Water-Gas Shift Reaction on Alumina-Supported Pt-CeO_x Catalysts Prepared by Supercritical Fluid Deposition

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Abstract

Alumina-supported platinum catalysts, both with and without ceria, were prepared by supercritical fluid deposition and evaluated for activity for water-gas shift reaction. The organometallic precursor, platinum(II) acetylacetonate, was deposited from solution in supercritical carbon dioxide. Analysis of the catalysts by high resolution scanning transmission electron microscopy indicated that platinum was present in the form of highly dispersed metal nanoparticles. Pretreatment of the alumina-supported ceria in hydrogen prior to the deposition of the platinum precursor resulted in more platinum nucleated on ceria than non-pretreated alumina-supported ceria but varied in both particle size and structure. The ceria-containing catalyst that was not pretreated exhibited a more uniform particle size, and the Pt particles were encapsulated in crystalline ceria. Reaction rate measurements showed that the catalyst was more active for water-gas shift, with reaction rates per mass of platinum that exceeded most literature values for water-gas shift reaction on Pt-CeO_x catalysts. The high activity was attributed to the significant fraction of platinum/ceria interfacial contact. These results show the promise of supercritical fluid deposition as a scalable means of synthesizing highly active supported metal catalysts that offer efficient utilization of precious metals.

1. Introduction

Synthesis gas, or syngas, is a fuel gas generated by steam reforming or partial oxidation of fossil fuels or biofuels. Its composition is largely hydrogen and carbon monoxide, the ratio of which depends on the source fuel and the processing method. Syngas currently represents the most significant source of hydrogen that could potentially support widespread use of hydrogen fuel cell technologies. However, if the H₂ is to be used in such applications, the concentration of CO must be reduced significantly to prevent poisoning of the fuel cell catalyst and maintain performance. In a fuel processing train to generate H₂ for mobile, small scale operations, water-gas shift (WGS) reaction offers the benefit of reducing the CO content while simultaneously increasing H₂ content:

WGS is a slightly exothermic reaction ($\Delta H = -41.1$ kJ/mol), and as a result the achievable equilibrium conversion of CO decreases with increased temperature. In industrial applications, WGS is normally performed in two steps, both a high temperature and low temperature shift. At low temperatures, high conversions are achievable but are limited due to slow kinetics. Reaction rates are faster at high temperatures, however, equilibrium constraints limit conversion. Industrial catalysts include copper/zinc oxide and ferrochrome-based catalysts. These catalysts are not suited for mobile or small-scale operations due to safety and technical constraints. The requisite size of the catalyst bed, durability during start-up and shut-down, and hazards related to their pyrophoric nature are all prohibitive factors.[1] The search for WGS catalysts that can be safely and reliably implemented in logistical, fuel cell-related technologies points toward platinum or gold used in conjunction with ceria or other partially reducible oxides.[2-7] For economic feasibility, maximizing the activity per mass of precious metal required is vital. To achieve the highest specific activity,

two surface characteristics are needed. One is high metal dispersion, meaning that a large fraction of the metal atoms are available on the surface as active sites with smaller particles resulting in higher dispersion. Significant interface between the metal particles and the partially reducible oxide surface is also important, as these interfacial sites are crucial to rate enhancement, as discussed below.

While the mechanism by which reducible metal oxides promote the activity of noble metals for water-gas shift remains a matter of scientific investigation and debate, the importance of the promotion is well established.[8-11] In the case of platinum/ceria catalysts, there are two proposed mechanisms by which WGS may occur. One suggestion is a redox mechanism that takes advantage of the oxygen storage capacity of ceria.[3] The other involves adsorbed formate intermediates on platinum sites adjacent to ceria. The degree of promotion in both mechanisms is dependent upon interfacial area between active metal sites and oxides. Consequently, methods of synthesizing supported catalysts with intimate contact between the two are essential.[12-17] This high interfacial area also serves to stabilize metal particles and reduce agglomeration, thus extending the life of the catalyst.

Advances in transmission electron microscopy have made possible the characterization of supported metals down to the atomic scale, and the potential offered by even single-atom catalysts for reactions such as WGS can now be investigated.[4, 18-20] These results indicate that the active sites are primarily metal atoms or ions strongly bound on the reducible oxide surface.[21, 22] Therefore, the possibility exists to yield active catalysts with exceedingly low loading of precious metals. Multiple authors make note of the need for scalable catalyst synthesis techniques that can take advantage of their findings.[4, 20]

Using supercritical fluid (SCF) solvents to synthesize functional nanostructured supported metals has been a topic of increasing interest and research for the past decade.[23-28] The properties of supercritical fluids can be described as hybrid between those of liquids and

gases.[29, 30] Their densities approach those of liquids, providing the ability to act as process solvents[31-36] yet exhibit mass transfer properties that are much more akin to those of gases. Low viscosities and high diffusivities make them attractive for processes dependent upon transfer through a solvent medium.[37] The absence of surface tension makes them especially suitable for interfacial processes, particularly those involving transport through high-surface-area porous solids. Among compounds whose critical temperature and pressure are reasonably accessible, carbon dioxide stands out as the most commonly utilized supercritical fluid due to characteristics that render it particularly safe for use – it is non-toxic, nonflammable, and nonreactive under most conditions. As a result, it has been promoted as a “green” solvent.[34, 35, 38] While the environmental benignity of CO₂ as a solvent is a positive trait, it is the implications of the process advantages, notably high diffusion rates and lack of surface tension, that are more crucial to the work in this paper.

Deposition of metals from supercritical fluids presents an attractive alternative to wet methods for yielding highly dispersed metal particles. The first step in the process is dissolution of organometallic precursors, often complexes of β -diketones or cyclic octadienes, in the SCF, usually carbon dioxide.[39-41] While the solubilities of these precursors in supercritical CO₂ are very low (on the order of 10⁻⁵ to 10⁻⁴ mole fraction), they are generally sufficient to achieve appreciable metal loading on the supports.[42-45] Further, the low solubility should serve to increase the dispersion of precursor on the support since deposition of single molecules rather than clusters should occur.

The next step is the adsorption of the organometallic precursor from the supercritical fluid on to a solid support. Synthesis of metal nanoparticles via supercritical fluid deposition (SCFD) has been studied on carbon nanotubes[46, 47], silica and carbon aerogels,[39, 48-50], and on more traditional supports such as bulk alumina and silica.[49, 51, 52] Following adsorption, the solvent is vented from the system, leaving the precursor behind on the

support. Thus, the solvent evaporation step necessary with wet impregnation, which results in both concentration and precipitation of precursors and metal aggregates is avoided.[53] The metal complex is subsequently reduced by thermal or chemical treatment, a step often carried out prior to depressurization. The method of reduction has been found to influence particle size.[54] Furthermore, substrates with higher surface area have been shown to result in smaller particle sizes,[55, 56] and functionalization of the support can be used to reduce particle agglomeration.[57]

The use of materials prepared by SCFD for catalysis is a promising application, and several recent reports highlight their potential. Supported palladium catalysts for alkylation[58] and supported ruthenium catalysts for hydrogenation[59] have been synthesized using supercritical CO₂. The authors note high catalytic activity and the ease with which reaction conversion and selectivity can be tuned by adjusting synthesis parameters. Electrocatalyst materials produced using platinum deposition from supercritical CO₂ on carbon nanotubes,[60-62] graphene sheets,[63] and carbon black[64] have shown considerable promise as direct methanol fuel cell electrode catalysts. A report of a catalyst of copper and platinum on ceria prepared by SCFD suggests that its activity for preferential oxidation of carbon monoxide is the highest reported.[65] The activity for all catalysts prepared by this method has been attributed to the high dispersion of the metal.

The aforementioned works show promising results, but many opportunities still exist to demonstrate the catalytic activity of materials prepared by deposition of metal precursors using supercritical carbon dioxide, especially on oxide supports. In this work, we explore the use of SCFD to prepare water gas-shift catalysts of platinum and ceria supported on γ -alumina. A motivation for the study was that SCFD should generate catalysts with a high specific activity per mass of platinum due to high dispersion of metal nanoparticles on the

support. A further goal was to investigate the effect of treatments before and after deposition on the nature and interaction of the platinum and ceria in materials made by this method.

2. Experimental

2.1 Materials

Platinum(II) 2,4-pentanedionate (Alfa Aesar, 97%) and cerium(III) chloride heptahydrate (Acros Organics, 99%) were used as received. Catalyst supports were high-surface-area cylindrical γ -alumina pellets from Alfa Aesar, having a diameter of 1/8 inch and a specific surface area of 255 m²/g. Research grade carbon dioxide from Airgas was used for catalyst synthesis.

2.2 Catalyst preparation

The ceria precursor was deposited onto γ -alumina pellets using incipient wetness impregnation. An appropriate amount of cerium(III) chloride heptahydrate to prepare a nominal 5 % Ce by weight was dissolved in deionized water. Metal loadings chosen were for comparison purposes to published literature values. The solution was then added drop-wise on approximately 2 g of alumina pellets until they were completely saturated. The pellets were then dried overnight, and the process was repeated until the solution was depleted. The pellets were calcined in air at 400°C for 6 hours.

Prior to deposition of the platinum precursor, some of the pellets were pretreated in a flowing stream of 16% H₂ in N₂ at 300°C for 4 hrs. The pellets were then cooled in flowing N₂ and loaded immediately into the deposition vessel described below.

The platinum precursor was deposited using SCFD. The experimental apparatus for the deposition is depicted in Figure 1. The vessel is a 500-mL Parr reactor constructed of 316 stainless steel. Fitted to the reactor is a K-type thermal couple, pressure indicator, vent line, and rupture disk assembly. The reactor was placed inside a temperature-controlled heating jacket atop a magnetic stirrer.

For each deposition, a suitable amount of platinum precursor to achieve a nominal 1.25 % Pt by weight was placed in the bottom of the reactor with a magnetic stir bar. According to reported solubility values, the amount of precursor used is soluble in supercritical CO₂ at deposition conditions.[42] Approximately 2 grams of catalyst pellets (Al₂O₃, CeO_x/Al₂O₃, or pretreated CeO_x/Al₂O₃) were placed in a mesh basket suspended well above the bottom of the reactor to ensure that the support did not contact the solid precursor. The vessel was sealed and the air was flushed from the reactor with CO₂ from a high-pressure syringe pump (ISCO Model 500D). The vessel was then slowly heated and pressurized to 60°C and 140 atm. The contents of the vessel were allowed to remain at these conditions for 20 hrs. The vessel was then vented (4 atm/min) and cooled to room temperature. Importance was placed on avoiding the liquid region to ensure deposition occurred only from the supercritical phase.

After deposition, samples were calcined in air at 400°C for 4 hours. They were then reduced in flowing 5% H₂ in N₂ at 350°C.

2.3 Catalyst characterization

Elemental analysis was performed using atomic emission spectroscopy (Agilent 4100 MP-AES) calibrated with appropriate single-element standards. Approximately 100 mg of catalyst was digested in 6 mL each of HCl (1 M) and HNO₃ (1 M). The mixture was stirred at 65°C until the solution ran clear (approximately 20 hours) to ensure complete dissolution.

Samples were then diluted to appropriate concentrations and elemental analysis was conducted.

Catalysts samples underwent temperature-programmed reduction in a Quantachrome ChemBET chemisorption analyzer. Each sample was crushed, sieved to remove particles smaller than 500 μm , and loaded into a quartz U-tube in amounts ranging from 0.1 to 0.3 g. Reduction took place under a constant flow of 5% H_2 in N_2 . Temperature ramps were set at $10^\circ\text{C}/\text{min}$. A cold trap removed any condensable reduction products formed. The uptake of H_2 was measured for a temperature range of $40\text{--}500^\circ\text{C}$.

Following reduction, CO pulse titration was conducted on each sample. The samples were heated to 350°C under 5% H_2 in N_2 flow for 1 hr to ensure complete reduction, followed by a helium flush to remove chemisorbed hydrogen. The sample tube was then immersed in a dry ice-acetone bath to reduce the sample temperature to -78°C . The low temperature was used to suppress CO spillover to the ceria to mitigate falsely high dispersion measurements. CO was pulsed in 266 μL increments.

High-angle annular dark field (HAADF) high-resolution scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) were performed using an aberration-corrected JEOL 2200FS STEM.

2.4 Catalyst activity measurement

Reaction measurements were performed in a 6-mm OD quartz tube reactor in a temperature-controlled tube furnace. Reactor feed composition was 16%/32%/32%/20% $\text{CO}/\text{H}_2/\text{H}_2\text{O}/\text{N}_2$. Gases were metered through mass flow controllers (MKS, 200 SCCM maximum flow), and water was fed from a syringe pump into a preheater to generate steam. The combined gas streams were also preheated before entering the reactor. The total gas

flow rate through the reactor was 250 SCCM. Gas hourly space velocity for these experiments was approximately $75,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

The catalyst pellets were crushed and sieved to remove particles smaller than $500 \mu\text{m}$ before they were loaded in the reactor tube, and the bed was held in place with quartz wool. The amount of catalyst in the reactor was approximately 200 mg. In a given experiment, reactor temperature was initially set at the high end of the temperature range and lowered through the experiment. Samples were taken over a range of temperatures from 450°C down to 250°C , depending on the conversion achieved. The temperature range required for measureable CO conversion was higher for the catalyst without ceria. Temperature was measured both at the inlet and the outlet of the catalyst bed.

Samples of the reactor effluent were drawn from the stream exiting the reactor using a $100 \mu\text{L}$ gas-tight syringe. Composition was determined using a gas chromatograph (Agilent 7820A) equipped with a Supelco Carboxen-1010 PLOT column ($30 \text{ m} \times 0.53 \text{ mm ID}$) and a thermal conductivity detector. Using helium as the carrier and reference gas impaired the precision of measuring the hydrogen peak, so analyses were based on the CO peak relative to the N_2 peak. A sample chromatogram and method can be found in Supplemental Materials.

3. Results and discussion

3.1 Catalyst composition

Based on the amount of cerium and platinum precursors used in the preparation of catalysts, nominal catalyst compositions were 1.25% Pt and 5% Ce. Elemental composition based on atomic emission spectroscopy is provided in Table 1. Pt contents ranging from 0.83% to 0.95% by mass indicate that approximately 70% of the precursor loaded into the

deposition vessel was deposited on the support. Recent reports showing that the adsorption behavior of organometallic compounds in supercritical fluids follows equilibrium adsorption isotherms. [66] Given the 20 hours allowed for adsorption, it is likely that the amount adsorbed corresponds to equilibrium concentrations established between the surface and the fluid phase. Silver nitrate tests did not indicate any significant residual chloride following deposition of platinum and calcination.

3.2 Platinum dispersion

The dispersion of platinum, defined as the fraction to total platinum atoms available as active surface sites, was evaluated using CO pulse chemisorption, and values are provided in Table 1. This technique determines the number of metal atoms accessible as active sites based on the amount of gas adsorbed. A 1:1 stoichiometry is assumed for Pt and CO. Dispersion is calculated as

$$\%D = \frac{\text{moles of CO adsorbed}}{\text{moles of Pt in catalyst sample}} \times 100\%$$

The metal dispersion values in Table 1 correspond to average crystal diameters of less than 1 nm. The average dispersion is higher for the catalyst without ceria. When ceria is present, chemisorption indicates a somewhat higher metal dispersion for the catalyst with reducing pretreatment prior to metal deposition than the one without pretreatment. Pulse chemisorption evaluates the number of metal sites available, but it does not provide information regarding the environment of those metal sites. Because the most important surface sites in Pt/CeO_x water-gas shift catalysts are those at the interface between Pt particles and ceria, analysis using electron microscopy was performed to further understand the nature of the catalyst surface.

The catalyst samples were investigated by high-resolution HAADF-STEM, a technique which has the ability to resolve single metal atoms. Z-contrast, which distinguishes between elements in electron micrographs based on their atomic masses, can be employed to differentiate between Pt and Ce in the images. In Figure 2, where some example micrographs are provided, the brightest dots are platinum atoms, and cerium atoms. All catalysts exhibited distribution of platinum throughout the alumina support, as shown in images A, C, and E in Figure 2. Images at smaller scales showed differences between the three surfaces. Additional image of all three catalysts are available as Supplemental Materials, along with images of $\text{CeO}_x/\text{Al}_2\text{O}_3$ prior to platinum deposition. In the catalyst without ceria, most of the Pt is distributed in small, somewhat organized clusters, or even smaller groups of atoms without organization, rather than in discrete nanoparticles. An example of these clusters is shown in Figure 2B. The histogram in Figure 3A shows the distribution of cluster sizes, but it is important to remember the significant difference in the density of Pt atoms in the clusters compared to that in Pt nanoparticles.

The two catalysts containing ceria showed variations in surface particles resulting for the pre-deposition treatment of ceria with hydrogen. Those exhibited some ceria crystals with an average size of approximately 20 nm, visible in Figures 2C and 2E. In the catalyst that was not pretreated, shown in Figure 2C and 2D, platinum was distributed in the form of spherical nanoparticles. The diameter of these particles is mostly in the 2 to 4 nm range, and the distribution is shown in Figure 3B. The nanoparticles in this material are crystalline, as indicated by the lattice visible on the Pt particle in Figure 2D. Another interesting feature of this catalyst is the collection of crystalline ceria around the platinum nanoparticles, also depicted in Figure 2D. The accumulation of ceria around the platinum nanoparticles is further illustrated by EDS in Figure 2G, whose scale is shown in Figure 2H.

The pretreated catalyst, depicted in Figures 2E and 2F, exhibited a greater variation in structure of the platinum. Platinum clusters (1 nm) and platinum nanoparticles (2 nm – 4 nm) were present throughout the support, along with both atomically dispersed cerium and large ceria crystals (20 nm). The platinum clusters can account for the higher dispersion measured by CO pulse titration of the pretreated ceria-containing catalyst. A greater fraction of the platinum appears to have nucleated on ceria crystals than non-pretreated ceria-containing catalysts (Figure 2F), but the migration and accumulation around platinum observed in the other catalyst does not appear to have taken place. A particle size distribution analysis is provided in Figure 3C, but it should be noted that it is not only size that distinguishes the particle morphology here, but that the Pt atoms were present in the forms of disorganized groups, clusters without crystal structure, and crystalline nanoparticles.

The pretreatment of the supported ceria with H₂ prior to deposition of the Pt precursor was performed in order to create high-energy oxygen vacancies to promote the deposition of Pt on the ceria. The goal was to increase the interfacial area between the Pt and ceria in order to maximize the promoting catalytic effect of the ceria for WGS reaction. These results suggest that the pre-reduction of the ceria does affect the deposition of the Pt precursor, most notably in the fraction of the Pt that is nucleated on ceria. However, these catalysts also exhibited less uniform platinum particles, both in size and crystallinity. A possible explanation is that the surface oxygen vacancies resulted in local environments where deposited Pt(acac)₂ was more highly concentrated, enabling agglomeration of nanoparticles upon calcination and reduction. The other two catalysts, both the non-pretreated and the Pt-only catalysts show more uniform Pt particles.

3.3 Temperature-programmed reduction

Temperature-programmed reduction scans for all three catalysts, as well as for ceria on alumina without platinum and alumina exposed to supercritical CO₂, are provided in Figure 4. H₂-TPR measures the consumption of hydrogen by a material as the temperature is increased. The signal is proportional to hydrogen consumption, and because the temperature is ramped at a constant rate, higher signals indicate faster rates of reduction. Qualitatively, TPR can be used to compare interactions between metals and support surfaces. Stronger interaction between a particular metal and its support results in higher reduction temperatures.

For all TPR traces where Pt is present (A, B, and C) in Figure 4, the lower temperature peaks can be attributed to the reduction of platinum oxides to metallic platinum supported on ceria or alumina.[67, 68] For the material containing ceria on alumina (scan D), the small H₂ consumption peak centered at 360°C can be attributed to reduction of surface ceria. The higher temperature peaks result from interaction of CO₂ and the alumina support as shown in scan E. Desorption of CO₂ in the temperature range was confirmed by TGA-MS.

For the catalysts containing both platinum and ceria (A and B), the maximum rate of platinum reduction occurs at approximately 300°C. For the platinum catalyst without ceria (C), this maximum is at a lower temperature of approximately 270°C. The higher temperature required to reduce the platinum when ceria is present suggests a stronger stabilizing interaction with ceria than with alumina alone, confirming interaction between the platinum oxides and the ceria. While the reduction of surface ceria is also taking place in scans A and B, it is negligible in comparison to the reduction of Pt in those experiments, as can be seen by comparison to curve D.

3.4 Catalyst activity

Catalysts synthesized by the three preparation methods were evaluated over a range of temperatures for activity for WGS reaction. Reaction results are provided in Figure 5, along with a curve representing equilibrium conversion of CO based on feed composition. No methane formation or carbon deposition was observed in any of the experiments carried out and all CO conversion is attributed to water-gas shift reaction. The measured conversions are well below equilibrium conversions, as contact time was limited in order to measure reaction conversions that were kinetically limited.

Rates of reaction per mass of platinum are plotted in Figure 6 as a function of temperature. At a given temperature, the rate of the CO conversion follows the order Pt-CeO_x > Pt-pre-reduced CeO_x > Pt. Significant rate promotion is observed for the ceria-containing catalysts, as expected. Because the amount of Pt is similar, the difference between the two Pt-CeO_x catalysts must be attributed to the environment or the morphology of the Pt. Of particular interest is the ratio of platinum nucleated on ceria to that on alumina and the average ceria-interacting platinum particle size. Both of these characteristics affect the number of active Pt sites able to interact with ceria.

Differences between the ceria-containing catalysts that were observed by electron microscopy can be used to explain the differences in activity. While the catalyst pretreatment in H₂ did appear to result in more deposition of Pt in ceria-rich regions, it also resulted in greater particle variability. The pretreated catalyst exhibited some Pt clusters in addition to crystalline nanoparticles. The migration of ceria to form crystalline shells around the Pt nanoparticles in the non-pretreated catalyst served to increase the number of active interfacial sites, reportedly the active site of CO oxidation.[6, 21] Thus, the results indicate that rate

promotion due to platinum/ceria contact as well as the size distribution of platinum particles contribute to the differences in catalyst activity.

For comparison of the catalysts in this work to catalysts made by other means, examples of water-gas shift reaction studies using Pt/ceria catalysts under similar temperature, pressure, and feed composition were found. To ensure a fair comparison, the reported rates were adjusted to match the temperature and feed compositions in this study using a reported empirical rate law suited to these conditions:[17]

$$r = k \frac{P_{\text{CO}}^{0.1} P_{\text{H}_2\text{O}}}{P_{\text{CO}_2}^{0.1} P_{\text{H}_2}^{0.5}} \left[1 - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{K_{eq} P_{\text{CO}} P_{\text{H}_2\text{O}}} \right]$$

In each calculation, the equilibrium constant at the experimental temperature was used. Rates were adjusted where necessary to 260°C using the reported activation energies. The details of the calculations are provided in the Supplemental Materials.

The adjusted reaction rates and turnover frequencies are compared in Table 2. As the table demonstrates, the rates for the Pt-CeO_x/Al₂O₃ catalyst without pretreatment measured in this work are comparable to or slightly higher than most reported values for Pt-CeO_x catalysts. They are somewhat lower than the fastest rates in the table, both of which were Pt-CeO_x/Al₂O₃ measured in a coated in a microchannel reactor to facilitate heat and mass transfer.[69, 70] We propose that our rates are higher than most reported rates due to both the degree of platinum/ceria interaction and small platinum particle sizes. Comparison to those rates that are fastest suggests that investigation of internal mass transfer effects by variation of catalyst particle size is a promising next step.

Apparent activation energies were calculated using the Arrhenius plots in Figure 7. The rates plotted are calculated based on CO conversion and elemental analyses. To avoid including effects of concentration on rates in activation energy calculations, the highest conversions measured are not included in the plot. We note that the activation energy of the Pt-only catalysts is markedly higher than literature values. This can be attributed to strength

of interaction between the highly dispersed platinum clusters and the Al_2O_3 surface.[17]
With the addition of ceria to the Pt, the apparent activation energy drops significantly.
Between the two Pt-CeO_x catalysts, the activation energies are similar and comparable to other studies.

4. Conclusions

Pt-CeO_x/Al₂O₃ catalysts prepared using supercritical fluid deposition were synthesized and evaluated for activity for the water-gas shift reaction. Reaction rates per mass of platinum were highest for the catalyst in which post-deposition reduction and calcination results in migration of cerium atoms and collection of crystalline ceria around platinum nanoparticles having an average diameter of approximately 3 nm. Further studies are needed to fully elucidate the role of calcination and reduction in catalyst syntheses employing supercritical CO₂ for precursor deposition on oxide supports. The rates for the most active catalyst were comparable to some of the highest values found in the literature. These results demonstrate the potential of supercritical fluid deposition as a scalable technique for preparation of highly active and efficient precious metal catalysts for energy applications.

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Figure 1. Experimental apparatus for supercritical fluid deposition of organometallic precursor on catalyst support.

Figure 2. Images of catalysts prepared by supercritical fluid deposition, showing distribution of Pt and relative location of Pt and ceria. A and B: Pt/Al₂O₃, C and D: Pt-CeO_x/Al₂O₃ (not pretreated in H₂), E and F: Pt-CeO_x/Al₂O₃ (pretreated in H₂). G and H: EDS of non-pretreated Pt-CeO_x catalyst showing accumulation of ceria around Pt nanoparticles (ceria – red, Pt – blue) and corresponding STEM image.

Figure 3. Histograms representing particle and cluster size distribution on catalysts (assuming approximately circular shape). A: Pt/Al₂O₃ ($\bar{x} = 1.15$ nm, $\sigma = 0.27$), B: Pt-CeO_x/Al₂O₃ (not pretreated in H₂, $\bar{x} = 3.38$ nm, $\sigma = 0.78$), C: Pt-CeO_x/Al₂O₃ (pretreated in H₂, $\bar{x} = 1.42$ nm, $\sigma = 0.46$). Ceria analysis was performed qualitatively.

Figure 4. Temperature-programmed reduction scans for catalysts prepared using supercritical fluid deposition of $\text{Pt}(\text{acac})_2$, following calcination. Reducing gas is 5% H_2 in N_2 , and heating rate is 10 K/min. A: $\text{Pt-CeO}_x/\text{Al}_2\text{O}_3$ (pretreated in H_2), B: $\text{Pt-CeO}_x/\text{Al}_2\text{O}_3$ (not pretreated), C: $\text{Pt}/\text{Al}_2\text{O}_3$, D: $\text{CeO}_x/\text{Al}_2\text{O}_3$, E: Al_2O_3 exposed to supercritical CO_2 .

Figure 5. Conversion of CO via the WGS reaction on supported Pt catalysts: • Pt/Al₂O₃, ■ Pt-CeO_x/Al₂O₃, ▲ Pt-CeO_x/Al₂O₃ (pretreated). Reaction conditions: 1 atm, GHSV = 75,000 mL·g⁻¹·h⁻¹. Feed composition: 16% CO, 32% H₂, 32% H₂O, 20% N₂. Solid line represents thermodynamic equilibrium conversion.

Figure 6. Rates of WGS reaction on supported Pt catalysts: ● Pt/Al₂O₃, ■ Pt-CeO_x/Al₂O₃, ▲Pt-CeO_x/Al₂O₃ (pretreated). Conditions as noted with Figure 4.

Figure 7. Arrhenius plots used to calculate apparent activation energies for WGS reaction on supported Pt catalysts: • Pt/Al₂O₃, ■ Pt-CeO_x/Al₂O₃, ▲Pt-CeO_x/Al₂O₃ (pretreated). Conditions are as noted with Figure 4.

Table 1
Summary of catalyst characteristics and activity

Catalyst	Elemental Analysis	Pt Dispersion	Rate (mmol CO/g Pt/s)	TOF ^a (s ⁻¹)	Temperature (°C)	E _A (kJ/mol)
Pt/Al ₂ O ₃	0.85% Pt	75%	4.1	1.1	420	151±1
Pt-CeO _x /Al ₂ O ₃	0.95% Pt 6.0% Ce	54%	6.8	2.4	300	71±6
Pt-CeO _x /Al ₂ O ₃ (pretreated)	0.83% Pt 7.2% Ce	64%	3.8	1.2	300	74±10.

^a Turnover frequencies calculated as

$$TOF = rate \left(\frac{\text{mol CO}}{\text{g Pt} \cdot \text{s}} \right) \times \frac{195.09 \text{ g Pt}}{\text{mol Pt}} \times \frac{1}{dispersion} \left(\frac{\text{mol Pt}}{\text{mol surface Pt}} \right)$$

Table 2. Comparison of literature values for rates and turnover frequencies.

Catalyst composition	Rate ^a (mmol CO/ g Pt/s)	TOF ^a (s ⁻¹)	E _A (kJ/mol)	Preparation method ^b	Feed gas composition (%)						Ref.
					CO	CO ₂	H ₂	H ₂ O	CH ₄	inert	
0.3%Pt/CeO _x	1.3	1.1	72.7	DP	11	8	26	26	-	29	[6]
0.8%Pt/CeO _x	1.3	0.7	85.2	DP	11	8	26	26	-	29	[6]
1.1%Pt/CeO _x	1.5	0.6	84.6	UGCP	11	8	26	26	-	29	[6]
1.2%Pt/CeO _x	1.2	0.9	83.2	IWI	11	8	26	26	-	29	[6]
1%Pt/CeO ₂	2.1	1.4	75	IWI	6.8	8.5	37.3	22.0	-	25.4	[17]
0.49%Pt/CeO ₂	0.7	0.2	-	IWI	4.4	8.7	28.0	29.6	0.1	29.2	[16]
0.56%Pt- 6.7%Ce/TiO ₂	1.1	0.4	-	IWI	4.4	8.7	28.0	29.6	0.1	29.2	[16]
1.4%Pt- 8.3%Ce/Al ₂ O ₃	5.6	0.7	86	SG	9.6	8.4	32.2	23.0	-	26.8	[69]
0.79%Pt- 3.4%Ce/Al ₂ O ₃	7.8	0.7	76.8	IWI	10	10	30	20	-	30	[70]
0.95%Pt- 6.0%Ce/Al ₂ O ₃	2.4	0.9	71	SCFD	16	-	32	32	-	20	This work

^a If measured at temperatures other than 260°C, rates and TOFs are adjusted to 260°C using reported activation energies. Adjustments are also made for variation in feed composition.

^b DP = deposition precipitation, UGCP = urea gelation/co-precipitation, IWI = incipient wetness impregnation, SG = sol-gel, SCFD = supercritical fluid deposition