CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalytic Activity of Commercial Catalyst

Firstly, the WGS catalytic activity was tested with a commercial catalyst as a benchmark for gold-ceria catalysts and used as a reference data for lab-scale experiment. In all tests, the CO was converted to CO_2 and no methanation reaction was observed on both HTS and LTS reactions.

4.1.1 High-Temperature Water-Gas Shift Activity

Firstly, HT-WGS catalytic activity was performed to determine the outlet concentration of CO after HT-WGS unit before passing through the LTS unit.
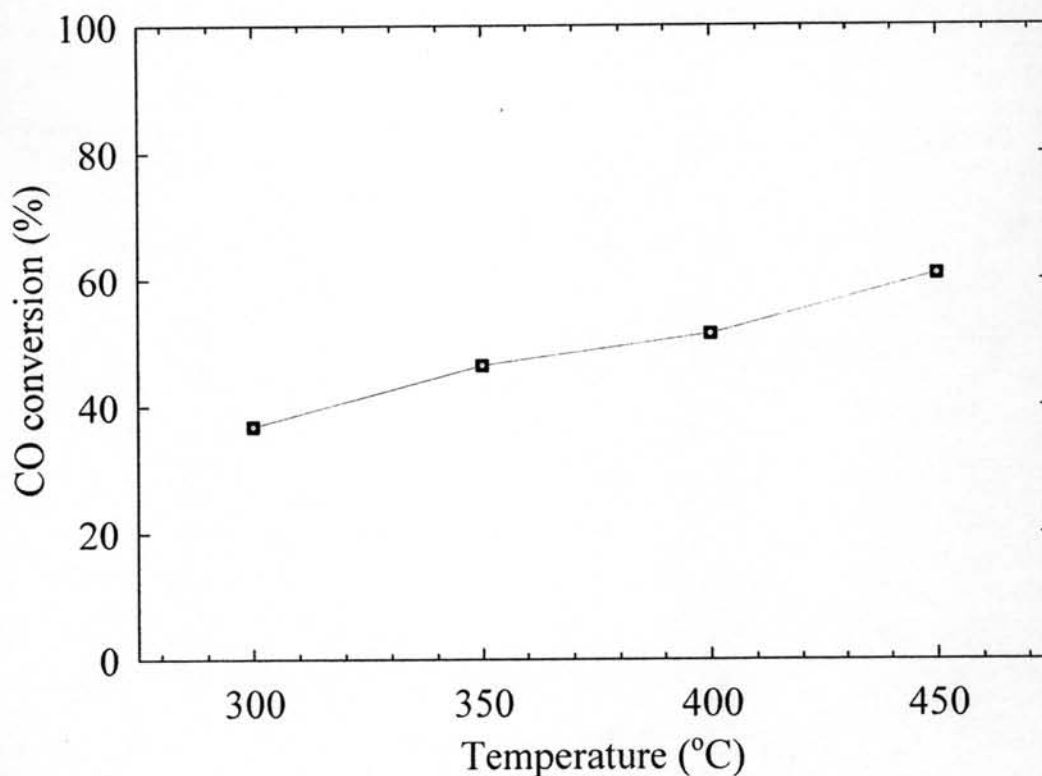
Figure 4.1 The HT-WGS catalytic activity of commercial catalyst, Shiftmax 120 at $SV = 50,000$ ml·h^{-1}·g^{-1} as a function of the reaction temperature. Reaction condition: 8% CO and 8% H_2O balanced with helium.

The HT-WGS commercial catalyst obtained from Süd-Chemie, Shiftmax 120, was used in this experiment with 8% CO concentration and 8% H_2O in form of steam.

The initial CO concentration was 8% which is generally in range of the outlet concentration from steam reforming unit (7-12 %CO). The reaction was performed at temperature range from 300 to 450° C with a space velocity of 50,000 $ml \cdot h^{-1} \cdot g^{-1}$. The catalytic activity of Shiftmax 120 is shown in Figure 4.1. The CO conversion slightly increased from 36.8 % up to 60.87 % from 300 to 450°C (~4% CO left) without methanation. This is because the exothermic behaviors of water-gas shift reaction.

4.1.2 Low-Temperature Water-Gas Shift Activity

For LT-WGS catalytic activity, the CO outlet concentration from HT-WGS unit was used as a CO inlet concentration of LT-WGS unit. The 4% CO
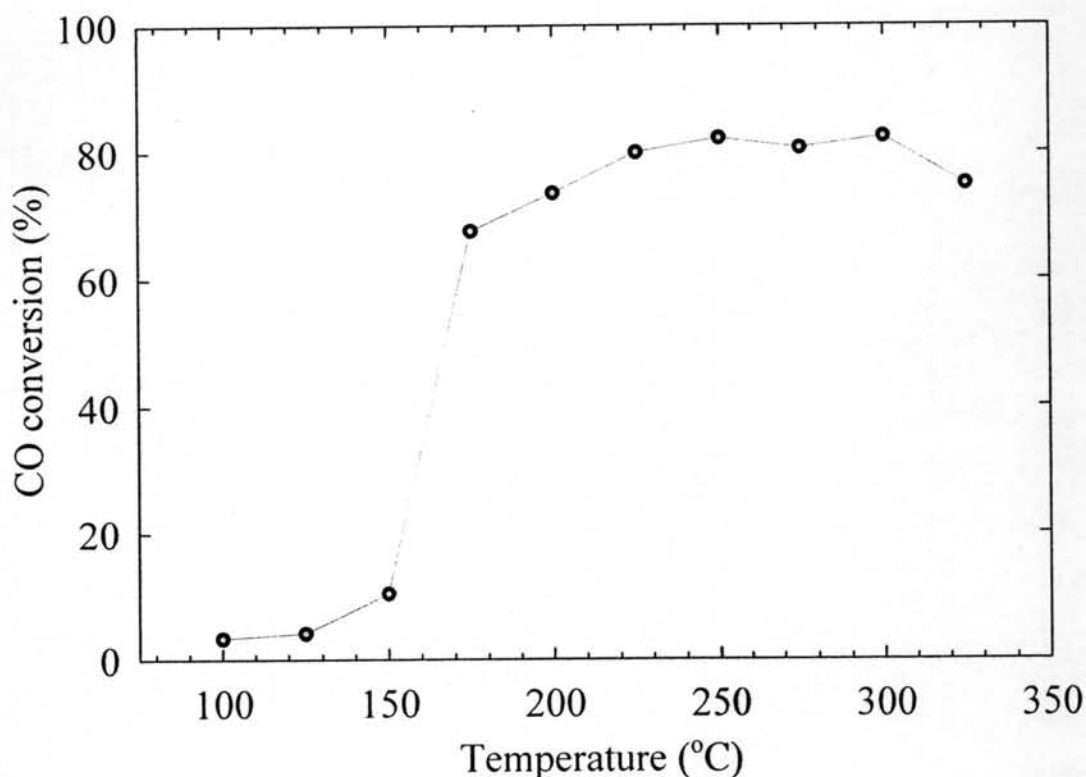

Figure 4.2 The LT-WGS catalytic activity of commercial catalyst, Shiftmax 230 at SV = 30,000 $ml \cdot h^{-1} \cdot g^{-1}$ as a function of the reaction temperature. Reaction condition: 4% CO and 8% H_2O balanced with helium.

balanced with helium was mixed with steam before getting through the reactor. The commercial LTS catalyst, Shiftmax 230, was used as a benchmark for the prepared gold-ceria catalyst. 0.16 g (0.148-0.224 mm) of Shiftmax 230 was used. The total flow rate was 80 ml/min, 32 ml/min of 10% CO/He and 48 ml/min of helium (to get 4% of CO) at the temperature range of 100-325° C with a space velocity of 30,000 $ml \cdot h^{-1} \cdot g^{-1}$. The catalytic activity of Shiftmax 230 is shown in Figure 4.2. From the results, the LT-WGS of Shiftmax 230 exhibited the high CO conversion, 67.63%, at above 175 °C and could reduce the CO concentration from 4% to less than 1%.

4.2 Catalytic Activity of Au/CeO$_2$ Catalysts

A series of 1-5 % gold loading over LS-ceria and HS-ceria catalysts (DP) was studied in LT-WGS with an exact inlet CO concentration amount (4%). All of the effects were studied in lab-scale. The reactant flow was adjusted to meet the desired composition while the amount of catalyst was kept constant. The gold-ceria-LS catalysts were used first in the first three variables which are the effect of space velocity, gold loading, and H_2-pretreatment. Whereas, the gold-ceria-HS samples were used to study the effect of water to CO ratio, H_2-mixing on the catalytic performance and stability test was also carried out.

4.2.1 Effect of Space Velocity

From other previous literature works, the LT-WGS activity with gold-ceria catalyst was normally tested at low space velocities. In 2002, Andreeva *et al.* studied the gold-ceria catalysts with varied space velocities, 4,000, 8,000, and 12,000 h^{-1} while Tabakova *et al.* (2004) studied the preparation effect of gold-ceria catalysts at space velocity of 4,000 h^{-1}. Not only gold-ceria catalyst was studied at low space velocity but other metal in IB group (Ag and Cu) were also investigated on LTS reaction by Tabakova *et al.* at the same space velocity in 2006. The copper on ceria catalyst was also studied by Zerva *et al.* (2006) at very low space velocity, 750 h^{-1}, whereas gold on high surface mesoporous zirconia (Au/ZrO$_2$) was recently investigated on LTS reaction by Idakiev *et al.* (2006) at space velocity of 4,000 h^{-1}. Therefore, the prepared gold-ceria catalyst was primarily tested with the several of space

velocities to investigate the efficiency of the prepared catalyst comparing with Shiftmax 230. 0.45 g of 2% gold-ceria-LS catalyst was used without any pretreatment condition. The velocity of reactant gas was varied among 30, 60 and 90 ml/min in order to get the exact space velocity of 4,000, 8,000, and 12,000 $ml \cdot h^{-1} \cdot g^{-1}$ respectively while at 30,000 $ml \cdot h^{-1} \cdot g^{-1}$, the reactant condition was as same as the condition of Shiftmax 230, the steam was carried by helium as same ratio as CO amount (4 vol. %).
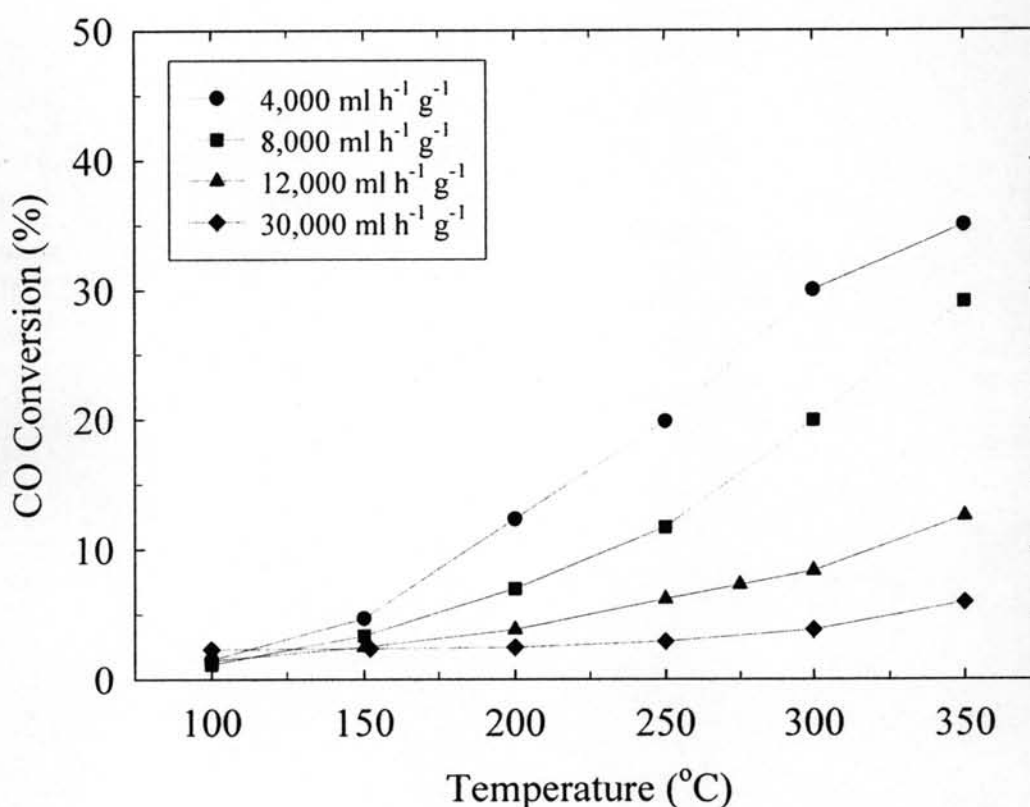

Figure 4.3 Effect of space velocity on the LT-WGS activity of 2% Au/CeO$_2$ –LS catalyst at different space velocities as a function of the reaction temperature. Reaction condition: 4% CO and 4% H$_2$O balanced with helium.

Figure 4.3 shows the LT-WGS activity of 2% gold-ceria-LS catalyst at different space velocities. Increasing the space velocity resulted in the anticipated decrease in the conversion. At space velocities of 30,000 and 12,000 $ml \cdot h^{-1} \cdot g^{-1}$, CO conversion was almost independence from temperature reaction but at lower space

velocities of 4,000 and 8,000 ml·h^{-1}·g^{-1}, CO conversion was significantly increased as reaction temperature increased. At 30,000 ml·h^{-1}·g^{-1}, CO conversion of the prepared gold-ceria catalyst was very low, 5.93% even in high temperature range while Shift-max 230 showed very high CO conversion after 175 °C, 67.73% at the same space velocity. Nevertheless, the highest CO conversion of 2%Au/CeO$_2$-LS was achieved at 4,000 ml·h^{-1}·g^{-1}. The maximum CO conversion was 35% at 350° C.

From the result, the efficiency of the prepared gold-ceria catalyst was still less than the Shiftmax 230 which can be performed at higher space velocity with excellent physical strength. The CO conversion of gold-ceria catalyst was valued below 12,000 ml·h^{-1}·g^{-1}. This may be from the increasing of contact time between reactant gas and active site resulting to the more CO conversion. The effect of space velocity is in the same trend with previous work reported by Andreeva et al. (2002) but much less efficient. However, Sakurai et al. (2005) showed that gold-ceria catalyst had higher activity than the commercial catalyst, CuO/ZnO/Al$_2$O$_3$.

4.2.2 Effect of Gold Loading

Since Au/Fe$_2$O$_3$ and Au/Al$_2$O$_3$ catalysts has been first investigated on LT-WGS reaction (Andreeva et al., 1996), most of previous works have concerned with the amount of gold loading and the diameter of gold particle on the activity of LT-WGS reaction (Sakurai et al., 1997, Fu et al., 2001, Andreeva et al., 2002, Jacob et al., 2005).

To study the LT-WGS activity and characteristic of ceria support which were affected from the different amount of gold loading, 1%, 2%, and 5% of gold were loaded onto a commercial ceria-LS, DP method and were investigated in LT-WGS reaction at SV = 4,000 ml·h^{-1}·g^{-1} in the temperature range of 100-350 °C. The composition of reactant was 4% CO and 4% H$_2$O balanced with helium.

The CO conversion of 1%, 2%, and 5% gold loading on ceria-LS is presented in Figure 4.4. From the result, it can be noticed that the activity of 2% gold-ceria sample has comparable to 5% gold-ceria sample while the activity of 1% gold-ceria sample was much lower. The commercial ceria-LS catalyst was also tested in the same condition but it was almost inactive at any temperature for the WGSR.
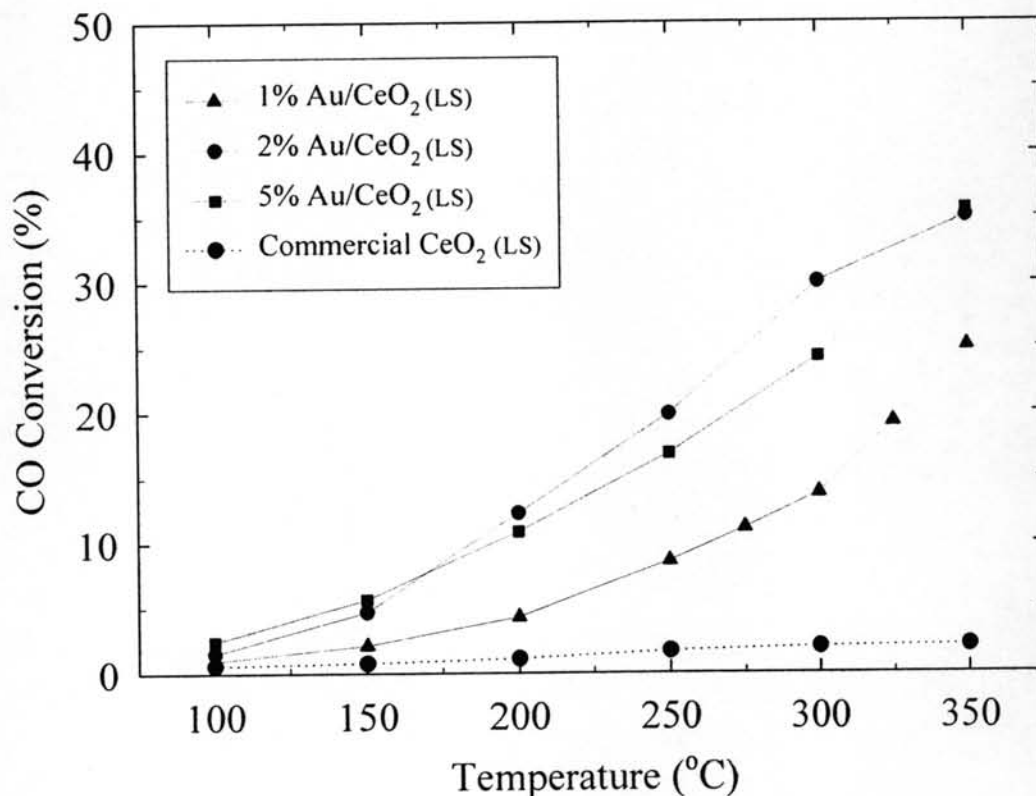
Figure 4.4 Effect of gold loading on the LTS activity of 1%, 2%, and 5% Au/CeO₂ - LS catalysts at SV = 4,000 ml g⁻¹ h⁻¹ as a function of the reaction temperature. Reaction condition: 4% CO and 4% H₂O balanced with helium.

The catalyst characterization was then performed to investigate the characteristic of samples. The XRD technique was used to identify the presence of Au and the crystallinity of the prepared catalysts.

XRD patterns of the prepared catalyst using ceria low surface area (CeO₂-LS) as a support is presented in Figure 4.5. The prepared catalysts are 1%, 2%, and 5% gold-ceria-LS compared with the commercial ceria-LS support. The distinct diffraction peak of ceria was observed in all samples. The CeO₂ peaks at 28.6° and 47.5° respecting to plane (111) and (220), the major peak of CeO₂, were almost unchanged after the addition of gold. For the diffraction peak of gold, the peak at ~ 38° was only observed in 2% and 5% Au/CeO₂ samples as a small broad peak corresponding to Au (111) while 1% gold-ceria sample did not reveal the evidence of gold
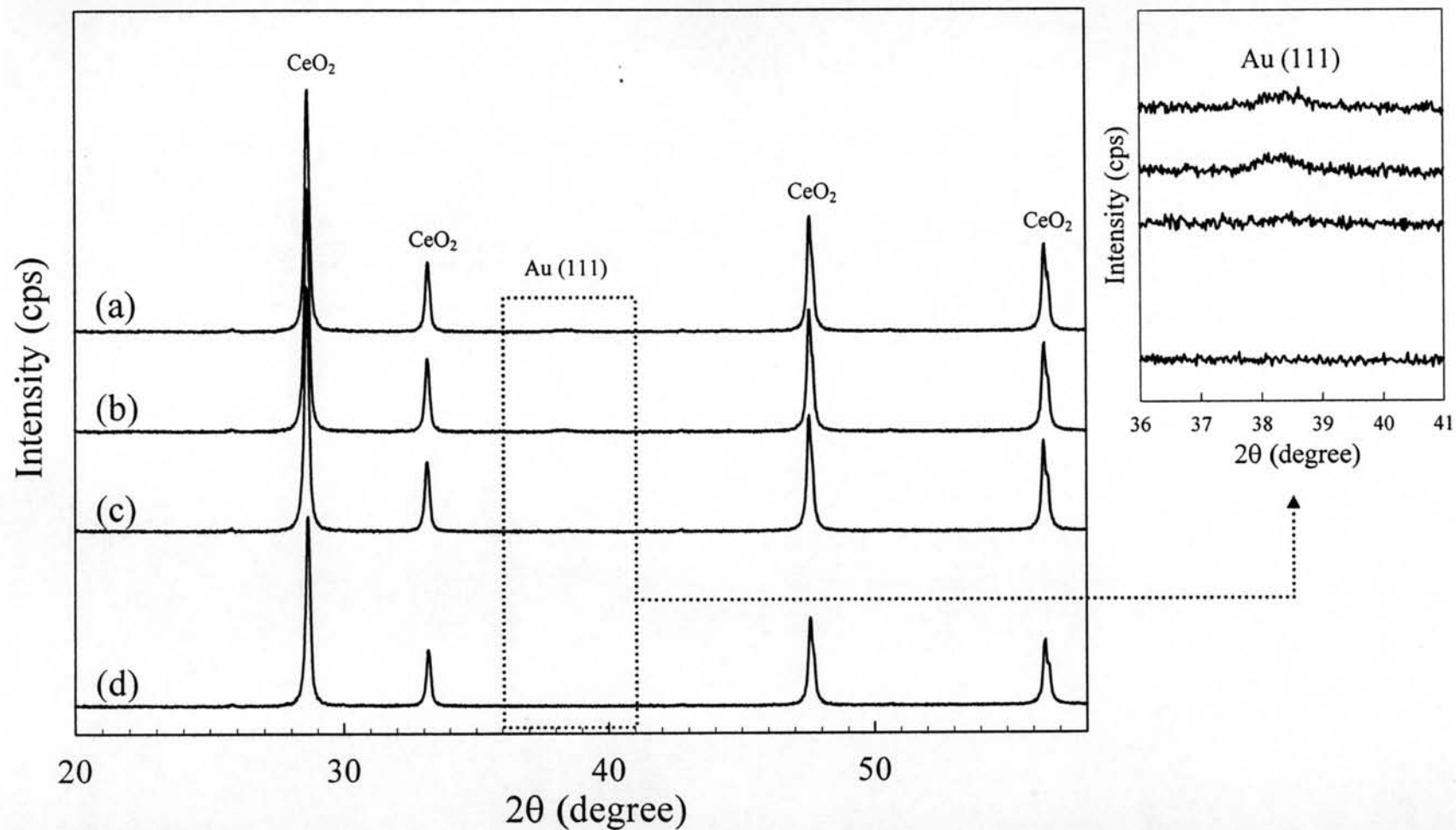
Figure 4.5 XRD patterns of (a) 5% Au/CeO$_2$-LS (b) 2% Au/CeO$_2$-LS (c) 1% Au/CeO$_2$-LS (d) CeO$_2$-LS in the range of 2θ from 20° to 60° with scan speed 5 degrees/minute and scan step 0.02 degree. The small graph shows magnification of XRD patterns from 36° to 41°.

particles. With increasing gold loading, the gold diffraction peak is more pronounced, but the full width at half peak maximum (FWHM) remains unchanged. This could be attributed to the fact that the gold particle size is too small and also that is under detection limit of this technique. For the secondary diffraction peak of Au at ~ 44° which attributed to Au plane (200), the peak could only be detected from the XRD pattern of 5% gold-ceria sample plausible to the higher amount of gold loading in the sample. Transmission electron microscopy (TEM) was also used to study the sample morphology and to determine the gold particle size.

The size distribution of gold metal is one of the important factors which are influence to CO oxidation reaction (Okamura et al. 1997) and also LT-WGS reaction (Andreeva et al. 1996 and 1998). Considering of the mechanism of WGS reaction on gold catalyst is made difficult. However, one of the evidently proposed of WGS mechanisms has been published that the reaction proceed at the boundary between metallic gold particle and ceria, where CO adsorption on gold and H_2O dissociation on ceria defects take place, see Figure 2.5 (Bocuzzi et al., 1999 and Tabakova et al., 2003). Following from this hypothesis, the smaller gold particle size should provide the higher activity because of the increasing of active sites.

The TEM images show the distribution of gold at different magnifications of prepared catalysts, 1%, 2%, and 5% Au/CeO_2-LS, respectively as shown in Figure 4.6 – 4.8 while Figure 4.9 presents the estimated particle size distribution of gold for each sample. The images of LS-samples clearly showed the deposition of gold particles on larger ceria particles. From the taken images, the gold distribution of 1% gold-ceria sample thoroughly dispersed along the ceria particles with very small particle with an average particle size of 10.12 nm. Most of them are less than 15 nm and the most fraction of gold particle is in the range of 6-10 nm while no gold particle size more than 30 nm was observed (see Figure 4.9).
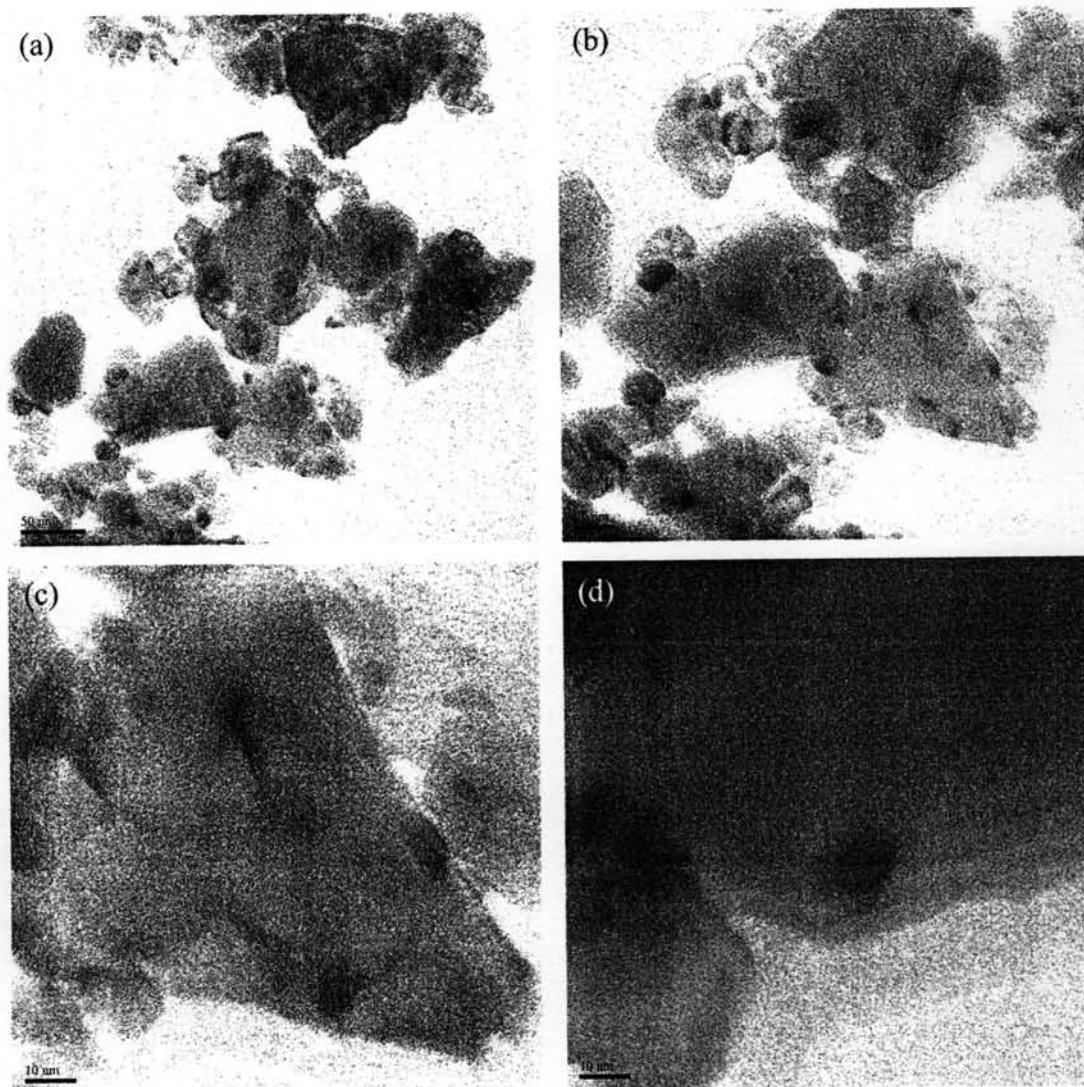
Figure 4.6 TEM images of 1%Au/CeO$_2$-LS catalyst at different magnifications; (a) at 50,000 magnification with 50 nm scale, (b) at 80,000 magnification with 20 nm scale, (c) at 200,000 magnification with 10 nm scale, (d) at 200,000 magnification with 10 nm scale.

For 2% gold-ceria sample, the dispersion of gold was less than that of 1% gold-ceria sample. As can be observed from Figure 4.7 (a), some of ceria particles had no deposition of gold on them so; most of them are in the range of 6-20 nm. However, the most fraction of gold particle is still in the range of 6-10 nm with the average particle size of 13.23 nm. The distribution tended to move to the bigger gold particle size when amount of gold loading increased. As can be observed, the fraction

at 1-5 nm was decreased while the fraction at more than 30 nm was observed (see Figure 4.9).
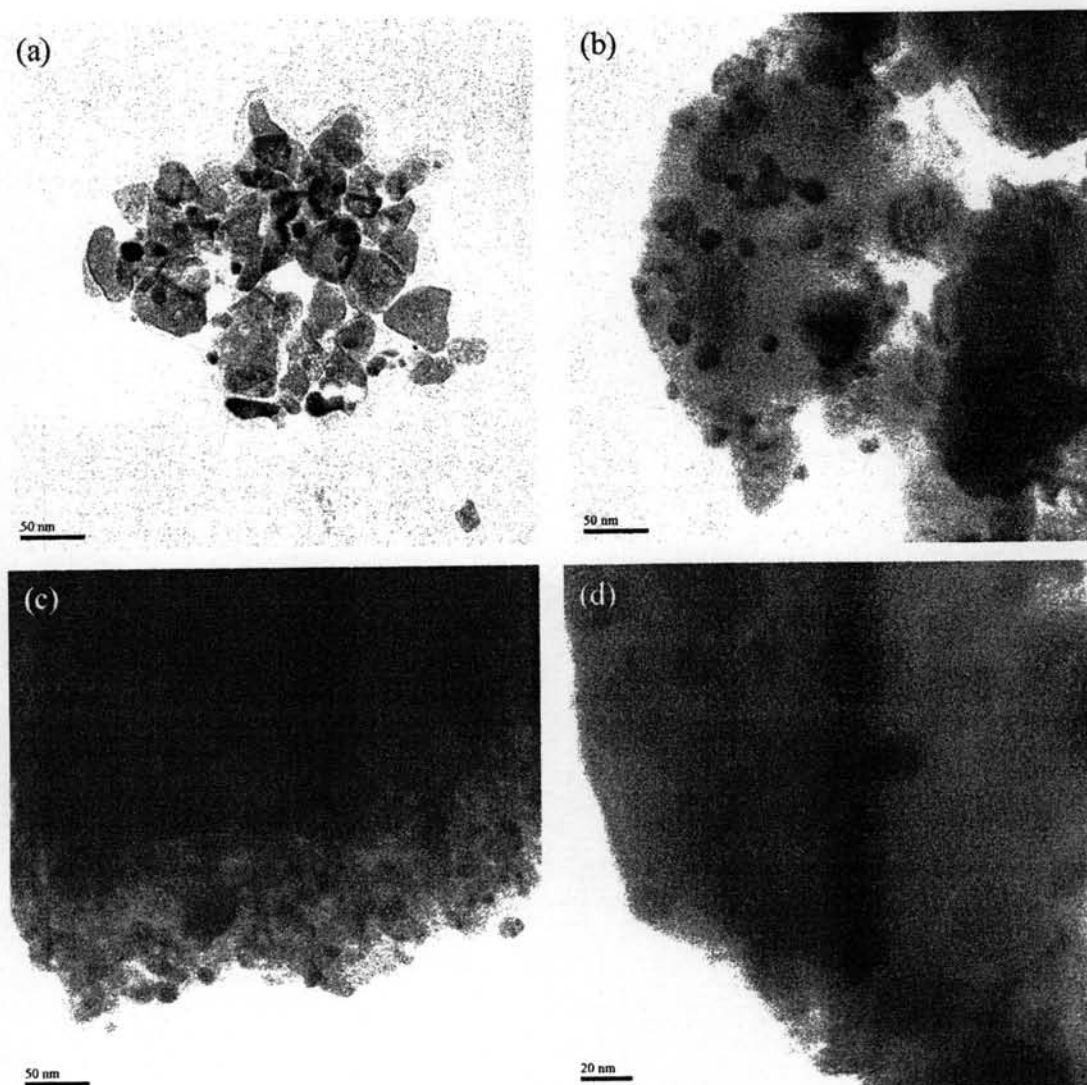

Figure 4.7 TEM images of 2%Au/CeO$_2$-LS catalyst at different magnifications; (a) at 50,000 magnification with 50 nm scale, (b) at 50,000 magnification with 50 nm scale, (c) at 50,000 magnification with 50 nm scale, (d) at 100,000 magnification with 20 nm scale.
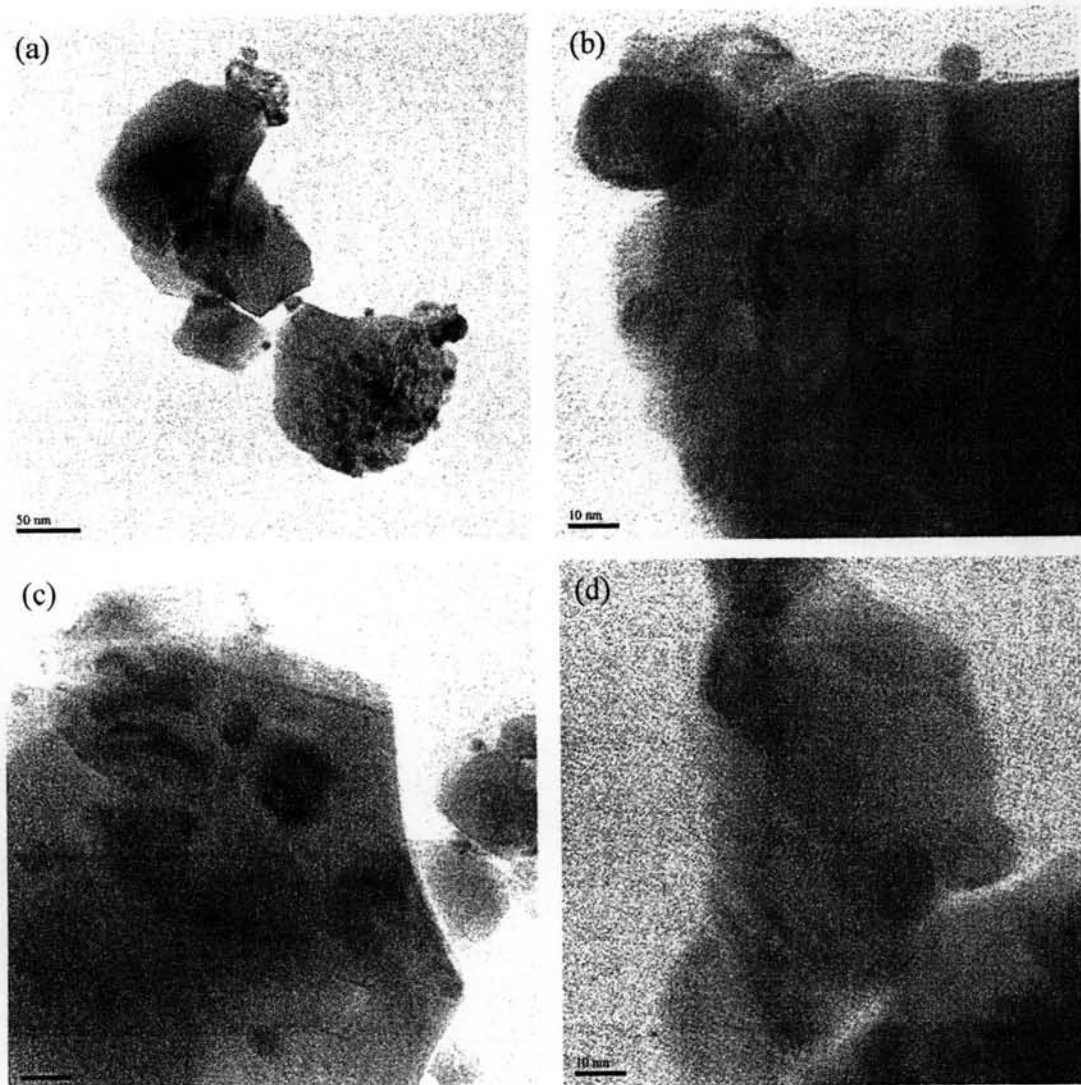
Figure 4.8 TEM images of 5%Au/CeO$_2$-LS catalyst at different magnifications; (a) at 50,000 magnification with 50 nm scale, (b) at 200,000 magnification with 10 nm scale, (c) at 100,000 magnification with 20 nm scale, (d) at 200,000 magnification with 10 nm scale.

From TEM images of 5% gold-ceria sample, large particle was clearly observed as well as the low dispersion of gold particles. There are many agglomerated particles which are bigger than 15 nm in the TEM images. As shown in Figure 4.9, the distribution of gold particle size was in a broad range. The presence of particle bigger than 30 nm was increased and the fraction of gold particle size in the range of 1-5 nm was the lowest when compared with 1% and 2% gold-ceria sample. The

most fractions shifted to 11-15 nm. The overall distribution of gold particle size was significantly broadened.
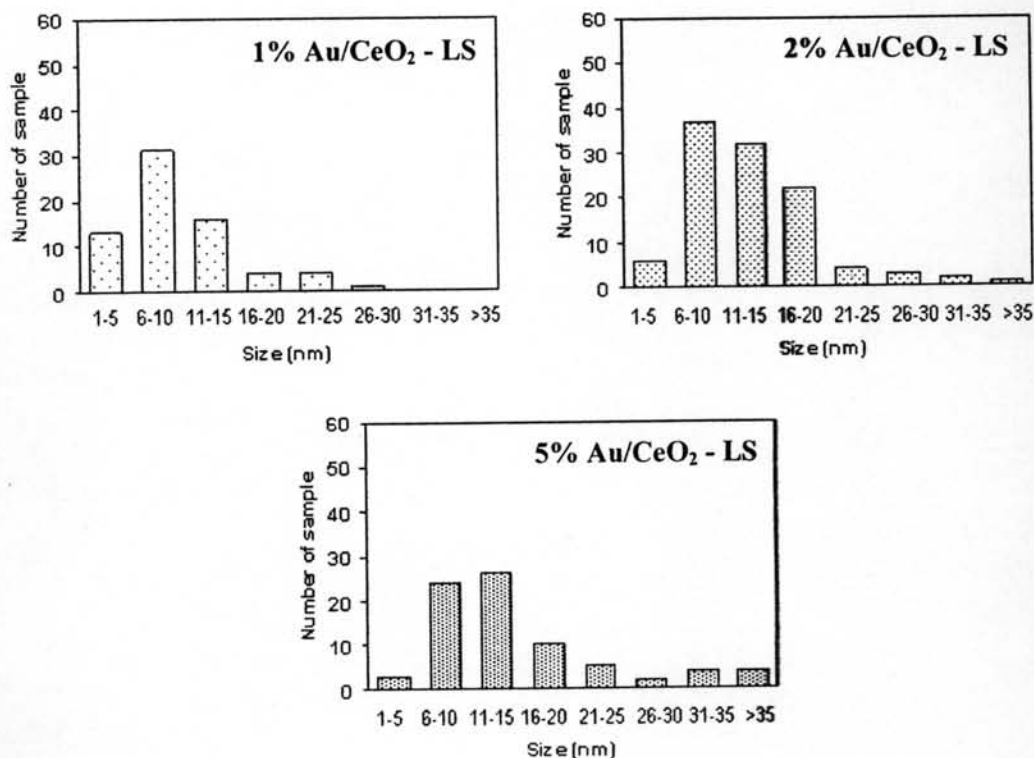

Figure 4.9 Particle size distributions of Au/CeO₂-LS catalysts from TEM analysis

The Characteristic of 1%, 2%, and 5% Au/CeO₂–LS catalysts including with commercial CeO₂ support are presented below in Table 4.1. From BET specific surface area, the measured surface area values were different in a small range (maximum different ~ 1.13 m²/g) as well as the crystallite size of ceria which almost unchanged after the gold was loaded. Therefore, it can be assumed that the addition of gold has no effect on the size and structure of ceria.

As discussed above, the gold particle size from TEM images which is larger than 35 nm can be observed only for 5% gold-ceria-LS sample. TEM images of 5% gold-ceria sample showed some agglomerated gold particles which led the increased average gold particle size up to 15.43 nm. This can be explained why the activity of 5% gold-ceria was comparable to 2% gold-ceria. In addition, the XRD patterns of gold peak insisted the presence of gold for 2% and 5% gold-ceria samples.

For 5% gold-ceria-sample, two peaks of gold can be observed at 38.62° (plane 111) and 44.26° (plane 200) while for 2% gold-ceria sample only one peak at 38.20° (plane 111) can be observed. This can be assumed that the 5% gold-ceria sample had more gold loading than 2% gold-ceria sample.

Table 4.1 Characteristic of Au/CeO_2 – LS catalysts compared with a commercial CeO_2-LS support

Sample	Crystallite size (nm)[a]			Au particle size, nm[b]	BET Surface area, m^2/g
	Au		CeO_2		
	(111)	(200)	(111)		
CeO_2 - LS	-	-	43.62	-	7.80
1% Au/CeO_2 - LS	No peak	No peak	43.62	10.12	6.67
2% Au/CeO_2 - LS	89.47	No peak	43.62	13.23	7.05
5% Au/CeO_2 - LS	71.32	72.66	40.80	15.43	7.61

a: determined by XRD using Scherrer equation
b: determined by TEM

From other previous work with effect of gold loading, Fu and co-workers (2001) studied the activity of high gold loadings (5-8%) on ceria catalysts for LT-WGS with two preparation methods, DP and co-precipitation (CP). The LT-WGS activity increased when gold loading was increased. They concluded that the addition of gold significantly increased the reducibility of the ceria surface oxygen which was controlled by the crystallite size of ceria. The Au/CeO_2 catalytic activity correlated well with its reducibility. However, our work is in good agreement with Andreva et al. (2002). They found that the 3% and 5% Au/CeO_2 has comparable LT-WGS activity, ~90% and stability. The stability of gold-ceria after three months remains stable, suggesting from TPR result that the reduction/oxidation process take place readily in the presence of gold and 3%Au/CeO_2 has the optimal ratio between surface gold active centers and ceria surface being capable to produce oxygen.

4.2.3 Effect of H$_2$-Pretreatment

The effect of H$_2$-pretreatment of gold-ceria catalyst was studied with 2% gold-ceria catalyst-LS. The catalyst was pretreated with 5.32% H$_2$/N$_2$ at 250 °C at a heating rate 10 °C/min for 2 hours prior to the LT-WGS reaction.

Figure 4.10 showed the LT-WGS activity of 2% gold-ceria and H$_2$ pretreated 2% gold-ceria catalysts. The H$_2$ pretreated catalyst exhibited slightly higher CO conversion than the fresh catalyst, ~5% increased.
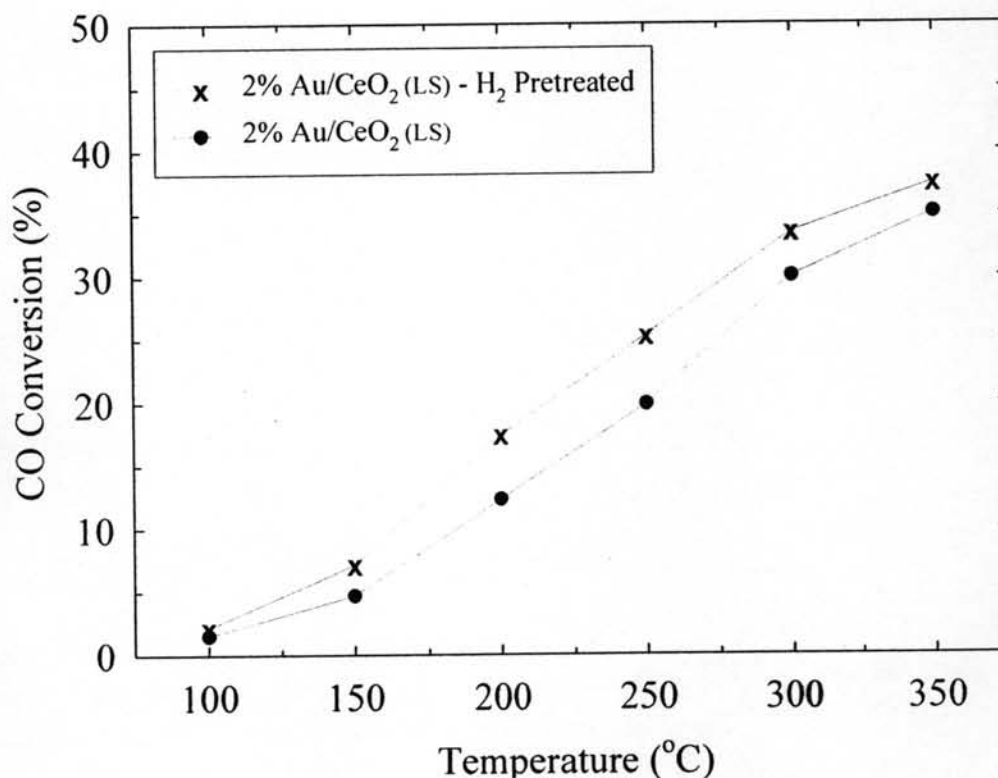

Figure 4.10 Effect of H$_2$-Pretreatment on the LTS activity of 2% Au/CeO$_2$ - LS catalyst at SV = 4,000 ml g^{-1} h^{-1} as a function of the reaction temperature. The sample was pretreated in 5.32% H$_2$/N$_2$ at 250° C for 2 hours. Reaction condition: 4% CO and 4% H$_2$O balanced with helium.

This can be explained that the H$_2$ reduced cationic gold (Au$^{\delta+}$) to the more active form, metallic gold (Au^0). Although other studies have provided evidence that cationic gold in the absence of metallic gold exhibited high catalytic activity for CO oxidation (Fierro-Gonzales *et al.*, 2004). For WGS reaction, Fu *et al.*

(2003, 2005) examined gold-ceria catalyst and found that cationic gold species strongly bound to ceria, Au_n-O-Ce, are the catalytically relevant species whereas the coexisting metallic gold nanoparticles do not participate in the WGS reaction. This was proved by the same activity measurements for cyanide-leached samples devoid of gold nanoparticles. However, our work is in a good agreement with the recent study by Manzoli et $al.$ (2007) which was confirmed that the increasing of the CO oxidation reactivity on H_2-pretreated gold-ceria catalyst by FT-IR technique. The different reactivity of Au^0 and $Au^{\delta+}$ both adsorb CO with different strengths and they react with oxygen to produce CO_2, but the Au^0 species are much more active than $Au^{\delta+}$ species which bind CO more strongly than Au^0.

4.2.4   Effect of Type of CeO_2

In order to study the effect of the nature and structure of ceria support, two type of commercial ceria supports, micro-powder and nano-powder ceria, were examined with the same amount of gold loading by DP method. The prepared 2% gold-ceria-LS and 2% gold-ceria-HS catalysts and also ceria support themselves were performed in the same LT-WGS reaction condition without any pretreatment. The LT-WGS condition was performed at SV = 4,000 ml g^{-1} h^{-1} as a function of the reaction temperature with the reaction composition, 4% CO and 4% H_2O balanced with helium.

Figure.4.11 shows the LT-WGS activity of 2% gold-ceria-LS, 2% gold-ceria-HS, LS-ceria, and HS-ceria samples as a function of temperature. At initial temperature, CO conversions of high surface samples were slightly higher than that of low surface samples. The activity of HS-catalyst was more conversion than LS-catalyst as temperature was increased. Especially at maximum temperature, the CO conversion of HS-catalyst was reached 55% while only 35% was obtained for LS-catalyst. As well as the activity of ceria supports, ceria-HS also showed higher CO conversion than ceria-LS due to the higher surface area which led the better of CO oxidation reaction.

The result showed that the nature and structure of ceria support also affected to the WGS activity. In addition, 2% gold-ceria-HS and 2% gold-ceria-LS

were characterized by XRD, TEM, BET, and H_2-TPR to investigate the effect of type of ceria to the characteristic of gold which can lead to the improved of WGS activity.
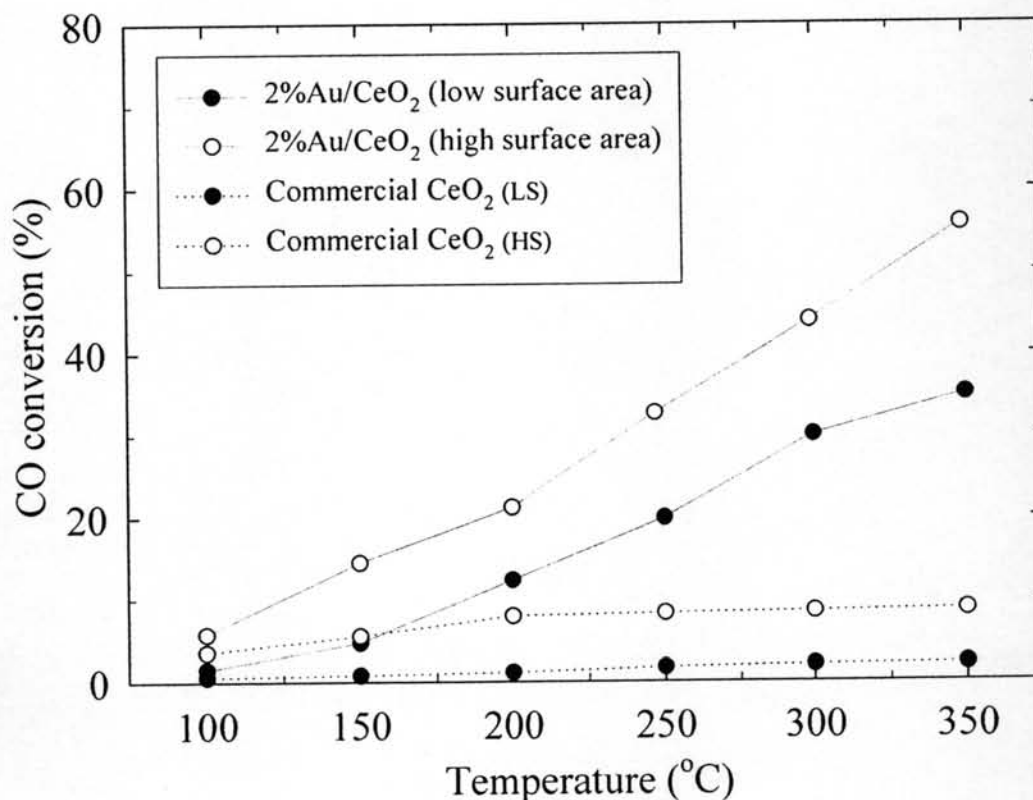

Figure 4.11 Effect of type of ceria on the LT-WGS activity of 2% Au on LS and HS CeO_2 at SV = 4,000 ml g^{-1} h^{-1} as a function of the reaction temperature. Reaction condition: 4% CO and 4% H_2O balanced with helium.

The characteristic of the prepared catalyst and commercial ceria supports are presented in Table 4.2. From the BET surface area results, the specific surface area of HS-ceria has almost ten times higher than that of LS-ceria (70.34 m^2/g for HS-ceria and 7.8 m^2/g for LS-ceria). The much higher in specific surface area could enhance the ability of reducibility of surface ceria support. This is in good agreement with the study WGS reaction with ceria supported precious metal by Gorte and Zhao in 2005, both formate intermediate and reduction oxidation mecha-

nisms were used adsorption sites of ceria as a pathway of oxygen exchanged. As the specific surface area of ceria increased, the adsorption sites were increased too.

Table 4.2 Characteristic of low surface and high surface of 2% Au/CeO_2 catalysts including commercial CeO_2 supports

Sample	Crystallite size (nm)			Au particle size, nm	BET Surface area, m^2/g
	Au		CeO_2		
	(111)	(200)	(111)		
CeO_2 - LS	-	-	43.62	-	7.80
2% Au/CeO_2 - LS	89.47	No peak	43.62	13.23	7.05
CeO_2 - HS	-	-	34.89	-	70.34
2% Au/CeO_2 - HS	59.64	No peak	31.65	9.48	75.65

From calculated crystallite size, the gold crystallite sites of 2% gold-ceria-HS catalyst were significantly lower than that of 2% gold-ceria-LS catalyst. This could be concluded that the nano-powder ceria reduced the crystallite size of gold due to the more specific surface area facilitated better dispersion of gold particle
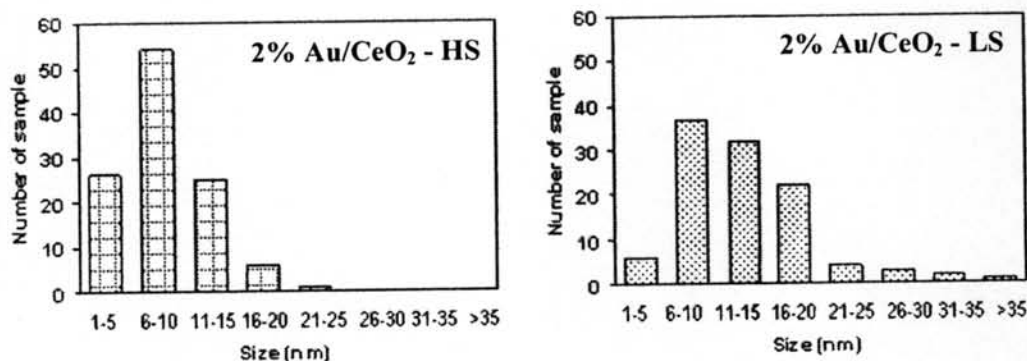

Figure 4.12 Particle size distributions of 2% Au/CeO_2-HS and 2% Au/CeO_2-LS catalysts.

(see Table 4.2) while the dominant crystallite of ceria support (plane 111) was also unchanged for HS catalyst as same as LS catalyst when Au was loaded. This can be

explained from the preparation method that the metal prepared by DP technique should not be affected to the crystallite size and structure of ceria as in agreement with Fu *et al.* (2001).

Figure 4.12 presents the gold particle size distribution of both HS and LS catalysts. The majority of distribution peak is at 6-10 nm range for 2% gold-ceria-HS resulting to the lowest average particle size (9.48 nm) which is much smaller than from 2% gold-ceria-LS, 13.43 nm especially, no gold particle size bigger than 25 nm was observed for 2% gold-ceria-HS. This confirmed the well dispersion of gold particle on high surface ceria support. The observed Au particles smaller than 6 nm was 26 particles which are 23.21% of all observed particles, while other gold-ceria catalysts prepared by other groups have the mean diameter in the range of 1-3 nm (Tabakova *et al.*, 2004 and Sakurai *et al.*, 2005). Based on this result over Au/CeO_2, our catalyst showed lower activity than Au/CeO_2 reported in the earlier literature.
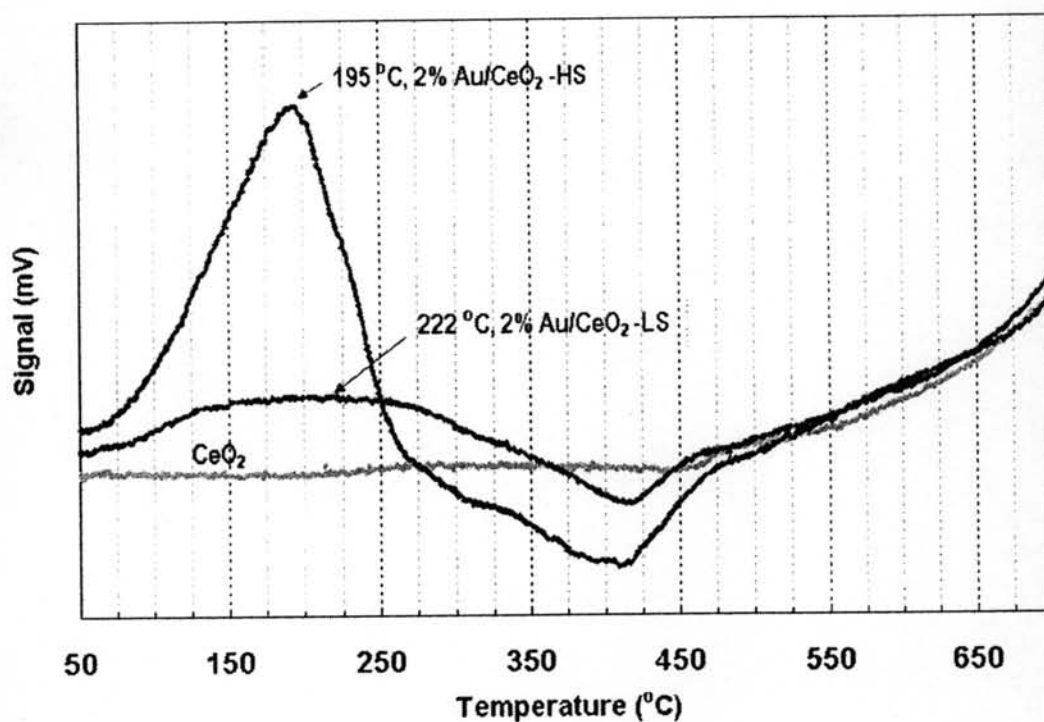

Figure 4.13 H_2-TPR Profile of 2% Au/CeO_2 – HS, 2% Au/CeO_2 – LS, and commercial CeO_2. Test condition: 5.32% H_2/N_2, 20 cm^3; 10 °C/min. Catalysts were pretreated in N_2 at 250 °C for 30 minutes.

The result is in a good agreement with Lai *et al.* (2006), the high surface ceria stabilized gold at high dispersion. Highly dispersed gold promotes the CO oxidation by activating CO in the former case and by assisting the dissociation of adsorbed oxygen in the latter.

Figure 4.13 confirms the enhancement of reducibility of high surface ceria. The peak start from 50 °C to 400°C corresponding to the reduction of surface capping oxygen of ceria in the HS-catalyst. It became much sharper than LS-catalyst and shifted to lower temperature. For the peak at 700 °C corresponding to the reduction of bulk oxygen of CeO_2 remains unchanged for all samples. The presence of gold metal facilitates both the restoration of the surface oxygen anions and their removal by CO at lower temperature. Increasing the surface area was found to enhance the oxygen storage capacity of ceria support. Moreover, decreasing the CeO_2 crystallite size leads to greater metal-ceria interaction.

4.2.5 Effect of Water to CO Ratio

Effect of water/CO ratio in the reactant feed was investigated between the 1/1 and 3/1 water/CO ratio. 2% gold-ceria-HS was used to study the effect of water/CO ratio without any pretreatment at SV = 4,000 ml g^{-1} h^{-1}. The reaction composition was 4% CO and with varied %vol. of H_2O (12%, 4%, 0%) balanced with helium.

As mentioned in introduction part, the WGS reaction is a reversible reaction. The equilibrium of reaction will be changed if the reactant and/or product are changed. Water in form of steam is accounted for the reactant in the WGS reaction. From WGS reaction, one mole of water reacts with one mole of CO.

Therefore, increasing the amount of water in LTS feed should improve the WGS activity. The result was shown in Figure 4.15. The effect of water/CO ratio was studied with 3/1, 1/1 and 0/1. The WGS activity of 3/1 water/CO ratio is slightly higher than 1/1 water/CO ratio. This is in agreement with Andreeva *et al.* (2002) that the catalytic activity slightly increases as a function of the H_2O/CO ratio. The other suggestions, referred from the studying of the redox properties of water on the oxidized and reduced model surface of CeO_2 (111), is that the exposure of water to the ceria support can increase the surface reduction. This can be ex-

plained by a bulk-to-surface diffusion of oxygen vacancies and this diffusion is promoted by H_2O/OH. For the 0/1 water/CO ratio or in the absence of water, the CO conversion was significantly decreased to ~ 7-13%.
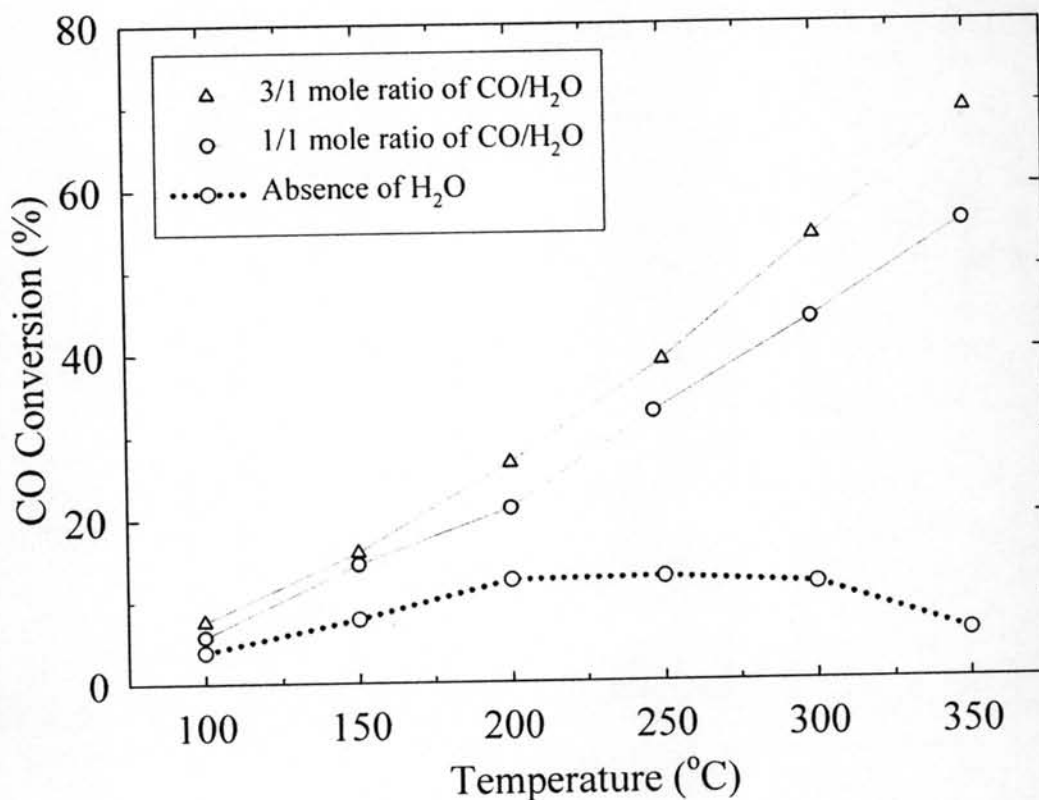

Figure 4.14 Effect of Water/CO ratio on the LTS activity of 2% Au/CeO$_2$-HS catalyst at SV = 4,000 ml g^{-1} h^{-1} as a function of the reaction temperature. The 3/1, 1/1, and 0/1 (absence of water) water/CO ratios were examined. Reaction condition: 4% CO and vary amount of H$_2$O balanced with helium.

From the properties of ceria support, it has oxygen storage property and some of CO receives oxygen from ceria surface to produce CO$_2$ as well as CO oxidation reaction.

4.2.6 Effect of H$_2$ Mixing

H$_2$ is known as product of WGSR, but the presence of H$_2$ in the LTS feed is possible due to the continuous feed stream from steam reforming and HTS units. Therefore, the effect H$_2$ mixing in the feed was investigated. The 60% H$_2$, which is considered as a general fraction in H$_2$ production from steam reforming unit, was added into reactant feed before mixing with steam and getting through the LT-WGS reactor was added into reactant feed before mixing with steam and getting through the LTS reactor. 2% Au/CeO$_2$-HS catalyst was used without any pretreatment at SV = 4,000 ml g^{-1} h^{-1}. The reaction composition was 4% CO, 4% H$_2$O and 60% H$_2$ balanced with helium.
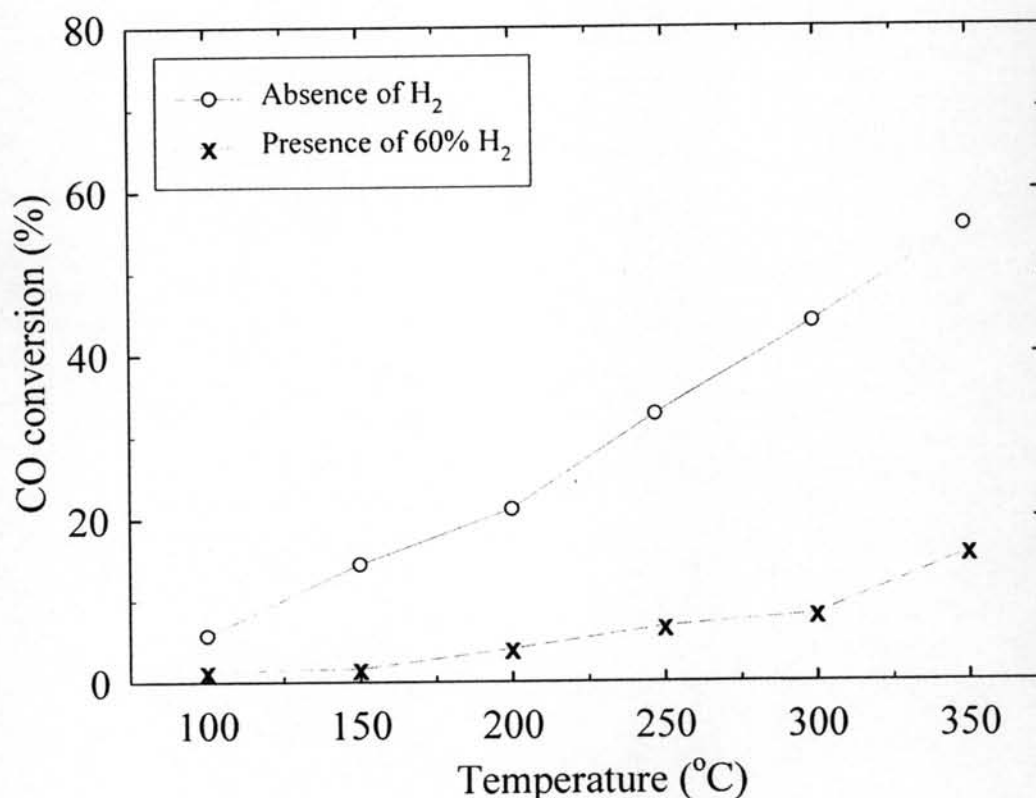

Figure 4.15 Effect of H$_2$-mixing in the reactant feed on the LTS activity of 2% Au/CeO$_2$ - HS catalyst at SV = 4,000 ml g^{-1} h^{-1} as a function of the reaction temperature. Reaction condition: 4% CO, 4% H$_2$O and 60% H$_2$ balanced with helium.

From the result in Figure 4.15 below, the presence of H_2 was also affected to the equilibrium of WGSR as same as the effect of water/CO ratio. When the dynamic equilibrium was interfered, the change in equilibrium was occurred. The result showed that the CO conversion of H_2-mixing feed was steeply dropped to nearly 10% CO conversion. This can be explained that the reverse water-gas shift was possibly occurred due to the inducement from a large H_2 fraction in the feed. However, this work showed difficult trend with the work reported by Sakurai et al. (2005). They found that when H_2 was added to the reactant gas ($CO+H_2O$), the CO conversion greatly increased. It was proposed that the presence of H_2 in the reactant gas thus promotes the reduction of ceria by consuming CO, on the other hand, Kim and Thompson (2005) found that the presence of H_2 did not affect the deactivation characteristic of Au/CeO_2 catalyst.

4.2.7 Stability Test

The stability test of H_2-pretreated of 2% gold-ceria-HS was performed at 250 °C in the presence of 60% H_2 in the feed for 500 minutes.

Figure 4.16 shows the stability of H_2-pretreated of 2% gold-ceria-HS catalyst on LT-WGS reaction at 250 °C. The initial CO conversion of ~42% was observed; however, after 500 minutes of time-on-stream, around 10% of conversion was dropped. The same trend of CO conversion reduction was found in the study of Denkwitz et al. (2007) with reaction condition: 1% CO and 99% H_2 (dry basis) with 2% H_2O at 180 °C. The 4.7 gold-ceria prepared with the same condition as our catalyst (DP, calcined at the 400 °C for 2 hours) was used. Almost 10% of conversion was dropped after 500 minutes of LTS reaction.

The non-stability of catalyst can be explained from many reasons. First, some of cationic gold which is likely cannot fully be reduced. Therefore, continuing reduction of the catalyst during the reaction will counteract, an at least partly compensate for, deactivation of the catalyst. Secondly, the long term reaction led to the agglomeration of gold particles, which is responsible for at least part of the deactivation (Bond et al., 2006). Alternatively, Kim and Thompson (2005) reported that CO and H_2 in the reactant are likely sources for the formation of carbonaceous de-

posits [formats, carbonates and carboxylates] resulting in the deactivation behavior of Au/CeO_2 catalyst was observed.
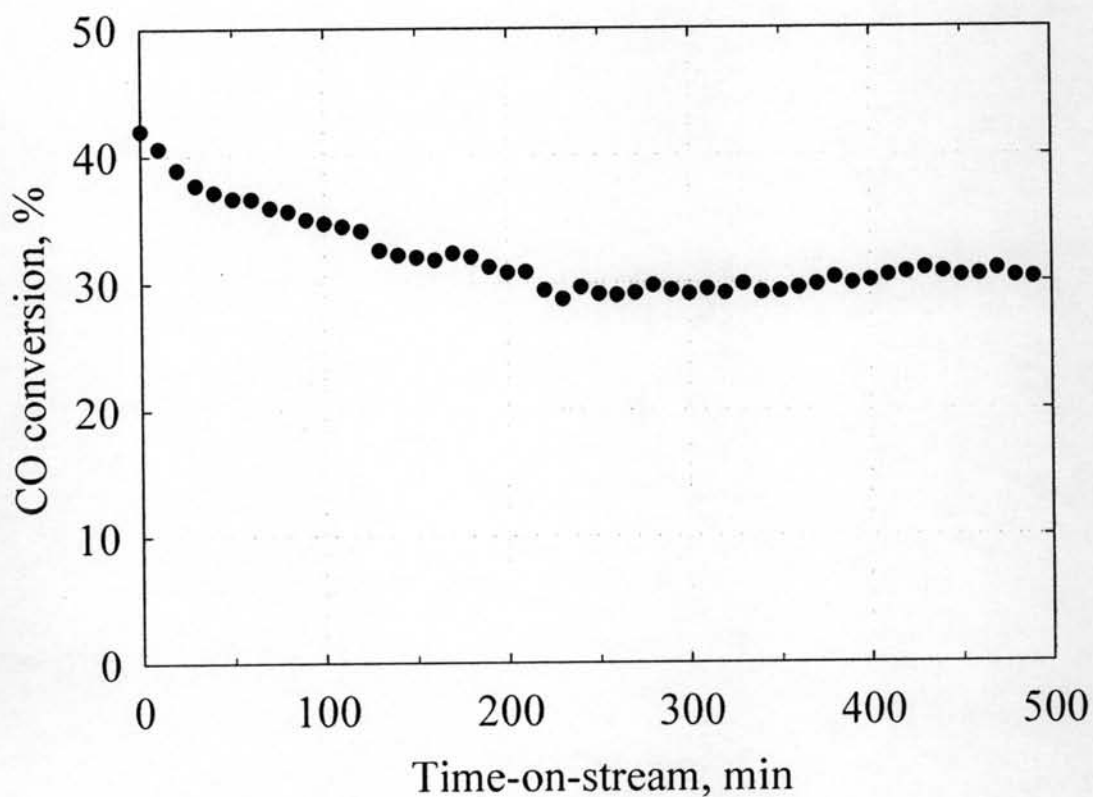

Figure 4.16 Effect of H_2-Pretreated on the LTS activity of 2% Au/CeO_2 - HS catalyst at SV = 4,000 ml g^{-1} h^{-1} as a function of the reaction temperature. The sample was pretreated in 5.32% H_2/N_2 at 200° C for 2 hours. Reaction condition: 4% CO and 4% H_2O balanced with helium.

4.5 Bench-Scale Experiment

Bench-scale experiment integrated H_2 production unit (steam reforming) and CO treatment units (water-gas shift and preferential oxidation) together. Each unit was continuously connected and built in the same structure. Figure 4.17 shows the design of H_2 production system. The purpose of this bench-scale experiment is to study the prepared gold-ceria catalyst and commercial catalyst, Shiftmax 230, with realistic feed. The starting gas material is natural gas.
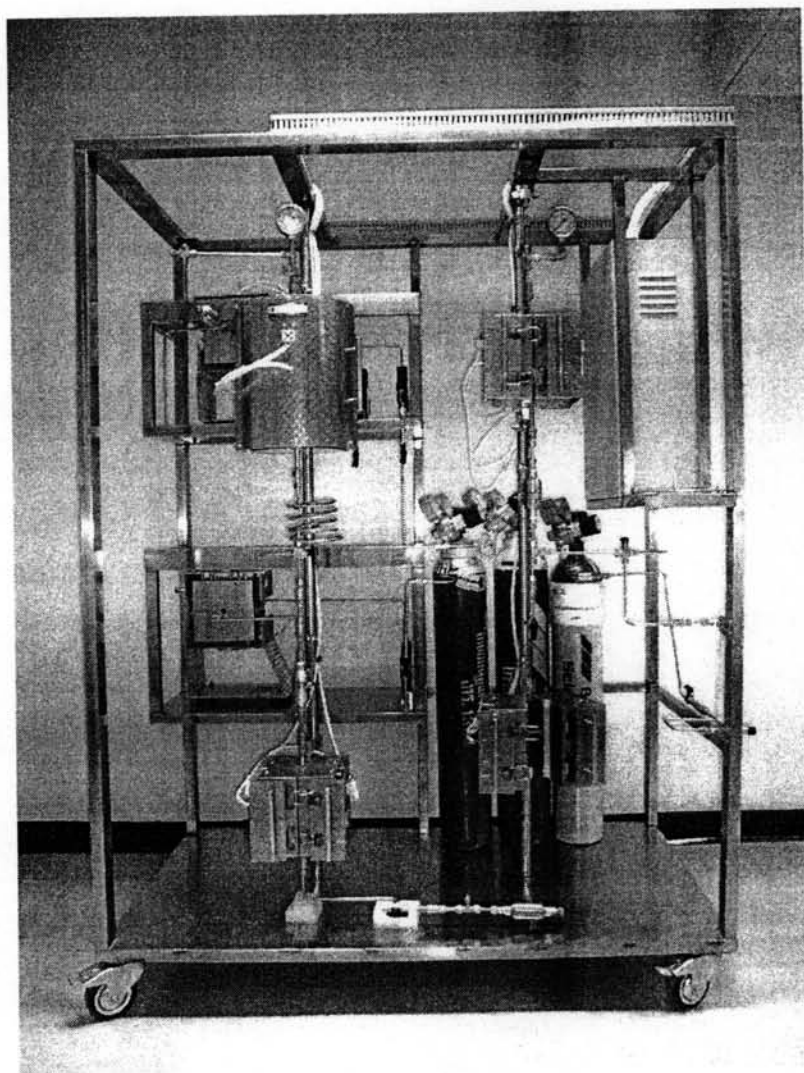

Figure 4.17 H_2 production system uses natural gas as a raw material which composed of SRM unit, HTS unit, LTS unit, ProX unit, and two vaporizer units.
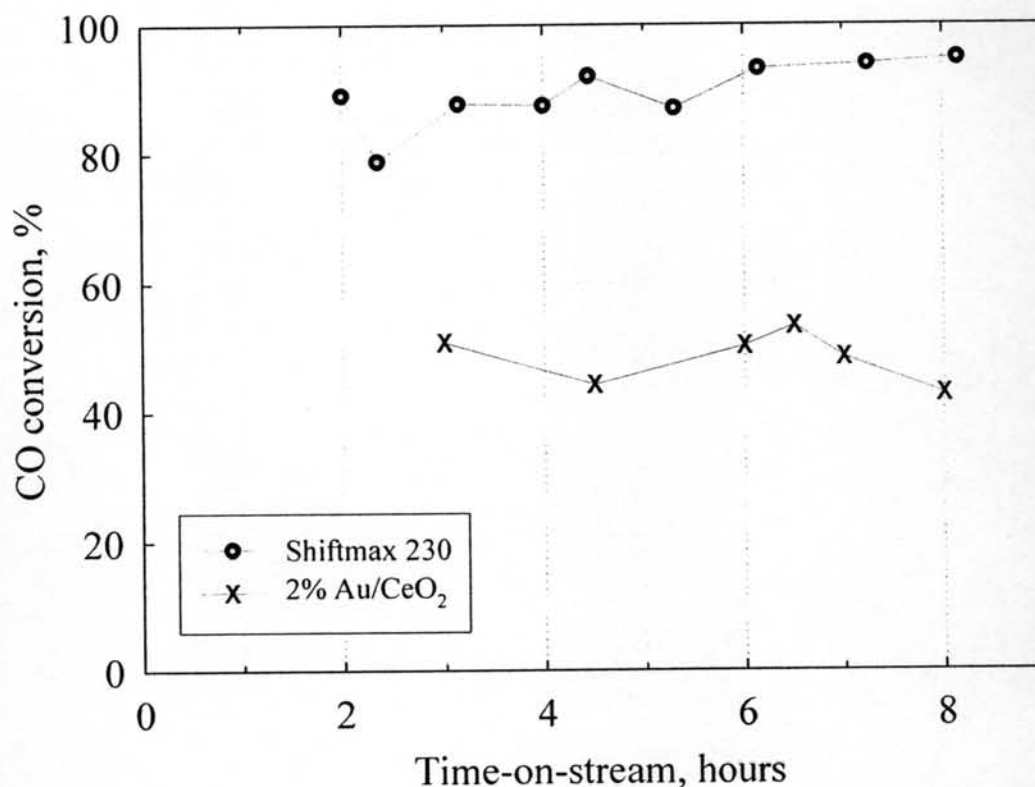
Figure 4.18 Comparison of CO conversion of Shiftmax 230 and H_2 pretreated 2% Au/CeO$_2$ samples on bench-scale experiment as a function of time on stream. Reaction condition: ~4% CO, ~60% H_2 in continuous natural gas feed after passing through the SRM (steam reforming unit) and the HTS unit with 12% H_2O added.

The H_2 production unit composed of four unit in this system, steam reforming (SRM), high-temperature water-gas shift (HT-WGS), low-temperature water-gas shift (LTS), and Preferential Oxidation (ProX). For SRM and ProX units, they were responsible for other researchers and were also investigated by prepared catalyst. For LTS unit, the commercial and prepared gold-ceria catalysts were used while only a commercial catalyst was used in HTS unit.

In bench scale, 4.5 g of catalyst was used with 20-60 mesh. The space velocity was set to ~ 4,000 ml g^{-1} h^{-1}. The LT-WGS reaction was performed at 250 °C for ~500 minutes. Figure 4.18 shows the CO conversion of commercial catalyst,
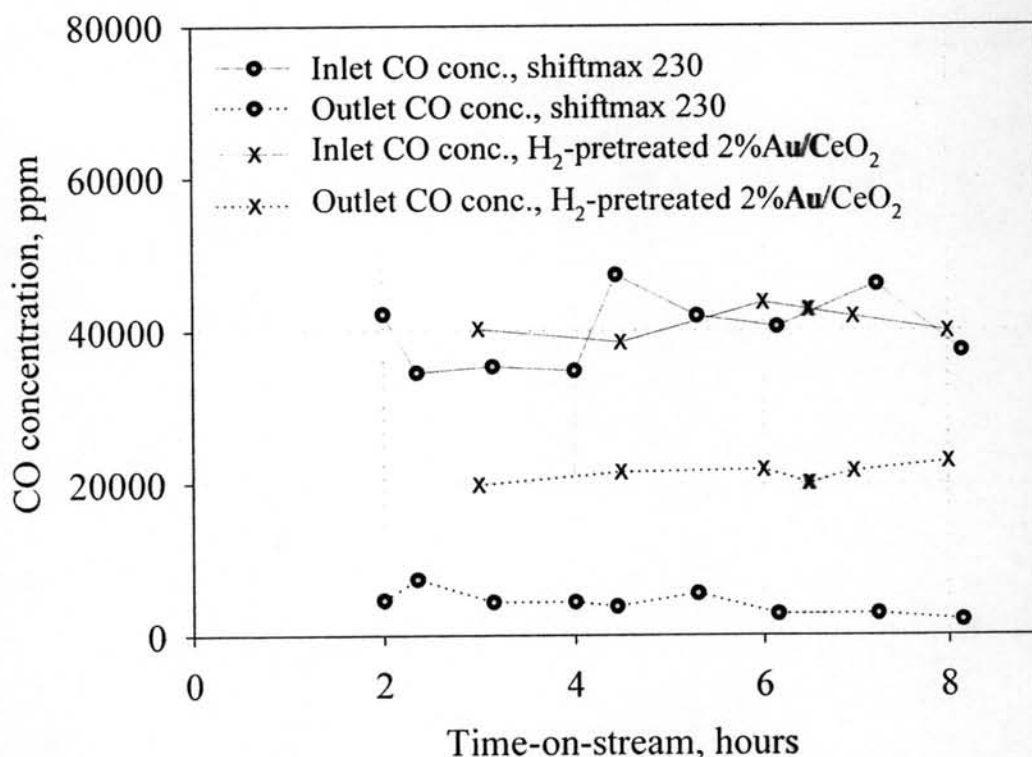
Figure 4.19 Comparison of inlet and outlet CO concentration of Shiftmax 230 and H_2 pretreated 2% gold-ceria samples before and after passing through the LTS unit as a function of time on stream. Reaction condition: ~4% CO, ~60% H_2 in continuous natural gas feed after passing through the SRM and the HTS unit with 12% H_2O added.

Shiftmax 230 and H_2- pretreated 2% gold-ceria-HS, the 2% gold-ceria-HS was pretreated in 5.32% H_2/N_2 at 250 °C (heating rate 10 °C/min) for 2 hours before taking into LT-WGS reaction. The CO conversion of prepared gold-ceria sample was about half of commercial catalyst CO conversion. The CO conversion of gold-ceria sample was better than that of in presence of 60% H_2 in the lab-scale (~58-60% H_2 was detected in the bench-scale feed). However, the commercial catalyst still presented more activity than gold-ceria sample. This result conflicted with other previous work. Figure 4.19 presents the inlet and outlet of CO concentration of LT-

WGS unit. The outlet CO concentration from the reaction of gold-ceria was still high (around 20,000 ppm) while the commercial achieved the better conversion and CO concentration can be reduce to less than 8,000 ppm before passing through ProX unit.