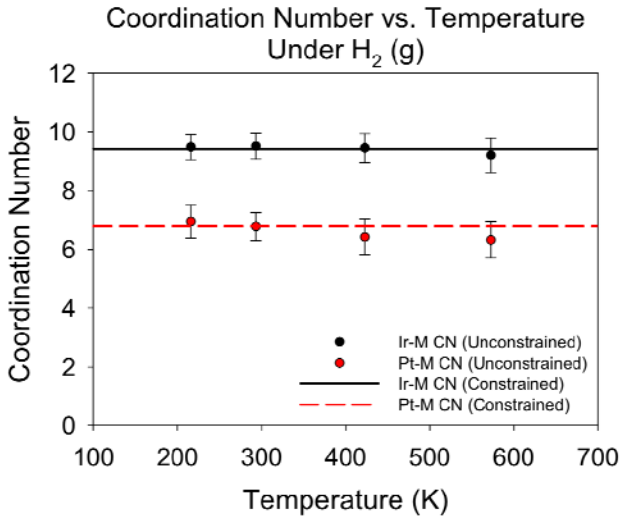
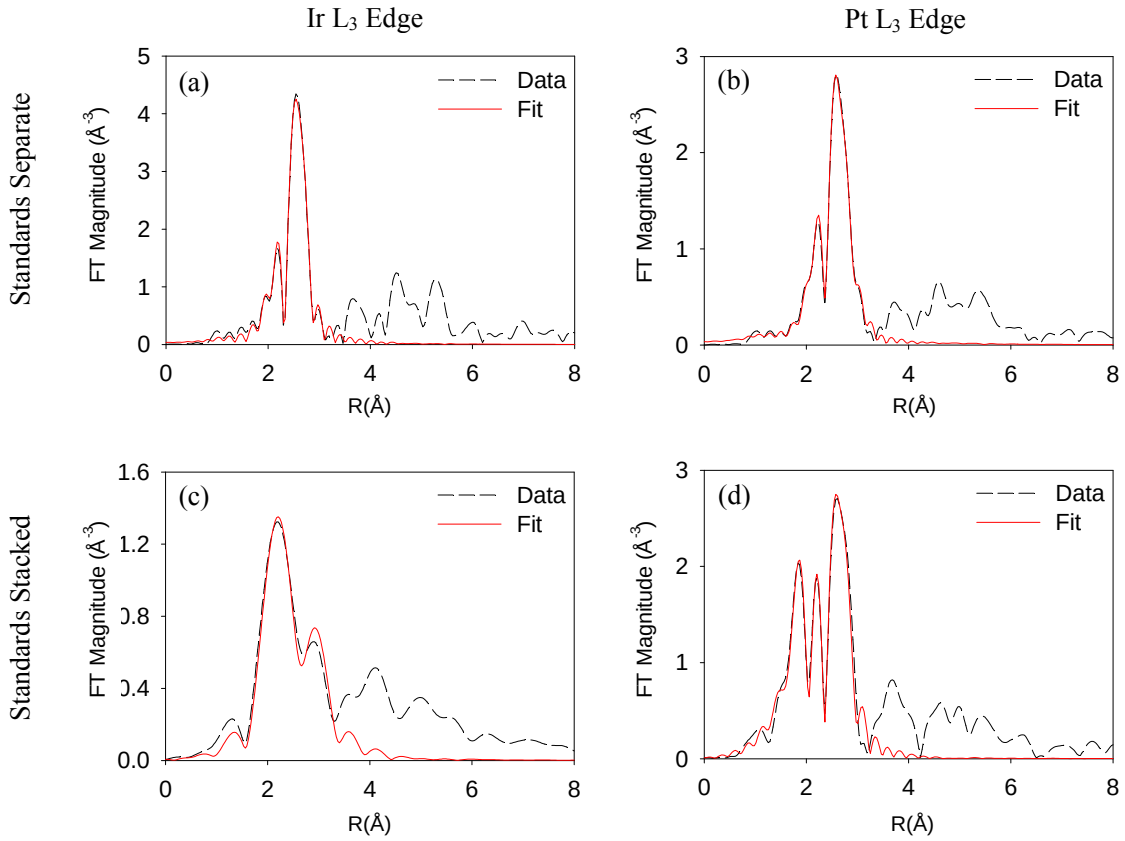
a.)



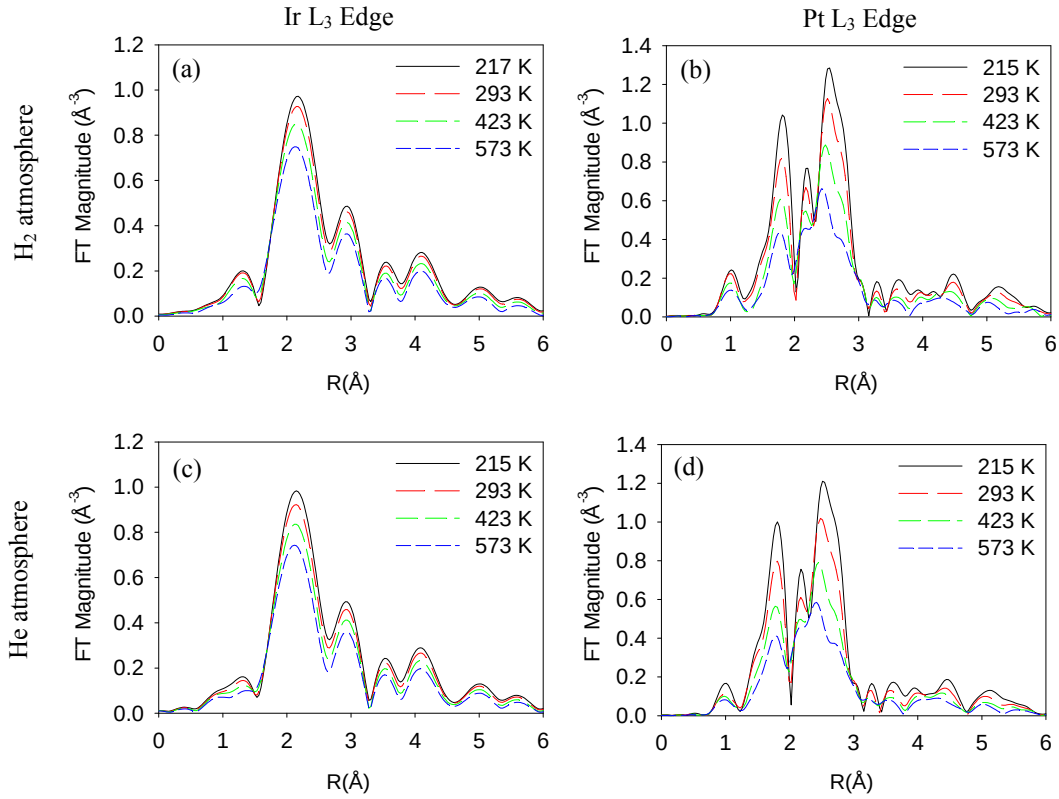
b.)



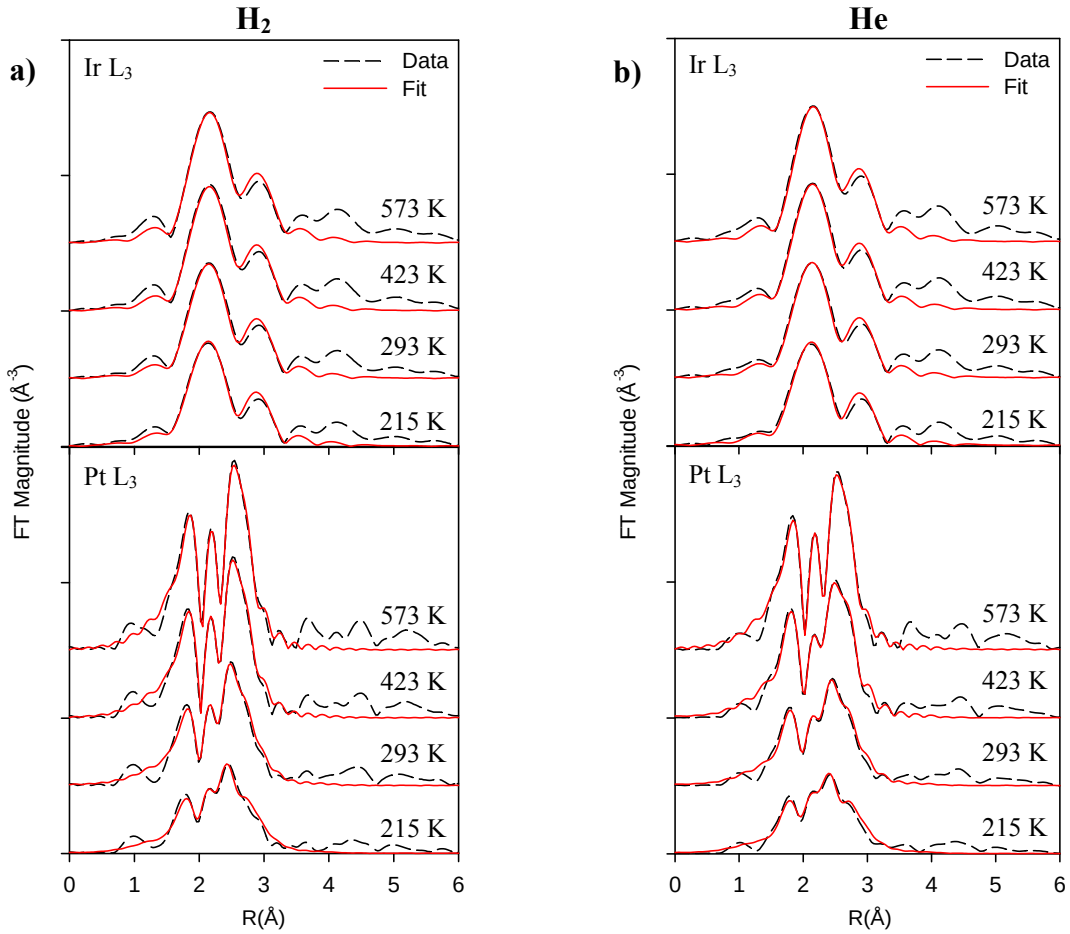
S.I. Figure 1. The plot shows the relative consistency in coordination number under (a) He and (b) H_2 for both the Ir-M and Pt-M contributions when the coordination numbers are left unconstrained with respect to temperature during the fitting process. The straight lines (black, Ir-M; and red dashed, Pt-M) represent the fit values obtained for the coordination number of Ir-M (9.4 ± 0.2) and Pt-M (6.7 ± 0.3) when the coordination numbers were constrained to be one value.



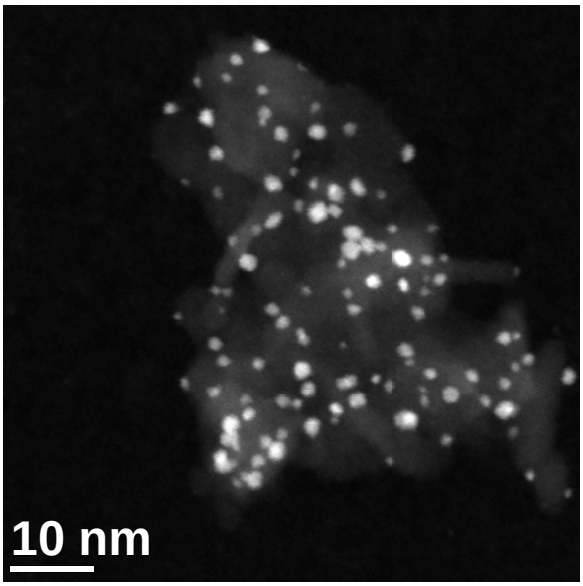
S.I. Figure 2. Comparison of EXAFS data and first shell fits for isolated (a) Ir black and (b) Pt foil standards [k^2-weighted, k=2.0-18.0 Å^{-1}, R=1.8-3.0 Å]. Comparison of EXAFS data and two-edge, three-component fits for stacked Ir and Pt standards at (c) the Ir L_3 edge [k^2-weighted, k=2.7-8.7 Å^{-1}, R=1.2-3.1 Å] and (d) the Pt L_3 edge [k^2-weighted, k=2.7-16.0 Å^{-1}, R=1.2-3.0 Å].



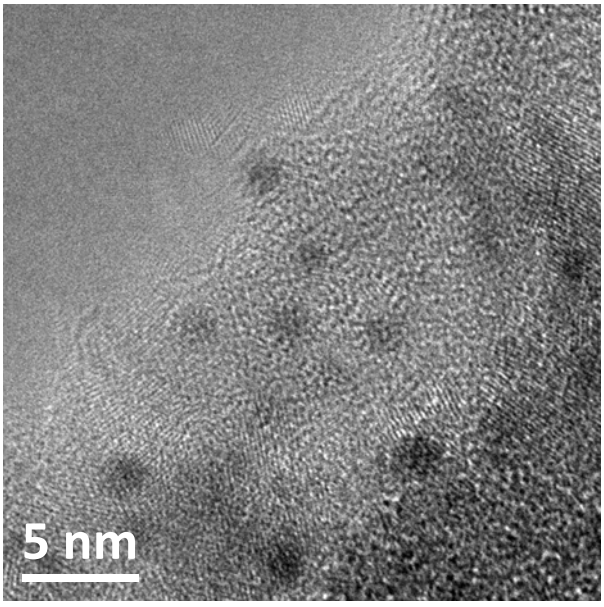
S.I. Figure 3. EXAFS spectra measured at different temperatures for Ir-Pt/Al_2O_3 under a 4% H_2 atmosphere at the (a) Ir L_3 and (b) Pt L_3 edges. EXAFS spectra measured at different temperatures for Ir-Pt/Al_2O_3 under a He atmosphere at the (c) Ir L_3 and (d) Pt L_3 edges. Spectra at the Ir L_3 edge are k^2-weighted and Fourier transformed over a k range of 2.0-8.7 $Å^{-1}$ while Pt L_3 spectra are k^2-weighted and Fourier transformed over a k range of 2.0-16.3 $Å^{-1}$.



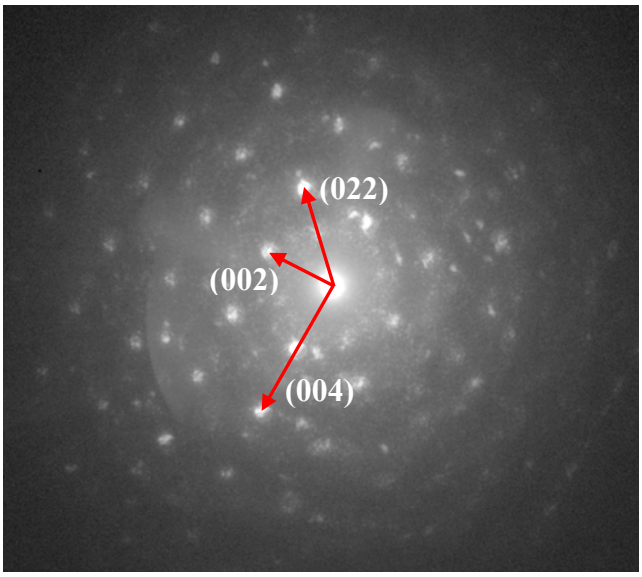
S.I. Figure 4. (a) Comparison of data and fits for Ir-Pt/Al_2O_3 under a 4% H_2 atmosphere measured at multiple temperatures at the Ir L_3 and Pt L_3 absorption edges. At the Ir L_3 edge the data were transformed over k=2.7-8.7 Å^{-1} and fit over R=1.2-3.1 Å. At the Pt L_3 edge the data were transformed over k=2.7-17.1 Å^{-1} and fit over R=1.3-3.0 Å. All spectra were k^2-weighted. (b) Comparison of data and fits for IrPt/Al_2O_3 under a He atmosphere measured at multiple temperatures at the Ir L_3 and Pt L_3 absorption edges. At the Ir L_3 edge the data were transformed over k=2.7-8.8 Å^{-1} and fit over R=1.2-3.1 Å. At the Pt L_3 edge the data were transformed over k=2.7-16.5 Å^{-1} and fit over R=1.3-3.0 Å. All spectra were k^2-weighted.



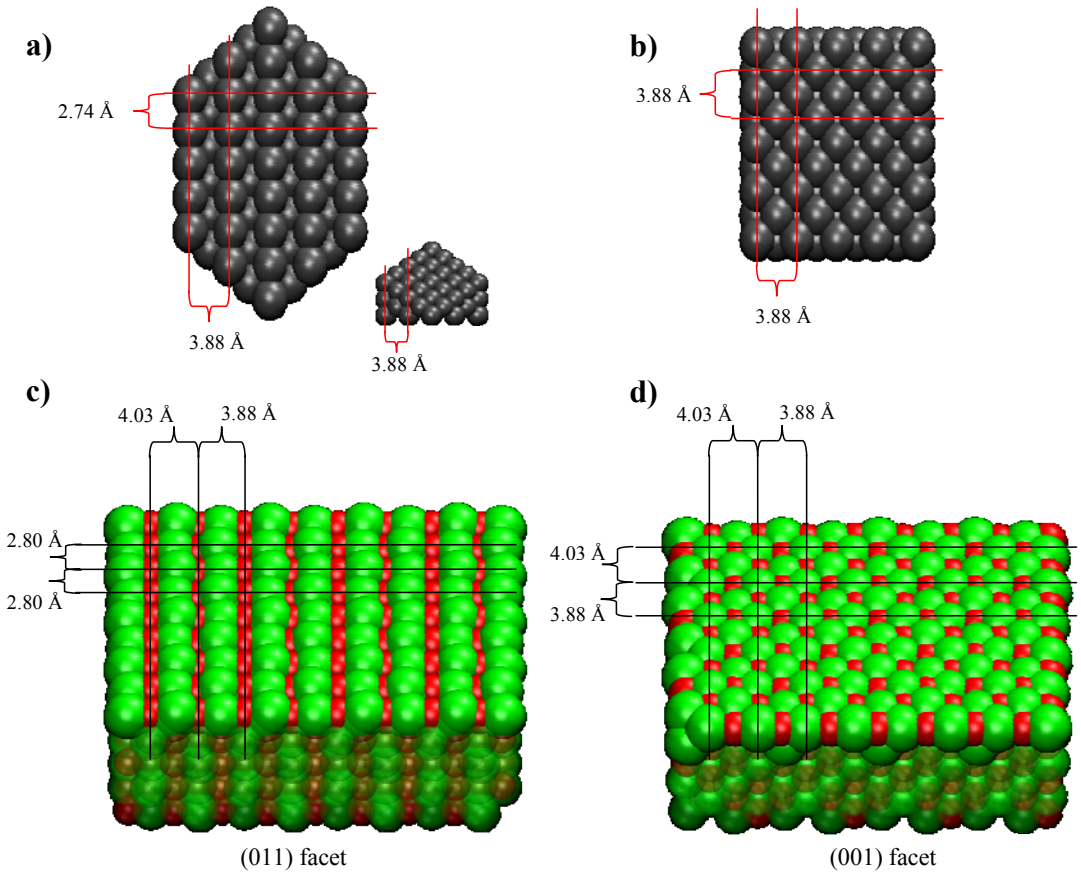
S.I. Figure 5. Representative STEM image showing dispersion of the Ir-Pt nanoparticles on the γ-Al_2O_3 support.



S.I. Figure 6. HRTEM micrograph image showing the presence of many domains on the γ-Al_2O_3 support.



S.I. Figure 7. NBD pattern showing a [001] zone axis orientation for the γ-Al_2O_3 support. Arrows and parenthetical numbers highlight diffraction spots corresponding to specific lattice planes.



S.I. Figure 8. Model structures showing the (011) and (001) planar truncations for an fcc cluster with atomic spacing equivalent to an Ir-Pt alloy ((a) and (b), respectively) and for γ-Al_2O_3 ((c) and (d), respectively). Lines and distances show the spacing between rows of atoms in all images.

Parameter	Temperature			
	215 K	293 K	423 K	573 K
N_{Ir} [a]	9.4(2)	9.4(2)	9.4(2)	9.4(2)
N_{Pt} [a]	6.8(3)	6.8(3)	6.8(3)	6.8(3)
$\Delta E_{0,Ir}$ (eV) [a]	5.8(3)	5.8(3)	5.8(3)	5.8(3)
$\Delta E_{0,Pt}$ (eV) [a]	6.6(6)	6.6(6)	6.6(6)	6.6(6)
R_{Ir} (Å)	2.687(4)	2.686(4)	2.681(6)	2.677(6)
R_{Pt} (Å)	2.731(6)	2.724(7)	2.717(7)	2.713(7)
σ^2_{Ir} (Å^2)	0.0047(1)	0.0055(2)	0.0065(3)	0.0078(3)
σ^2_{Pt} (Å^2)	0.0055(2)	0.0061(2)	0.0072(3)	0.0089(3)
$\sigma^{(3)}_{Ir}$ (Å^3)	0.00000(3)	0.00005(4)	0.00007(5)	0.00012(7)
$\sigma^{(3)}_{Pt}$ (Å^3)	0.00005(5)	0.00005(6)	0.00010(7)	0.00020(8)

[a] indicates a temperature independent parameter.

S.I. Table 1. EXAFS fitting results for Ir-Pt/Al_2O_3 nanoparticles under H_2.

Parameter	Temperature			
	215 K	293 K	423 K	573 K
N_{Ir} [a]	9.4(2)	9.4(2)	9.4(2)	9.4(2)
N_{Pt} [a]	6.7(3)	6.7(3)	6.7(3)	6.7(3)
$\Delta E_{0,Ir}$ (eV) [a]	5.9(3)	5.9(3)	5.9(3)	5.9(3)
$\Delta E_{0,Pt}$ (eV) [a]	6.4(6)	6.4(6)	6.4(6)	6.4(6)
R_{Ir} (Å)	2.671(4)	2.669(4)	2.670(5)	2.672(5)
R_{Pt} (Å)	2.706(7)	2.695(7)	2.696(8)	2.695(9)
σ^2_{Ir} (Å^2)	0.0049(2)	0.0056(2)	0.0067(3)	0.0080(3)
σ^2_{Pt} (Å^2)	0.0057(2)	0.0064(2)	0.0078(3)	0.0095(4)
$\sigma^{(3)}_{Ir}$ (Å^3)	0.00000(3)	0.00001(4)	0.00008(5)	0.00014(7)
$\sigma^{(3)}_{Pt}$ (Å^3)	0.00000(6)	0.00004(6)	0.00010(8)	0.0002(1)

[a] indicates a temperature independent parameter.

S.I. Table 2. EXAFS fitting results for Ir-Pt/Al_2O_3 nanoparticles under He.

S.I. Calculation 1. Based on the work of Savargaonkar, et al.[1], the parameters: E_{des} = 66 kJ/mol, k_a = 2.3×10^5 Pa^{-1} s^{-1}, k_d = 20 s^{-1} and T = 333 K were used to calculate the hydrogen coverage at different temperatures using the Langmuir model for dissociative adsorption:

$$KP_{H_2} = \frac{\theta_H{}^2}{(1-\theta_H)^2} \quad (1)$$

were K is the ratio of the adsorption and desorption coefficients, P_{H_2} is the pressure of H_2 and θ_H is the surface coverage. Theoretical coverages of hydrogen were calculated to be 1.00 at 215 K and 0.13 at 573 K for 573 K for a 4% H_2 atmosphere.

References

1. Savargaonkar, N.; Uner, D.; Pruski, M.; King, T. S. *Langmuir* **2002**, *18*, 4005.