CHAPTER IV

INVESTIGATION OF DOUBLE-STAGE PREFERENTIAL CO OXIDATION REACTOR OVER BIMETALLIC Au–Pt SUPPORTED ON A-ZEOLITE CATALYST[*]

4.1 Abstract

This article presents experiment data on the preferential CO oxidation (PROX) in a hydrogen-rich stream, currently the most practical method for CO removal induced by a double-stage process. The reaction was carried out in a microreactor testing unit using Au and Pt supported on an A zeolite catalyst in the temperature range of 50–300 °C under atmospheric pressure. The reactant gas mixture contained CO (1%), O_2 (1%), H_2 (40%), CO_2 (0–10%), and H_2O (0–10%), with the balance being He, at a total flow rate of 50 mL/min. The results clearly show that the addition of the second stage significantly reduces the H_2 loss and the O_2 requirements while greatly increasing the CO selectivity from ~48 to ~58%. The addition of CO_2 and H_2O in the feed slightly reduces the CO oxidation activity both in single- and double-stage processes. Moreover, the double-stage process shows a CO removal efficiency of over 99% during 60 h of testing at a reaction temperature of 170 °C in the simulated reformed gas (CO_2- and H_2O-free).

Keywords: Preferential CO oxidation; Double-stage reactor; Au-Pt catalyst

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4.2 Introduction

In recent years, proton-exchange membrane fuel cells (PEMFCs) have been used as a clean alternative for automobile applications because of their high efficiency, zero emissions, low noise, and rapid startup. Currently, almost all hydrogen is produced via the steam reforming of natural gas at oil refineries. A number of attempts have been made to develop an on-board fuel processor, including steam reforming (SR) of hydrocarbons over, typically, a Ni catalyst on a ceramic support;[1,2] the water—gas shift (WGS) reaction, and CO removal methods. In the first step, natural gas is exposed to a high-temperature steam to produce H_2, CO, and CO_2. Unfortunately, CO, which acts as an impurity in a PEMFC, results in incredible losses in efficiency.[3,4] In the second step, the WGS reaction, CO is converted by the steam to produce additional H_2 and CO_2. However, the CO concentrations in the reformate are greater than acceptable levels (<10 ppm) for PEMFC applications. Many processes have been proposed to remove the CO content in H_2 fuel, such as pressure swing adsorption,[5] membrane filtration,[6] methanation,[7] and the preferential oxidation of CO (PROX). PROX seems to be the most practical process for automotive applications. The majority of researchers have mainly focused on the improvement of a high performance catalyst for this process.[8,9] A suitable catalyst should be active and very selective to the conversion of CO to CO_2 at a relatively low temperature, while minimizing the hydrogen oxidation to water. Pt-based catalysts are well known to effectively catalyze the preferentially oxidized CO to CO_2 at high temperatures,[10–14] whereas Au-based catalysts present a great potential for achieving a high conversion at low temperatures, when the size of the Au metal is smaller than 5 nm.[15–18] Previously, Haruta and co-workers reported that only nanosized Au particles can catalyze the CO oxidation reaction.[19] A few years later, Igarashi et al.[20] investigated Pt supported on zeolites for the PROX of CO. Various types of zeolites—A zeolite, mordenite, X zeolite, and alumina—were used as supports. The effects of support on the selectivities of CO oxidation and H_2 oxidation were investigated, and the selectivity toward CO oxidation was found to decrease in the order of A zeolite > mordenite > X zeolite > alumina. Rosso et al.[9] developed catalysts comprising noble metals supported on A zeolite employing 1 % Pt, Pd and

Ru as the active metal and 3-, 4- and 5-A zeolite as a catalyst support. The Pt catalyst showed a complete CO conversion and a remarkably high selectivity. From our previous results,[21] the presence of Au in a Pt/A zeolite catalyst can slightly improve the catalytic activities. The temperature of the maximum CO conversion was shifted 40 °C lower, and the CO selectivity was increased. However, the addition of Au by coimpregnation yielded large Au particles that were unable to oxidize CO in the presence of H_2. The addition of a multistaged PROX system offers better CO conversion and CO selectivity, and is considered an alternative method to improve the performance of the PROX process.[22–24] The process performance can also be enhanced by adjusting several variables, such as the reaction temperature of each stage, the oxygen split ratio, the amount of catalyst in each reactor, and so on.

In this present work, we have attempted to optimize the overall operating conditions in the double-stage process for the preferential CO oxidation unit in order to effectively remove CO from H_2 fuel and minimize H_2 losses in the simulated reformate stream by using a AuPt/A zeolite as a catalyst. The purpose of this article is to present the recent results of the double-stage reactor in the PROX unit for application directly to on-board fuel processor applications.

4.3 Experimental Section

4.3.1 Materials and Catalyst Preparation

$HAuCl_4 \cdot 3H_2O$ (Alfa AESAR, Au 49.5%) and $H_2PtCl_6 \cdot xH_2O$ (Aldrich Chemical Co., Pt 37.5%) were used as the sources of Au and Pt, respectively. The 1% (1:2) AuPt/A zeolite catalyst was prepared via conventional coimpregnation. [21] The mixture of precursor aqueous solutions was impregnated onto a NaA zeolite support. Then, the catalyst was dried at 110 °C overnight and subsequently calcined in air at 500 °C for 5 h.

4.3.2 Catalyst Characterization

X-ray diffraction was performed on a Rigaku X-ray diffractometer system (RINT-2200) with a Cu tube for generating Cu Kα radiation (1.5406 Å) in order to determine the phase of Au and Pt on the A zeolite as a catalyst support. The actual metal loading was determined using a Perkin-Elmer Optima 4300 DV inductively coupled plasma–optical emission spectrometer (ICP-OES). The morphology was investigated by transmission electron microscopy (TEM) using a JEM 2010 instrument operating at an accelerating voltage of 200 kV in bright- and dark-field modes. The BET surface area was obtained by the physisorption of N_2 at -196 °C using a Sorptomatic 1990 instrument. Prior to the BET measurement, each sample was outgassed by being heated under a vacuum at 300 °C for 6 h in order to eliminate the adsorbed species on the surface. The metal dispersion was determined by H_2 chemisorption at 50 °C.

4.3.3 Catalytic Activity Measurement

The preferential catalytic reactors were connected in series, as shown in Figure 4.1. The effluent from the first reactor was passed directly to the second reactor. The reaction in each stage was carried out in a fixed-bed U-tube microreactor, with 50 mg of the catalyst packed in each stage. Each reactor was individually equipped with a temperature controller and an O_2 supply. A thermocouple was placed at the bottom of the catalyst bed. Helium (He) gas was used to flush out the remaining water at 110 °C for 1 h, and the catalyst bed was cooled to room temperature before being heated to the desired reaction temperature. The catalytic activity and process performance were investigated at various temperatures in the range of 50–300 °C. The overall reactant gas mixture contained 1% CO, 1% O_2, 40% H_2, 0–10% CO_2, and 0–10% H_2O, with the balance being He; the total flow rate was 50 mL/min (λ=2) with a space velocity of the total gas mixture (GHSV) of 30,000 h^{-1}. The amount of O_2 entering each stage was varied at split ratios of 20:80, 40:60, 50:50, 60:40, and 80:20. The concentrations of H_2, O_2, CO, and CO_2 in the effluent gas from the reactor were analyzed by autosampling in an online gas chromatograph (carbosphere column, 80/100 mesh, 10 ft x ⅛ in.) using He as the carrier gas. The CO and O_2 conversions were calculated based on the consumption of reactant gases along the preferential CO oxidation reaction. The CO selectivity was defined as the O_2 consumption for the desired CO oxidation reaction divided by the total O_2 consumption.

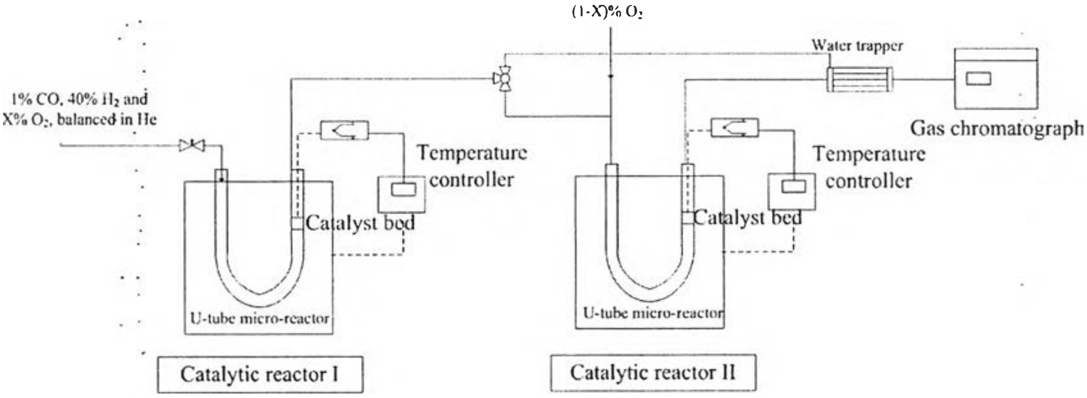

Figure 4.1 Schematic of double-stage process for the preferential CO oxidation reaction.

4.4 Results and Discussion

4.4.1 Catalyst Characterization

The X-ray diffraction patterns of Au and Pt were observed at 2θ values of 38.5° and 39.8° (not shown here), respectively, indicating the Au(111) and Pt(111) reflections for Cu Kα radiation. TEM results confirmed the formation of Au metal and Pt metal on the catalyst surface, indicating that the Au metal particles were larger than the Pt metal particles; however, the Au was not well dispersed on the surface. The crystallite sizes of the Au were about 200 nm, whereas the crystallite sizes of the Pt were almost uniform in size at 70 nm. The observations agreed well with the fact that the Pt crystallite size was 71.3 nm, calculated from the half-width of the main peak Pt(111) according to Scherrer's equation. In addition, the Pt metal particles had a higher dispersion than the Au metal particles, and they appeared to be phase separated, as can be seen in Figure 4.2 a,b. These results indicate that the Au and Pt metal particles are not combined into an alloy metal. The actual total metal loading is close to the calculated value, as confirmed by ICP. The BET surface area and the metal dispersion were determined to be 606 m^2/g and 26.7%, respectively.

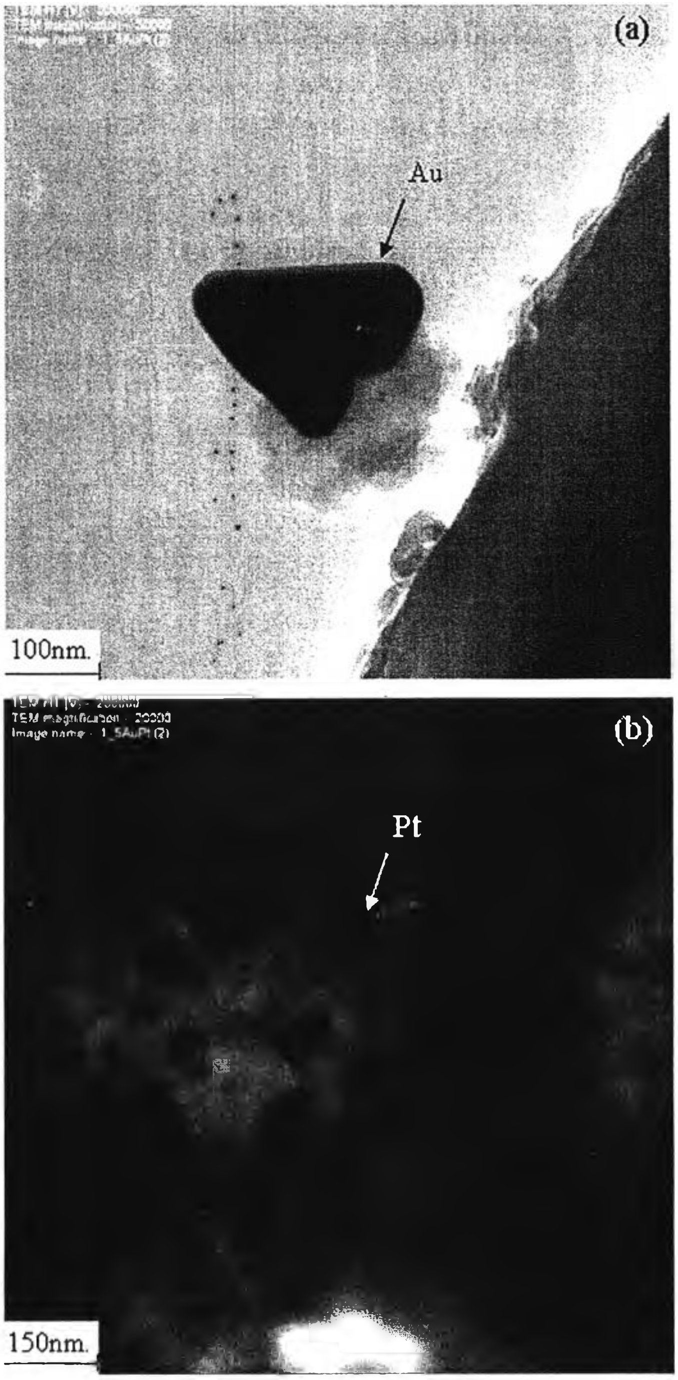

Figure 4.2 TEM micrographs of 1% (1:2)AuPt/A zeolite: (a) Au metal and (b) Pt metal.

4.4.2 Catalytic Activities

4.4.2.1 Comparison of Single and Double-Stage Reactors

In regard to the CO, O_2 conversions and CO selectivity, a comparison of the overall activity from the single- to double-stage reactors is shown in Figure 4.3. The double-stage experiment was performed under the same reaction conditions as the single-stage process except for the fractionation of an amount of O_2, which was introduced into each reactor in the double-stage reactor to oxidize a portion of the CO in the simulated reformate. In the double-stage process, the O_2 split ratio was controlled at 50:50. The results clearly show that the addition of the second stage provided a significant improvement in the overall process performance, especially in reducing the H_2 loss, whereas the double-stage process used the same amount of catalyst as in the single stage. In other words, the H_2 loss was more pronounced in the single-stage reactor. At a temperature of 170 °C, the double-stage reactor achieved a 99.80% CO conversion and a 58.01% CO selectivity, compared to 100.00% CO conversion and 48.00% CO selectivity in the single-stage reactor. No byproducts (methane) were observed in these experiments.

The difference in process performance between the single stage and the double stage can be explained in that the gas hourly space velocities (GHSVs) between the single- and the double-stage processes were slightly different. Even though the total flow rate of reactant in the two processes was fixed at 50 mL/min, the GHSV in the double-stage process was greater than that in the single-stage process. The contact time of the catalyst and reactant gas decreased with increasing GHSV, resulting in a slightly decreased CO conversion. This result agrees well with the work of Srinivas and Gulari,[23] who conducted experiments on the PROX reaction operating in a two-stage system over 2%Pt/γ-Al_2O_3. They reported that the two-stage system provided a higher CO selectivity (~49.72–49.94%) than the single-stage system (49.3%); however, complete O_2 consumption was still observed. In our work, the oxygen consumption in the double-stage process was less than that in the single-stage process, around 20%. Hence, the CO selectivity was found to be much higher than that expected from the result obtained in a single-stage process. Conversely, such oxygen was completely consumed by the oxidation reaction in the single-stage process.

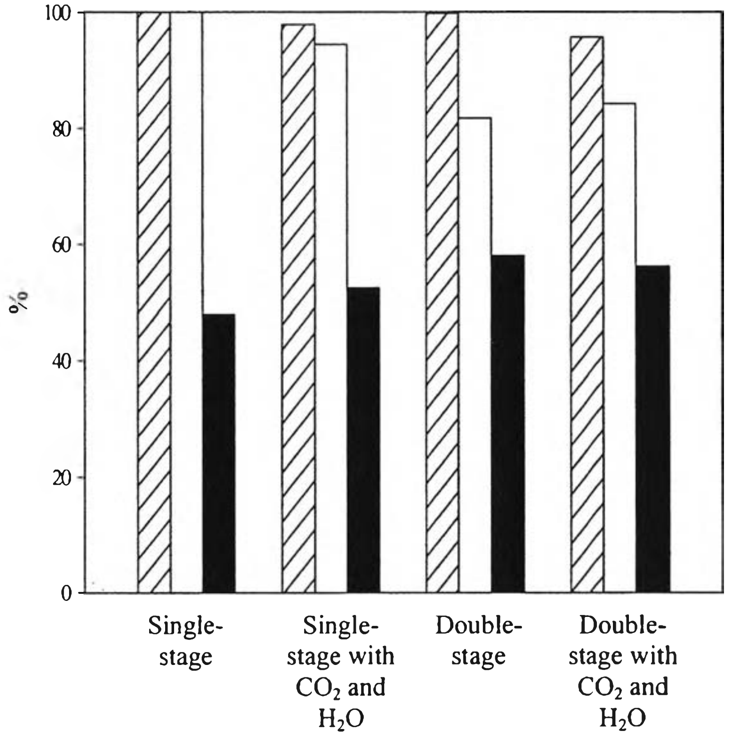

Figure 4.3 Comparison of the overall activities of the single- and double-stage processes with and without CO_2 and H_2O for preferential CO oxidation: (▨) CO conversion, (□) O_2 conversion, and (■) CO selectivity. The reaction temperature and O_2 split ratio of the double-stage process were controlled at 170 °C and 50:50, respectively.

The incremental increase in the CO selectivity might be caused by the O_2 partition, which is suitable for the CO oxidation reaction rather than for the H_2 oxidation reaction or for the total oxidation reaction. These results could be confirmed by the reduction of O_2 consumption at 170 °C and are consistent with the reported results by Igarashi et al.[20] and Ahluwalia et al.[22] They suggested that the selectivity can be enhanced by fractionizing the oxygen addition to a multistage reactor, resulting in a large reduction of the total amount of oxygen required to oxidize CO in the H_2-rich stream, which could be reduced to 0.7% by using a two-stage reactor,[20] whereas a single-stage reactor system required 1.5% oxygen to completely oxidize 1% of the CO in the reformate.

It is obvious that the AuPt/A-type zeolite had superior activity for PROX in the absence of CO_2 and H_2O in the feed; therefore, the presence of 10%CO_2 and 10%H_2O in the feed was also considered in order to observe the catalytic activities and process performance under more realistic conditions (Figure 4.3). The addition of CO_2 and H_2O slightly decreased the CO conversion in both the single- and double-stage processes. The CO conversion obtained in the presence and absence of CO_2 and H_2O reached 100% at the same reaction temperature. The results from our previous work found that the addition of water vapor into the feed did not have a significant effect on the CO conversion, but had a positive effect on the CO selectivity at high temperatures. The phenomenon in this present work can be explained by the competitive adsorption of CO with the CO_2 molecules on the Au active sites or at the interface between Au and the support.[25] Additionally, the O_2 consumption in the single-stage reactor with CO_2 and H_2O in the feed was less than that in their absence, resulting in an increased CO selectivity (~5%). The increase in CO selectivity might be caused by the increasing number of hydroxyl groups on the catalyst surface, which are better oxidants than the O_2; this can be confirmed by the reduction of O_2 consumption. In contrast, in the double-stage process, the O_2 consumption slightly increased when CO_2 and H_2O were added to the feed stream, whereas the CO selectivity was only slightly impacted. However, the double-stage process offered a higher CO selectivity than the single-stage process even in the presence of both CO_2 and H_2O.

4.4.2.2 Effect of Reaction Temperature

For the optimization of the operating conditions for a double-stage reactor in the PROX reaction to achieve the appropriate overall performance, the reaction temperature is an important factor. Therefore, we also investigated the effect of reaction temperature of each reactor on the catalytic performance. For these experiments, the first stage was controlled at constant temperatures (50, 130, 170, and 210 °C), and then the second-stage temperature was varied in the range of 50–

300 °C. The O_2 split ratio was constant at 50:50. Figure 4.4 shows the CO conversion profiles; it seems to be the same pattern for all first-stage reaction temperatures. The CO conversion increased with increasing temperature in the second stage in the range of 50–200 °C; then, the tendency of the CO conversion remained almost constant in the high-temperature range (200–250 °C). For CO selectivity, a high value (~100%) was observed for low second-stage temperatures (50–100 °C), and then the CO selectivity rapidly dropped with increasing temperature in the range of 130–200 °C. At high temperatures (200–250 °C), the CO selectivity remained constant. From the primary screening experiments, setting the temperatures of both the first and the second stages at 170 °C gave the best performance. Based on these results, another advantage of the double-stage process is that this process can be operated in a wide range of reaction temperatures (170–250 °C), at which CO is also completely removed.

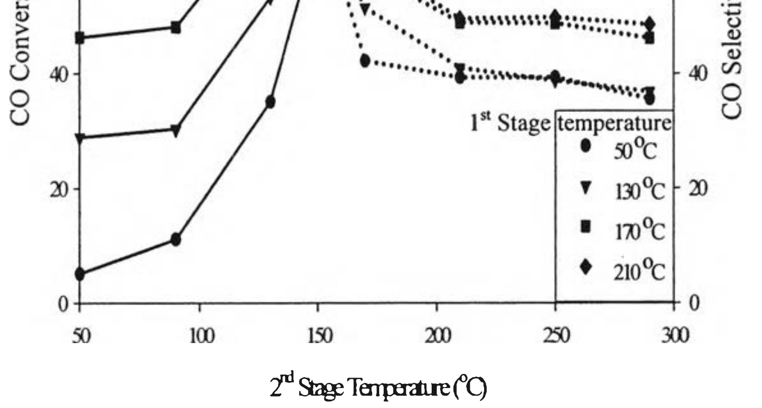

Figure 4.4 CO conversion (solid line) and CO selectivity (dotted line) as functions of reaction temperature of each reactor at an O_2 split ratio of 50:50. The first-stage reaction temperature was varied in the range of 50–210 °C.

A summary of the catalytic activities of the catalysts prepared in the present work compared to the catalysts reported in the literature is provided in Table 4.1. As mentioned above, the effect on the catalytic activity of adding Au to Pt catalyst is documented in the literature.[21] The improvement in the catalytic performance of the AuPt catalyst in the double-stage process was observed in terms of a lower operating temperature and a higher selectivity compared to those of the Pt-based catalysts. However, the 1% Pt/Al_2O_3 and 5.9% Pt/mordenite catalysts achieved very high CO conversions (~100% CO conversion) at 200 °C.

Table 4.1 Overall optimum process performance of each researcher group

Catalyst	Percentage of total metal loading (%)	Catalyst weight in each reactor (g)	Operating Temperature (°C)		O_2 split ratio	CO conversion (%)	CO selectivity (%)
			first stage	second stage			
AuPt/A zeolite[a]	1	0.05	170	170	50:50	99.80	58.01
Pt/γ-Al_2O_3[b]	2	0.06	230	170	60:40	99.88	49.94
Pt/mordenite[c]	5.9	0.05	200	200	70:30	100.00	ni[d]

[a] Gas composition = 1% CO, 1% O_2, 40% H_2, and balance He; flow rate = 50 mL/min (this work).

[b] Gas composition = 1% CO, 1% O_2, and 60% H_2 in Ar; flow rate = 180 mL/min.[23]

[c] Gas composition = 1% CO, 0.7% O_2, and balance H_2; flow rate = 25 mL/min.[20]

[d] Not indicated.

4.4.2.3 Effect of O_2 Split

One of many ways to improve the PROX process performance is by adjusting the amount of O_2 entering each reactor in order to remove the CO completely from a simulated H_2-rich stream. During the operation in a double-stage reactor, a total O_2/CO ratio of 1/1 was maintained. O_2 split ratios were investigated for value of 20:80, 40:60, 50:50, 60:40, and 80:20, as shown in Figure 4.5.

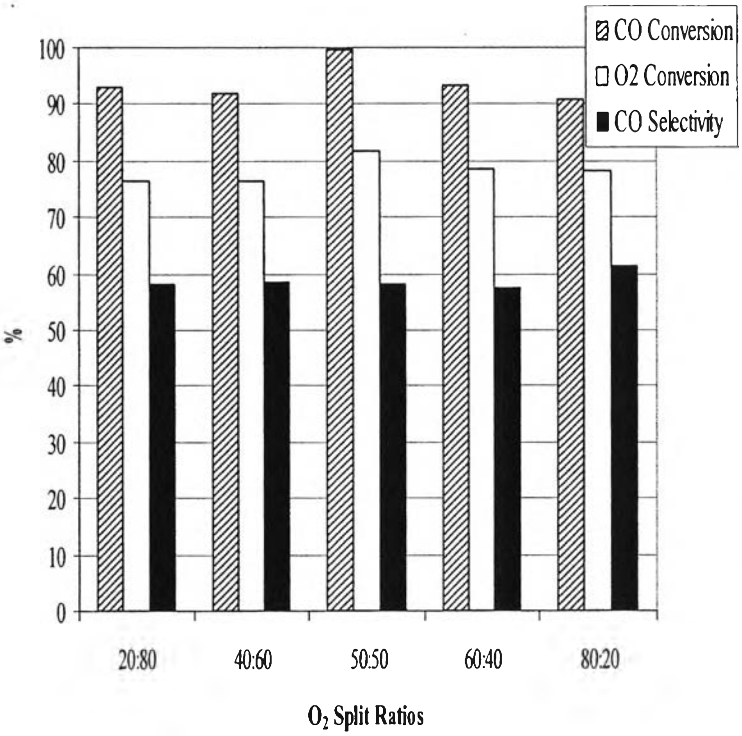

Figure 4.5 Catalytic activities of 1% (1:2) AuPt/A zeolite in a double-stage reactor with various O_2 split ratios at a reaction temperature of 170 °C under atmospheric pressure.

The temperatures of both stages were controlled at 170 °C. Studies of the O_2 split ratios revealed that the O_2 split ratio does not affect the subsequent CO selectivity (58–61%). In this study, we saw a trend toward improvement in CO conversion at an O_2 split ratio of 50:50 (~97%); however, 100% CO conversion could not be achieved for any values of the O_2 split. Although the maximum CO selectivity was obtained at an O_2 split ratio of 80:20 (~61%), at this ratio, the CO conversion was lower than that for the other O_2 split ratios. The slight difference in process performance due to the oxygen stoichiometry in each stage for various O_2 split ratios was very little changed. Our study shows consistent results in favor of the double-stage reactor process for most outcome measures, including selectivity improvement and almost complete CO conversion.[20,23] Srinivas and Gulari[23] found that, at a split ratio of 60:40, with the first stage operating at 230 °C and the second stage at 170 °C, the best conditions were achieved, whereas Igarashi et al.[20] reported that a split ratio of 70:30 operating at 200 °C provided the best conditions. At this stage, the overall process performance in this present work is not quite good enough, so the development and investigation of other parameters in this process have to be carried out further.

4.4.2.4 Stability Testing

To assess the capability of this process to be applied in automotive fuel cell applications, stability testing is an important factor to consider. The catalytic activity was isothermally investigated at a temperature of 170 °C for 60 h. Under these operating conditions, the CO concentrations in the simulated reformate remained low. As evidenced by Figure 6, no degradation was observed over the AuPt/A zeolite with the double-stage reactor for the preferential CO oxidation reaction during 60 h of testing. This phenomenon can be explained in that the cagelike pores of A-type zeolite can prevent the sintering of metals during the preferential CO oxidation reaction that better than that of the straight channels in other types of zeolite. Zeolite with channel-like pores can facilitate the migration of metal in the catalyst.[26] BET measurements and XRD analysis were conducted on the spent catalysts and were compared to the results for the fresh catalyst. The surface area was still considered to be relatively high, indicating that the structure did not collapse under PROX conditions.

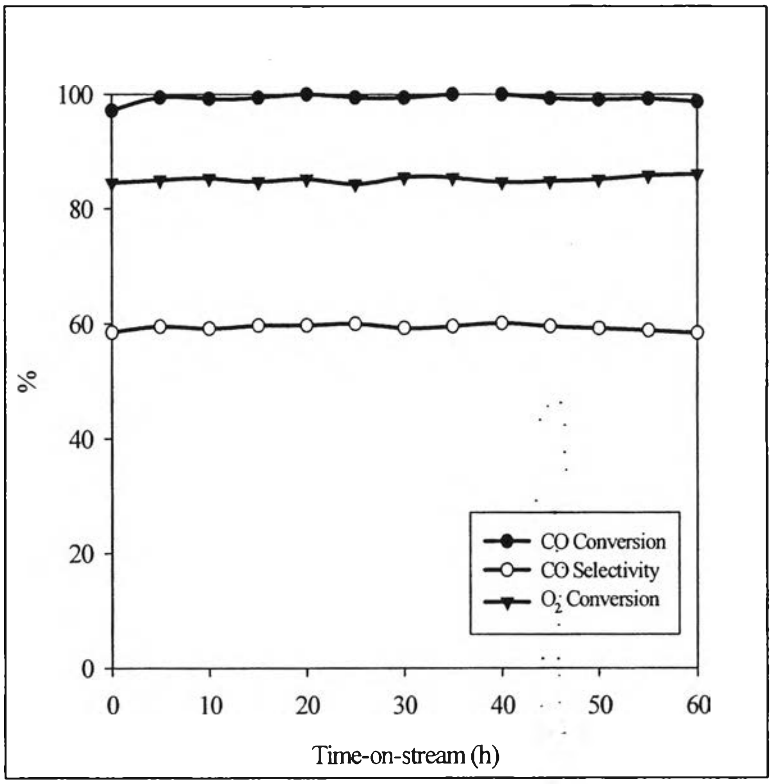

Figure 4.6 Stability testing of the 1% (1:2) AuPt/A zeolite catalyst in a double-stage reactor at 170 °C under atmospheric pressure, and an O_2 split ratio of 50:50.

4.5 Conclusions

The catalytic activities of AuPt/A zeolite catalyst for the PROX reaction in single- and the double-stage reactors were studied in the temperature range of 50–300 °C. The double-stage reactor gained more process efficiency than the single-stage reactor in terms of CO selectivity. In the double-stage process, the effect of reaction temperature is more pronounced than the effect of oxygen split ratio. The conditions were optimized with a reaction temperature in both stages of 170 °C and an oxygen split ratio of 50:50, which provided the maximum CO conversion (99.80%) combined with a CO selectivity of 58.01%. The stability of the catalyst behavior was tested at 170 °C in a double-stage process without CO_2 and H_2O, which showed stable performance of the high catalytic activities without any degradation for 60 h.

4.6 Acknowledgements

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