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Deactivation Mechanisms for Pd/Ceria During the Water-Gas Shift Reaction

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Abstract

The mechanism responsible for the irreversible deactivation of ceria-supported precious metals for the water-gas-shift reaction has been investigated through accelerated aging tests. It is shown that deactivation of Pd/ceria occurs more rapidly at 673 K compared to 523 K when operating with an integral reactor in 25 torr each of CO and H_2O. By heating a fresh catalyst in H_2, H_2O, CO, or CO_2, it was shown that deactivation occurs due to the presence of CO. Measurements of metal dispersion by CO adsorption and by x-ray diffraction show that deactivation on Pt/ceria and Pd/ceria catalysts in our studies was due to a loss of metal surface area. Finally, water-gas-shift rates on a series Pd/ceria catalysts with ceria crystallite sizes ranging from 7.2 to 40 nm and Pd loadings of either 1 wt% or 6 wt% demonstrated that rates were strictly proportional to the Pd surface area. Based on these observations, ceria-supported precious metals could be active and stable for the water-gas-shift reaction if steps are taken to avoid metal particle-size growth.

Introduction

Several reports have suggested that ceria-supported precious metals (PM) may be of interest as water-gas-shift (WGS) catalysts [1-5]. The activity of these catalysts can approach and even exceed that of conventional, low-temperature WGS catalysts like Cu/ZnO under some conditions. Moreover, the reaction orders on the precious-metal catalysts are favorable for achieving low CO concentrations [2]. Because the precious metals tend to be saturated with CO to low CO partial pressures, the rate expression tends toward zeroth-order in CO, rather than a positive order as found with Cu/ZnO catalysts, so that the ceria-supported PM catalysts exhibit high rates even at low CO pressures.

However, another recent report has claimed that the ceria-supported metals are not practical for the WGS reaction because of the high rate at which these catalysts deactivate [6]. The authors of this paper state that deactivation is due to the irreversible over-reduction of ceria in H_2 and imply that it will not be possible to stabilize ceria-supported metals for the WGS reaction. Obviously, developing a better understanding of these catalysts and how they deactivate is crucial for establishing whether or not ceria-based catalysts can be used for this application and for developing methods to stabilize these materials. For example, if deactivation were due to a loss of surface area in either the ceria or the precious metal, it should be possible to stabilize materials by proper catalyst design.

In this note, we will show that deactivation of Pd/ceria and Pt/ceria catalysts for the WGS reaction is likely due to the loss of metal surface area. High-temperature reduction in pure H_2 had no effect on the catalyst activity. Heating the catalyst in CO or a WGS reaction mixture did cause deactivation, but we observed a strictly linear relationship between activity and metal surface area. Finally, we measured rates using a series of ceria supports having a range of surface areas and crystallite sizes and found that the rates were independent of the ceria properties for calcination temperatures up to 1223 K.

Experimental

All of the catalysts used in this study were prepared at the University of Pennsylvania. In all cases, the supports were pure ceria, although the surface areas and crystallite sizes of the ceria were varied. For most of the samples, the ceria was prepared by simply decomposing $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.5%) in air. Samples with a range of surface areas could be prepared by varying the calcination temperature. To achieve a higher surface area for one

sample, ceria was precipitated from an aqueous solution using ammonium hydroxide, washed thoroughly with distilled water, dried overnight at 383 K, and finally calcined in air at 623 K. Table 1 shows a listing of the properties of the various ceria samples that were used in this study. Both Pt and Pd catalysts were prepared by wet impregnation of either $Pd(NH_3)_4(NO_3)_2$ (Aldrich 99.99%) or $PtCl_4$ (Alfa Aesar, 99.9%) onto the various ceria supports. Because the results for both Pt and Pd catalysts were similar and most of our effort was expended on the Pd catalysts, only selected results from Pt/ceria will be shown.

Kinetic measurements for the WGS reaction were performed in a ¼-inch, Pyrex glass, tubular reactor using approximately 0.10 g of catalyst. Water was introduced by saturation of a He carrier gas flowing through a de-ionized water saturator. While the reactor pressure was always atmospheric, the partial pressures of CO, H_2O and He were controlled by adjusting the relative flow rates of each component. All of the reaction measurements in this study were collected with partial pressures for CO and H_2O of 25 torr. For all measurements where rates are reported, the conversions of CO and H_2O were kept well below 10%, so that differential conditions could be assumed. Before analyzing the products, we always allowed the reaction to run for at least 30 min to avoid potential transients associated with catalyst conditioning. To ensure that the results were reproducible, the rates at each point were measured at least three times. The concentration of the effluent from the reactor was determined using an on-line gas chromatograph, SRI8610C, equipped with a Hayesep Q column and a TCD detector.

The Pd and Pt dispersions were determined by CO adsorption at room temperature. Because oxygen from ceria can react with CO adsorbed on Pd at near room temperature [2,7] and because CO_2 can adsorb on reduced ceria [7], a fixed pretreatment procedure was used on each of the catalysts. Specifically, 0.2 g catalyst was loaded into a sample cell and evacuated at 673 K. While holding the sample at 673 K, it was exposed to 200 torr of O_2 for several minutes, evacuated, and re-exposed to 200 torr O_2 and evacuated twice more. Afterwards, the sample was reduced in 200 torr H_2 for several minutes at 623 K, three times, to transform Pd to its metallic form. Finally, the sample was evacuated at 623 K and cooled to room temperature. CO uptakes were then determined by adding small pulses of CO until a rise in the pressure of the sample cell was detected. Because of the small volume above the sample, the accuracy of the endpoint determination was approximately 2%. For ceria samples without Pd or Pt, we observed no measurable adsorption of CO. In determining the Pd dispersion, we assumed an adsorption

stoichiometry of one CO molecule per surface Pd [8,9]. In the absence of precious metals, adsorption of CO on ceria was negligible.

Temperature-programmed-oxidation (TPO) measurements were performed on several samples to determine whether carbon formed on the catalyst after heating in CO or CO_2 and the temperature at which this carbon could be removed. These experiments used a tubular flow reactor with a mass spectrometer as the detector, similar to the apparatus used in pulse reactor studies described elsewhere [7]. These measurements demonstrated that any carbon-containing species formed on Pd/ceria catalysts in this study were removed by heating in O_2 below 673 K.

Results

Deactivation of the Pd/ceria, WGS catalysts at our normal testing temperature of 523 K was slow and difficult to measure over the period of 12 h. Therefore, in order to examine a range of variables that could be responsible for deactivation, it was necessary to establish a procedure for accelerated aging of the catalyst and for testing the effects of that aging. Fig. 1 illustrates a typical set of aging measurements performed on a catalyst with 1 wt% Pd on the ceria that had been calcined to 873K (surface area of 37 m^2/g). The sample size in this experiment was 0.10 g and the gas flow rate was maintained at 120 ml/min. For the first 200 min, the reaction was carried out at 523 K with 25 torr of both CO and H_2O in He and a stable conversion of 25% was observed. After 200 min, the temperature was increased to 673 K in the same reactant mixture, held at this temperature for 120 min, then cooled back to 523 K. After the high-temperature excursion, the conversion dropped to 15%, showing that substantial catalyst deactivation had occurred. After an additional 180 min in the WGS conditions, we again raised the sample temperature to 673 K and changed the reactant stream to 100 mL/min of pure O_2 for ~100 min. If impurities or over-reduction of ceria were responsible for catalyst deactivation, we reasoned that this oxidation step should have restored activity. However, when the temperature was again lowered to 523 K and the CO-H_2O reactant mixture restored, the CO conversion had increased to only 16%. An attempt to regenerate the catalyst in pure O_2 at 873 K for ~100 min increased the conversions to ~17%, but this is still significantly below the initial conversion of 25%.

In order to understand what species are responsible for catalyst deactivation, we performed a set of experiments similar to that described in Fig. 1. Again, the conversion of CO was measured for 25 torr each of CO and H_2O in He at 523 K on a fresh sample from the same catalyst batch as that used for the data in Fig. 1. After 150 min, the temperature of the sample

was raised to 673 K and the gas composition was changed to include only one of the reactants or products from the WGS reaction. After 90 to 120 min, the temperature was lowered to 523 K and the gas composition returned to the initial CO-H_2O-He mixture. Fig. 2a) shows the effect of treating the sample in 50 torr of H_2O at 673 K. The conversion of CO in the WGS environment was between 25 and 27% both before and after the H_2O treatment, demonstrating that heating in pure H_2O has little effect on the catalyst. Similar experiments for H_2 are shown in Fig. 2b). Again, there is no evidence for deactivation of the catalyst by heating it in pure H_2 at 673 K and there may even have been an increase in the conversions after the H_2 treatment. Fig. 2c) suggests that there is some effect on the catalyst of heating it in pure CO_2 at 673 K, but the change in conversion was again minimal compared to the changes observed in Fig. 1.

The effect of heating the catalyst to 673 K in pure CO had a dramatic effect on the catalyst activity, as shown in Fig. 2d). After this treatment, the WGS conversion at 523 K decreased from 25% to less than 3%. Calcination in pure O_2 at 873 K for 180 min partially restored the activity and a WGS conversion of ~18% was observed after oxidation. However, we were not able to restore the catalyst to its fresh activity after it had been heated in CO. Indeed, heating the catalyst in CO for 600 min at 673 K resulted in a further decrease in catalyst activity. Even after oxidation of the catalyst at 873 K, the conversion of CO in WGS at 523 K was still less than 12% after this long exposure to CO.

To determine what changes had occurred on the Pd/ceria catalyst after the various treatments, we measured the Pd dispersions using CO adsorption, the total surface areas using 2-propanol adsorption [10], and the ceria crystallite sizes using x-ray diffraction. This data is listed in Table 2, along with the corresponding CO conversions in WGS at 523 K. Based on the data in this table, it seems clear that the none of the pretreatments had any major effect on either the total surface area or the crystallite size of ceria. Rather, there was a marked decrease in the apparent Pd dispersion, as measured by CO adsorption uptakes, for the samples treated in either CO or CO_2. It is noteworthy that calcination in O_2 at 873 K increased the CO adsorption uptakes. While this could be consistent with removal of impurities from the Pd surface, TPO results indicated that all carbon impurities were removed by the pretreatments used in preparing the samples for the adsorption measurements. Furthermore, with Pd catalysts, re-dispersion of the metals under oxidizing conditions is well known [11].

In order to demonstrate the reliability of CO adsorption for measuring Pd dispersion, we prepared a second Pd/ceria catalyst with 6 wt% Pd on the ceria calcined to 873 K so that particle sizes could be determined by XRD line broadening. In agreement with the Pd dispersions determined from CO adsorption capacities, we observed an increase in the Pd particle size from ~3 nm to 8 nm after treating it in CO at 673 K for 10 hrs. Finally, it is interesting to compare our results to those of Shen and coworkers [12], who found a large increase in the size of Pd particles supported on ceria when the catalyst was used for methanol synthesis. The reactant species and temperatures used for methanol synthesis are obviously very similar to those used in WGS conditions.

We found similar results for on a 1-wt% Pt/ceria catalyst, although the rate of deactivation for the Pt catalysts is somewhat slower. The fresh catalyst, which had a dispersion of 45%, exhibited a WGS conversion of 23% using the same reaction conditions as those of Fig. 1. After heating the catalyst in flowing CO for 10 hr at 673 K, the WGS conversion at our standard conditions dropped to 18% and the Pt dispersion was found to have dropped to 28%.

To better understand how Pd dispersion and ceria crystallite size might affect WGS activities, we prepared a series of catalysts with 1 wt% Pd using each of the ceria samples listed in Table 1. We then measured the Pd dispersions with room-temperature CO adsorption and the differential rates for WGS at 523 K on 0.1 g of each of these materials. The WGS rates were measured at 25 torr each of CO and H_2O in He. We also measured differential rates on the deactivated samples in Table 2 and on the 6-wt% Pd sample used in the XRD measurements. All of this data is shown in Fig. 3, with rates plotted as a function of the CO adsorption capacity. All of the data fall along a straight line that goes through the origin. The obvious interpretation of Fig. 3 is that, for pure ceria, the rates depend only on the metal surface areas. While Pd dispersions tended to be higher on the ceria sample with higher surface areas, the rates did not seem to otherwise depend on the ceria crystallite size or surface area. The size of the Pd particles, calculated from the Pd dispersion, also did not play a major role in affecting the rates of the WGS reaction, at least for the range of parameters used in our study.

Discussion

Deactivation mechanisms for industrial reactions like WGS are difficult to establish because the loss in activity often occurs over a period of weeks, making it difficult to relate changes in catalyst properties to catalytic performance. In this paper, we propose an accelerated

aging test for ceria-supported precious metals that seems to mimic observations from long-term, WGS deactivation studies very well. While simulated aging studies cannot replace long-term testing under industrial conditions, they provide very useful information about the properties of catalysts. Our studies demonstrate that the deactivation of Pd/ceria and Pt/ceria catalysts under WGS reaction conditions is likely due to a loss of the metal surface area and probably not to any fundamental changes in the ceria. It seems highly unlikely that over-reduction of ceria can be a major deactivation mechanism, since high-temperature treatments in H_2 do not affect activity and since high-temperature oxidation does not restore the activity of deactivated catalysts.

It is somewhat surprising that WGS reaction rates vary so linearly with Pd surface area over such a wide range of Pd particle sizes. Given that the WGS reaction on Pd/ceria appears to be due to bi-functional mechanism, with ceria supplying oxygen from water to the Pd and CO oxidation occurring on the Pd surface [13], one might expect that the rates would depend on the circumferential area at the interface between Pd and ceria, similar to what has been reported for ceria-mediated rates of CO oxidation on Rh/ceria catalysts [14]. However, based on a recent paper by Smirnov and Graham [15], who showed that Pd particles were completely oxidized by a ceria-zirconia film upon mild heating in vacuum, it seems reasonable that the entire surface of the Pd particles could be effective for catalyzing the oxidation reaction if the rates of oxygen transfer from ceria to Pd were comparable to the overall reaction rate.

It is also noteworthy that the ceria crystallite size had no effect on the rates, at least for the range of ceria crystallite sizes, between 7.2 and 40 nm, used in this study. In previous work, it had been shown that ceria, when it has been heated to high temperatures, loses its ability to transfer oxygen [13,16]. WGS catalysts prepared from ceria that has been deactivated in this way showed catalytic activities that were orders-of-magnitude less active than their fresh counterparts [13]. However, it appears that ceria deactivation occurs rather abruptly following calcination above 1270 K, rather than decreasing progressively with crystallite size [13,16]. In both earlier studies from our laboratory and from the results shown here, we do not observe a dependence on rates so long as the ceria has not been treated so harshly that it is completely deactivated. It has been suggested that deactivation of ceria might be associated with removal of defects in the structure and that removal of defects occurs in a narrow temperature range [17]. If this mechanism is proven to be correct, it would tend to confirm that crystallite size of ceria is not an important parameter.

It is at first somewhat surprising that treatment of Pd/ceria catalysts in CO under such mild conditions should result in the dramatic growth of Pd particles, even though others have reported this effect earlier [12]. However, several mechanisms for Pd particle growth are possible. First, it is known that CO adsorption on Pd single crystals can cause the movement of surface Pd atoms at even lower temperatures than that used for our deactivation studies [18]. Second, reduction of Pd-ceria catalysts in CO has been shown to lead to carbonates on the ceria surface and these carbonates can be removed by re-oxidation in either O_2 or H_2O [2]. The restructuring of the ceria support could well result in Pd particle growth.

Despite remaining questions about how Pd particles grow under WGS conditions, the results of our present study indicate that the rates on Pd/ceria catalysts have an intrinsic value that can be modified by increasing the metal dispersions and are probably unaffected by ceria structure so long as ceria is not treated too harshly [13]. The effect of promoters on Pd/ceria can be dramatic [19], but attempts to stabilize these ceria-based catalysts also requires focussing on methods for maintaining metal dispersions. There is clearly a large amount of expertise available for accomplishing this in industrial catalysts, so that ceria-supported, precious metals could indeed find application as stable water-gas-shift catalysts for specialty applications.

Summary

Based on accelerated aging studies, deactivation of Pd/ceria and Pt/ceria catalysts for the water-gas-shift reaction is due to the growth of metal particles in CO. We find no evidence for deactivation by over reduction of ceria. Since it should be possible to develop stable water-gas-shift catalysts based on ceria-supported metals by introducing methods for maintaining the metal surface areas, we disagree with recent claims that arguing that these catalysts cannot be stabilized.

Acknowledgement

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Figure Captions

Fig. 1. An accelerated aging test for deactivation for a 1 wt% Pd/ceria catalyst prepared using ceria calcined to 873 K. The CO conversions were obtained using an integral reactor at 523 K with 25 torr each of CO and H_2O in a He carrier. The accelerated aging was accomplished using the following temperatures and gas compositions:

A) 673 K in 25 torr each of CO and H_2O;

B) 673 K in pure O_2 flow;

C) 873 K in pure O_2 flow.

Fig. 2. Accelerated aging tests for 1 wt% Pd/ceria catalysts, prepared using ceria calcined to 873 K, when heated in the presence of individual reactant or products gases. The CO conversions were obtained using an integral reactor at 523 K with 25 torr each of CO and H_2O in a He carrier.

a) Effect heating Pd/ceria in 50 torr H_2O vapor at 673 K.

b) Effect of heating in pure H_2 flow at 673 K.

c) Effect of heating in pure CO_2 flow at 673 K.

d) Effect of heating in pure CO flow at 673 K, followed by re-calcination in pure O_2 flow at 873 K.

Fig. 3. A plot of differential, water-gas-shift rates as a function of CO adsorption capacity for a series of Pd/ceria catalysts in 25 torr each of CO and H_2O at 523 K. Data are shown before and after deactivation for some of the catalysts. The symbols correspond to the following catalysts: ◆ 1 wt% Pd/ceria, with ceria calcined at 873 K; ■ 6 wt% Pd/ceria with ceria calcined at 873 K; Δ 1 wt% Pd/ceria with ceria precipitated and calcined at 623 K; ● 1 wt% Pd/ceria with ceria calcined at 1073 K; ▲1 wt% Pd/ceria with ceria calcined at 1223 K.

Table 1 Properties of the ceria supports.

Catalyst Calcination Temperature (K)	Surface Area (m^2/g)[a]	Crystallite Size (nm)[b]
623[c]	65	7.2
873	37	11.
1073	10	32.
1223	3	40.

a) The surface areas were determined from the amount of 2-propanol that adsorbed irreversibly at room temperature, as discussed in Reference [10].
b) Determined using the XRD line width of CeO_2(111), using the Scherrer equation.
c) This ceria was prepared by precipitation using methods described in the text.

Table 2 Summary of the catalyst properties following the accelerated aging tests in Figs. 1 and 2.

Catalyst	Fresh Catalyst	After WGS at 673 K for 120 min[a]	H_2O 673 K	H_2 673 K	CO 673 K[a]	CO_2, 673 K[a]
WGS, CO Conversion (%)	25	15 (18)	25	27	After 2 hrs: 3 (17) After 10 hrs: 2 (12)	2 hrs: 22 10 hrs: 16 (23)
Pd Dispersion (%)	23	14 (19)	25		After 10 hrs: 3 (10)	10 hrs: 16 (23)
Surface Area[b] (m^2/g)	37	37			After 10 hrs: 32	10 hrs: 32
Ceria Crystallite size (nm)	11.3	11.0	11.0	10.6	10.7	10.7

a) Values in parenthesis were obtained after calcination in pure O_2 at 873 K.
b) Determined from 2-propanol adsorption [10].

Figure 1

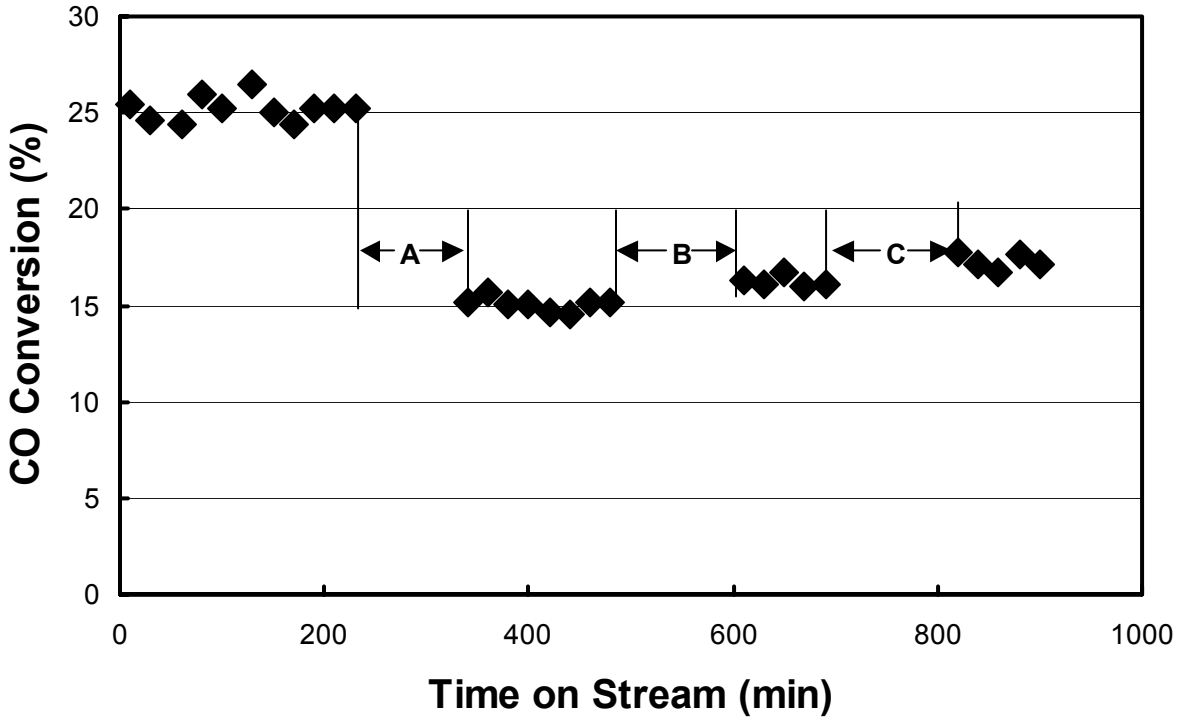
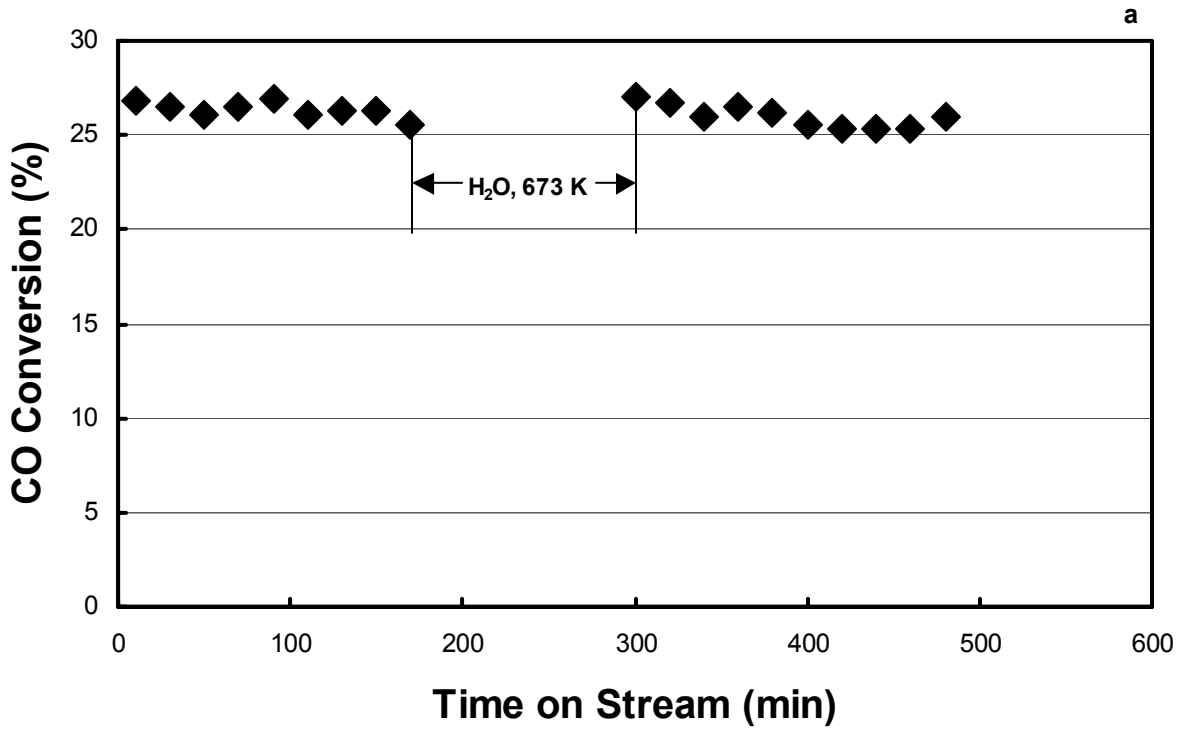

30
25
20
15
10
5
0
CO Conversion (%)
A
B
C
0
200
400
600
800
1000
Time on Stream (min)

Figure 2 a)


a
30
25
20
15
10
5
0
CO Conversion (%)
H2O, 673 K
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100
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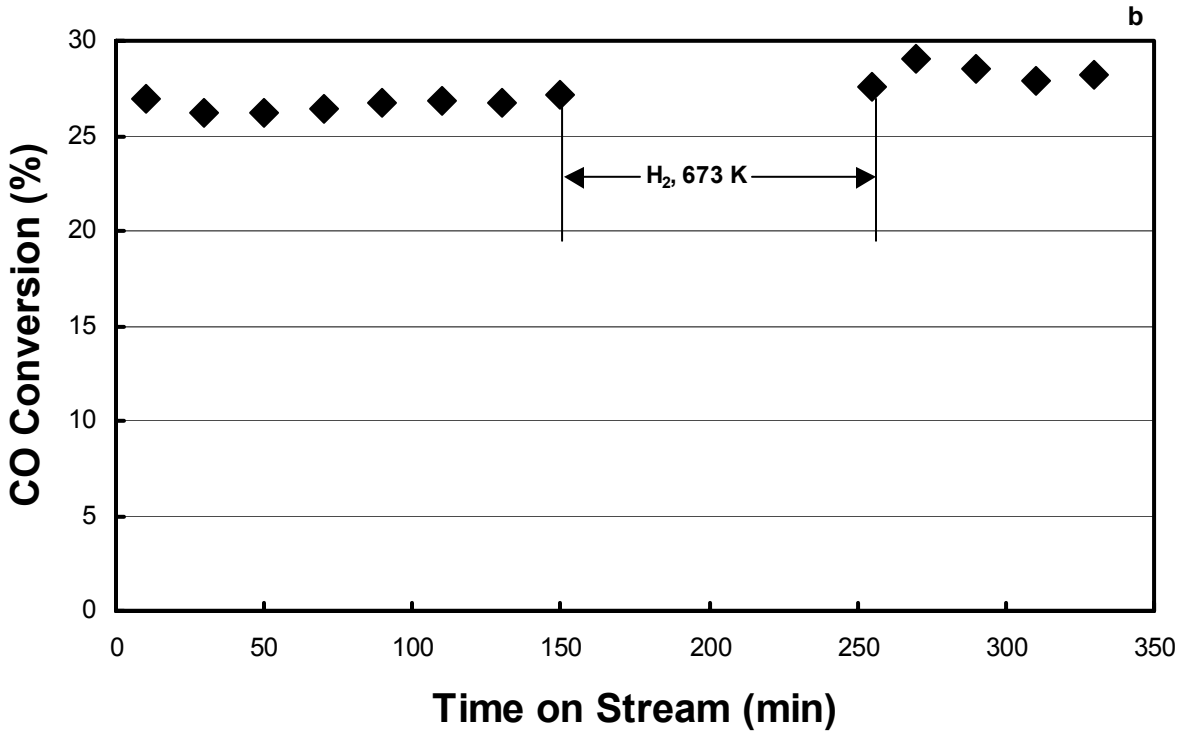
300
400
500
600
Time on Stream (min)

Figure 2b)


b
30
25
20
15
10
5
0
CO Conversion (%)
H2, 673 K
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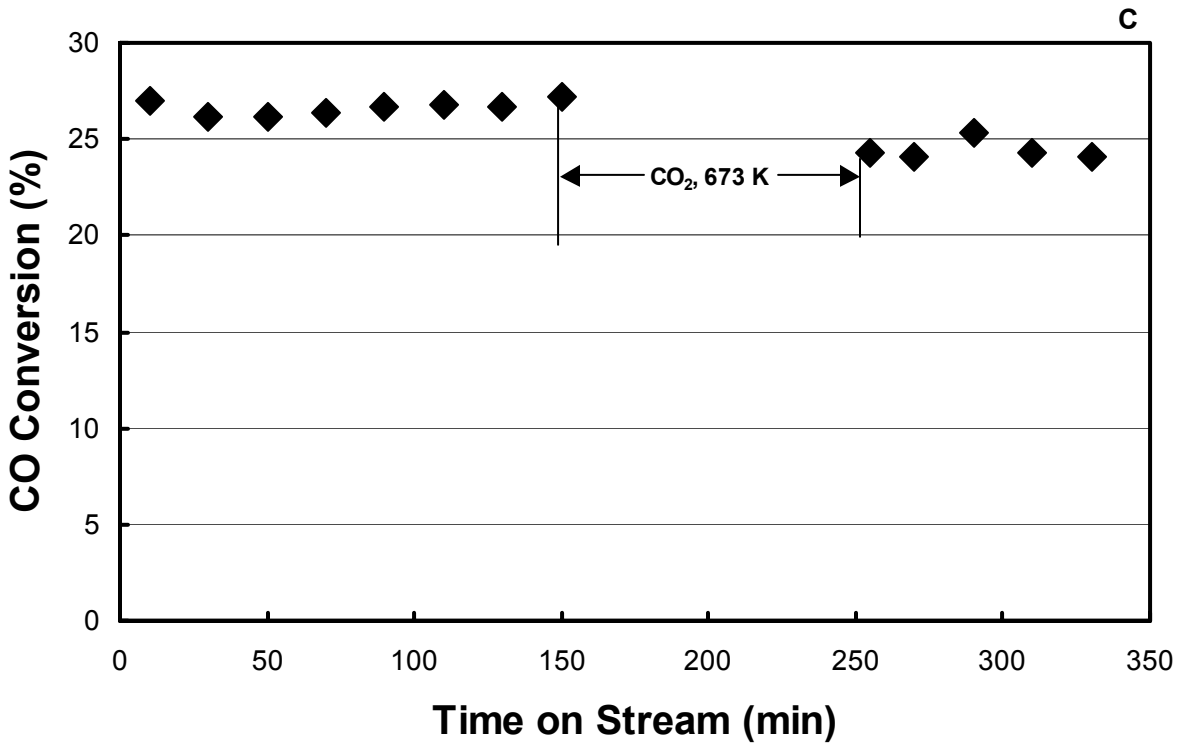
50
100
150
200
250
300
350
Time on Stream (min)

Figure 2c)


C
30
25
20
15
10
5
0
CO Conversion (%)
CO2, 673 K
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50
100
150
200
250
300
350
Time on Stream (min)

Figure 2d)

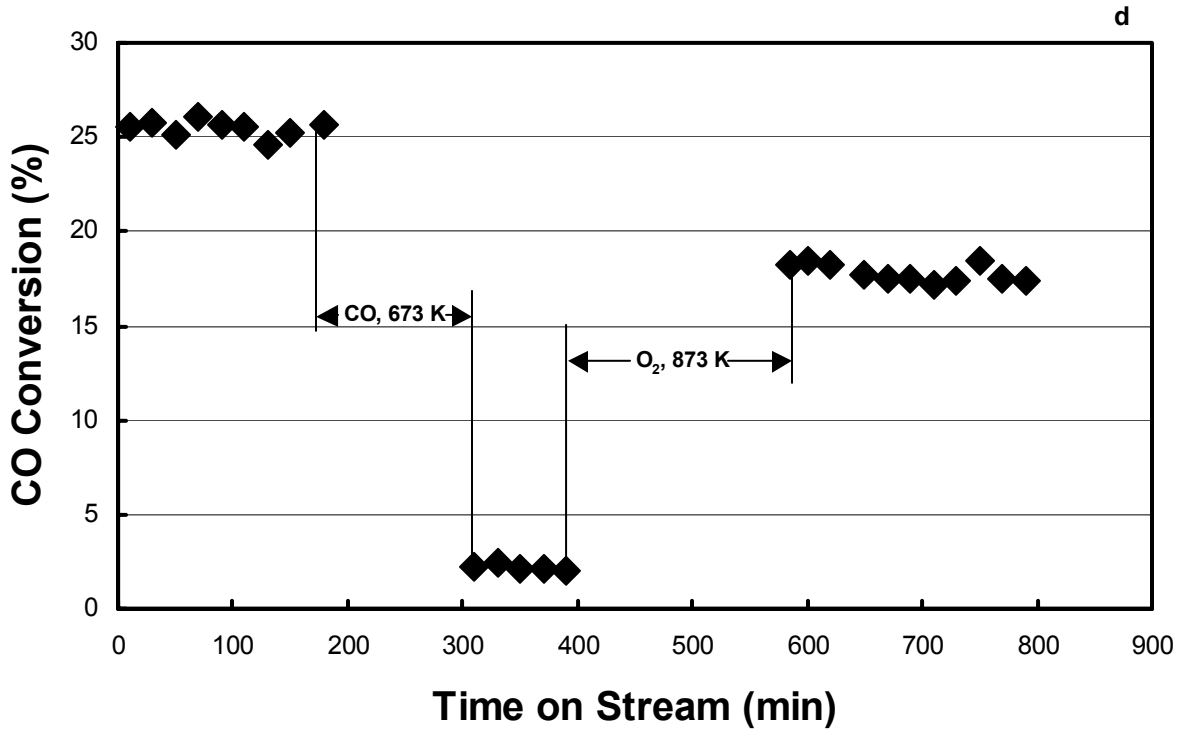
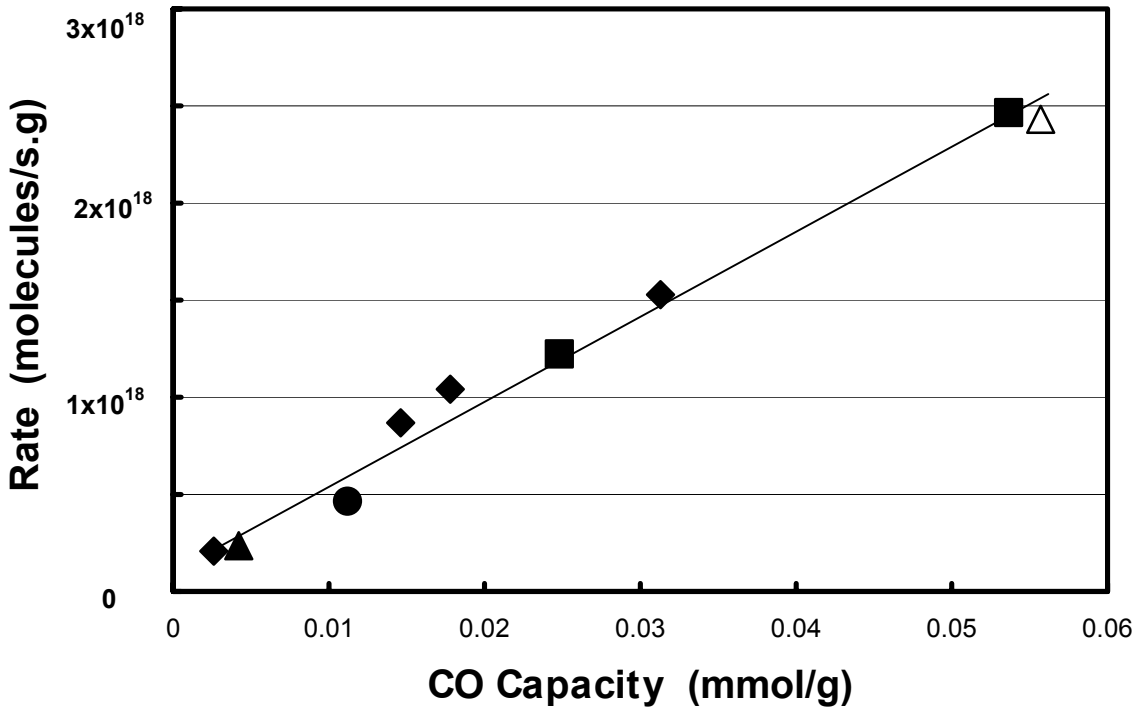

d
CO Conversion (%)
Time on Stream (min)
CO, 673 K
O2, 873 K
0
5
10
15
20
25
30
0
100
200
300
400
500
600
700
800
900

Figure 3


3x10^18
2x10^18
1x10^18
0
Rate (molecules/s.g)
0
0.01
0.02
0.03
0.04
0.05
0.06
CO Capacity (mmol/g)