

# A Common Single-Site Pt(II)–O(OH)<sub>x</sub>– Species Stabilized by Sodium on “Active” and “Inert” Supports Catalyzes the Water-Gas Shift Reaction

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## S Supporting Information

**ABSTRACT:** While it has long been known that different types of support oxides have different capabilities to anchor metals and thus tailor the catalytic behavior, it is not always clear whether the support is a mere carrier of the active metal site, itself not participating directly in the reaction pathway. We report that catalytically similar single-atom-centric Pt sites are formed by binding to sodium ions through –O ligands, the ensemble being equally effective on supports as diverse as TiO<sub>2</sub>, L-zeolites, and mesoporous silica MCM-41. Loading of 0.5 wt % Pt on all of these supports preserves the Pt in atomic dispersion as Pt(II), and the Pt–O(OH)<sub>x</sub>– species catalyzes the water-gas shift reaction from ~120 to 400 °C. Since the effect of the support is “indirect,” these findings pave the way for the use of a variety of earth-abundant supports as carriers of atomically dispersed platinum for applications in catalytic fuel-gas processing.

The search for atom-efficient heterogeneous metal catalysts has intensified in recent years, especially as applied to the expensive platinum group metals and gold catalysts, in the hope that new industrially relevant, low-cost catalysts will be developed for a variety of applications that encompass fuel processing and hydrogen and chemicals production.<sup>1,2</sup> Of particular interest are novel single-site metal and alloy catalysts that can be stabilized on a variety of supports, as discussed in several recent reviews.<sup>1,2</sup> This search has met with success in the case of the low-temperature water-gas shift (WGS) reaction by the identification of the exclusive active sites as isolated Au–O<sub>x</sub> species on ceria,<sup>3,4</sup> titania,<sup>5</sup> and most recently on “inert” oxide supports such as zeolites, alumina, and silica after the addition of sodium–oxygen ligands.<sup>6</sup> These diverse catalysts are distinguished by a similarly structured gold species with the same intrinsic activity (turnover frequency (TOF)) and the same apparent activation energy (45 ± 5 kJ/mol) for the WGS reaction irrespective of the support used.<sup>7</sup> Along a similar line, Ir atoms supported on FeO<sub>x</sub> are active and stable in the WGS reaction up to 300 °C.<sup>8</sup> For platinum catalysts, even though it

has been known for a number of years that isolated Pt–O<sub>x</sub> species on ceria catalyze the WGS reaction,<sup>3,9</sup> it has been difficult to prepare them in an exclusively single-site manner without interference from Pt nanoparticles (NPs) that include a large number of spectator atoms,<sup>10</sup> especially on supports other than ceria. With supports such as zeolites, it has been a daunting task to prepare Pt as single-site isolated Pt–O<sub>x</sub> and to retain it in this (active) form at higher than the ambient temperature. In elegant work reported recently, Kistler et al.<sup>11</sup> prepared 1 wt % Pt(II)–oxo species ligated to two Al sites of a KLTL zeolite. This single-site cationic species was active for the CO oxidation reaction at up to 150 °C. No such report exists for Pt–O<sub>x</sub> species on zeolites catalyzing the WGS reaction. To date, any attempt to activate Pt supported on zeolites for this reaction has failed.

We report that Pt–O<sub>x</sub> species can now be prepared in stable single-site form in zeolites and mesoporous silica when the preparation is conducted with the addition of a sodium oxide precursor. The synthesis is simple, from Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and NaOH, the latter added in a second step by solid-state impregnation in nitrogen in amounts such that the Na/Pt atomic ratio is about 10:1 (see Materials and Methods in the Supporting Information (SI)). Previous work has shown the importance of adding alkali metal ions to Pt catalysts for the WGS reaction on various “active” supports such as ceria,<sup>12</sup> zirconia,<sup>13</sup> and titania<sup>14,15</sup> as well as on “inert” alumina and silica<sup>16</sup> and carbon nanotubes (CNTs).<sup>17,18</sup> However, the catalyst typically contains a large fraction (>50%) of the Pt in nanocluster and NP form, which is not easy to remove by leaching techniques, thus preventing a determination of the true TOF of the reaction. The apparent activation energies of the reaction on all of these Pt catalysts were similar (70 ± 5 kJ/mol), indicating a similarly structured Pt active site irrespective of the support.<sup>16</sup> By means of a facile incipient wet impregnation (IWI) method, the platinum species can be dispersed as 20-atom clusters,<sup>19</sup> and a distribution of 1–13-atom clusters on the KLTL zeolite has been reported.<sup>20</sup> Arguably, even if some of the Pt is present in isolated Pt–O<sub>x</sub>–

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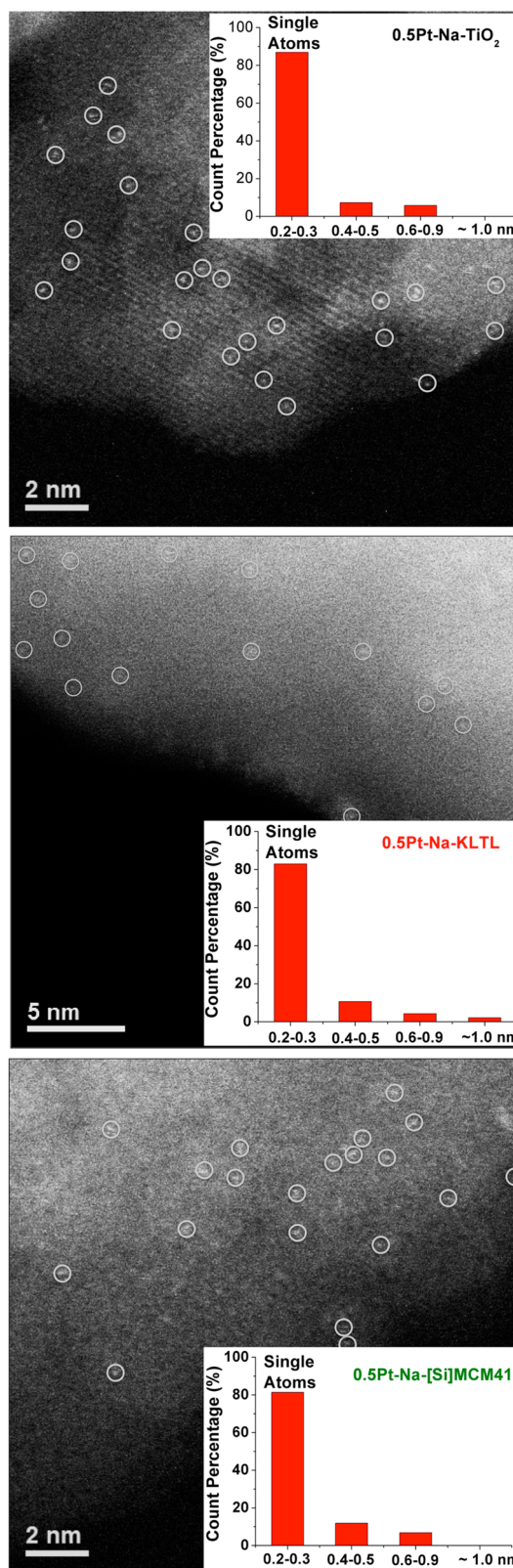
form bound to alkali ions through  $-O$  ligands, it remains unclear how well these species would catalyze the WGS reaction and whether they would remain stable under the reducing atmospheres and elevated temperatures (up to 400 °C) of the reaction.

Another fundamental question that must be addressed and finally resolved for alkali-containing Pt catalysts on all supports, including the “active” ones like titania, is whether the alkali metals modify the titania to create more Pt–oxygen vacancy– $Ti^{3+}$  sites<sup>14</sup> or the electron-deficient platinum is stabilized by the nearby  $Na-O_x$  moieties.<sup>15</sup> No direct experimental evidence was provided on either side to distinguish the Pt active center from the abundant Pt NPs on the titania surface. Interestingly, the work of Pazmiño et al.<sup>21</sup> shows that a similarly active platinum in an unspecified structure was formed on  $Al_2O_3$  or  $TiO_2$  supports upon Na addition (Na/Pt atomic ratio ranging from 7 to 90). Divergent Pt dispersions from 6 to 70% in these unoptimized samples with spectator Pt structures present may distort the characterization data significantly, so a definitive answer to these questions was not possible. The work of Zhai et al.,<sup>16</sup> with a combination of experiment and theory, has shown that atomically dispersed Pt– $O_x(OH)_xNa$  species are formed and that they stabilize both the Pt atom and the  $NaO_x$  species under the WGS reaction conditions and against washing away in aqueous solutions.

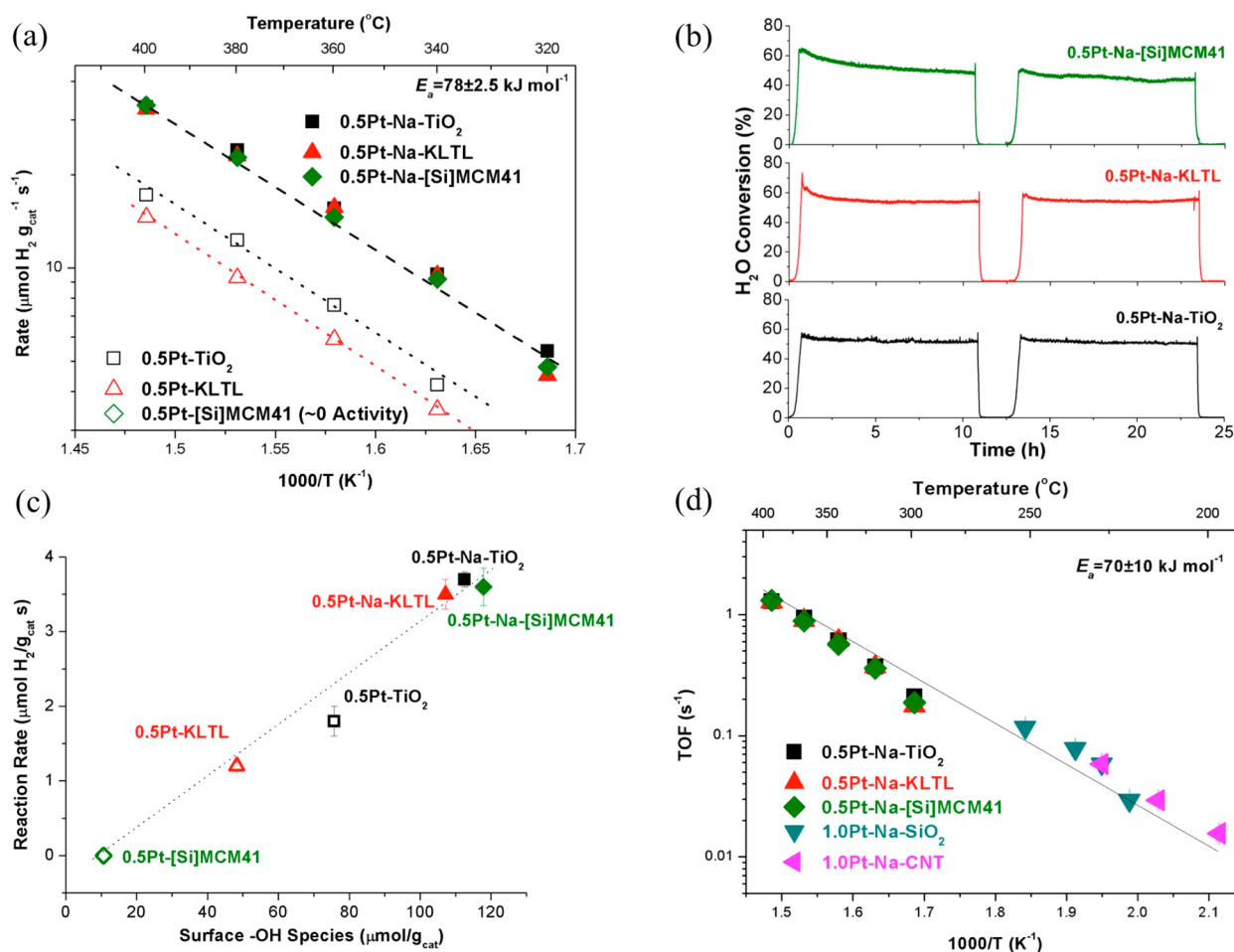
Since all of the previously prepared Pt catalysts contained both active and inactive Pt structures, here we set out to prepare exclusively single-site Pt– $O_x$  species with the addition of alkali ions on zeolite and titania supports. We also included mesoporous silica as a support in order to generalize our findings irrespective of the support porosity. Thus, a high-surface-area anatase ( $TiO_2$ ), a microporous K-type L-zeolite (KLTL), and mesoporous silica MCM-41 ( $[Si]MCM41$ ) were the different supports used in this work. Their properties before and after impregnation are shown in Table S1 and Figures S1–S3 in the SI. While the Na-free Pt catalysts have an abundance of Pt NPs on the all three supports (Figures S4–S7), their Na-containing counterparts are free of Pt NPs. As shown in Figures 1 and S8–S10, more than 80% of the Pt is present as isolated atoms on all three supports. No nanoclusters of Pt were observed. The few Pt species on the subnanometer scale do not show any organized planes and are actually isolated atoms sitting on the support close to each other without Pt–Pt bonding, as will be discussed below on the basis of the X-ray absorption spectroscopy (XAS) data analysis.

In the Na-free samples, Pt NPs abound (Figure S7), resulting in low WGS activity, as shown in Figure 2a. The WGS reaction rate for the Na-containing catalysts with the same 0.5 wt % Pt loading was the same for all three supports, and the rate data merged onto one line in the Arrhenius-type plot shown in Figure 2a. Noteworthy is the invariance of the apparent activation energy of the reaction ( $E_a \approx 78$  kJ/mol) on all of the supported Pt catalysts with or without sodium addition. This finding is similar to what was reported previously for Pt on other supports,<sup>3,16,18</sup> clearly pointing to a similarly structured Pt– $O_x$  site surrounded by Ti ions or, in the case of inert surfaces, by alkali ions that can stabilize the active Pt center through  $-O$  bonds. The big jump in activity when sodium is present (Figure 2a) must then be due to a higher number of such active Pt– $O_x$  sites.

The Na-containing Pt-catalysts were stable and gave similar CO conversions (50–60%) during cyclic 10 h tests at 275 °C with shutdown at room temperature (Figure 2b). The used



**Figure 1.** Aberration-corrected high-angle annular dark-field scanning transmission electron micrographs of the Na-containing Pt catalysts. Circles are drawn around isolated Pt atoms. The size distributions (insets) are based on over 150 observed platinum species counted from the high-magnification images (recorded at 5–10 M $\times$  original magnification).



**Figure 2.** WGS reactivities of Pt catalysts on various supports. The values shown in the labels are wt % Pt. (a) Arrhenius-type plot of reaction rates of the Na-free and Na-containing samples in a simulated reformat gas mixture (11% CO, 26% H<sub>2</sub>O, 7% CO<sub>2</sub>, and 26% H<sub>2</sub>, balance He). (b) Stability test in two 10 h cycles, each reaction at 275  $^{\circ}\text{C}$  in a product-free gas mixture (10% CO, 3% H<sub>2</sub>O, balance He; shutdown to room temperature in 3% H<sub>2</sub>O in He). (c) Linear relationship between the WGS reaction rate (reformat gas conditions, 300  $^{\circ}\text{C}$ ) and the amount of surface -OH species associated with the Pt (based on CO TPR at 50–300  $^{\circ}\text{C}$ ). (d) TOF plot of the WGS reaction rates over the Na-containing catalysts on various supports (data for 1.0Pt-Na-SiO<sub>2</sub> and 1.0Pt-Na-CNT are from ref 18).

catalysts retained their initial Pt-O<sub>x</sub>-Na structure. Indeed, atomically dispersed Pt was still the dominant species even for the slightly less stable 0.5Pt-Na-[Si]MCM41 catalyst after use at 300–400  $^{\circ}\text{C}$  for 6 h (Figure S11). A direct Pt-O<sub>x</sub>-Na interaction was reported on the basis of Na 1s X-ray photoelectron spectroscopy (XPS) measurements on Na-containing Pt catalysts supported on carbon nanotubes.<sup>17</sup> XPS conducted on the present fresh and used catalysts identified the same Na-O<sub>x</sub>- interaction with Pt, whereas in Pt-free samples the sodium species do not interact with the support, but with the gas phase existing mainly as carbon-containing compounds on all three supports (Figure S13).

CO temperature-programmed reduction (TPR) tests were conducted to titrate the WGS-active and regenerable hydroxyls on the surface (Figure S12). The addition of Na dramatically increased the amount of these hydroxyls and correspondingly the overall WGS activity of the catalyst within the same temperature window (from <150 to 300  $^{\circ}\text{C}$ ), regardless of support type. When the steady-state reaction rates measured in the kinetic-control regime were plotted as a function of the integrated amount of regenerable -OH below 300  $^{\circ}\text{C}$ , a linear relationship was found (Figure 2c). This provides a quick-and-easy method to rank-order catalysts on the basis of their low-

temperature surface -OH concentrations. Hence, the active center is, more precisely, a Pt-O(OH)<sub>x</sub>- species, with the -OH vicinal to the Pt atom made available either by an “active” metal oxide such as ceria or titania or by sodium oxide when the support is “inert” (i.e., cannot supply the active -OH species). Of course, the TOF of the reaction can be determined by proper counting of the single Pt atoms on various supports, a more difficult undertaking but one that is possible for well-prepared atomic-scale catalysts. This concept is corroborated by Figure 2d, where we calculated the TOFs by dividing the reaction rates of the Na-containing Pt catalysts by the amounts of Pt atoms. The TOFs over these atomic Pt catalysts are similar, independent of the support type and the preparation conditions. Therefore, we conclude that the “support effect” in the WGS reaction catalyzed by Pt is indirect.

The exclusive presence of Pt atoms on the present catalysts allows us to characterize the chemical valence and coordination structure of the active Pt centers without interference from spectator Pt NPs. XPS results (Figure S14a) show a shift of Pt(IV) to Pt(II) after use in the product-free reaction gas mixture up to 400  $^{\circ}\text{C}$ , with no contribution from Pt(0). *In situ* XAS experiments were conducted from room temperature to 275  $^{\circ}\text{C}$ , where stable and similar activities were found for all

three Na-containing Pt samples (Figure 2b). By both linear combination of X-ray absorption near-edge structure (XANES) spectra (Figure S15) and extended X-ray absorption fine structure (EXAFS) analysis (Table S2 and Figures S14b and S16), we found a transformation of Pt(IV) to Pt(II) upon the initiation of the WGS reaction with a ~55% decrease of first-shell Pt–O coordination from ~4 to 2, while no metallic Pt–Pt bonds were formed. These findings were the same on all three different supports investigated here. EXAFS analysis of a platinum catalyst prepared with addition of sodium on an open silica support,<sup>16,18</sup> 1.0Pt–Na–SiO<sub>2</sub>, also corroborates these findings (Table S3 and Figure S17).

In conclusion, we have demonstrated how to prepare single-atom-centric Pt sites stabilized by sodium through –O ligands and that the sites are active and stable in realistic WGS reaction mixtures from ~120 to 400 °C. These properties are invariant to the choice of the support, be it an “active” or “inert” oxide with respect to its ability to supply regenerable –OH species at low temperatures. Without the interference from spectator Pt NPs, a common low-coordination platinum species, namely, atomic Pt(II)–O(OH)<sub>x</sub>–, has been found. The 100% atomic Pt dispersion of these catalysts in both the fresh and used states is promising for the development of practical catalysts containing only small amounts of costly platinum that remains stable under severe reaction conditions. These catalytic centers may be useful for other reactions in both fuel processing and the production of chemicals.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Materials and Methods, supplementary text, Figures S1–S17, Table S1–S3, and additional references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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