Stabilization of super electrophilic Pd$^{+2}$ cations in small-pore SSZ-13 zeolite

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ABSTRACT: The results of our combined experimental (FTIR, XPS, HAADF-STEM, EXAFS) and density functional theory study reveals that Pd ions in zeolites, previously identified as Pd$^{+3}$ and Pd$^{+4}$, are in fact present as super electrophilic Pd$^{+2}$ species (ion pairs with the negatively charged framework oxygens). In this contribution we re-assign the spectroscopic signatures of these species, discuss the unusual coordination environment of “naked” (ligand-free) Pd$^{+2}$ in SSZ-13, and their complexes with CO and NO. With CO, non-classical, highly positive [Pd(CO)]$^{+2}$ ions are formed with the zeolite framework acting as a weakly coordinating anion (ion pairs). Non-classical carbonyl complexes also form with Pt$^{+2}$ and Ag$^+$ in SSZ-13. The Pd$^{+2}$(CO)$_2$ complex is remarkably stable in zeolite cages even in the presence of water. Dicarbonyl and nitrosyl Pd$^{+2}$ complexes, in turn, serve as precursors to the synthesis of previously inaccessible Pd$^{+2}$-carbonyl-olefin [Pd(CO)(C$_2$H$_4$)] and -nitrosyl-olefin [Pd(NO)(C$_2$H$_4$)] complexes. Overall, we provide novel insight into the interactions of divalent metals with the zeolite framework, and show the new chemistry of Pd/SSZ-13 system with implications for adsorption and catalysis.
with CO at 400 °C prior to CO adsorption. The IR spectra showed an increase in the intensity of the 1990 cm⁻¹ band. Upon vacuum-induced desorption, the center of this band red-shifted due to the elimination of dipole-dipole coupling interactions present at higher coverages (Fig. S3). As such, we ascribe the peak at ~1990 cm⁻¹ to CO adsorbed linearly on small Pd clusters, whereas bands below 1900 cm⁻¹ represent doubly- and possibly triply-bridged CO on such clusters that are formed in small amounts (<0.5% of total Pd).

Note that in agreement with works by Stair and co-workers and Hadjiivanov and co-workers, the molar extinction coefficients of CO bands for CO-containing species dramatically increases as the temperature goes down. For example, for metallic Pt-bound CO, it was found that the 2090 cm⁻¹ band has ~8 times higher molar extinction coefficient than the 2110 cm⁻¹ belonging to ionic Pt.

The 2214 and 2193 cm⁻¹ bands belong to CO stretching vibrations previously assigned to Pd(III)(CO)₂ complexes by the Bell group and later Hadjiivanov group on Pd/ZSM-5. Unlike those systems in which CO adsorption produced a wealth of species, in our 1 wt% Pd/SSZ-13 (Si/Al=6) these species are formed selectively (~90%) at room temperature. These Pd(CO): species are stable in the presence of CO, O₂ or inert atmosphere, and fully decompose only above 140 °C. This means that the high uniformity of Pd in small-pore SSZ-13 enables the selective production of this species. Indeed, the symmetric and asymmetric CO bands grow and, upon evacuation, disappear in concert (Fig.1, Fig. S3), suggesting they belong to the same species. The assignment of these bands to dicarboxyls of Pd is further confirmed by isotopic labeling of the adsorbate (¹³CO) (Fig. S4). In contrast, the stabilization of the Pd⁻² in zeolite would require at least 3 Al atoms in either 6-membered or 8-membered rings of the SSZ-13 structure (which is highly unlikely) or Pd⁻²-OH fragment held by 2 proximal Al atoms. To explain the observed high wavenumbers, we modeled unique Pd⁻⁴(CO)₂(O) and Pd⁻⁴(CO)(OH) complexes (Tables 1 and S1). In the case of Pd⁻⁴(CO)₂(O) spontaneous formation and desorption of carbon dioxide is observed. The calculated vibrational frequencies of the other complex, Pd⁻⁴(CO)(OH) were notably lower than 2200 cm⁻¹: 2141 and 2114 cm⁻¹. The structure of Pd(IV) was more stable with 0 unpaired electrons and for this reason, we included it. In that case CO₂ molecule leaves the complex. These results do not agree with the experimental data. Additionally, Pd⁻³(CO): complex (1 unpaired electron) has calculated symmetric and asymmetric C-O stretching vibrations at 2103 and 2063 cm⁻¹, significantly lower than the observed values.

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Non-classical metal carbonyls have received attention in the organometallic literature. Due to pioneering efforts coming from the Aubke group, for example, it was demonstrated that non-classical, superelectrophilic transition metal carbonyls can be produced from Pd or Pt compounds in toxic/corrosive magic acids HSO₃F/SBF₅ in the absence of moisture and under CO pressures. (As noted by Olah and Klumpp, a variety of cationic species from organo-cations to metal cations should be called “superelectrophilic” due to the labile and weakly coordinating nature of fluorosulfonate or similar weakly coordinating anions produced in the “magic”/supercarboxyl). For example, Pd⁻⁴(CO)(SO₃F)₂ was obtained, in which Pd⁻⁴(CO) fragments were weakly interacting with the anion. On the basis of single-crystal XRD data Pd⁻⁴(CO)₂ fragments were proposed to stabilize via secondary contacts of CO with basic SO₃F⁺ groups dispersed in the crystallographic structure. These compounds were stable only in the complete absence of moisture and decomposed immediately in the presence of traces of water or above 130 °C. The frequencies of the υasym and υsym vibrations were observed at 2220 and 2199 cm⁻¹ in solution. Note, that the split between these two bands is identical to that has been previously assigned to Pd(III)(CO):. Thus, we may reassign the 2214 and 2193 cm⁻¹ signatures to Pd⁻⁴(CO): non-classical carbonyl, charge-balanced by 2 negative charges associated with Al pairs and weakly interacting with the basic O ions of the zeolite, in principle similar to Pd⁻⁴(CO)₂(SO₃F). XPS data (vide infra) in addition to EXAFS data showing Pd⁻² in an oxygen environment confirm this result. The slight red shift from 2220 to 2194 cm⁻¹ reflects either a higher basicity of zeolite oxygen compared with SO₃F⁺ anions or, alternatively the effect of confinement. The more correct annotation for this sample would then be a charge-transfer/ion-pair complex between [Pd(CO)₉]²⁻ and two O-Zeolite. Indeed, CO adsorption on the pink-colored Pd⁻²(O-Zeo): produces a purple-colored [Pd(CO)₉]²⁻(O-Zeo): complex (Fig. S5) indicating significant charge-transfer in the ~520 nm UV-Vis spectral region of both species. We tried to model this complex with DFT calculations (Table S1, Figs. S6-S9 for structures of various modeled Pd complexes). The results from DFT calculations show significant disagreement with respect to the observed frequencies and in the split between the CO bands. The calculated CO signatures are 2172 and 2138 cm⁻¹ with a 34 cm⁻¹ split. However, among all Pd(CO)₂ fragments this is the only one that shows a C-O stretching vibrational feature above that of gas-phase CO.
attempted to model the non-classical complex with the known crystallographic structure (i.e., Pd$^{2+}$(CO)$_4$(SO$_3$F)$_2$). The Pd(CO)$_2$(SO$_3$F)$_2$ structure was optimized and the calculated frequencies were 2199 and 2164 cm$^{-1}$, once again lower than the experimental values of 2220 and 2199 cm$^{-1}$. The calculated split was 35 cm$^{-1}$, larger than the experimentally measured split of 20 cm$^{-1}$ (the same as for modeled Pd$^{2+}$(CO)$_2$ in zeolite). Again, these computational estimates give $\sim$30-40 cm$^{-1}$ lower frequencies than the experiment. We suggest that the non-classical and/or superelectrophilic nature of such Pd complexes complicates their modeling by DFT. However, based on the provided evidence, this Pd/SSZ-13 system selectively forms non-classical Pd$^{2+}$(CO)$_2$ fragments and not Pd$^{3+}$(CO)$_2$ as previously proposed in the literature$^{1,12,24,25}$.

The non-classical nature of this complex is further indirectly corroborated by the fact that its infrared signature does not depend on zeolite type to any significant extent and presents a Pd$^{2+}$(CO)$_2$ fragment stabilized as ion pairs (with the Al-associated negative oxygen atoms of zeolite acting as a negative part of the ion pair, whereas Pd$^{2+}$ and Pd$^{3+}$(CO)$_2$ are the positive +2-charged part of the ion pair) in a small (~0.85 nm) SSZ-13 cage (Fig. S10).$^{11,12,24,25}$ Zeolites with larger cavities do not seem to selectively stabilize this fragment, yet it is observable$^{11,12}$ in conclusion, semi-free non-classical, superelectrophilic, Pd$^{2+}$(CO)$_2$ is formed in the micropores of SSZ-13, and is probably stabilized by secondary interactions between its CO ligands and the basic oxygen of zeolite framework.

The interactions of CO fragments with framework sites (stabilization) withdraws it from Al and suggests that it may exist as a semi-free [Pd(CO)$_2$]$^{2+}$ ion weakly interacting with the framework (the framework itself can thus be regarded as a weakly coordinating macro-anion). All other non-classical carbonyl complexes prepared in HSO$_3$F/SbF$_5$ exist only in the complete absence of moisture.$^{19-23}$ We extended our work to 1 wt% Pt and 3 wt% Ag in SSZ-13 (Si/Al = 6) as well (Fig S16 for HAADF-STEM images of 1 wt% Pt/SSZ-13). In Pt/SSZ-13, non-classical Pt$^{2+}$(CO)$_2$: with CO frequencies 2186 and 2153 cm$^{-1}$ is formed in addition to two classical Pt$^{2+}$-CO monocarbonyls (Fig. 3). DFT modeling of classical Pt$^{2+}$ monocarbonyl complexes allows us to unambiguously assign the 2133 cm$^{-1}$ band to Pt$^{2+}$(CO) in the 8-membered ring, whereas the ~2118 cm$^{-1}$ band belongs to Pt$^{2+}$(CO) in the 6-membered ring (Fig. S17, Tables 2 and S2). These results clearly demonstrate the confinement of isostructural Pt$^{2+}$-CO which leads to the downshift of its IR signature. These bands cannot belong to the dicarbonyl species because they grow independently from each other. The fact that 2186 and 2153 cm$^{-1}$ bands change in concert upon evacuation is a clear indication that they belong to the same species, which, analogously with Pd$^{2+}$(CO)$_2$, can be assigned to Pt$^{2+}$(CO)$_2$. Surprisingly, DFT modeling found two energetic minima for two isostructural and isoelectronic Pt$^{2+}$(CO)$_2$ complexes in the 8-membered ring with very similar stabilities but different frequencies (2156 and 2108, and 2179 and 2136 cm$^{-1}$, respectively). The likely reason for this is that in one of the complexes CO molecules are close to the zeolite framework with O-O distances of 240 pm. This unusual finding that two essentially isoelectronic and isostructural M-CO complexes could have significantly different C-O stretching frequencies is notable.

The Aubke group has also reported the ability to form a non-classical [Pd$^{2+}$(CO)$_4$] complex under higher CO pressures.$^{19-23}$ We have therefore modeled two tetracarbonyl complexes of Pd$^{2+}$ cation and of Pd$^0$ in the CHA structure (Table S1). Interestingly, in the Pd$^{2+}$(CO)$_4$zer structure the carbon of one of the CO molecules is bound to an oxygen center from the zeolite with O-C distance of 141 pm. Despite the fact that we were successfully able to model and construct these unusual homoleptic structures, we find no evidence that they are formed under our experimental conditions.

We extended our work to 1 wt% Pt and 3 wt% Ag in SSZ-13 (Si/Al = 6) as well (Fig. S16 for HAADF-STEM images of 1 wt% Pt/SSZ-13). In Pt/SSZ-13, non-classical Pt$^{2+}$(CO)$_2$: with CO frequencies 2186 and 2153 cm$^{-1}$ is formed in addition to two classical Pt$^{2+}$-CO monocarbonyls (Fig. 3). DFT modeling of classical Pt$^{2+}$ monocarbonyl complexes allows us to unambiguously assign the 2133 cm$^{-1}$ band to Pt$^{2+}$(CO) in the 8-membered ring, whereas the ~2118 cm$^{-1}$ band belongs to Pt$^{2+}$(CO) in the 6-membered ring (Fig. S17, Tables 2 and S2). These results clearly demonstrate the confinement of isostructural Pt$^{2+}$-CO which leads to the downshift of its IR signature. These bands cannot belong to the dicarbonyl species because they grow independently from each other. The fact that 2186 and 2153 cm$^{-1}$ bands change in concert upon evacuation is a clear indication that they belong to the same species, which, analogously with Pd$^{2+}$(CO)$_2$, can be assigned to Pt$^{2+}$(CO)$_2$. Surprisingly, DFT modeling found two energetic minima for two isostructural and isoelectronic Pt$^{2+}$(CO)$_2$ complexes in the 8-membered ring with very similar stabilities but different frequencies (2156 and 2108, and 2179 and 2136 cm$^{-1}$, respectively). The likely reason for this is that in one of the complexes CO molecules are close to the zeolite framework with O-O distances of 240 pm. This unusual finding that two essentially isoelectronic and isostructural M-CO complexes could have significantly different C-O stretching frequencies is notable.
C-O stretch at 2135/2136 cm\(^{-1}\) is much lower than the observed 2153 cm\(^{-1}\). Moreover, the observed experimental frequencies for Pt\(^{2+}(CO)\) are below those of Pd\(^{2+}(CO)\) (which is in perfect agreement with the observation by Aubke group, with the split between band for Pt\(^{2+}(CO)\) (34 cm\(^{-1}\)) larger than for Pd\(^{2+}(CO)\) (21 cm\(^{-1}\)).\(^{19-23}\) Thus, the formation of non-classical Pt\(^{2+}(CO)\) fragment is confirmed. Although the intensities of the bands belonging to classical Pt monocarbonyls are higher than for the Pt\(^{2+}(CO)\) species, due to the aforementioned significantly higher molar extinction coefficients of CO complexes with downshifted vibrational frequencies, the Pt\(^{2+}\)-CO complexes may not be present as the major species.\(^{42,43,53}\) Moreover, it is important to note that this is the first observation of Pt\(^{2+}(CO)\) fragment on a solid support. Non-zeolitic solid support do not seem to provide any evidence for its existence. However, in some previous literature, the Pt\(^{2+}(CO)\) was claimed to exist in ZSM-5 zeolite (noteworthy, unlike in our case, metal nanoparticles were always present in those systems alongside cationic Pt sites): in one report by Hadjiivanov and co-workers, the 2165 and 2150 cm\(^{-1}\) bands with the split between them equal to 15 cm\(^{-1}\), were assigned to Pt\(^{2+}(CO)\); interestingly, the bands at 2204 and 2168 cm\(^{-1}\) in Y-zeolite\(^{55}\) in another report by the same group at 2211 and 2175 cm\(^{-1}\) in ZSM-5, correspondingly were assigned to Pt\(^{3+}(CO)\). Based on our new understanding of the system, it is highly unlikely that Pt\(^{3+}\) ions would be present in ZSM-5 or Y with Si/Al ratio 10-15 due to the fact that this would require 3 Al sites to be in very close proximity either in the same ring or in nearby rings (although it is possible, statistically, their amount would be very low). In those works the observed split ~34-35 cm\(^{-1}\) corresponds exactly to the split we observe for Pt\(^{2+}(CO)\) fragment confined in SSZ-13. Thus, the signatures assigned to Pt\(^{3+}(CO)\) in previous works with split between CO bands of 34-35 cm\(^{-1}\) have to be re-assigned to Pt\(^{2+}(CO)\). The 2165 and 2150 cm\(^{-1}\) assigned previously to Pt\(^{2+}(CO)\), thus, belong to some other Pt carbonyl complexes, and not Pt\(^{2+}(CO)\).

In the case of Ag/SSZ-13, non-classical silver [Ag(CO)]\(^{+}\) with a C-O stretch at 2186 cm\(^{-1}\), and, at higher CO pressures (>1 Torr), non-classical [Ag(CO)]\(^{+}\) species with a C-O stretch at 2177 cm\(^{-1}\) is also formed in SSZ-13 at room temperature (Fig. 4).\(^{25,26,45}\) This is in excellent agreement with the work by the Strauss group.\(^{22,23}\) Indeed, they found that the Ag\(^{+}\) salt of the weekly coordinating anion [Nb(OTeF\(_5\))\(^{-}\)] can form Ag(CO)\(^{+}\) and Ag(CO)\(^{2+}\) with CO signatures of 2208 and 2198 cm\(^{-1}\), respectively, in good agreement with CO split between mono- and dicarbonyl Ag complexes in SSZ-13. Only under pressures above 13 atmospheres could the authors observe the formation of [Ag(CO)]\(^{-}\). Similarly to Pt and Pd, the CO stretches with Ag in the confined microvoids of SSZ-13 are downshifted.

These complexes do not decompose in the presence of significant amounts of water signifying a general trend for SSZ-13 to stabilize such complexes selectively with remarkable stability in the presence of water (Fig. 5).
performance of such materials in PNA applications in the presence of NO molecules. This is why, for example, water can inhibit the dehydration of samples, the Pd 3d 5/2 feature was shifted by about 2.7 eV compared to typical PdO and over 2.3 eV for Pd2+ XPS features observed for typical Pd hydrated or tetramine compounds. At first glance, this seems to indicate a significantly different oxidation state of Pd compared to typical Pd2+. Thus, we decided to explore XPS of 0.1 wt% and 1 wt% Pd/SSZ-13 (Si/Al=6) in greater details (Tables S3, S4, Figs. S16-S24). Both feature atomically dispersed Pd as evidenced by previous HAADF-STEM, EXAFS, XRD, FTIR and DFT data. We also note that upon dehydrogenation either in He or O2, the color of the sample changes from light yellow to light pink (Fig. S3). This is due to Pd interaction with water vapor. (It is known that water can interact with Pd ions in zeolite (analogous to Cu/SSZ-13) and it actually decreases its propensity to interact with NO molecules. This is why, for example, water can inhibit the performance of such materials in PNA applications in the presence of NO molecules adsorbed onto them (or inserted between the framework and Pd2+, which breaks up the Pd2+ 2: Ozeolite ion pair). Indeed, our DFT calculations demonstrate that H2O binding to Pd cations is favorable (Table S1). Upon heating, we observe water removal from Pd2+ and formation of a light pink Pd-zeolite system with isolated superelecrophilic Pd2+ cations: their superelecrophilic nature is evident based on the extremely high shift of the binding energy of Pd2+ feature by 2.3 to 339.6 eV. This process is reversible, as evidenced by the restoration of the yellow color in the presence of water vapor.

We also investigated the interaction of the non-classical Pd2+(CO)2 complex in the SSZ-13 zeolite with ethylene. In many catalytic applications (e.g., automotive exhaust abatement) the active centers can bind a number of adsorbates from the complex gas mixture they are exposed to. Therefore, identifying and characterizing the adsorbed species that can form in Pd/SSZ-13 in a gas mixture containing both CO and a hydrocarbon (e.g., ethylene) is of great interest. The possible formation of olefin complexes, similar to the cation of the Zeise salt, is of fundamental interest. When the Pd2+(CO)2/SSZ-13 system was exposed to C2H4 at ambient temperature it completely lost its pink color, suggesting the formation of a new complex. (Fig S5). The series of FTIR spectra collected in situ during the exposure of Pd2+(CO)2 to ethylene show the gradual decrease in intensity of the two dicarbonyl bands (2193 and 2214 cm⁻¹), and the concomitant development of a new, intense feature centered at 2143 cm⁻¹ (Fig. 6).

This could indicate two things: the transformation of Pd2+ into Pd ions with a higher oxidation state, or the removal of water coordinated to some of the Pd cations and subsequent transformation to Pd2+ sites with unusually high binding energy (BE). In the case of Rh prepared from Rh(CO)2(Acac) and anchored as Rh(CO)2: classical fragments strongly bound to the HY framework, a single Rh(I)(CO): is upshifted by 1 eV compared to the parent Rh(CO)2: and about ~25 cm⁻¹ in the FTIR spectra – a notable high value. The zeolite, thus, indeed may act as a macroligand in whose cages/microchannels the complex sits. However, the 2.3 eV shift is perhaps too great to be explained by the simple ligand effect. The possibility where Pd2+ is oxidized to Pd4+ can only be envisioned perhaps too great to be explained by the simple ligand effect. The possibility where Pd2+ is oxidized to Pd4+ can only be envisioned perhaps too great to be explained by the simple ligand effect.
Figure 7. FTIR spectra obtained from Pd(II)(CO)2/SSZ-13 (1 wt% Pd and Si/Al=6) during sequential ethylene adsorption at 298 K. (P_{C2H4, max}=2 Torr)

Very similar bands are observed in Rh complexes with pi-ethylene as well as Pt²⁻C₂H₄ and Cu-C₂H₄ pi-complexes (Fig. S27). This complex is stable at room temperature and does not decompose under high vacuum (Figs. S28, S29).

The classical nature of this complex is fully supported by the results of DFT calculations showing excellent agreement of the calculated C-O stretching frequencies with the experimental ones. The minor shoulder at lower C-O frequencies (2110-2120 cm⁻¹) can be attributed to the Pd²⁺(CO) species. DFT calculations reveal that CO binding on Pd²⁺-CO is energetically favorable by 87 kJ/mol, whereas CO binding energy on Pd(CO)(C₂H₄) increases to 151 kJ/mol (almost two times). Comparing the binding energy of ethylene in the Pd(C₂H₄) fragment without CO, (58 kJ/mole), to that in the Pd(CO)(C₂H₄) (98 kJ/mole), clearly explains the stability of this fragment. It is of great importance in the context of so-called passive hydrocarbon traps: the new concept aimed at alleviating hydrocarbon emissions during vehicle cold start. Ethylene binding to naked Pd cations is much weaker than that in the presence of CO (CO is always present in the exhaust), which makes ethylene binding more favorable. Furthermore, ethylene desorption temperature shifts to a higher value, which is beneficial for passive HC trap materials. These results illustrate how the adsorption strength of one adsorbate can be controlled by the presence of another adsorbate.

Attempts to restore the original Pd²⁺(CO)₂ were unsuccessful (Fig. S28) even under elevated CO pressure: we speculate that when the complex is locked in its specific framework-tethered position it is not possible for it to move back to the non-classical [Pd²⁺(CO)₂]. However, one may argue that energies could potentially be responsible for this effect: comparing energies from DFT calculations (Table S1), adsorption of two CO ligands on Pd²⁺ is exothermic in 215 kJ/mol in electronic energies, whereas adsorption of CO and C₂H₄ simultaneously is 209 kJ/mol favourable. Although, as we demonstrated earlier, DFT predictions for non-classical [Pd²⁺(CO)₂] differ from the real observations, even if we assume weaker binding of CO, there should at least be some reversibility of this exchange, which is not observed. Therefore, it is indeed probable that the formation of the locked-in Pd(CO)(C₂H₄) entity bound to the framework strongly prevents its conversion back to non-classical [Pd²⁺(CO)₂].

Motivated by the discovery of this mixed carbonyl/ethylene complex of Pd²⁺ in SSZ-13, we set out to investigate the possibility of the formation of other mixed-ligand ethylene complexes. To this end, we exposed a Pd²⁺-NO complex formed via Pd²⁺/SSZ-13 interaction with NO to ethylene and observed similar changes in the N-O stretching vibrational region as we have shown above for the carbonyl complex (Fig. 8).

Figure 8. FTIR spectra recorded from Pd-NO/SSZ-13 (1 wt% Pd and Si/Al=6) during sequential ethylene adsorption at 298 K. (P_{C2H4, max}=2 Torr)

The band belonging to Pd²⁺-NO (1865 cm⁻¹) decreased in intensity, while a new N-O stretching vibrational feature developed at 1774 cm⁻¹, indicating the transformation of Pd²⁺(NO) to Pd²⁺(NO)(C₂H₄) in the presence of ethylene. This is the first palladium²⁺ nitrosyl/olefin complex observed. The assignment of the new IR band was supported by the results of DFT calculations that predicted a shift of the NO stretching vibrational frequency in the Pd²⁺-NO complex to lower wavenumbers upon its interaction with ethylene. This resulted in the formation of the Pd(NO)(C₂H₄) complex.

The exposure of the Pd(NO)(C₂H₄) to CO results in the formation of detectable Pd(CO)(C₂H₄) complex, while evacuation restores the Pd(NO) complex (Fig. S30) via ethylene desorption. These results are consistent with the prediction of DFT calculations, i.e., weaker binding of C₂H₄ in the Pd(NO)(C₂H₄) complex compared with Pd(CO)(C₂H₄): C₂H₄ binding energy on nitrosyl complex is 79 kJ/mol while it is 98 kJ/mol for the carbonyl complex (Table S1).

The changes in the CH-stretching region are also very interesting (Fig. 9). The low intensity of the C-H stretching band for pi-coordinated ethylene in Pd(CO)(C₂H₄) is as expected since the bands in that region have very low molar extinction coefficients. However, for Pd(NO)(C₂H₄), the C-H stretching region has a higher intensity with bands very different than the ones observed for Pd²⁺(CO)(C₂H₄) (normalized for both sample preparations).
These differences seem to indicate the catalytic formation of compounds (with specific C-H stretching vibrations) during the exposure of Pd^{2+}NO to ethylene. In contrast, we did not see the development of these features on Pd(CO)(C_2H_4), indicating that the zeolite itself is not responsible for the formation (Figs 7, S31) of this compound. The developing bands during the exposure of the Pd^{2+}NO complex to ethylene did not match the characteristic features of either polyethylene or butenes. However, when a 5% butadiene/He gas mixture was introduced onto the SSZ-13, bands Pd(II)(CO)_{2} exposed to ethylene under identical conditions. (P_{C2H4}, max=2 Torr).

REFERENCES

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Figure 9. FTIR spectra (in the C-H stretching region) of Pd(II)(NO)(C_2H_4)/SSZ-13 (1 wt% Pd and Si/Al=6) during sequential ethylene adsorption (top) and comparison of the same region for Pd(II)(CO)(C_2H_4) exposed to ethylene under identical conditions. (P_{C2H4}, max=2 Torr).
Supporting Information

Stabilization of super electrophilic Pd$^{2+}$ cations in small-pore SSZ-13 zeolite

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METHODS

Na-SSZ-13 with Si/Al = 6 and ion-exchanged twice with 2 M NH₄NO₃ aqueous solution at 80 °C for 3 hours yielding the ammonium forms of SSZ-13. NH₄-SSZ-13 was subsequently dried under ambient conditions and then at 80 °C. Samples with 0.1 and 1 wt% Pd, 1 wt% Pt and 3 wt% Ag loadings were prepared by modified ion exchange (for Pd and Pt) with 10 wt% Pd(NH₃)₄(NO₃)₂ solution (Sigma-Aldrich 99.99%) with NH₄-SSZ-13, and platinum(II) tetraamine nitrate solution, and regular ion exchange for AgNO₃ (99.99%) solution with H-SSZ-13 (produced by decomposition of NH₄-SSZ-13 in air at 550 °C). More specifically, minimum amount of the Pd(II) or Pt(II) precursor solution was added to zeolite in the amount approximately equivalent to the total pore volume of the zeolite. The thick paste was mixed and stirred vigorously for 30 minutes, followed by calcination in air at 650 °C for 5 h (ramping rate 2 °C/min) in case of Pd and 350°C in case of Pt. H-forms of zeolites could be used as well with identical results: in that case, Pd and Pt tetramine salts were dissolved in the minimum amount of dilute ammonium hydroxide solution (pH=11.5), mixed with zeolite to form thick paste (mixed vigorously), followed by drying and calcination in air at 650 °C for Pd and 350 °C for Pt. In the case of Ag, 1 g of H-SSZ-13 was dispersed in water and stirred with ~20 ml of 0.1 M silver nitrate solution for 3 hours; then the sample was purified by 5 successive centrifugation-redispersion cycles and dried at 80 °C overnight. To avoid silver auto-reduction under high vacuum in the FTIR cell, the sample was heated to 180 °C to remove residual water from Ag/SSZ-13 as quickly as possible and then immediately cooled down prior to IR measurements.

The in situ static transmission IR experiments were conducted in a home-built cell housed in the sample compartment of a Bruker Vertex 80 spectrometer, equipped with an MCT detector and operated at 4 cm⁻¹ resolution. The powder sample was pressed onto a tungsten mesh which, in turn, was mounted onto a copper heating assembly attached to a ceramic feedthrough. The sample could be resistively heated, and
the sample temperature was monitored by a thermocouple spot welded onto the top center of the W grid. The cold finger on the glass bulb containing CO was cooled with liquid nitrogen to eliminate any contamination originating from metal carbonyls, while NO was cleaned with multiple freeze–pump–thaw cycles. Prior to spectrum collection, a background with the activated (annealed, reduced or oxidized) sample in the IR beam was collected. Each spectrum reported is obtained by averaging 256 scans.

HAADF-STEM was used to probe the dispersion of Pd and Pt in prepared samples. The analysis was performed with a FEI Titan 80-300 microscope operated at 300 kV. The instrument is equipped with a CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows for imaging with 0.1 nm resolution in scanning transmission electron microscopy mode (STEM). The images were acquired with a high angle annular dark field (HAADF) detector with inner collection angle set to 52 mrad.

Standard NOx adsorption tests were conducted in a plug-flow reactor system with powder samples (120 mg, 60–80 mesh) loaded in a quartz tube, using a synthetic gas mixture that contained ~200 ppm of NOx or (200 ppm of NOx, 200 ppm CO, 3 vv% H2O and 14% O2) balanced with N2 at a flow rate of 310 sccm (corresponding to 330,000 h⁻¹).

All the gas lines were heated to over 100 °C. Concentrations of reactants and products were measured by an online MKS MultiGas 2030 FTIR gas analyzer with a gas cell maintained at 191 °C. Two four-way valves were used for gas switching between the reactor and the bypass. Prior to storage testing at 100 °C, the sample was pretreated in 14% O2 balanced in N2 flow for 1 h at 550 °C and cooled to the target temperature in the same feed. The gas mixture was then switched from the reactor to the bypass, and 200 ppm of NOx was added to the mixture. Upon stabilization, the gas mixture was switched back from bypass to the reactor for storage testing for 10 min. The sample was then heated to 600 °C at a rate of 10 °C/min to record the desorption profiles of gases in the effluent.

XAS spectra were collected at X-ray beamline 9-1 of the Argonne National Laboratory. The storage ring electron energy was 7 GeV and the ring current was in the range of 495-500 mA. Prior to these measurements, each powder sample was loaded into a cell. The XAS data were collected in the fluorescence mode. Samples were scanned at energies near the Pd K absorption edge (24,350 eV). Standards (PdO, Pd foil and K2[PdCl6] were scanned as well. PdO and K2[PdCl6] were mixed with BN prior to scanning).

X-ray Photoelectron Spectroscopy (XPS) experiments were performed using a Physical Electronics Quantera scanning X-ray microprobe. This system uses a focused monochromatic Al Ka X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 32 element multichannel
detection system. The 80 W X-ray beam focused to 100 μm diameter was rastered over a 1.1 × 0.1 mm rectangle on the sample. The X-ray beam was incident normal to the sample and the photoelectron detector was at 45° off-normal. High-energy-resolution spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. Note that the samples experienced variable degrees of charging. Low-energy electrons at ∼1 eV, 20 μA and low-energy Ar⁺ ions were used to minimize this charging. First, the 0.1 and 1 wt% Pd samples were measured as is. The samples then were heated in 10% O₂/He for 1 h at 600 °C (ramping rate 10 °C/min), followed by cooling down in O₂/He to room temperature in a flow cell attached to the XPS system. The pretreated samples were immediately transferred into the UHV chamber without exposure to the open air for the first XPS analysis. Note that following the heating treatment, adventitious carbon, ideal for binding energy (BE) calibration, became absent. Therefore, all binding energies were referenced to a Si 2p BE of SSZ-13 of 102.7 eV.

Computational Details and Models

We performed periodic DFT calculations using the PW91 exchange-correlation functional with dispersion correction (PW91-D2).[1,2] Vienna ab initio simulation package (VASP) [3,4] was employed for these calculations. Ultrasofter pseudopotentials [5,6] were used as implemented in the VASP package. The large size of the unit cell (see below) allowed us to sample the Brillouin zone using the Γ point only [7]. A plane-wave basis was used with a cutoff energy of 400 eV.

The monoclinic unit cell of the CHA framework consists of 36 T atoms. It was optimized for the pure silicate structure with dimensions: a = b = 13.675 Å, c = 14.767 Å; α = β = 90°, γ = 120° [8]. Two Si atoms in the unit cell located in one six-member ring were replaced with Al. The negative charges around the Al sites were compensated by the M²⁺ ion or M⁺ (M = Pd or Pt) and H⁺ cations or their complexes. All atoms were allowed to relax until the force on each atom was less than 5×10⁻² eV/Å during the geometry optimization.

The total binding energy BE of all neutral ligands (CO, NO, H₂O, and C₂H₄) is calculated as follows:

\[ BE = E[ZEO/M(L1)ₙ(L2)ₘ] - E[ZEO/M] - n \times E(L1) - m \times E(L2) \]

where ZEO/M(L1)ₙ(L2)ₘ (n = 1, 2 or 3) is the energy of the optimized zeolite system together with the metal (M = Pd or Pt) cation and the adsorbed molecule(s); E[ZEO/M] are the energies of the pristine zeolite system, where the framework negative charges are compensated by various cationic species considered, while E(L1) and E(L2) are the energies of the adsorbate molecule(s) in the gas phase.
The adsorption energies of certain ligand (L1 or L2) in the M (M = Pd or Pt) complexes M(L1)n(L2)m, (n=1-3, m = 0 - 2) located in the pores of CHA zeolite are calculated as follows:

\[ BE_{L1} = E[ZEO/M(L1)_{n}(L2)_{m}] - E[ZEO/M(L1)_{n-1}(L2)_{m}] - E(L1) \]

\[ BE_{L2} = E[ZEO/M(L1)_{n}(L2)_{m}] - E[ZEO/M(L1)_{n}(L2)_{m-1}] - E(L2) \]

in the cases where there are two types of adsorbed ligands, L1 and L2 corresponds to the order of the ligands in the notation of the structure. For example in Pd\(^{2+}\)(CO)(C2H4) structure CO is first ligand (L1) and C2H4 is the second one (L2).

Consistent with these definitions, negative values of BE imply a favorable interaction.

The vibrational frequencies were calculated using a normal mode analysis where the elements of the Hessian were approximated as finite differences of gradients, displacing each atomic center by \(1.5 \times 10^{-2}\) Å either way along each Cartesian direction. All calculated C-O vibrational frequencies were shifted by the difference of the calculated harmonic frequency of the free CO obtained with the same computational approach and the experimentally measured (anharmonic) frequency of CO in the gas phase (i.e., 2143 cm\(^{-1}\)):

\[ \nu(C-O)_{\text{calc}} = \nu_{\text{calculated}} - \nu_{\text{calculated(CO-gas)}} + 2143. \]

In this case, the calculated \(\nu_{\text{CO}}\) frequencies are corrected for both the anharmonicity (which is 35 cm\(^{-1}\) for gas phase CO) and the systematic error of the computational method, as reported earlier [9]. Such correction cannot be applied for the N-O vibrational frequencies due to the change in the oxidation state, when NO ligands are adsorbed to the metal species.

References


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**Figure S1.** XANES region at the Pd K-edge of standards PdO, [Pd(NH$_3$_4)(NO$_3$_2), K$_2$[PdCl$_6$] and comparison with air calcined 1 wt% Pd/SSZ-13.
**Figure S2.** Cryo-HAADF-STEM images of 1 wt% Pd/SSZ13 with Si/Al ratio 6 showing very high dispersion of Pd (no agglomeration).
Figure S3. FTIR spectra under vacuum (from 5 Torr CO adsorbed to 0.001 Torr) on 1 wt% Pd/SSZ-13 with Si/Al=6 pre-reduced in the presence of CO (10 Torr) at 400 °C for 1 hr in the infra-red cell.
Figure S4. FTIR spectra during 5 Torr $^{13}$CO adsorption on 1 wt% Pd/SSZ-13 with Si/Al=6 exposed to 5 Torr $^{12}$CO prior to that.

Figures S5. Visual changes to 1 wt% Pd/SSZ-13 with Si/Al ratio 6 single-atom material: a). in the presence of moisture b). dehydrated under helium or oxygen (note that these changes are reversible; when the pink sample is stored in the glove box in the absence of moisture it retains its colour; as soon as water is added in the glovebox or the sample is taken out of the glovebox, the colour changes to yellowish) c). Pd/SSZ-13 exposed to CO d). Pd(II)(CO)$_2$/SSZ-13 exposed to a single pulse of ethylene with the formation of classical colourless (in the VIS region) Pd(II)(CO)(C$_2$H$_4$) complex.
Figure S6. Optimized structures of selected Pd⁺ complexes located in a six-membered ring of CHA: (a) Pd⁺(CO); b) Pd⁺(CO)₂, c) Pt⁺(CO)₃, d) Pd⁺(NO), e) Pd⁺(NO)₂ and f) Pd⁺(NO)₃. For visual clarity only local structure around the complex is shown and in some cases different views of the complexes are presented. Color coding: Si – gray; O – red; Al – green; H – white; C – yellow; N – purple; Pd – cyan.
Figure S7. Optimized structures of selected Pd$^{2+}$ complexes located in a six-membered ring of CHA: (a) Pd$^{2+}$(CO); b) Pd$^{2+}$(CO)$_2$, c) Pd$^{2+}$(CO)$_4$ zeo, d) desorbed Pd$^0$(CO)$_4$ unit; e) Pd$^{2+}$(NO), f) Pd$^{2+}$(NO)$_2$ and g) Pd$^{2+}$(NO)$_3$; mixed complexes: h) Pd$^{2+}$(CO)$_2$(NO), i) Pd$^{2+}$(CO)(NO)$_2$. For visual clarity only local structure around the complex is shown and in some cases different views of the complexes are presented. Color coding: Si – gray; O – red; Al – green; H – white; C – yellow; N – purple; Pd – cyan.
Figure S8. Optimized structures of selected Pd$^{2+}$ complexes located in a six-membered ring of CHA: a) Pd$^{2+}$(CO)(OH), b) Pd$^{2+}$(CO)$_2$(OH), c) Pd$^{2+}$(NO)(OH), d) Pd$^{2+}$(CO)(H$_2$O), e) Pd$^{2+}$(NO)(H$_2$O), f) Pd$^{2+}$(CO)(C$_2$H$_4$), g) Pd$^{2+}$(NO)(C$_2$H$_4$), h) Pd$^{2+}$(NO)(C$_2$H$_4$)$_2$ and i) Pd$^{2+}$(NO)(C$_4$H$_8$). Models with Pd$^{2+}$(O)Pd$^{2+}$ dimer: j) pristine dimer, k) Pd$^{2+}$(CO)(O)Pd$^{2+}$(CO), l) Pd$^{2+}$(CO)$_2$(O)Pd$^{2+}$(CO)$_2$ (one CO$_2$ is desorbed). Color coding: Si – gray; O – red; Al – green; H – white; C – yellow; N – purple; Pd – cyan.
**Figure S9.** Optimized structures of selected Pd$^{3+}$ and Pd$^{4+}$ complexes located in a six-membered ring of CHA: a) Pd$^{3+}$(CO)(OH), b) Pd$^{3+}$(CO)$_2$(OH), c) Pd$^{3+}$(NO)(OH), d) Pd$^{4+}$(C$_4$H$_8$)(O) and e) Pd$^{4+}$(NO)(C$_4$H$_8$)(O). Color coding: Si – gray; O – red; Al – green; H – white; C – yellow; N – purple; Pd – cyan.

**Figure S10.** Crystallographic structure of SSZ-13 (chabazite) material. The diameter of the cavity is ~0.85 nm.

**Figure S11.** FTIR of sequential 6 Torr H$_2$O adsorption on Pd(II)(CO)$_2$ and Pd(NO)(CO) in SSZ-13 (1 wt% Pd, Si/Al=6). Both complexes are stable in the presence of water (6 Torr added).
Figure S12. NO adsorption (0.2 Torr) on Pd(CO)\textsubscript{2}/SSZ-13 with Si/Al=6.

Figure S13. NO adsorption on 1 wt% Pd/SSZ-13 with Si/Al=6.
**Figure S14.** FTIR spectra collected during step-wise addition of 0.5 Torr CO adsorption on an NO saturated 1wt% Pd/H-SSZ-13 sample.

**Figure S15.** NOx and CO abatement performance of 1 wt% Pd SSZ-13 with Si/Al = 6. NOx adsorption at 100 °C for 10 min (after 10 min bypass) followed with TPD (10 °C/min). The feed gas mixture contains 200 ppm of NOx, 14% O2, 3 % H2O with 200 ppm CO.
Figure S16. HAADF-STEM images of 1 wt% Pt/SSZ13 with Si/Al ratio 6.

Table S1. Binding energies of the neutral ligands (in kJ/mol), vibrational frequencies of diatomic ligands ($\nu(L)$ in cm$^{-1}$), elongation of the bond length(s) in the ligands with respect to isolated molecule in gas phase, Pd-ligand and Pd-O$_{zeo}$ distances ($\Delta d$(A-B), d(Pd-L), d(Pd-O$_{zeo}$), respectively, in pm), and number of the unpaired electrons in the systems, $N_s$.

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Pd$^{2+}$(CO)$_4$ one CO ligand desorbs

Pd$^{2+}$(NO)$_4$ desorbed
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<td>Pd²⁺(NO)(C₄H₈)₂</td>
<td>-149</td>
<td>1897</td>
<td>-2.3</td>
<td>203/215</td>
<td>212/224</td>
<td>0</td>
<td></td>
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<tr>
<td>Pd³⁺(CO)(OH)</td>
<td>-117</td>
<td>2158</td>
<td>-0.3</td>
<td>192/195</td>
<td>210/211</td>
<td>1</td>
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<tr>
<td>Pd³⁺(CO)(OH)</td>
<td>-160</td>
<td>2141/2114</td>
<td>0.0/0.1</td>
<td>194/194/217</td>
<td>213/213</td>
<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pd³⁺(NO)(OH)</td>
<td>-149</td>
<td>1897</td>
<td>-2.3</td>
<td>203/215</td>
<td>212/224</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Pd³⁺(CO)</td>
<td>-254</td>
<td>-113</td>
<td>1836</td>
<td>-0.8</td>
<td>199</td>
<td>237/237</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Superscripts:

- a: shifted by +35 cm⁻¹ since the calculated CO in gas phase 2108 cm⁻¹ is lower by 35 cm⁻¹ with respect to the experimental value, 2143 cm⁻¹; the calculated frequencies of NO are not shifted. Part of the data have been reported as Supporting information in ref. [9] and here they are reported for comparison with the new data.

- b: elongation with respect to the isolated ligand

- c: relative energy with respect to Pd²⁺ structure

- d: elongation of the bound CO molecule to one O from the zeolite

- e: elongation of OH with respect to Pd²⁺(OH)/zeo complex

Hydrogen bond between the H from OH and O from the zeolite: c 204 pm; d 203 pm.

Hydrogen bond between the H from H₂O and O from the zeolite: b 147.8 pm; i 149.0 pm; j 154.5 pm.

- With respect to two molecules ethylene
Figure S17. Optimized structures of selected Pt$^{2+}$ complexes located in a six-membered ring of CHA: (a) Pt$^{2+}$; b) Pt$^{2+}$(CO); c) Pt$^{2+}$(CO)$_2$ and d) Pt$^{2+}$(CO)(OH), as well as located in eight membered ring of CHA: e) Pt$^{2+}$; f) Pt$^{2+}$(CO)$_a$; g) Pt$^{2+}$(CO)$_2$ a; h) Pt$^{2+}$(CO)$_2$ b. For visual clarity only local structure around the complex is shown and in some cases different views of the complexes are presented. Color coding: Si – gray; O – red; Al – green; H – white; C – yellow; Pt – blue.
Table S2. Binding energies of all the neutral ligands (BE, in kJ/mol) and of the second adsorbed ligand (BE_{L2}, in kJ/mol), vibrational frequencies of diatomic (C-O) ligands (x(L) in cm^{-1}), elongation of the C-O bond length(s) in the ligands with respect to the isolated CO molecule in gas phase, Pt-ligand distances (in pm) (Pt-L), distances between Pt cation and zeolite O centers (Pt-O_{zeo}) and number of the unpaired electrons in the systems, N_{s}.

<table>
<thead>
<tr>
<th>Str.</th>
<th>BE</th>
<th>BE_{L2}</th>
<th>x(L)^a</th>
<th>Δd(A-B)^b</th>
<th>d(Pt-L)</th>
<th>d(Pt-O_{zeo})</th>
<th>N_{s}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt^{2+}</td>
<td>206;206;212;212</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Pt^{2+}(CO)</td>
<td>-134</td>
<td>2108</td>
<td>0.8</td>
<td>185</td>
<td>208;211;211</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pt^{2+}(CO)_{2}</td>
<td>-318</td>
<td>-184</td>
<td>2182;2136</td>
<td>-0.1;0.0</td>
<td>189;189</td>
<td>209;209</td>
<td>0</td>
</tr>
<tr>
<td>Pt^{2+}(OH)</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
<td>202;210;211</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Pt^{2+}(CO)(OH)</td>
<td>-181</td>
<td>2146</td>
<td>0.1</td>
<td>188;194</td>
<td>209;209</td>
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<tr>
<td>Pt^{2+} 8 mem. ring</td>
<td>200;206;211</td>
<td>0</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pt^{2+}(CO)_{a} 8 mem. ring</td>
<td>-309</td>
<td>2138</td>
<td>0.5</td>
<td>186</td>
<td>202;211;212</td>
<td>0</td>
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<tr>
<td>Pt^{2+}(CO)_{b} 8 mem. ring</td>
<td>-309</td>
<td>2134</td>
<td>0.4</td>
<td>186</td>
<td>202;211;213</td>
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<tr>
<td>Pt^{2+}(CO)_{2-a} 8 mem. ring</td>
<td>-481</td>
<td>-173</td>
<td>2156;2108</td>
<td>0.2;0.5</td>
<td>190;190</td>
<td>206;210</td>
<td>0</td>
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<tr>
<td>Pt^{2+}(CO)_{2-b} 8 mem. ring</td>
<td>-479</td>
<td>-170</td>
<td>2179;2135</td>
<td>0.0;0.1</td>
<td>189;190</td>
<td>205;210</td>
<td>0</td>
</tr>
</tbody>
</table>

^a^ the frequencies are shifted by +35 cm^{-1} since the calculated C-O vibrational frequency for a CO molecule in gas phase 2108 cm^{-1} is lower by 35 cm^{-1} with respect to the experimental value, 2143 cm^{-1}.

^b^ elongation with respect to the isolated ligand in gas phase
Table S3. XPS data acquisition parameters.

<table>
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<th>XPS wide scan data acquisition parameters:</th>
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<td><strong>No</strong></td>
<td><strong>Transition</strong></td>
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<tr>
<td>1</td>
<td>S1s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XPS narrow (high energy resolution) scan data files:</th>
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</thead>
<tbody>
<tr>
<td><strong>No</strong></td>
<td><strong>Transition</strong></td>
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<tr>
<td>6</td>
<td>O1s</td>
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<tr>
<td>5</td>
<td>C1s</td>
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<tr>
<td>4</td>
<td>Pd3d</td>
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<tr>
<td>3</td>
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<tr>
<td>2</td>
<td>Al2p</td>
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<tr>
<td>1</td>
<td>Si2p</td>
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</table>

Table S4. Calculated weight % of each element for 1 and 0.1 wt% Pd/SSZ-13 with Si/Al=6 “as is” and after various treatments.

<table>
<thead>
<tr>
<th>Weight % Table (Calculated from XPS data)</th>
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</thead>
<tbody>
<tr>
<td><strong>Area Comment</strong></td>
</tr>
<tr>
<td>1wt% Pd/SSZ-13 Si/Al=6 (batch 1) As is</td>
</tr>
<tr>
<td>1wt% Pd/SSZ-13 Si/Al=6 (batch 1) 600C O2</td>
</tr>
<tr>
<td>1wt% Pd/SSZ-13 Si/Al=6 (batch 1) NO RT</td>
</tr>
<tr>
<td>0.1wt% Pd/SSZ-13 Si/Al=6 As is</td>
</tr>
<tr>
<td>0.1wt% Pd/SSZ-13 Si/Al=6 600C O2</td>
</tr>
<tr>
<td>0.1wt% Pd/SSZ-13 Si/Al=6 600C NO RT</td>
</tr>
</tbody>
</table>
Figure S18. Wide-line XPS scan of 1 wt% Pd/SSZ-13 with Si/Al=6 as is.
**Figure S19.** Wide-line XPS scan of 1 wt% Pd/SSZ-13 with Si/Al=6 calcined at 600 °C (taken at the first sample area).

**Figure S20.** Wide-line XPS scan of 1 wt% Pd/SSZ-13 with Si/Al=6 calcined at 600 °C (taken at the 2nd sample area, different than the first one).

**Figure S21.** Wide-line XPS scan of 0.1 wt% Pd/SSZ-13 with Si/Al=6 calcined at 600 °C.
Figure S22. High-resolution XPS scan of Si2p region for 1 wt% Pd/SSZ-13 with Si/Al=6 as is and treated under various conditions.
Figure S23. High-resolution XPS scan of Al2p region for 1 wt% Pd/SSZ-13 with Si/Al=6 as is and treated under various conditions.
Figure S24. High-resolution XPS scan of C1s region for 1 wt% Pd/SSZ-13 with Si/Al=6 as is and treated under various conditions.
Figure S25. High-resolution XPS spectra for 0.1 wt% Pd/SSZ-13 with Si/Al ratio 6 before (red) and after heating in oxygen at 600ºC (experiments performed in-situ).
Figure S26. High-resolution XPS spectra for 1 wt% Pd/SSZ-13 with Si/Al ratio 6 before (red) and after heating in oxygen at 600°C (experiments performed in-situ).
Figure S27. C-H stretching regions of Rh(C₂H₄)₂ on zeolite (blue line), alumina (red line) and Rh(CO)(C₂H₄)(Acac) (green line).
Figure S28. FTIR spectra of the CO adsorption (10 Torr) on the Pd(II)(CO)(C$_2$H$_4$)/SSZ-13 with Si/Al ratio 6.

Figure S29. FTIR spectra of the high vacuum (10$^{-6}$-10$^{-7}$ Torr) on the Pd(II)(CO)(C$_2$H$_4$)/SSZ-13 with Si/Al ratio 6.
Figure S30. FTIR spectra of applying high vacuum on the Pd(II)(NO)(C_2H_4)/SSZ-13 with Si/Al ratio 6.

Figure S31. FTIR spectra of the comparison between Pd(II)(CO)(C_2H_4) (black spectrum) and Pd(NO)(C_2H_4)/SSZ-13 (blue spectrum) with Si/Al ratio 6 after C_2H_4 adsorption on Pd carbonyl and nitrosyl complexes: CO/NO stretching and C=C vibrations regions are shown in addition to C-H stretching region in the main text.
Figure S32. C-H stretching region of 5% butadiene adsorption on zeolite (blue line before adsorption, red line after butadiene-1,3 adsorption).