CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Gases

The gases used in this research were

a) 24.85% carbon monoxide in helium from Thai Industrial Gas Public Co., Ltd.

b) 20% carbon dioxide in helium from Praxair (Thailand) Co., Ltd.

c) 99.5% carbon dioxide from Bangkok Industrial Gas Co., Ltd.

d) 8% oxygen in helium from Thai Industrial Gas Public Co., Ltd.

e) High purity oxygen (99.7%) from Praxair (Thailand) Co., Ltd.

f) Ultra high purity hydrogen (99.99%) from Thai Industrial Gas Public Co., Ltd.

g) High purity nitrogen from Thai Industrial Gas Public Co., Ltd.

h) High purity helium from Thai Industrial Gas Public Co., Ltd.

i) Ultra high purity helium from Praxair (Thailand) Co., Ltd.

3.1.2 Chemicals

The chemical reagents used for catalyst preparation were as follow

a) Hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$), ACS, 99.99% purity from Alfa Aesar A Johnson Matthey Company.

b) Titanium dioxide P-25 (TiO_2) from Degusssa Corporation.

c) Titanium dioxide (TiO_2) Anatase AR grade of 99.0% purity from Sigma-Aldrich Company.

d) Titanium (IV) butoxide or Tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$) AR grade from Fluka Co., Ltd.

e) Methanol (CH_3OH) AR grade of 99.8% purity from Labscan Asia Co., Ltd.

f) Nitric acid (HNO_3) AR grade of 65% purity from Riedel-deHaen Co., Ltd.

g)   Ammonium hydroxide (28-30%NH_4OH) from J.T. Baker.

h)   Gold atomic spectroscopy standard solution (1000 ppm Au) from Fluka Co., Ltd.

i)   Tri-Magnesium Dicitrate Nanohydrate ($C_{12}H_{10}Mg_3O_{14}.9H_2O$) from Fluka Co., Ltd.

3.2 Equipment

The experimental setup as shown schematically in Figure 3.1 was divided into 3 main parts:

3.2.1 Gas Blending System

The reactant gas mixture was composed of CO, H_2, CO_2, and O_2 balanced in He.   Each gas was supplied from a compressed gas cylinder at initial pressure approximately of 2000 psig.   Each stream was passed through the micron line filter to remove particles and check valve to prevent reverse flow.   The stream flow rates were controlled by 840 Sierra Instruments model mass flow controllers to achieve the desired composition.   The reactant gases were mixed in the mixer and bubbled through water to humidify before sending to the reactor.

3.2.2 Catalytic Reactor

The selective CO oxidation was employed at atmospheric pressure in a Pyrex glass U-tube microreactor with an inside diameter of 4 mm.   The catalyst was packed between glass wool plugs in the middle of the reactor.   The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a chromel-alumel thermocouple (Type K).

3.2.3 Analytical Instrumentation

The effluent gas from the reactor was analyzed qualitatively and quantitatively by autosampling with a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD).   The column utilized in the chromatograph was carbosphere, 80/100 mesh, 10 ft x 1/8 inch
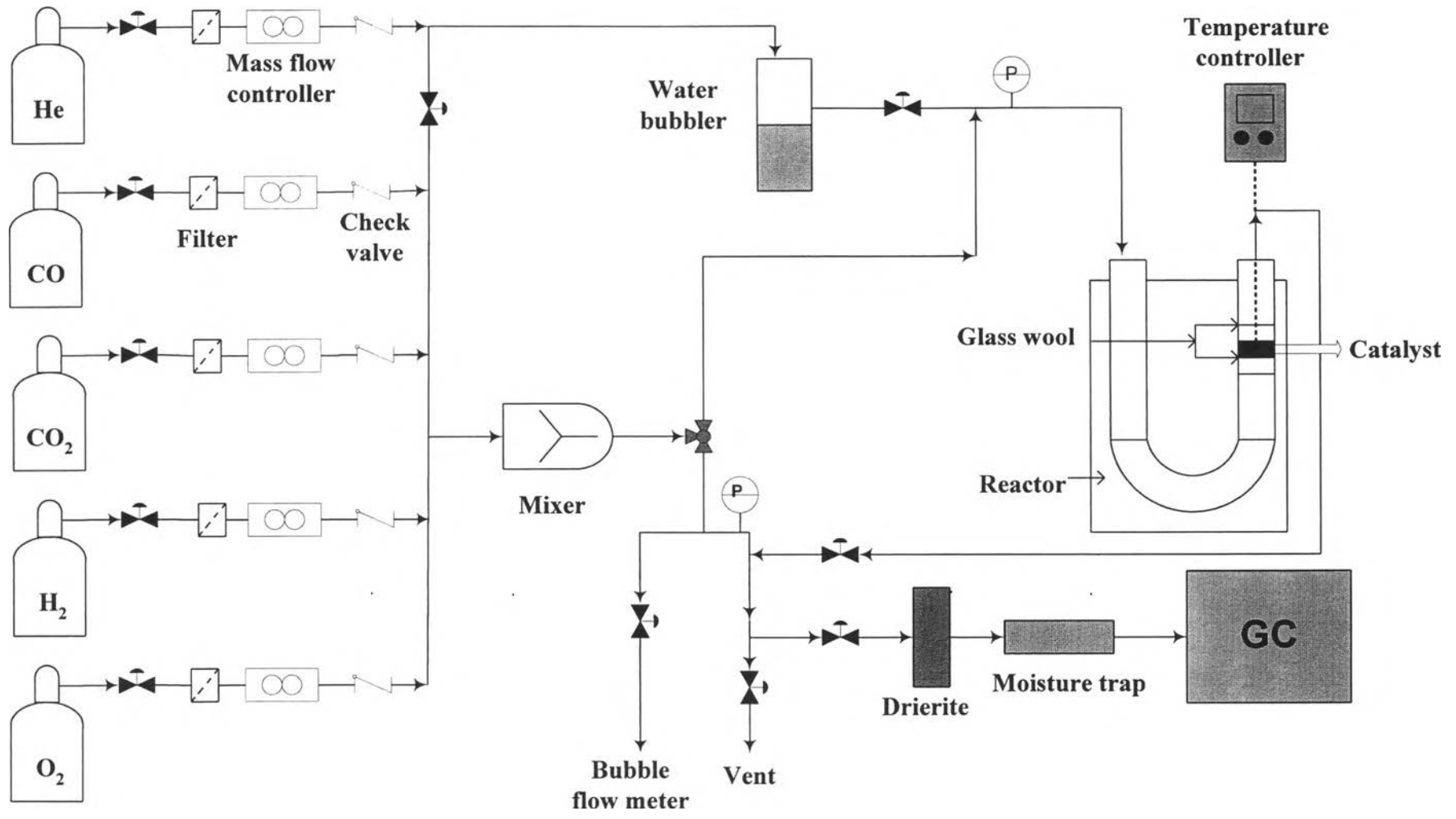
Figure 3.1 The schematic flow diagram of experimental equipment.

stainless steel packed column. The temperature of the oven, injector, and detector was maintained at 55, 110, and 175°C, respectively. The output of chromatograph was recorded by a Hewlett Packard 3365 series II chemstation.

3.3 Catalyst Preparation Procedure

The catalysts were prepared by deposition-precipitation method and impregnation on sol-gel method. In this research work, gold supported on titanium dioxide (Au/TiO_2) was synthesized and the amount of Au was varied in the range of 0.5 to 5 wt%.

3.3.1 Deposition-precipitation Method

Au/TiO_2 catalysts were prepared by deposition-precipitation method. There are 2 sources of titanium dioxide (TiO_2) support in this work: Degussa P-25 and Sigma. Degussa P-25 has a mixture of anatase and rutile type at the ratio 3:1 with BET surface area approximately 60 m^2/g. Sigma has only anatase form of TiO_2 with BET surface area approximately 12 m^2/g.

a) The appropriate amount of hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$) was dissolved in distilled water under continuous stirring and heating at 70°C.

b) The pH of the aqueous solution was adjusted to a fixed point of 8 by adding NH_4OH.

c) The amount of TiO_2 supported was added into the mixed solution.

d) The amount of TiO_2 was suspended and aged for one hour.

e) The suspension was separated by centrifuge at 2000 rpm for 5 min and washed by hot distilled water.

f) In order to eliminate the excess ions, washing procedure was repeated several times until the conductivity change of supernatant being constant.

g) The precipitate was dried at 110°C for 24 h and then calcined in air by varying temperature for 5 h.

h)   The sample was ground to powder, then sieved to 80/120 mesh size and kept in a dessicator before being used.

3.3.2 Deposition-precipitation Method with Addition of Mg Citrate (DP with Addition of Mg Citrate)

These catalysts were prepared in the same manner described above, except that some of catalysts were treated with Mg citrate. The Mg citrate was added to the stirring slurry with Mg/Au ratio=18 after adding TiO_2 support (Tsubota *et al.*, 1991).

3.3.3 Impregnation on Sol-gel Method (ISG)

Support TiO_2 was prepared by the sol–gel method with following steps.

a)   Two solutions were prepared, the first solution consisted of the amount of titanium (IV) butoxide (TBOT) dissolved in methanol.

b)   The second solution consisted of distilled water, nitric acid (65wt%) and methanol.

c)   The latter were added to the TBOT solution in a closed system, under N_2 atmosphere with vigorous stirring.

d)   The translucent gels were aged for 19-20 h to increase the rigidity of the gel network by successive polycondensation reaction.

e)   The support was dried at 110°C for 24 h and calcined in air at temperature of 400°C for 5 h.

f)   The desired amount of hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$) was weighed and dissolved in distilled water.

g)   The calcined support was impregnated with a solution of $HAuCl_4.3H_2O$ by adding a few droplets to support.

h)   The sample was dried again at 110°C for 24 h and calcined in air by varying temperature for 5 h.

i)   The sample was ground to powder, then sieved to 80/120 mesh size and kept in a dessicator before being used.

3.4 Catalyst Characterization

The characteristics of the prepared catalysts were investigated by 4 techniques described below.

3.4.1 Surface Area Measurement (BET)

The surface area, total pore volume and average pore diameter of all prepared catalyst samples have been determined by Brunauer-Emmet-Teller (BET) method using Autosorb-1 Gas Sorption System (Quantachrome Corporation). N_2 gas with cross-sectional area of 16.2 x 10^{-20} m^2/molecule was used as the adsorbate at liquid N_2 temperature (77K). All samples were outgassed by heating under vacuum to eliminate volatile absorbents in the surface at 200°C for at least 2 h before measurement. The surface area of each catalyst was calculated from five point adsorption isotherm. The average pore diameter and pore volume were determined at P/P_0 ratio close to unity. The results were analyzed by Autosorb ANYGAS Software Version 2.10, which uses the BET equation as shown in Equation 3.1.

$$\frac{1}{W \times \left(\frac{P_0}{P} - 1\right)} = \frac{1}{(W_m \times C)} + \frac{C-1}{W_m \times C} \times \frac{P}{P_0}$$

(3.1)

where:

W = weight of gas adsorbed

W_m = weight of adsorbate constituting a monolayer of surface coverage

P = the pressure of gas

P_0 = the saturated vapor pressure at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorption, in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area was calculated by Equation 3.2.

$$S = \frac{W_m \times A_{nitrogen} \times \left(6.02 \times 10^{23}\right)}{M_{w,nitrogen}}$$

(3.2)

where:

S = surface area (m^2/g)

$A_{nitrogen}$ = cross-sectional area of one molecule nitrogen

= 0.162 nm^2 (at 77K)

$M_{w,nitrogen}$ = molecular weight of nitrogen (28).

3.4.2 X-ray Diffraction (XRD)

The X-ray diffractometer has been used to identify the internal structure, bulk phase, and composition of crystalline catalysts. X-ray diffraction (XRD) is based upon the fact that the X-ray diffraction pattern is unique for each crystalline substance. If there are peaks in the scattering pattern presence of crystalline phases can be assumed. The identity of the crystalline phase can be found by matching the pattern of the unknown and authentic sample. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. For the same crystalline substance, the higher intensity shows higher content of that phase.

A Rigaku X-ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for generating a Cuk_α radiation (1.5406 Å) was used to obtain the XRD patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_α filter. The goniometer parameters were: divergence slit = $1°$ (2θ); scattering slit = $1°$ (2θ); and receiving slit = 0.3 mm. The sample was ground to a fine homogeneous powder and held in the beam in a thin-walled glass container. A scan speed of $5°$ (2θ)/minute with a scan step of 0.02 (2θ) was used during a continuous run in the 5 to $90°$ (2θ) range. The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to a on-line microcomputer to record and subsequent data analysis. Crystallite size was calculated by using Scherrer equation in Equation 3.3.

$$D_b = K\lambda / B_d \cos \theta \qquad (3.3)$$

where:

λ = the X-ray wavelength (Å)

K = the Scherrer constant which is equal to 1

B_d= the angular width of the peak in the terms of $\Delta(2\theta)$(Radian)

θ = the Bragg angle of the reflection (degree)

D_b= the mean crystallite diameter (Å).

3.4.3 Atomic Absorption Spectroscopy (AAS)

The AAS, VARIAN model 300/400 was used to determine the actual content Au loading on the support. The necessary amount of catalyst was dissolved with aqua regia solution (hydrochloric acid to nitric acid of 82 to 18 ratios) and then heated to 100°C for one hour. Several standard solutions were made from stock solution of 1000 ppm to establish a calibration curve. The metal solution was diluted to the measuring range. The amount of Au loaded on the supports was obtained by measuring the absorbance of the prepared solution.

3.4.4 Transmission Electron Microscope (TEM)

In this work, TEM was used to investigate the average particle size of Au because Bethke and Kung (2000) studied that optimal average particle size of Au about 5-10 nm gave the best activity. Characterization of TEM samples was performed using a JEOL 2010, operating at an accelerating voltage of 200 kV. The samples were prepared by sonicating the powder in ethanol for 2-3 min, followed by deposition of a few drops of the resulting suspension on the holey carbon film grids. Bright-field images were taken at magnifications between 150-200 K with an objective aperture in place. TEM works much like a slide projector. A projector shines a beam of light through the slide, as the light passes through it is affected by the structures and objects on the slide. These effects resulted in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam was then projected onto the viewing screen, forming an enlarged image of the slide. Crystallinity and crystal structure of the samples were evaluated from selected area electron diffraction patterns. Images processing for constrast enhancement and image evaluation were done by means of the programs Digital Micrograph.

3.5 Activity Measurement

Selective CO oxidation reaction was carried out in the fixed bed reactor. The reactant gases were flowed passing through the sample of catalyst in the reactor containing 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balanced in He at the total flow rate of 50 ml/min (SV = 30,000 $mlg^{-1}h^{-1}$) and at atmospheric pressure. The amount of catalyst was 100 mg with 80/120 mesh size and reaction temperatures were set between 50 to 190°C.

3.5.1 Effect of Catalyst Pretreatment

Catalyst pretratment can change in the structure of the catalyst leading to the changes in the activity and selectivity.

a) The calcined catalysts were pretreated with

- 50 ml/min of pure H_2 at 200°C for 2 h
- 50 ml/min of pure O_2 at 200°C for 2 h
- 50 ml/min of pure He at 200°C for 2 h.

b) Samples were placed in the reactor and cooled down to the reaction temperature under pure He.

3.5.2 Effect of Calcination Temperature

Calcination was the last step in the preparation method in order to form structure and eliminate undesired product. The difference in catalyst structure caused some changes in the activity and selectivity.

The effect of calcination temperature on catalyst was conducted using 100 mg of catalyst calcined at different temperatures, which were 300, 400 and 600°C for 5 h. The reactant gas contained 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balanced in He flowing at 50 ml/min and under atmospheric pressure.

3.5.3 Effect of Metal Loading

The amount of Au loading has an effect on the catalyst activity. Thus, different metal Au loadings of 0.5, 1, 3, and 5% by weight were examined using 100

mg of each catalyst. The reactant gas contained 1%CO, 2%CO$_2$, 1%O$_2$, 2.6%H$_2$O, and 40%H$_2$ balanced in He flowing at 50 ml/min and under atmospheric pressure.

3.5.4 Effect of Catalyst Preparation

The preparation methods for highly dispersed Au catalysts have been developed in order to improve the catalyst activity. The effect of catalyst preparation method on catalyst activity was tested using 100 mg of each catalyst prepared by different methods. The catalysts were prepared by 2 techniques, which were deposition-precipitation and impregnation on sol-gel method.

3.5.5 Effect of CO$_2$

Hoflund *et al.* (1995) found that the retention of CO$_2$ led to the increase of surface coverage by intermediate species. Therefore, the activity test was examined using 100 mg of catalyst by varying the concentration of CO$_2$ in order to investigate the effect of CO$_2$.

3.5.6 Effect of H$_2$O

Generally, the catalyst activity is depressed in the presence of water vapor. Thus, the activity was tested using 100 mg of catalyst by varying the concentration of water vapor in the reaction gas mixture.

3.5.7 Deactivation Test

It is necessary to investigate the stability of catalyst. Therefore, catalyst deactivation was tested for 48 h under reaction condition for selective CO oxidation.

3.6 Calculations

The CO conversion and selectivity were calculated by Equation 3.4 and 3.5, respectively.

$$\% \text{ CO Conversion} = \frac{[CO]_0 - [CO]}{[CO]_0} \times 100 \qquad (3.4)$$

$$\% \text{ Selectivity} = \frac{[O_2]_{COoxi^n}}{[O_2]_{COoxi^n} + [O_2]_{H_2oxi^n}} \times 100 \qquad (3.5)$$

where:

$[CO]_O$ = Amount of CO in reactant gas

$[CO]$ = Amount of CO after reaction

$[O_2]_{COoxi^n}$ = Amount of O_2 for CO oxidation

$[O_2]_{H_2oxi^n}$ = Amount of O_2 for H_2 oxidation.

3.7 Experimental Plan

Condition : 100 mg of catalyst (80-120 mesh size)

Reactant gas : 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balanced in He

Flow rate : 50 ml/min

Space velocity : 30,000 $mlg^{-1}h^{-1}$

Reaction temperature : 50-190°C

Reaction pressure : atmospheric pressure

3.7.1 Effect of Catalyst Pretreatment

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1
- Impregnation on sol-gel method: ISG

Calcination condition: 400°C for 5 h

Table 3.1 summarizes the experimental plan for effect of catalyst pretreatment.

Table 3.1 Experimental plan for effect of catalyst pretreatment

Run No.	Type of catalyst	Pure H_2	Pure O_2	Pure He
1-3	1%Au/TiO$_2$ (DP1)	*	*	*
4-6	1%Au/TiO$_2$ (ISG)	*	*	*

3.7.2 Effect of Calcination Temperature

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1
- Depostion-precipitation method (Sigma): DP2
- Impregnation on sol-gel method: ISG

Pretreatment condition

- Pure O_2 at 200°C for 2 h for DP1 and DP2
- Pure H_2 at 200°C for 2 h for ISG

Table 3.2 summarizes the experimental plan for effect of calcination temperature.

Table 3.2 Experimental plan for effect of calcination temperature

Run No.	Type of catalyst	300°C	400°C	600°C
7-8	1%Au/TiO$_2$ (DP1)	*	*	-
9-10	1%Au/TiO$_2$ (DP2)	*	*	-
11-13	1%Au/TiO$_2$ (ISG)	*	*	*

3.7.3 Effect of Metal Loading

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1
- Impregnation on sol-gel method: ISG

Pretreatment condition

- Pure O_2 at 200°C for 2 h for DP1
- Pure H_2 at 200°C for 2 h for ISG

Table 3.3 summarizes the experimental plan for effect of metal loading.

Table 3.3 Experimental plan for effect of metal loading

Run No.	Type of catalyst	0.5%Au	1%Au	3%Au	5%Au
14-17	1%Au/TiO$_2$ (DP1)	*	*	*	*
18-20	1%Au/TiO$_2$ (ISG)	*	*	*	-

3.7.4 Effect of Catalyst Preparation

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1
- Depostion-precipitation method (Sigma): DP2
- Impregnation on sol-gel method: ISG

Pretreatment condition

- Pure O$_2$ at 200°C for 2 h for DP1 and DP2
- Pure H$_2$ at 200°C for 2 h for ISG

Table 3.4 summarizes the experimental plan for effect of catalyst preparation.

Table 3.4 Experimental plan for effect of catalyst preparation

Run No.	Type of catalyst	DP1	DP1 +Mg citrate	DP2	ISG
21-24	Au/TiO$_2$	*	*	*	*

3.7.5 Effect of CO$_2$

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1

Pretreatment condition: Pure O$_2$ at 200°C for 2 h for DP1

Table 3.5 summarizes the experimental plan for effect of CO$_2$.

Table 3.5 Experimental plan for effect of CO_2 (reactant gas: 1%CO, 1%O_2, 2.6%H_2O, and 40%H_2 balanced in He)

Run No.	Type of catalyst	0%CO_2	2%CO_2	10%CO_2
25-27	1%Au/TiO$_2$ (DP1)	*	*	*

3.7.6 Effect of H_2O

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1

Pretreatment condition: Pure O_2 at 200°C for 2 h for DP1

Table 3.6 summarizes the experimental plan for effect of H_2O.

Table 3.6 Experimental plan for effect of H_2O (reactant gas: 1%CO, 1%O_2, 2%CO_2, and 40%H_2 balanced in He)

Run No.	Type of catalyst	0%H_2O	2.6%H_2O	10%H_2O
28-30	1%Au/TiO$_2$ (DP1)	*	*	*

3.7.7 Deactivation Test

Catalyst preparation method

- Depostion-precipitation method (Degussa P-25): DP1

Pretreatment condition: Pure O_2 at 200°C for 2 h for DP1

Table 3.7 summarizes the experimental plan for deactivation test.

Table 3.7 Experimental plan for deactivation test

Run No.	Type of catalyst	Deactivation test
31	1%Au/TiO$_2$ (DP1)	*