Electronic Supplementary Material (ESI)

Dynamic Structural Evolution of MgO-Supported Palladium Catalysts: From Metal to Metal Oxide Nanoparticles to Surface then Subsurface Atomically Dispersed Cations

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Experimental and Computational methods

Synthesis of Pd/MgO samples. MgO powder (1000 mg, US Research Nanomaterials) was dispersed in 250 mL of ethanol (Sigma-Aldrich, reagent grade) in a 500-mL beaker with magnetic stirring. Aqueous Na₂PdCl₄, 60 mL of 0.14 mM ethanol solution, was transferred into the stirred beaker with a syringe pump at a rate of 5 mL/h.¹ The resultant solid was collected by centrifugation, washed with ethanol and distilled water, and then dried overnight in air in an oven at 80 °C, giving the sample designated as Pd/MgO_{wet}.

*Synthesis of Pd/MgO*₄₀₀, *Pd/MgO*₅₀₀, and *Pd/MgO*₇₀₀. The Pd/MgO_{wet} sample was calcined in flowing air (50 mL(NTP)/min) as the temperature was ramped from room temperature to 120 °C and held for 2 h to remove any residual water or organics. The sample was then further calcined in flowing air (50 mL(NTP)/min) as the temperature was ramped at a rate of 5 °C/min until a final temperature of 400, 500, or 700 °C was reached, and each respective sample was held for 4 h.

Synthesis of MgO_{web} MgO_{500} , and MgO_{700} . The MgO powders were treated under the same conditions used with the samples mentioned above, but without adding the palladium precursors. **X-ray Absorption Spectroscopy (XAS)**. *Experimental methods*. XAS experiments were conducted at beam line 9-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). Beamline 9-3 is a side-station of a 20-pole, 2-Tesla, wiggler insertion device, with rhodium-coated mirrors for collimation and harmonic rejection, and focusing of the X-ray beam. Photon energy selection was achieved with a double-crystal, liquid-nitrogen cooled Si (220), $\Phi = 0$, monochromator, and the harmonic rejection was set to 29 keV. The storage ring was operated at 3 GeV with a ring current of 495–500 mA in top-up mode. Palladium K-edge (24350.0 eV) XAS data were collected in fluorescence detection mode with a PIPS detector. A palladium foil spectrum was collected in transmission geometry simultaneously with each sample spectrum for energy calibration during the analysis. The ionization chambers used to measure the X-ray beam intensity were filled with argon and operated with a 700 VDC negative polarity bias.

In experiments characterizing the catalyst calcination, approximately 50 mg of catalyst powder was loaded in a flow-through cell consisting of a quartz tube (outside diameter = 3.0 mm, inside diameter 2.6 mm) with resistive coil heaters.² The upstream side of the flow cell was connected to a LabVIEW controlled process gas control manifold, and the outlet of the cell was connected

to a Hiden mass spectrometer for effluent gas analysis. EXAFS spectra of the Pd/MgO_{wet} sample in helium flowing at 20 mL(NTP)/min were collected at room temperature to characterize the asprepared catalyst. After the initial characterization, the sample was exposed to 20% O₂/helium flowing at 20.0 mL(NTP)/min, while the temperature was ramped from room temperature to 700 °C at a rate of 2 °C/min with a 1 h dwell at 700 °C with the gas flow continuing. EXAFS spectra were collected throughout the temperature ramp and dwell. The reactor was cooled to room temperature, and the gas feed was switched to helium flowing at 20 mL(NTP)/min, and EXAFS spectra were collected characterizing the sample after the calcination.

Ex-situ XAS data were collected in fluorescence detection mode using a PIPS detector with samples pressed into pellets at 25 °C.

Conventional XAS data analysis. The EXAFS and XANES data were analyzed with the Demeter package.³ Data alignment, edge calibration, deglitching, normalization, and background subtraction were done with Athena. The energy at the Pd K-edge was determined by the first inflection point of the absorption edge data characterizing the reference palladium foil, calibrated to the reported energy, 24350.0 eV. EXAFS data were modeled with the Artemis package in Demeter. S_0^2 was determined to be 0.88 ± 0.04 for the Pd K-edge from fitting the palladium foil (Fig. S8 and Table S2). Fitting was carried out taking into account k^1 , k^2 , and k^3 weightings. Models were selected on the basis of goodness of fit.

QuantEXAFS analysis. The automated EXAFS analysis was done using the recently developed QuantEXAFS¹ workflow that uses Xray Larch⁴ modules for the alignment, edge calibration, data normalization, and an in-house code (atoms2FEFF) for creating FEFF input files from DFT-optimized structures. FEFF was used for calculating the scattering paths. Seaborn was used for plotting the fitting results, and the SciPy optimizer code in Python was used to optimize the estimated fractions of the models representative of the Pd/MgO₅₀₀ sample. For these calculations, we used DFT structures obtained using the PBEsol functional. These structures and the calculation protocols are available on our GitHub [https://github.com/kul-group/kul-repository/tree/main/repo_2023_Pd-MgO].

Transient XANES Analysis. The CatXAS Python package was used to import, calculate the absorption coefficient, calibrate, and normalize the 230 XAS spectra collected during the *in-situ*

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calcination of the Pd/MgO_{wet} sample and time correlate the XAS spectra to the signals measured from the mass spectrometer.⁵ The normalized XAS spectra and the correlated spectra-process conditions data were exported for further analysis. To improve the signal-to-noise ratio in the data, a rolling average filter, using a window of nine spectra, was applied to the normalized XANES and XAS-process correlation data sets. Principal component analysis and multivariate curve resolution-alternating least squares analysis were performed on the filtered normalized XANES spectra with an energy range of 24,300–24,450 eV using a modified version of the TXM Wizard software.⁶ The number of components for the MCR-ALS analysis was determined on the basis of the knee in the scree plot with a percentage cumulative variance explained being greater than 99.95%; non-negative eigenspectral and non-negative concentration constraints were applied during the analysis.

IR Spectroscopy. Transmission IR spectra of the powder samples in the v_{O-H} region were determined with a Bruker IFS 66v/S spectrometer with a resolution of 2 cm⁻¹. Approximately 10 mg of sample was pressed between two KBr windows, and spectra were recorded at room temperature with the sample under vacuum, with an average of 128 scans per spectrum.

Catalysis Performance Testing. Ethylene hydrogenation was carried out in a conventional temperature-controlled once-through quartz tubular plug-flow reactor (inside diameter = 4 mm) at atmospheric pressure and various temperatures. The products were analyzed with an online Agilent 6890 gas chromatograph equipped with a 50 m × 0.53 mm PLOT Alumina "M" capillary column. Samples of catalyst powder (5–50 mg) that had passed through a 40–60 mesh sieve were loaded into the reactor, with the upstream and downstream sections packed with quartz wool. When the catalyst was Pd/MgO_{wet}, the sample mass was 5.0 mg (mixed with 45 mg of MgO_{wet}). When the catalyst was Pd/MgO₅₀₀ or Pd/MgO₇₀₀, the sample mass was 50.0 mg. In catalysis experiments, the feed was a mixture of H₂ flowing at 4.0 mL(NTP)/min + C₂H₄ flowing at 4.0 mL(NTP)/min + helium flowing at 32 mL(NTP)/min; the pressure was atmospheric. The feed flow rates were controlled with mass flow controllers (Brooks). These values and the catalyst masses were chosen to give ethylene conversions < 7%, which were in the differential range, to determine reaction rates directly. The catalytic reaction experiments were carried out at various temperatures with the same feed gas to provide near-steady-state conversions at various

temperatures. Catalytic reaction rates at various temperatures are based on 6 h of near steadystate operation.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) images of Pd/MgO samples loaded onto copper TEM grids were recorded with a Hitachi H-7700 transmission electron microscope at an acceleration voltage of 100 kV.

STEM Imaging. The microstructure of the sample was characterized with STEM and STEM-EDS. The atomic-resolution STEM images of Pd/MgO₇₀₀ were collected at Oak Ridge National Laboratory using a JEOL 200CF (NEOARM) microscope with an acceleration voltage of 200 kV. Further atomic-resolution STEM images were collected at Purdue University using a FEI Themis Z microscope with an acceleration voltage of 300 kV. Low-magnification STEM images and EDS mappings were recorded with a FEI TALOS 200X instrument operated at 200 kV. *In-situ* heating TEM experiments were performed with a FEI TALOS 200X instrument with a sample holder for *in-situ* heating; the sample was heated from 400 to 700 °C at a rate of 5 °C /min. The samples for STEM imaging were prepared by dispersing the catalyst powder onto the lacey carbon copper grids. The sample used in the *in-situ* STEM heating experiments was prepared by dispersing the powder catalyst sample onto a molybdenum grid.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) of catalyst samples was done with a Perkin Elmer Pyris 1 TGA instrument with an online Clarus SQ8T mass spectrometer. In a typical experiment, 15 mg of sample was weighed into an alumina crucible and placed on the balance in the presence of air. The temperature was raised at a rate of 20 °C/min from room temperature to 700 °C with the sample in air flowing at a rate of 20 mL(NTP)/min.

XRD Crystallography. XRD patterns of the catalyst samples were collected with a Philips X'Pert Pro Super diffractometer with a monochromatized Cu K α radiation source and a wavelength of 0.1542 nm.

Inductively Coupled Plasma Atomic Emission Spectroscopy. The palladium loadings of the catalysts were determined by inductively coupled plasma-atomic emission spectroscopy with an Atomscan Advantage system, Thermo Jarrell Ash. The Pd/MgO samples were digested in aqua regia.

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DFT calculations. The Vienna *ab-initio* simulation package (VASP)⁷ with the projector augmented wave method (PAW) implemented was used for the periodic DFT calculations. Energies were calculated using a 500 eV plane-wave cutoff with a $2 \times 1 \times 1$ Monkhorst–Pack k-point grid. The convergence of electronic energies was achieved up to 10^{-6} eV, with all the structures relaxed to keep the forces less than 0.05 eV/Å. The calculation of the zero point and the entropic energies was done by using the finite displacement method (0.02 Å). For calculations related to the mechanism of ethylene hydrogenation, a 500 eV plane-wave cutoff with a RPBE- functional was used. Climbing image nudged elastic band was used to calculate the barriers.

The database of DFT structures and a notebook outlining how to access them is available on GitHub [https://github.com/kul-group/kul-repository/tree/main/repo_2023_Pd-MgO]. We have also included examples of the INCAR file for structure optimization as well as at the calculated geometries of the transition states on GitHub [https://github.com/kul-group/kul-repository/tree/main/repo_2023_Pd-MgO].

Table S1.	Experimental	results:	details	of Pd/M	gO samples.
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Sample	Calcination	Pd content	
	temperature	determined by	
	(°C) in air	ICP (wt%)	
	flowing at 50		
	mL (NTP)/min		
Pd/MgO _{wet}	-	0.097	
Pd/MgO ₄₀₀	400	0.10	
Pd/MgO ₅₀₀	500	0.097	
Pd/MgO ₇₀₀	700	0.095	



Fig. S1. TEM images of (a) Pd/MgO_{wet} ; (b) Pd/MgO_{400} ; (c) Pd/MgO_{500} ; and (d) Pd/MgO_{700} .



Fig. S2. XRD patterns of (a) Pd/MgO_{wet} ; (b) Pd/MgO_{400} ; (c) Pd/MgO_{500} ; and (d) Pd/MgO_{700} .



Fig. S3. IR spectra in v_{O-H} region collected with sample under vacuum at room temperature: Pd/MgO_{wet}; Pd/MgO₄₀₀; Pd/MgO₅₀₀; and Pd/MgO₇₀₀.



Fig. S4. TGA-MS data characterizing the thermal treatment of Pd/MgO_{wet} . The temperature was raised at a rate of 20 °C /min to 700 °C with the sample in air flowing at a rate of 20 mL(NTP) min⁻¹. The sample mass was 15 mg.



Fig. S5. (a, b) HAADF-STEM images of Pd/MgO_{wet}. (c) EDS elemental mapping image of Pd/MgO_{wet} sample. (d) EDS spectrum of Pd/MgO_{wet} sample in Area #1 in c.



Fig. S6. (a, b) HAADF-STEM images of Pd/MgO₄₀₀. (c) EDS elemental mapping image of Pd/MgO₄₀₀ sample. (d) EDS spectrum of Pd/MgO₄₀₀ sample in Area #1 in c.



Fig. S7. *Ex-situ* XANES spectra collected at the palladium K-edge at room temperature in air characterizing the Pd/MgO samples with reference spectra of a palladium foil and Po for comparison.



Fig. S8. EXAFS data characterizing reference palladium foil: data collected at palladium K-edge and fitted with conventional EXAFS modelling. The data and the fits are shown in black and red, respectively. The magnitude and the imaginary parts of the Fourier transform are shown as solid and dashed lines, respectively (k^3 -weighted).

Table S2. EXAFS fit parameters characterizing reference palladium foil determined byconventional fitting methods.

Scattering	CN ^a	<i>R^a</i> (Å)	Δσ² (x10³) ^a (Ų)	ΔE_0^a (eV)	<i>S</i> ₀ ²	R-factor
path						
	12.0	2.74		4 2 (0 2)	0.88	0.000
Ра-Ра	12.0	(0.00)	0.006 (0.0003)	4.2 (0.3)	(0.04)	0.003
^{<i>a</i>} CN, coordination number; <i>R</i> , distance between absorber and scatterer atoms; $\Delta\sigma^2$,						
disorder term; ΔE_0 , inner potential correction; S_0^2 , amplitude reduction factor. Details of						
data analysis for palladium foil: k range: 3.0–12.3 Å ⁻¹ ; R range: 1.4–3.3 Å. Estimated errors						
are reported in parentheses (accuracies).						



Fig. S9. EXAFS function (black) and results of conventional EXAFS modeling (red) (k^3 -weighted) characterizing Pd/MgO_{wet}.

	Scattering	CN ^a	<i>R^a</i> (Å)	$\Delta\sigma^{2a}$ (Å ²)	ΔE_0^a (eV)	R-factor
	path					
		0.4 (0.0)	2 74 (0 01)	0.007	47(06)	0.012
	Pu-Pu	9.4 (0.8)	2.74 (0.01)	(0.001)	4.7 (0.6)	0.013
	^a CN, coordi	nation num	ber; <i>R</i> , distan	ce between	absorber an	d scatterer atoms; $\Delta\sigma^2$,
disorder term; ΔE_0 , inner potential correction. Details of data analysis for Pd/MgO _{wet} : k						
range: 3.00–12.30 Å ⁻¹ ; <i>R</i> range: 1.4-3.3 Å. Estimated errors (accuracies) are reported in						
parentheses. The S_0^2 term was determined to be 0.88 by fitting of data characterizing						
palladium foil.						

 Table S3. EXAFS parameters determined by conventional fitting characterizing Pd/MgO_{wet}.



Fig. S10. EXAFS function (black) and results of conventional EXAFS modeling (red) (k^3 -weighted) characterizing Pd/MgO₄₀₀.

Scattering	CN ^a	<i>R^a</i> (Å)	$\Delta \sigma^{2 a}$ (Å ²)	ΔE_0^a (eV)	R-factor
path					
	4 2 (0 7)	1 00 (0 02)	0.002	6 2 (1 0)	
Pa–O	4.2 (0.7)	1.99 (0.02)	(0.002)	6.3 (1.9)	
Pd–Pd	4.0 (2.0)		0.011	6 2 (1 0)	
(oxide)	4.0 (3.0)	(0.006)		0.3 (1.9)	0.08
Pd–Pd	8.0 (2.0)	2 27 (0 04)	0.011	(2/10)	
(oxide)	8.0 (3.0)	3.37 (0.04)	(0.006)	6.3 (1.9)	
	E E (A A)	2 60 (0 07)	0.002	6 2 (1 0)	
Pu-O	5.5 (4.4)	5.00 (0.07)	(0.002)	0.5 (1.9)	
^{<i>a</i>} CN, coordination number; <i>R</i> , distance between absorber and scatterer atoms; $\Delta \sigma^2$,					

Table S4. EXAFS parameters determined by conventional fitting and characterizing Pd/MgO₄₀₀.

^{*a*}CN, coordination number; *R*, distance between absorber and scatterer atoms; $\Delta\sigma^2$, disorder term; ΔE_0 , inner potential correction. Details of data analysis for Pd/MgO₄₀₀: *k* range: 2.0–12.7 Å⁻¹; *R* range: 1.05–3.85 Å. Estimated errors (accuracies) are reported in parentheses. The S_0^2 term was determined to be 0.88 by fitting data characterizing palladium foil.



Fig. S11. EXAFS data collected at Pd K-edge and conventional EXAFS modelling of Pd/MgO₅₀₀. The data and the conventional fits are shown in black and red, respectively. (a) The magnitude and the imaginary parts of the Fourier transforms are shown as solid and dashed lines, respectively (k^3 -weighted). (b) EXAFS function and results of conventional EXAFS modeling (k^3 -weighted) characterizing Pd/MgO₅₀₀.

Table S5. EXAFS parameters characterizing Pd/MgO_{500} determined by conventional fitting method.

Scattering	CN ^a	<i>R^a</i> (Å)	$\Delta\sigma^{2a}$ (Å ²)	ΔE_0^a (eV)	R-factor	
path						
Pd–O	4.6 (0.5)	2.02 (0.01)	0.003	0.2 (0.7)	0.034	
			(0.002)	8.2 (0.7)		
Pd–Mg	10.4	2.01 (0.01)	0.007	0.2 (0.7)		
	(2.0)	3.01 (0.01)	(0.003)	8.2 (0.7)		
^a CN, coordi	nation num	ber; <i>R,</i> distan	ice between	absorber an	d scatterer atoms; $\Delta \sigma^2$,	
disorder ter	·m; ΔE ₀ , inn	er potential co	prrection. Det	ails of data a	nalysis for Pd/MgO ₅₀₀ : k	
range: 2.0–12.8 Å ⁻¹ ; R range: 1.0–3.2 Å. Estimated errors (accuracies) are reported in						
parentheses. The S_0^2 term was determined to be 0.88 by fitting data characterizing						
palladium foil.						



Fig. S12. (a, b) Magnified HAADF-STEM images of Pd/MgO₄₀₀.



Fig. S13. EXAFS data collected at palladium K-edge and conventional EXAFS modelling of Pd/MgO₇₀₀. The data and the conventional fits are shown in black and red, respectively. (a) The magnitude and the imaginary parts of the Fourier transforms are shown as solid and dashed lines, respectively (k^3 -weighted). (b) EXAFS function and results of conventional EXAFS modeling (k^3 -weighted) characterizing Pd/MgO₇₀₀.

Table S6. EXAFS parameters characterizing Pd/MgO₇₀₀ determined by conventional fitting method.

Scattering	CN ^a	<i>R^a</i> (Å)	$\Delta\sigma^{2a}$ (Å ²)	ΔE_0^a (eV)	R-factor	
path						
Pd–O	5.3 (0.6)	2.04 (0.03)	0.006 (0.002)	10.1 (0.5)	0.029	
Pd–Mg	13.5 (1.7)	3.01 (0.00)	0.006 (0.002)	10.1 (0.5)	0.028	

^{*a*}CN, coordination number; *R*, distance between absorber and scatterer atoms; $\Delta \sigma^2$, disorder term; ΔE_0 , inner potential correction. Details of data analysis for Pd/MgO₇₀₀: *k* range: 2.0–12.8 Å⁻¹; *R* range: 1.0–3.2 Å. Estimated errors (accuracies) are reported in parentheses. The S_0^2 term was determined to be 0.88 by fitting data characterizing palladium foil.



Fig. S14. EXAFS function (black) and results of QuantEXAFS modeling (blue) (k^3 -weighted) characterizing Pd/MgO₇₀₀.

Table S7. EXAFS fit parameters characterizing Pd/MgO₅₀₀ and Pd/MgO₇₀₀ modeled using QuantEXAFS. Pd/MgO₅₀₀ is the mixture of the [310]/pos1/*O₂ sites (ca. $63 \pm 5\%$) and the ([100]^{Mg-vac}/sub1sites (ca. $37 \pm 5\%$).

Sample	Structures		ΔE_0 (eV)	$10^3 \times \sigma_i^2 (\text{\AA}^2)$	
Pd/MgO ₅₀₀	2.09	2.97	167 - 26	Pd-O (6); Pd-O (1)	$2.7 \pm 1.0; 9.9 \pm 6.5$
	200 2.02	292 388 2,29 3.01 3.01	-15.7 ± 5.0	Pd-Mg (9)	1.0 ± 2.8
	2.05 2.00	2.99 3.03		Pd-O (6)	4.4 ± 0.8
	202 203 Mg.vs	3.01 2.99 4.02 Md 3.02	-10.6 ± 2.6	Pd-Mg (11)	8.0 ± 1.5
Pd/MgO ₇₀₀	2.00	3,00 2,97	-11.2 ± 1.7	Pd-O (6)	6.2 ± 1.0
	202 Date Mare 201	3.02 2.39 2.39 3.02 3.02 3.02		Pd-Mg (11)	5.3 ± 0.7



(c) Quality of fit for all

(d) Simultaneous fits for [310] and [100]Mg-vac

Fig. S15. EXAFS data and QuantEXAFS fits in *R*-space (k^3 -weighted) with the corresponding EXAFS fits based on [310]/pos1/*O₂ (a) and [100]^{Mg-vac}/sub1 (b) structures characterizing Pd/MgO₅₀₀ (*k*-range 2.8–12.8 Å⁻¹ and *R*-range 1.0–5.0 Å), showing the magnitude (fit: blue; experiment: black) and imaginary portions (fit: green; experiment: black) of Fourier transforms of the data. (c) Scipy optimizer fit to estimate the fractional contributions for each site (experiment: black; fit: blue; [310]/pos1/*O₂ : green; [100]^{Mg-vac}/sub1: red). (d) Simultaneous fits based on [310]/pos1/*O₂ and [100]^{Mg-vac}/sub1 structures characterizing Pd/MgO₅₀₀ (*k*-range 2.8–12.8 Å⁻¹ and *R*-range 1.0–5.0 Å), showing the magnitude (fit: blue; experiment: black) of Fourier transforms of the data. (c) Scipy optimizer fit to estimate the fractional contributions for each site (experiment: black; fit: blue; [310]/pos1/*O₂ : green; [100]^{Mg-vac}/sub1: red). (d) Simultaneous fits based on [310]/pos1/*O₂ and [100]^{Mg-vac}/sub1 structures characterizing Pd/MgO₅₀₀ (*k*-range 2.8–12.8 Å⁻¹ and *R*-range 1.0–5.0 Å), showing the magnitude (fit: blue; experiment: black) and imaginary portions (fit: green; experiment: black) of Fourier transforms of the data.

On the basis of our QuantEXAFS workflow, once we had identified the two most stable sites that best fitted EXAFS data characterizing Pd/MgO_{500} , we used Sicpy optimizer in Python to optimize the fractional contributions of each structure to determine the best representative spectra that matched the experimental spectra; the fit does not entirely represent the experimental spectra,



suggesting the presence of some minority sites that were not accounted for.

Fig. S16. PCA analysis of 9-spectra averaged normalized XANES collected at the palladium K-edge characterizing the Pd/MgO sample during the TPO experiment as the temperature was raised from room temperature to 700 °C with the sample in flowing 20% O_2 /helium with a ramp rate of 2 °C min⁻¹. (a) 9-spectra rolling average normalized XANES spectra used for the PCA; (b) scree plot of the components from the PCA; (c) the first 5 components of the PCA, stacked for visualization and arbitrarily scaled.



Fig. S17. (a) FEFF-simulated XANES spectra (red, S310: [310]/pos1/*O₂ site; S100: [100]^{Mg-vac}/sub1 site); eigenspectra generated XANES in the MCR-ALS analysis (blue); and experimental XANES results (black) for feasible DFT-calculated structures and metallic Pd and PdO. (b) FEFF-simulated XANES spectra (red), and experimental XANES results (black) for metallic Pd and PdO.

The XANES simulations used the DFT-optimized structures described above and were performed with FEFF10⁸⁻¹⁰ using SCF and FMS cutoff radii of 6 and 9 Å, respectively, which provided converged spectra. Given the simplicity of the systems, the atomic potentials were selected by atomic type. While the PdO and Pd in MgO simulations used the final-state rule approximation for the core-hole, the Pd metal simulations were done using the NOHOLE option in FEFF, based on previous experience with other noble metals.^{11,12} The self-energy was modeled using the density-dependent MPSE (many-pole self-energy) dielectric function approach based on a weighted average of the atomic loss functions.¹³ To provide converged results into the low EXAFS region, the default maximum angular momenta for the site basis set were raised to 5, 4, and 4 for Pd, O, and Mg, respectively.



Fig. S18. HAADF-STEM images of Pd/MgO_{400} under vacuum collected during heating; images were obtained in the same region of the sample at the temperatures shown.



Fig. S19. Activity data characterizing catalysts initially in the form of (a) MgO_{700} ; (b) MgO_{500} ; and (c) MgO_{wet} for ethylene hydrogenation in a once-through flow reactor operated at 80, 45, and 25 °C, respectively.



Fig. S20. Catalytic activity data characterizing the catalyst initially in the form of Pd/MgO_{wet} for ethylene hydrogenation in a once-through flow reactor operated at 25 °C.

The sample incorporating metallic palladium nanoparticles, Pd/MgO_{wet}, was tested at 25 °C. The sample attained steady-state operation in 80 h, and the conversions were chosen to be low enough (<7%) to be in the differential range, determining reaction rates directly. With an estimate of the percentage of palladium atoms exposed on the nanoparticle surfaces (28.5%),¹⁴ we calculated a TOF of 7.7 (molecules of ethylene converted) × (Pd atom × s)⁻¹ at 25 °C.



Fig. S21. Catalytic activity data characterizing (a) Pd/MgO_{500} and (b) Pd/MgO_{700} for ethylene hydrogenation in a once-through flow reactor operated at 45 and at 80 °C, respectively.



Fig. S22. Demonstration of differential conversion of ethylene; the catalyst was Pd/MgO_{700} . Reaction conditions: $H_2 + C_2H_4$ at 1:1 molar ratio at 80 °C and atmospheric pressure. The linearity of this plot, which passes through the origin, demonstrates that the data determine rates (TOF values) directly (as the slope of the line).



Fig. S23. EXAFS data characterizing the fresh and used Pd/MgO catalyst that had been calcined ((a) *k*-range 3.0–12.8) and (b) *R*-range 1.0–3.2 Å)) at 500 °C showing the magnitude (fresh catalyst: green; used catalyst: blue) of Fourier transforms of the data; and (c) (*k*-range 3.0–12.8) and (d) (*R*-range 1.0–3.2 Å)) calcined at 700 °C, showing the magnitude (fresh: yellow ; used: red) of Fourier transforms of the data. The EXAFS fits of the experimental results characterizing the fresh and used catalysts shown no changes in the Pd/MgO₅₀₀ sample or the Pd/MgO₇₀₀ as a result of exposure to the ethylene hydrogenation catalysis conditions.

Notes and references

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