

Alumina Over-coating on Pd Nanoparticle Catalysts by Atomic Layer Deposition: Enhanced Stability and Reactivity

Hao Feng · Junling Lu · Peter C. Stair ·
Jeffrey W. Elam

Received: 9 December 2010 / Accepted: 7 January 2011
© Springer Science+Business Media, LLC 2011

Abstract ALD Alumina was utilized as a protective layer to inhibit the sintering of supported nano-sized ALD Pd catalysts in the methanol decomposition reaction carried out at elevated temperatures. The protective ALD alumina layers were synthesized on Pd nanoparticles (1–2 nm) supported on high surface area alumina substrates. Up to a certain over-coat thickness, the alumina protective layers preserved or even slightly enhanced the catalytic activity and prevented sintering of the Pd nanoparticles up to 500 °C.

Keywords Atomic layer deposition · Alumina over-coat · Methanol decomposition · Pd nanoparticles · Sintering

1 Introduction

The stability of small particles against sintering has been a serious problem restraining the applications of metal nanoparticles (NPs). This problem is prominent for supported noble metal catalysts in which NP sintering at high temperature is a major contributor to catalyst deactivation

[1–4]. Methods have been developed to encapsulate noble metal NPs in various types of porous materials using techniques such as chemical vapor deposition (CVD), grafting, micro-emulsion, dendrimer encapsulation, etc. to form core–shell structures [5–12]. Encapsulated NPs showed good sintering resistance up to 800 °C. However, in most cases there is a decrease in catalytic activity due to the mass transfer resistance associated with the protective shell (usually tens of nm's thick). Furthermore, many of these NP encapsulation procedures must be carried out in solution making them inconvenient for supported NP catalysts. CVD, while a gas-phase technique, does not provide adequate control over the thickness or composition of the encapsulating shell due to non-self limiting reactions. In contrast to these previous methods, atomic layer deposition (ALD) is a multi-step gas phase chemical process based on self-limiting surface chemistry which provides the possibility for atomically controlled post-modification of supported catalyst particles by applying protective over-coats [13]. The self-limiting, layer-by-layer deposition feature of ALD enables precise control over the thickness of the protective layer; therefore it is a most promising way of solving the mass transfer resistance problem. Ma et al. [14] successfully stabilized gold NPs (~5 nm) on TiO₂ surfaces by applying ALD SiO₂ over-coats. However, the interaction between the gold NPs and the ALD SiO₂ protective layer was not studied in detail and a loss of catalytic activity could not be avoided. In this letter, we report a novel method for stabilizing ultra-small Pd NPs (1–2 nm) by performing multiple cycles of Al₂O₃ ALD to produce over-coats. Up to a certain over-coat thickness, the Al₂O₃ protective layers preserved or even slightly enhanced the catalytic activity. These ALD Al₂O₃ over-coats effectively prevent sintering of the Pd NPs up to 500 °C in an inert atmosphere.

H. Feng, J. Lu contributed equally to this work

H. Feng · P. C. Stair
Chemical Science and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

J. Lu · J. W. Elam (✉)
Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, USA
e-mail: jelam@anl.gov

P. C. Stair
Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

2 Experimental Section

The supported catalysts were synthesized starting from silica gel (Silicycle S10040 M, ~300 mg) with a specific surface area of 99.6 m²/g. The layer-by-layer growth of the catalyst support material (Al_2O_3), the Pd NP catalysts, and the Al_2O_3 over-coats were carried out in a viscous flow reactor at a deposition temperature of 200 °C [13, 15]. ALD Al_2O_3 was performed using alternating exposures to trimethyl aluminum (TMA, Aldrich, 99%) and de-ionized water while the ALD Pd used alternating exposures to palladium hexafluoroacetylacetate ($\text{Pd}(\text{hfac})_2$, Aldrich, 99.9%) and formalin (Aldrich, 37% HCOH and 15% CH_3OH in aqueous solution). The solid $\text{Pd}(\text{hfac})_2$ precursor was heated to 60 °C in a stainless steel bubbler while the other precursors were maintained at room temperature. Ultra high purity nitrogen (Airgas, 99.999%) was used as the carrier gas. The ALD timing sequences can be expressed as t1–t2–t3–t4, where t1 and t3 are the precursor exposure times and t2 and t4 are the nitrogen purge times following the precursor exposures and all times are in seconds. ALD Al_2O_3 was performed using the timing sequence 60–60–60–60 while Pd ALD used 400–400–400–400. 10 cycles of ALD Al_2O_3 were performed on the silica gel particles to deposit the support layer, followed by two cycles of ALD Pd to synthesize the supported catalyst NPs. Finally, the over-coated samples were prepared using 1, 2, 4, 8, 12, 20, and 32 cycles of Al_2O_3 ALD to generate the protective layers.

The methanol decomposition reaction was carried out in a micro flow reactor with an I.D. of ~4 mm. 10 mg of the bare catalyst was used. For the catalysts with over-coating layers, the amount of catalyst used was adjusted to match the Pd content in 10 mg of the bare catalyst. The catalyst was held in the middle of the reactor by a plug of quartz wool. A K-type thermal couple was positioned inside the reactor and was in contact with the catalyst layer to measure the temperature. The methanol vapor was introduced into the reaction system using an argon (Airgas, 99.99%) gas bubbler kept at room temperature. Pure argon was used as the balance gas to generate an argon stream with ~4% methanol. The catalysis tests were carried out at 250 and 270 °C at atmospheric pressure. Reaction products were analyzed by a HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD). Signals from the TCD were calibrated using certified standard gas mixtures (Scotty, 1.00% CO_2 , 0.999% CO, 1.00% H_2 , 0.998% CH_4 , balance of nitrogen).

Scanning transmission electron microscopy (STEM) measurements were performed on a JEOL JEM-2100F fast transmission electron microscopy system (EPIC at Northwestern University) operated at 200 kV. For the Pd particle size data presented in Fig. 3 the error bars represent the

standard deviations calculated from more than 200 Pd NPs in several different STEM images for each sample.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed at room temperature using a Thermo Nicolet Nexus 870 instrument with an MCT detector (KECKII at Northwestern University). A cold trap at ~−80 °C was used in the gas inlet line to remove all the iron carbonyls. The background spectra were taken after purging the sample with ultrahigh purity (99.999%) helium for 30 min at a flow rate of ~80 sccm. Pure CO (Airgas, research grade) at a flow rate of ~40 sccm was then introduced to the DRIFTS cell for 20 min to saturate the Pd surface. After the CO saturation, another 5 min of helium purge at a flow rate of ~70 sccm was performed to remove gas phase CO in the DRIFTS cell. The spectra were recorded (512 scans, a resolution of 4 cm^{−1}) after the helium purge.

3 Results and Discussion

The supported Pd NPs were synthesized on Al_2O_3 -coated silica gel by ALD using published methods [13, 16]. Most of the as-prepared Pd particles were 1–2 nm in diameter after 2 ALD Pd cycles at 200 °C. The Al_2O_3 over-coats were synthesized using sequential exposures to trimethyl aluminum (TMA) and water vapors. Different numbers of Al_2O_3 ALD cycles (1–32) were performed to generate protective layers of progressively increasing thickness on the supported Pd catalysts. A linear correlation between the relative sample weight gain and the number of applied over-coating cycles was observed (Fig. 1), consistent with a linear increase in the thickness of the Al_2O_3 protective

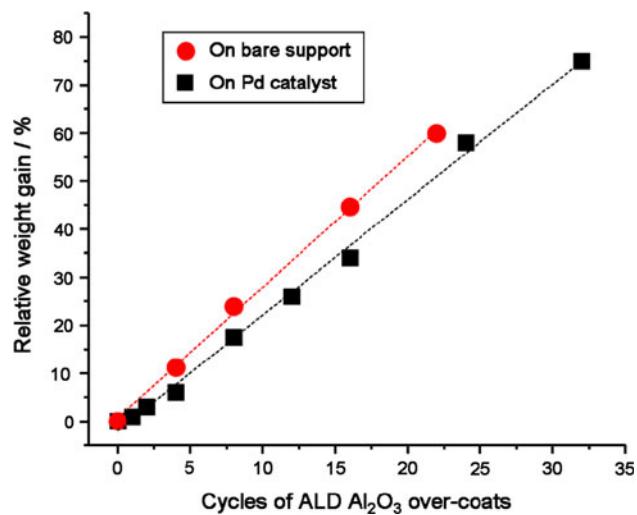


Fig. 1 Relative weight gain of Pd catalyst samples (squares) and bare support (circles) versus number of Al_2O_3 ALD over-coating cycles

layer with the number of over-coating cycles. An average thickness increase of 0.8 \AA/cycle can be deduced from the relative sample weight gain and the measured surface area of the support. This value was slightly smaller than the Al_2O_3 ALD thickness increase on the bare support ($\sim 1.0 \text{ \AA/cycle}$). This difference suggests that the ALD Al_2O_3 over-coats did not uniformly cover the catalyst surface. This is consistent with reaction by TMA with surface hydroxyls of the Al_2O_3 support but not with all of the Pd NP surface sites [12].

Methanol decomposition was carried out as a probe reaction to evaluate the effect of the ALD Al_2O_3 over-coats on the catalytic performance of the supported Pd NPs. Figure 2 displays the methanol conversion, which is defined as the percentage of methanol lost after passing through the reactor, measured at 250 and 270 °C for the Pd catalysts with 0 to 32 cycles of ALD Al_2O_3 over-coat recorded after 6 h of continuous running on stream. The weight of catalyst loaded in the reactor was adjusted to have the same Pd content. The catalytic performances fluctuated slightly during the first 10–25 min of testing but remained unchanged once stabilized: little deactivation was observed during the following 6 h of testing and CO (with trace amount of CO_2) and H_2 were the only detectable products which accounted for $100 \pm 3\%$ of the carbon and hydrogen balances. For the samples with 1c- to 16c- of ALD Al_2O_3 over-coat, the catalytic activity was essentially identical at each of the two reaction temperatures. Surprisingly, the catalysts prepared with ALD Al_2O_3 over-coats in the range 1–16 cycles showed slightly higher activities than the uncoated catalysts consistent with some sintering of the unprotected Pd NPs under reaction conditions. The catalytic activity started to decrease beyond 16 ALD Al_2O_3 over-coating cycles. At 20 cycles the catalyst

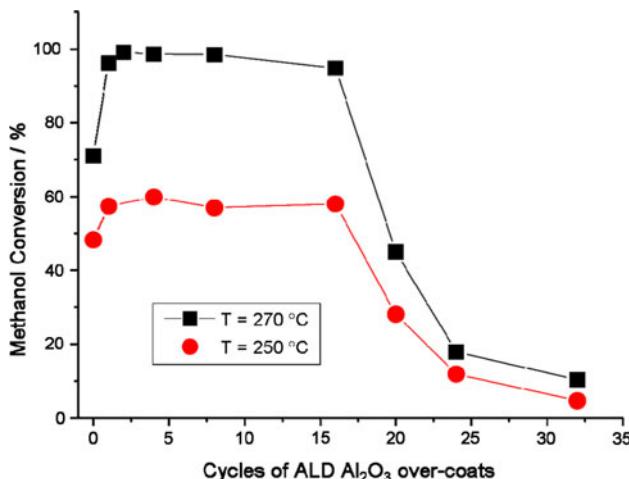


Fig. 2 Methanol conversion for Pd catalysts with 0–32 cycles of ALD Al_2O_3 over-coating in the methanol decomposition reaction carried out at 250 and 270 °C

had lost nearly half of its activity, compared to the uncoated sample, and the activity had dropped by more than 80% for 24 over-coating cycles.

Scanning transmission electron microscopy (STEM) measurements were employed to investigate the Pd NPs stabilization effects with different numbers of ALD Al_2O_3 over-coating cycles. As is shown in Fig. 3, the Pd sample without Al_2O_3 over-coat increased in size from 1.4 ± 0.7 to $2.3 \pm 1.1 \text{ nm}$ following the methanol decomposition reaction at 270 °C for 6 h. In contrast, sintering of Pd NPs was effectively inhibited by just one cycle of ALD Al_2O_3 over-coat: all the Pd catalysts with Al_2O_3 over-coats showed negligible changes in morphology after the methanol decomposition reaction.

Infrared (IR) spectroscopy of CO chemisorption on Pd NPs has been used extensively and the relationships between the IR features and the properties of Pd NPs are well understood [17–21]. Consequently, we employed diffuse reflectance IR spectroscopy (DRIFTS) to study CO chemisorption on the Pd samples with and without the Al_2O_3 over-coats. These measurements provide information on the accessibility of the Pd NPs after the Al_2O_3 over-coating as well as the effect of the Al_2O_3 ALD over-coating layers on the Pd NPs surfaces. As is shown in Fig. 4, the fresh Pd sample without Al_2O_3 over-coats exhibited two main peaks at 2095 and 1978 cm^{-1} and a pronounced broad shoulder near 1933 cm^{-1} . These three peaks can be assigned to linear CO on the Pd corner atoms, μ_2 bridge-bonded CO on the step and edge sites of Pd NPs, and μ_2 bridge-bonded CO on Pd (111) facets, respectively [17, 18]. In the methanol decomposition reaction two competing pathways exist. Dehydrogenation is rapid on Pd

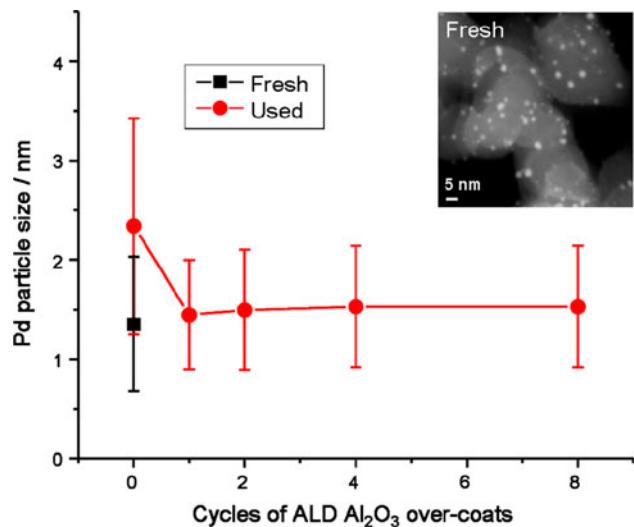


Fig. 3 Pd particle size for fresh (as-prepared) and used (following methanol decomposition reaction at 270 °C) catalysts versus number of ALD Al_2O_3 over-coating cycles. Inset shows representative STEM image of fresh Pd sample without Al_2O_3 over-coat

(111) sites, producing CO and H₂, while corners, steps, and edges catalyze C–O bond breakage producing adsorbed carbon and CH_x species (i.e. coke) [21]. In other words, the low coordination sites contribute negligibly to the methanol decomposition pathway. Therefore, we attribute the decrease of peaks at 2095 and 1978 cm⁻¹ after methanol decomposition experiments to coke formation on the low coordination sites [21, 22].

On the fresh ALD Al₂O₃ over-coated Pd samples, the intensity of the three peaks associated with CO chemisorption decreased steadily with increasing numbers of over-coating cycles. This behavior suggests that the Pd NPs become progressively covered by the ALD Al₂O₃ (solid spectra in Fig. 4). Comparing the spectra of the bare sample to those with the ALD Al₂O₃ over-coats, the change in the relative intensities of the three peaks was remarkable. On the bare sample, the peaks at 2095 and 1978 cm⁻¹ were much stronger than the peak at 1933 cm⁻¹. However, the intensities of the 2086 and 1973 cm⁻¹ peaks were nearly equal to that of the peak at 1933 cm⁻¹ with the over-coats. (Therein, the peaks at 2095 and 1978 cm⁻¹ decreased and shifted to 2086 and 1973 cm⁻¹, respectively.) These changes suggest that during the over-coating procedure the TMA precursor reacts not only with the hydroxyl groups present on the support, but also with the most energetic (e.g. edge and corner) sites of the Pd NPs. Consequently, the first few cycles of ALD Al₂O₃ deposit preferentially onto the low-coordination sites rather than uniformly blanketing the

particles entirely. Since the Pd atoms on the low-coordination sites contribute little to the catalytic methanol decomposition, the activities of the catalysts were not affected by the ALD Al₂O₃ over-coats. With increasing numbers of ALD Al₂O₃ over-coating cycles, the increasing amount of Al₂O₃ deposited on the defect sites and on the underlying support begins to intrude on the Pd (111) sites and eventually leads to the complete encapsulation of the Pd particles. In the DRIFTS data shown in Fig. 4, all three peaks nearly vanished when the number of Al₂O₃ ALD over-coating cycles exceeded 16. In other words, the Pd NPs were completely covered when ≥ 16 cycles of over-coating were performed. However, it is noteworthy that the peak at 1933 cm⁻¹ on all of the over-coated Pd samples restored to a certain degree after performing the methanol decomposition reaction (dotted spectra in Fig. 4), while restoration of the other two peaks was very limited. The intensity changes among these three peaks, before and after reaction, indicate that initially the ALD Al₂O₃ over-coats largely encapsulate the Pd NPs, but after reaction these Al₂O₃ over-coats have rearranged so that the Pd (111) facets become exposed. The reasons for this rearrangement may be the structure stabilization of the thin Al₂O₃ over-coating layers as well as the large lattice mismatch between the Pd (111) facets and crystalline Al₂O₃. The peak restoration was minimal for the Pd samples with 20 and 24 ALD Al₂O₃ over-coating cycles suggesting that the thicker Al₂O₃ layers do not rearrange sufficiently at these temperatures.

The activity increase associated with the 1c- to 8c- Al₂O₃ coated Pd samples shown in Fig. 2 was consistent with the STEM images and CO chemisorption results. However, the DRIFTS results of 16c-, 20c- and 24c- Al₂O₃ over-coated Pd samples could only explain the trend of the reactivity change of these samples, but not quantitatively, since the areas of the 1933 cm⁻¹ peak on these three samples were significantly smaller than those on the 1c- and 8c- Al₂O₃ coated Pd samples. The reason might be due to both the dramatic decrease in Pd loading and the difficulty of quantitative analysis with DRIFTS caused by the variation of absorption coefficient, scattering factor, and particle size after applying a large number of ALD Al₂O₃ overcoats [23].

To further investigate the effectiveness of ALD Al₂O₃ over-coats to inhibit sintering, a bare Pd catalyst sample and a sample with 16 ALD Al₂O₃ over-coating cycles were heated at 500 °C for 6 h in a flow of argon. Fig. 5 shows representative STEM images of the two samples. Fig. 5a shows obvious sintering of the bare Pd NPs: many large particles (10–20 nm) were formed during the heat treatment, accompanied by a remarkable decrease in the density of smaller (1–2 nm) particles. In contrast, Fig. 5b shows that the over-coated NPs did not sinter: little change in

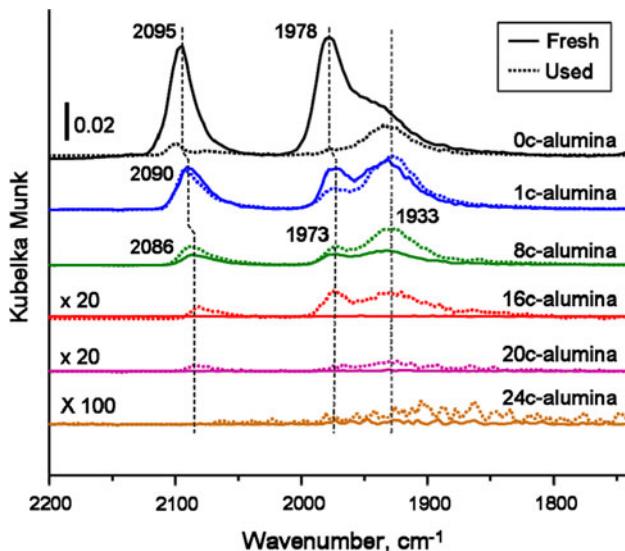


Fig. 4 DRIFTS spectra of CO chemisorbed to saturation coverage on fresh and used Pd catalysts with different numbers of ALD Al₂O₃ over-coating cycles (0c, 1c-, 8c-, 16c, 20c- and 24c-Al₂O₃). Spectra for fresh and used 16c- and 20c-Al₂O₃ samples were enlarged by $\times 20$. Spectra for fresh and used 24c-Al₂O₃ samples were enlarged by $\times 100$

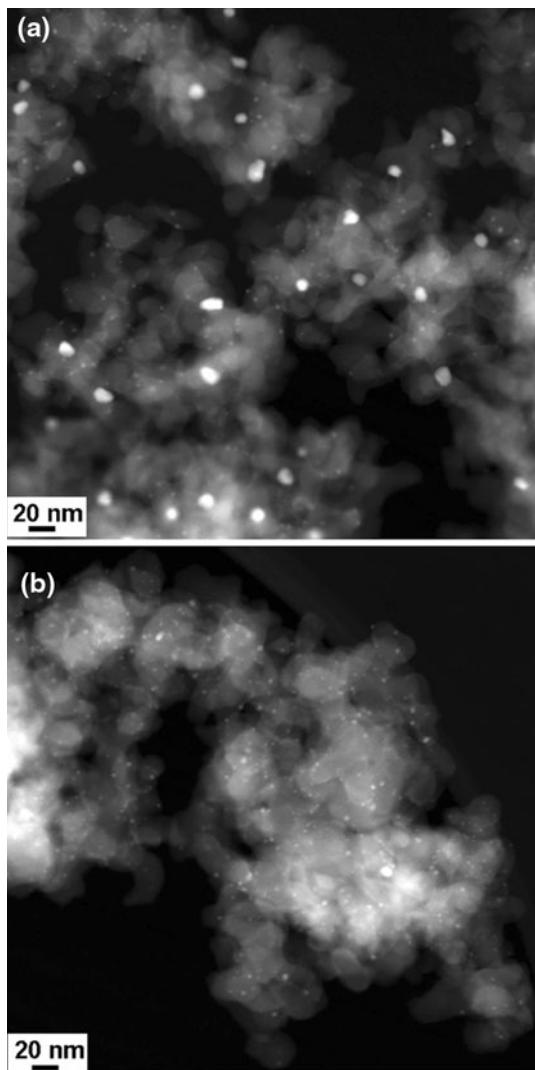


Fig. 5 STEM images of Pd catalysts after treatment in argon at 500 °C for 6 h with **a** no Al_2O_3 over-coat, and **b** 16 cycles of ALD Al_2O_3 over-coating

particle size or density was observed. It is generally believed that sintering of supported noble metal NPs is caused by particle migration and coalescence on the surface or by atom emission and re-capture (Ostwald ripening) [1, 5, 24]. The ALD Al_2O_3 over-coats could effectively inhibit sintering due to either mechanism. By applying the over-coats, the Al_2O_3 attached to the support as well as the low-coordinated sites on the Pd NPs to more effectively anchor the particles to the support. At the same time, bonding between Al_2O_3 overcoats and the corner, step, and kink sites on Pd NPs would increase the coordination number of these most unstable atoms thereby lowering the system free energy. This ALD over-coating technique could be extended to other supported metal NP systems and other metal oxides over-coats. If similar sintering protection and maintenance (or enhancement) of catalytic activity

are seen for these systems, then the ALD over-coating might provide a general solution to prevent sintering in supported metal NP catalysts.

4 Conclusions

In conclusion, we have demonstrated that the sintering of Pd NP catalysts can be effectively inhibited by ALD Al_2O_3 over-coats. The ALD Al_2O_3 over-coats enhanced the catalytic activities of Pd NPs for methanol decomposition by preventing the loss of active surface area during the reaction. Using CO as a probe molecule, we find that the ALD Al_2O_3 over-coats preferentially nucleate at corners, steps, and edges of the Pd NPs while leaving the catalytically active Pd (111) facets accessible for methanol conversion, and this site preference became more pronounced after reaction testing. To the best of our knowledge, this is the first example of stabilizing metal NPs with subnanometer/nanometer thick ALD oxide over-coats while preserving their catalytic activity. Furthermore, this preferentially blocking feature on metal NPs might also point out a new way to enhance the selectivity in catalytic reactions, especially those sensitive to the shape and facets of NPs.

Acknowledgments The work at Argonne National Laboratory was supported by the U.S. Department of Energy, BES-HFI, Chemical Sciences under Contract DE-AC-02-06CH11357. The work at Northwestern University was financially supported by The Dow Chemical Company under the Dow Methane Challenge Award.

References

- Bartholomew CH (2001) *Appl Catal A* 212:17
- Sault AG, Tikare V (2002) *J Catal* 211:19
- Datye AK, Xu Q, Kharas KC, McCarty JM (2006) *Catal Today* 111:59
- Bernal S, Calvino JJ, LoÁpez-Cartes C, Pintado JM, PeÁrez-Omil JA, RodróÁquez-Izquierdo JM, Hayek K, Rupprechter G (1999) *Catal Today* 52:29
- Park J-N, Forman AJ, Tang W, Cheng J, Hu Y-S, Lin H, McFarland EW (2008) *Small* 4:1694
- Kanazawa T (2006) *Catal Lett* 108:45
- Takenaka S, Matsumori H, Nakagawa K, Matsune H, Tanabe E, Kishida M (2007) *J Phys Chem A* 111:15133
- Zhao M, Sun L, Crooks RM (1998) *J Am Chem Soc* 120:4877
- Arnal PM, Comotti M, Schuth F (2006) *Angew Chem Int Ed* 45:8224
- Joo SH, Park JY, Tsung C-K, Yamada Y, Yang P, Somorjai GA (2009) *Nat Mater* 8:126
- Ott LS, Finke RG (2007) *Coord Chem Rev* 251:1075
- Seipenbusch M, Binder A (2009) *J Phys Chem C* 113:20606
- Feng H, Elam JW, Libera JA, Setthapun W, Stair PC (2010) *Chem Mater* 22:3133
- Ma Z, Brown S, Howe JY, Overbury SH, Dai S (2008) *J Phys Chem C* 112:9448
- Elam JW, Groner MD, George SM (2002) *Rev Sci Instrum* 2981
- Lu J, Stair PC (2010) *Langmuir*. doi:[10.1021/la101378s](https://doi.org/10.1021/la101378s)

17. Lear T, Marshall R, Lopez-Sanchez JA, Jackson SD, Klapotke TM, Baumer M, Rupprechter G, Freund HJ, Lennon D (2005) J Chem Phys 123:174706
18. Wolter K, Seifert O, Kuhlenbeck H, Baumer M, Freund HJ (1998) Surf Sci 399:190
19. Szanyi J, Kuhn WK, Goodman DW (1993) J Vac Sci Technol A Vac Surf Films 11:1969
20. Frank M, Baumer M (2000) Phys Chem Chem Phys 2:3723
21. Schauermann S, Hoffmann J, Johanek V, Hartmann J, Libuda J, Freund HJ (2002) Angew Chem Int Ed 41:2532
22. Schauermann S, Hoffmann J, Johanek V, Hartmann J, Libuda J, Freund HJ (2002) Phys Chem Chem Phys 4:3909
23. Smith BC (1995) Fundamentals of fourier transform infrared spectroscopy. CRC Press LLC, Boca Raton
24. Stone P, Pousston S, Bennett RA, Bowker M (1998) Chem Commun 1369