

# Combining in situ NEXAFS spectroscopy and CO<sub>2</sub> methanation kinetics to study Pt and Co nanoparticle catalysts reveals key insights into the role of platinum in promoted cobalt catalysis.

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## Supporting Information Placeholder

**ABSTRACT:** The mechanistic role of platinum and precious metals in promoting cobalt hydrogenation catalysts of the type used in reactions such as Fischer-Tropsch synthesis is highly debated. Here we use well defined monometallic Pt and Co nanoparticles and CO<sub>2</sub> methanation as a probe reaction to show that Pt nanoparticles deposited near to Co nanoparticles can enhance the CO<sub>2</sub> methanation rate by up to a factor of 6 times per cobalt surface atom. In situ NEXAFS spectroscopy of these same Pt nanoparticle plus Co nanoparticle systems in hydrogen shows the presence of nearby Pt nanoparticles is able to significantly enhance reduction of the Co at temperatures relevant to Fischer-Tropsch synthesis and CO<sub>2</sub> methanation. The mechanistic role of Pt in these reactions is discussed in light of these findings.

Platinum and other precious metals are known to promote cobalt catalysts for the reaction of CO and H<sub>2</sub> to hydrocarbons, Fischer-Tropsch synthesis. This reaction, initially developed by Franz Fischer and Hans Tropsch to the point of practical use in the early twentieth century, is considered to be a viable option to partially replace crude oil derived transportation fuels, and therefore of considerable current interest.<sup>1,2</sup> Industrial Fischer-Tropsch now produces > 200,000 bbl/d of synthetic oil.<sup>1</sup> Such catalysts have also been identified to be attractive as possible CO<sub>2</sub> hydrogenation catalysts<sup>3,4</sup> – an analogous reaction that is desirable as a means of utilizing the greenhouse gas CO<sub>2</sub> to generate useful products. The latter is useful both for offsetting the cost of CO<sub>2</sub> capture and removing the need for subsequent CO<sub>2</sub> storage in CO<sub>2</sub> emission reduction schemes.<sup>5</sup> In either case, the role of Pt in promoting Co catalyzed reactions of this type is generally not well understood, with a number of alternative explanations being offered for platinum's role. These can be classified as both structural and chemical effects – the former

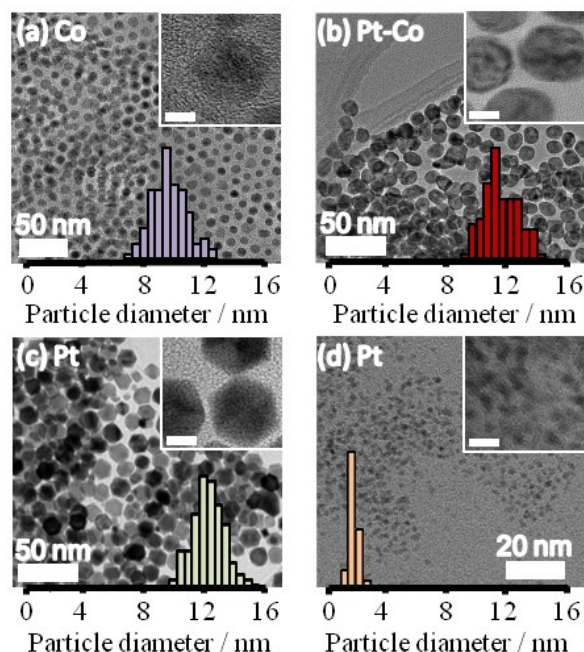
changing the dispersion of the Co and the latter influencing the catalytic chemistry.<sup>6</sup> It has been postulated this could include intimate contact between the two metals modifying the local band structure, ensemble type geometric effects, prevention of deactivation by carbonaceous deposits, and improvement in the reducibility of cobalt.<sup>7,8,9,10,11</sup> Interestingly for the present work, in a series of papers on Pd-Co sol-gel catalysts for CO hydrogenation, palladium is postulated to produce hydrogen that both facilitates cobalt reduction and participates in the reaction.<sup>12,13,14</sup> Considerable attempts have also been made using aberration corrected STEM (Scanning Transmission Electron Microscopy) to establish the possible role of precious metals in these reactions. In the impregnated commercial-type catalysts studied, platinum appeared as a surface atomic species within cobalt particles, but notably also improved the apparent reducibility of cobalt particles containing no precious metal atoms, suggesting hydrogen spill-over was occurring.<sup>15</sup> Although PtCo phases have been seen by XRD,<sup>10</sup> no isolated Pt particles have been observed in studies on commercial type catalysts. Nevertheless, it is useful to understanding the role of Pt to investigate what happens when isolated Pt particles are used as the promoter.

Controlled nanomaterials synthesis affords a new way to address such problems and has been employed to good effect in answering other key questions in catalysis.<sup>16</sup> The use of nanomaterials to address questions specifically in the study of cobalt based catalysts for Fischer Tropsch has recently been reviewed,<sup>17</sup> and we have already used size controlled cobalt nanoparticles to explore particle size effects in CO<sub>2</sub> hydrogenation.<sup>18</sup> To understand better the exact role of precious metals in these types of catalysts, we have recently reported on the preparation of Pt-Co bimetallic nanoparticles, where each nanoparticle contains an approximately 1:1 atomic of the two metals. However, we found that these particles were poor CO<sub>2</sub> methanation catalysts. We identified this was attributable to platinum segregating to the surface in reduc-

ing conditions as demonstrated by ambient pressure X-ray photoelectron spectroscopy and environmental transmission electron microscopy in  $H_2$ .<sup>3</sup>

Here, we identify a different, more realistic model for the catalyst structure involved in the Pt promotional effect. Instead of the two metals being present within a single nanoparticle, we have instead taken discrete monometallic nanoparticles of both Pt and Co and deposited them in close proximity within the pores of a mesoporous silica, MCF-17. This new structural model for the catalyst is a much better mimic for Pt promotion effects, exhibiting a methane production rate  $\sim 6$  times that of pure Co nanoparticles.

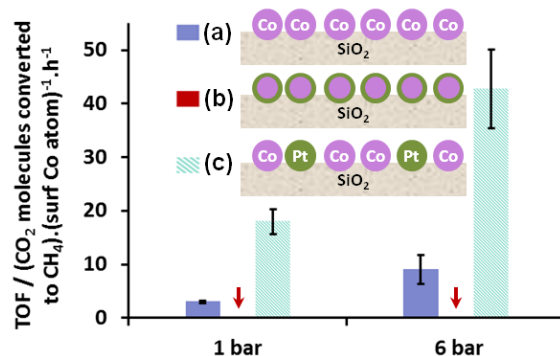
The various nanoparticles can be deposited in both a 3-D form (within the pores of a mesoporous silica, MCF-17) and in 2-D (on the native oxide surface of a silicon wafer). The 3-D and 2-D forms allow us to employ the same nanoparticles for catalytic and X-ray spectroscopy measurements, respectively. Figure 1 shows micrographs of all the nanoparticle samples used in this study: Co nanoparticles and Co-Pt bimetallic nanoparticles (as for our previous work on  $CO_2$  hydrogenation), but additionally 12 nm and 1.9 nm Pt nanoparticle samples, with good size control as indicated by the overlaid particle size distributions. We mostly focus on the sample that results from combining 12 nm Pt and 10 nm Co, as this is closely matched in size to the pure Co and CoPt samples considered previously.



**Figure 1.** Transmission electron micrographs of as prepared nanoparticles, overlaid with particle size distributions. Insets show HRTEM images for each system (5 nm scale bar). (a): 10 nm  $\pm$  1 Co nanoparticles; (b): 11 nm  $\pm$  1.5 Pt-Co alloyed nanoparticles (as previously reported); (c): 12 nm  $\pm$  1 Pt nanoparticles; and (d): 1.9 nm  $\pm$  0.3 Pt nanoparticles.

For the samples supported on MCF-17 used as catalysts in  $CO_2$  hydrogenation, the turnover frequency (TOF) values for methane production at 200  $^{\circ}C$  are shown in Figure 2, along with a schematic representation of the compositions of the catalysts. 200  $^{\circ}C$  was deliberately chosen as the reaction

temperature because of the typical range of commercial operating temperatures (200–250  $^{\circ}C$ ) for the analogous  $CO$  hydrogenation or Fischer-Tropsch reaction. As previously reported and discussed above, pure Co nanoparticles significantly outperform the Co-Pt bimetallic nanoparticles, attributable to Pt segregating to the surface of each particle and inhibiting the reaction. However, pure Pt nanoparticles located “near” to the pure cobalt nanoparticles (within the same mesoporous oxide support) result in a catalyst several times more active per cobalt site for the production of methane than their pure cobalt catalyst counterparts. It should be noted that this equates to around only 1 Pt nanoparticle for every 24 Co nanoparticles (based on their average size and the loadings determined by ICP-AES, the latter indicating a Pt:Co molar ratio of  $\sim 1:20$ ). This is slightly more than the often  $< 1:100$  molar ratio found in commercial type catalysts to allow us to characterize the Pt nanoparticles present with a range of techniques. We have previously demonstrated that the pure Pt nanoparticles are inactive for this reaction,<sup>3</sup> therefore we assume that all  $CH_4$  production is derived from the pure Co particles. The dramatic increase in rate is therefore the result of platinum nanoparticles enhancing the activity of the cobalt. Some production of  $CO$  is seen in all cases, along with very small traces of  $C_2$  and higher hydrocarbon products.

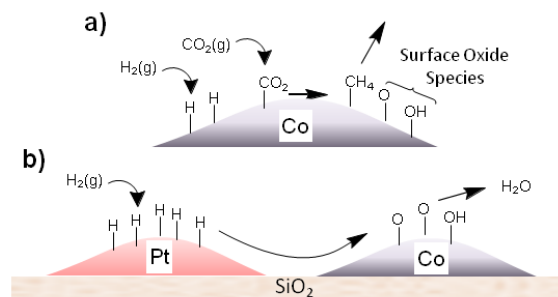


**Figure 2.** Turnover frequencies at 1 and 6 bar total pressure for the production of  $CH_4$  during catalytic  $CO_2$  hydrogenation (1:3  $CO_2$ :  $H_2$ ) at 200  $^{\circ}C$  for three catalyst samples: (a) 10 nm Co nanoparticles supported on MCF-17 mesoporous silica; (b) 11 nm Co-Pt binary nanoparticles supported on MCF-17; and (c) 10 nm Co and 12 nm Pt nanoparticles mixed in solution and subsequently supported on MCF-17. The red arrows denote the position of the data points for the Co-Pt binary nanoparticle sample (indicating only trace amounts of  $CH_4$ ). Schematic inset indicates overall structure of each sample.

One likely role for the platinum particles in this case is the efficient reduction of the cobalt particles’ surfaces, as is often postulated for the role of precious metals in promoting cobalt catalysts for Fischer Tropsch. Here, however, we pre-activated the cobalt catalyst by reduction at 450  $^{\circ}C$  in  $H_2$ , a treatment anticipated to afford fully reduced cobalt nanoparticles – we have previously reported a water loss / hydrogen adsorption temperature programmed reduction peak at this temperature for pure cobalt nanoparticle based catalysts.<sup>18</sup>

Oxidation by water (a reaction product) is often considered to be a possible deactivation mechanism during cobalt catalyzed hydrogenations,<sup>19,20</sup> although others have been unable to observe this during in situ NEXAFS spectroscopy of

cobalt crystallites in a 1 : 1 mix of  $\text{H}_2\text{O}$  and  $\text{H}_2$ .<sup>21</sup> However, if methane (or other hydrocarbon) formation occurs after breaking carbon-oxygen bonds in  $\text{CO}_2$ , oxygen may accumulate on (and beneath) the surface eventually leading to near surface oxidation before water is formed (Figure 3(a)). This will decrease the reaction rate, in agreement with findings on Co foils in vacuum for CO reduction, where hydrogenation and removal of surface oxide rather than the dissociation of CO were the rate limiting step.<sup>22</sup> It is also consistent with the recent observation using transient kinetic analysis for CO hydrogenation over a Co/MgO catalyst that oxygen (as well as carbon and hydrogen) builds up on the surface leading to more than a monolayer of adsorbed surface species under working conditions.<sup>23</sup>



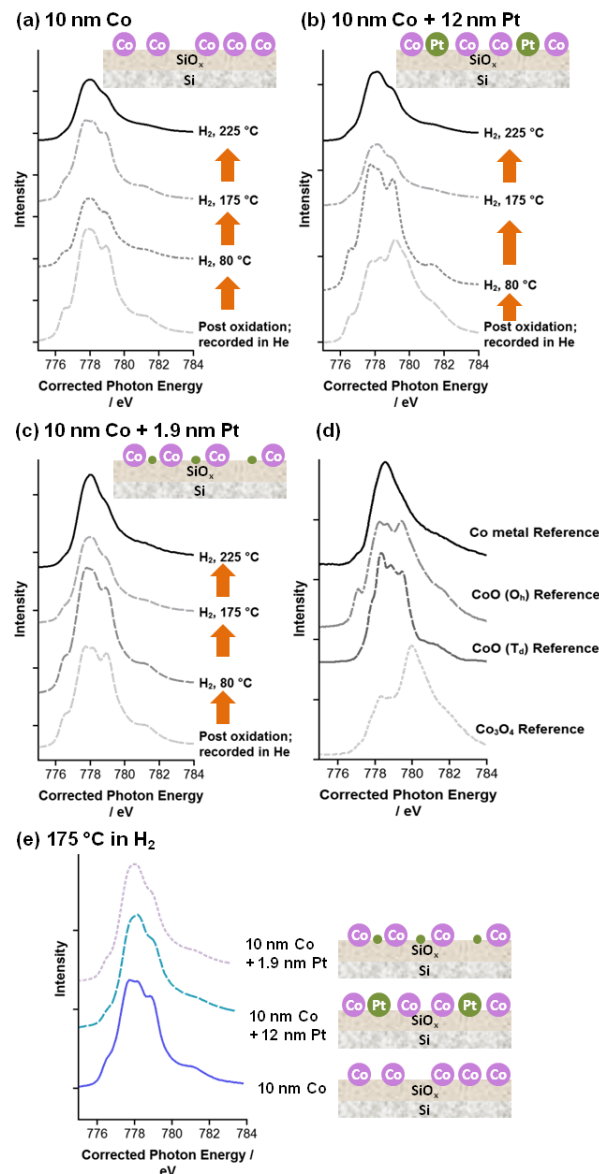
**Figure 3. Schematics showing (a) production of surface oxide from  $\text{CO}/\text{CO}_2$  hydrogenation, and (b) transfer of adsorbed hydrogen from Pt to Co via a spillover mechanism to re-reduce the cobalt oxide surface releasing water.**

Since Pt is very well known for dissociative chemisorption of  $\text{H}_2$ , we propose that hydrogen could be transferred between Pt and Co (as indicated in Figure 3(b)) to clean off surface oxygen/oxide under catalytic conditions. Such hydrogen transport processes theoretically involve the presence of surface hydroxyl groups, however it has been shown that silica surfaces typically have 6-7  $-\text{OH}$  per  $\text{nm}^2$  groups even after 450 °C treatment in vacuum.<sup>24</sup> This hydrogen migration would reverse the deactivation, increasing the observed rate, as found during the catalytic experiments when Pt nanoparticles are added. To investigate this further, we performed in situ NEXAFS spectroscopy during nanoparticle reduction for analogous 2D samples deposited on silicon wafers (Figure 4). Three samples were studied using NEXAFS: (1) pure Co nanoparticles; (2) Pure Co nanoparticles with the same 12 nm Pt nanoparticles (as used in the MCF-17 supported catalyst); and (3) pure Co nanoparticles, with smaller 1.9 nm Pt nanoparticles (see supporting information for ex-situ characterization). Samples were prepared by sequential dip-coating to yield films of individual Pt and Co nanoparticles. This last sample with smaller Pt nanoparticles was investigated to see whether the same effect would occur irrespective of Pt nanoparticle size (important in matching up to commercial catalysts, where only very small amounts of Pt are present').

By comparing the sample spectra in Figure 4 (a)-(c) with the reference spectra in (d), it is clear that a gradual change from the oxidized form towards a reduced cobalt metallic state occurs in all three samples as the temperature is increased. This can be seen especially clearly for the samples at 175 °C in Figure 4(e). It can also be seen in Figure 5, which shows the fraction of metallic cobalt observed under each

condition, obtained by using linear combinations of reference spectra to calculate the Co average valence, as is common for processing NEXAFS data of this kind.<sup>25</sup> At all temperatures investigated, it is clear that the fraction of cobalt reduced by  $\text{H}_2$  to the metallic state is significantly higher when Pt nanoparticles are added.

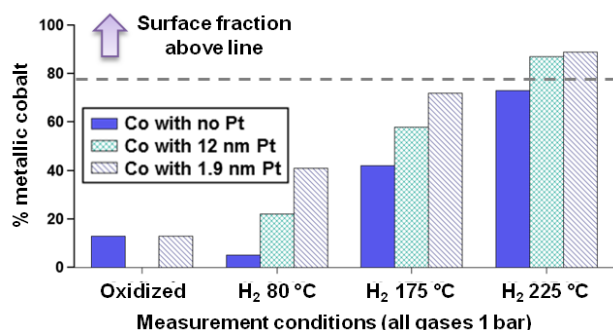
Since surface oxygen is more stable (imposes less lattice strain and decreases surface energy), it is reasonable to assume residual oxygen in the nanoparticle will preferentially diffuse to the surface on the timescale of our experiments, and therefore undergo reduction last. This means that the threshold for reducing a significant fraction of the surface cobalt atoms (marked in Figure 5) is achieved only in the presence of nearby Pt nanoparticles, even at the upper temperature in the present study.



**Figure 4. In situ Co  $L_3$ -edge NEXAFS spectra in  $\text{H}_2$  at increasing temperatures, following oxidation in a  $\text{He}/\text{O}_2$  mixture at 100 °C and cooling in He (a - c). A number of standard reference spectra obtained in vacuum are shown in (d), and the 175 °C spectra recorded in  $\text{H}_2$  are**

re-plotted in (e) to facilitate comparison. Schematics indicate the overall structure of each sample.

As a final aside it is worth noting that we have, to date, been unsuccessful in preparing a uniform bimetallic nanoparticle sample (in the > 6 nm range known to be active for CO and CO<sub>2</sub> hydrogenation) in which the Pt concentration is sufficiently low that Pt cannot cover most of the surface once segregated by the reducing atmosphere. When lower Pt concentration samples are targeted, a mixture of pure Co and Pt-Co nanoparticles with higher Pt concentrations are produced. We therefore speculate that the surface reduction of Pt and Co salts during wet impregnation (the technique typically used to prepare commercial supported catalysts) is subject to similar constraints. The alternative role of Pt found here may be a very important feature of the promotional role precious metals have in industrially employed catalysts.



**Figure 5.** Calculated % of metallic cobalt (Co<sup>0</sup>) during in situ reduction. Data points based on least square fitting of the Co L<sub>3</sub>-edge NEXAFS spectra to reference data shown in Figure 3(d). The area above the horizontal line show the fraction of the signal expected to originate from cobalt in the surface atomic layer – see supporting information. An example fitting and complete fitting results are also given in the supporting information.

In summary, while bimetallic nanoparticles comprising Pt and Co within a single particle are ineffective as CO<sub>2</sub> hydrogenation catalysts, supporting individual Pt and Co nanoparticles in close proximity on silica (even in a ~1:24 particle ratio) enhances the hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> per Co surface atom over Co nanoparticles by up to a factor of 6 times. In situ NEXAFS spectroscopy during Co nanoparticle reduction shows the addition of Pt nanoparticles is able to significantly enhance reduction of the Co at any given temperature. This allows us to tentatively suggest hydrogen atoms dissociated on Pt may be transferred to the Co nanoparticles via long distance hydrogen atom spillover, aiding their reduction. Given the similar temperature range of the catalytic and spectroscopic results, the same phenomenon can be expected to occur under reaction conditions and therefore likely enhances the rate of removal of surface cobalt oxide formed in the reaction, generating more reaction sites and therefore rationalizing the observed dramatic increase in CH<sub>4</sub> production. Given the similar mechanisms, this observation also has implications for the role of platinum in promoting the analogous and industrially important Fischer-Tropsch (CO hydrogenation) reaction.

## ASSOCIATED CONTENT

## Supporting Information

Methodology; NEXAFS Spectra Fitting; Ex situ characterization of NEXAFS 2D and silica supported Pt & Co 3D samples; Surface fraction calculations; ICP-AES. 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 interests.

## ACKNOWLEDGMENT

This work was supported by the Director, Office of Basic Energy Sciences, Materials Science and Engineering Division and the Division of Chemical Sciences, Geological and Biosciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors are also grateful to Hui Zhang at Beamline 7.0.1 for his practical assistance. SKB and NK gratefully acknowledge financial support by Total S.A. We are also thankful for valuable discussions with Daniel Curulla-Ferre (Total S.A.).

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TOC Graphic:

