

CHAPTER IV

EXPERIMENTAL

4.1 Sample preparations

4.1.1 Chemicals

The lists of chemicals used in this research are shown in the Table 4.1.

Table 4.1: Chemicals used for sample preparations

Chemical	Grade	Supplier
Titanium ethoxide	20%	Aldrich
Titanium isopropoxide	99.999%	Aldrich
Cobalt (II) nitrate hexahydrate	analytical	Aldrich
Re ₂ (CO) ₁₀	analytical	Pressure chemicals
NaBH ₄	+98%	Acros
Tetrahydrofuran	+99%	Aldrich
Ethanol	andhydrous	Aldrich
Cyclohexane	99%	EM science
<i>n</i> -Pentane	99%	Fisher
1,4-butanediol	analytical	Aldrich
Nitric acid	concentrate	Aldrich
JRC-TIO-1	reference	Science, Shimane University

4.1.2 Synthesis of TiO₂ nanocrystal in anatase phase via sol-gel based precipitate process

TiO₂ nanocrystals were synthesized via sol-gel process of titanium ethoxide. A specific amount of precursor was dissolved in ethanol, and mixed with a water-ethanol solution at water:alkoxide molar ratio equal to 165. A precursor solution was added drop-wise into the aqueous solution and was stirred by ultrasonic vibration at room temperature. White precipitates of hydrous oxides formed instantly and the mixture was stirred for at least two hours. The amorphous precipitates were separated from the mother liquor by centrifugation and were redispersed in ethanol for five times to minimize particle agglomeration. The resulting materials were then dried and calcined at 723 K in the studied atmospheres, respectively, for 2 hours with the heating rate at 10 K/min. To study the controlling of surface defect in the first step, %O₂ during calcination as the first studied parameter was varied from 0 to 100%. The water:alkoxide molar ratio used during sol-gel synthesis which is the second studied parameter was also varied from 4 to 165. Details of calculation for evaluating water:alkoxide molar ratio in this synthesis are given in Appendix A.

4.1.3 Synthesis of TiO₂ nanocrystal in anatase phase via sol-gel based peptization process

Titanium isopropoxide (417 ml) was hydrolyzed in 5000 ml of water to which 36.1 ml of concentrated nitric acid has been previously added. Precipitation occurred immediately. The suspension was peptized in order to obtain a clear sol. The sol was then dialyzed for 3–4 days using a sol to water ratio of 1 : 10 until a final pH of 3.5 was reached and then it was dried at 373 K for 2 h and subsequently calcined at 623 K for 2 h.

4.1.3 Synthesis of TiO₂ nanocrystal in anatase phase via solvothermal method

A specific amount of precursor was dissolved in 100 ml of 1,4-butanediol in a test tube and placed in 300 ml autoclave containing 30 ml of the same organic solvent. After the autoclave was completely purged with nitrogen, the contents were heated to the desired temperature (523 and 573 K) at the rate of 2.5 K/min and held at that temperature for 2 h. After the autoclave was cooled to room temperature, the product powders obtained in the test tube were washed repeatedly with methanol and dried in air.

4.1.4 Preparation of Co/TiO₂ catalyst

A 20 wt% of Co/TiO₂ was prepared by the incipient wetness impregnation¹⁹. A designed amount of cobalt nitrate [Co(NO₃)₂·6H₂O] was dissolved in deionized water and then impregnated onto prepared titania. The catalyst precursor was dried at 383 K for 12 h and calcined in air at 723 K for 4 h. Details of calculation of this preparation are given in Appendix A.

4.1.5 Synthesis of H₃Re₃(CO)₁₂

H₃Re₃(CO)₁₂ was synthesized from Re₂(CO)₁₀ by the method of Andrews et al. All handling was done in a glove box or by using standard Schlenk techniques to minimize exposure to O₂ and moisture at University of California, Davis, CA. H₃Re₃(CO)₁₂ was isolated by precipitation from a hot cyclohexane solution and washed with dry *n*-pentane and then stored in an N₂-filled glove box. The identity of the precursor in a CH₂Cl₂ solution was confirmed by IR spectra matching the literature spectrum.

4.1.6 Preparation of TiO₂ incorporating H₃Re₃(CO)₁₂

The preparation and sample transfers were performed using standard Schlenk techniques and a N₂-filled glove box at University of California, Davis, CA. H₃Re₃(CO)₁₂ was adsorbed on TiO₂ by slurring in *n*-pentane; each slurry was stirred at room temperature for 24 h and then evacuated at the same temperature for 24 h to remove the solvent. The resultant samples were stored under N₂ in a glove box until further use.

4.1.7 Preparation of TiO₂ with different initial crystallite size

To prepare TiO₂ with the different initial crystallite size via sol-gel based precipitate method, the water:alkoxide molar ratios of 165 and 50 were used. By using solvothermal method, the reaction temperatures of 523 and 573K were used for obtaining the different initial crystallite size.

4.1.8 Preparation of TiO₂ with different crystallite size

To prepare TiO₂ with different crystallite size for studying in the topic of crystal growth, the crystalline TiO₂ was placed into box furnace and heated it up to the desired temperature within the range of 673-1173, at the rate of 10K/min and holding it at that temperature for 1 h.

4.1.9 Preparation of perfective and defective TiO₂ nanocrystal by the second step creation method

To prepare perfective TiO₂, the crystalline TiO₂ was treated with O₂ at 723 K for 4 h. In case of defective TiO₂, the crystalline TiO₂ was treated under vacuum at 723 K for 4 h.

4.2 Characterization

4.2.1 Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) was performed by using a SIEMENS XRD D5000 connect with a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer. The measurements were carried out by using Ni-filtered CuK_α radiation. Scans were performed over the range from 10° to 80° with step 0.02° . To determine the average crystallite size, peak broadening analysis was applied to anatase (101) peak using Scherrer's equation.

The samples were also transferred from the glove box and pressed into the sample holder in air. X-ray diffraction (XRD) patterns of the samples were also collected with a Scintag XDS-2000 X-ray powder diffractometer by using filtered Cu $\text{K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) at University of California, Davis, CA. Each reported pattern was scanned in the range of 10 to 80° with 0.02° scanning steps.

4.2.2 Scanning electron microscope (SEM)

SEM and Energy dispersive X-ray spectroscopy (EDX) were used to determine the sample morphology and element distribution of the sample using JEOL JSM – 35CF. SEM was operated using the back scattering electron mode at 20 kV. After the SEM micrographs were taken, EDX was performed to determine the element distribution on the sample using Link Isis 300 software at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

4.2.3 Transmission electron microscopy and selected area electron diffraction

TEM and SAED characterizing the morphology, crystallite size, and diffraction patterns of the primary particles of the resulting TiO₂ samples were obtained using the JEOL JEM-2010 transmission electron microscope operated at 200 kV with an optical point to point resolution of 0.23 nm. The sample was dispersed in ethanol prior to measurement.

4.2.4 Brunauer-Emmett-Teller surface area (BET)

Surface area (BET) of the sample was measured using a micromeritics model ASAP 2000 using nitrogen as the adsorbate. Each sample was degassed under vacuum at < 10 $\mu\text{m-Hg}$ in the Micromeritics ASAP 2000 at 423 K for 4 hours prior to N₂ physisorption.

4.2.5 CO₂-temperature programmed desorption

TPD using CO₂ as a probe molecule (CO₂-TPD) was performed to determine the Ti³⁺ site on the surface of TiO₂. It was carried out using a 1 g of a TiO₂ sample. The sample was dosed by 1% CO₂ in He for 1 h in liquid nitrogen and then desorbed at a range of temperature from 123 to 253 K by level controlling. A Gow-Mac (Series 150) gas chromatograph equipped with a thermal conductivity detector was used to analyze CO₂.

4.2.6 IR spectroscopy

Each powder sample was pressed between two KBr windows in the glove box and mounted into a sealed cell. IR spectra were collected under vacuum, with a Bruker IFS 66v spectrometer operated with a resolution of 2 cm⁻¹ at University of California, Davis, CA. Each reported spectrum is the average of 64 scans.

4.2.7 Electron spin resonance spectroscopy

ESR was conducted at power 1mW and amplitude 2.5×10^4 without illumination using a JEOL, JES-RE2X electron spin resonance spectrometer at Chulalongkorn university, Thailand. It was performed to monitor the surface Ti^{3+} on the surface of the TiO_2 .

Samples were also loaded into EPR tubes in the glove box and then evacuated overnight and flame sealed. Data were collected with a Bruker ECS 106 X-band spectrometer equipped with a Bruker ER4116DM cavity at department chemistry, University of California, Davis, CA. Samples were cooled with liquid helium, and the temperature was controlled at 5 K with an Oxford ESR900 liquid helium cryostat and an Oxford ITC503 temperature controller.

4.2.8 Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) was used to determine the reduction behaviors and reducibilities of the supported catalysts. It was carried out using 50 mg of a sample and a temperature ramp from 35 to 1073 K at 5K/min. The carrier gas was 5% by volume H_2 in Ar. A cold trap was placed before the detector to remove water produced during the reaction. The thermal conductivity detector (TCD) was used for measuring the amount of hydrogen consumption. The operating condition of the TCD is shown in the Table 4.2. Details of calculation for reducibility of the sample are given in Appendix B.

4.2.9 Hydrogen chemisorption

Static H_2 chemisorption at 100°C on the reduced sample was used to determine the number of reduce surface cobalt metal atoms and percentage overall cobalt dispersion. H_2 chemisorption was carried out following the procedure described by Reuel and Bartholomew using a Micromeritics Pulse Chemisorb 2700 instrument at the Analysis Center of department of chemical engineering, faculty of engineering,

chulalongkorn university. Prior to chemisorption, the samples were reduced at 350°C for 10 h. Details of calculation of the total hydrogen chemisorption and dispersion are given in Appendix C.

4.2.10 X-ray absorption spectroscopy

The powder samples formed by adsorption of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ on titania were characterized by X-ray absorption spectroscopy at the Re L_{III} edge (10535 eV). Data were collected in fluorescence mode at beamline X18-B of the National Synchrotron Light Source (NSLS), USA and at beam line 2-3 of the Stanford Synchrotron Radiation Laboratory (SSRL), USA. Si(111) and Si(220) double-crystal monochromators were used at the respective synchrotrons, with respective spectral resolutions of 1.0 and 0.5 eV.

Samples in an argon-filled glove box were packed into a sample holder and sealed with Kapton® tape. The measurements were done at room temperature with a N_2 -filled ion chamber used to measure the incoming X-rays and a 13-element germanium detector used for the fluorescence; the germanium detector window was set for the L_{α} lines (8652 and 8586 eV). The monochromator was detuned 25% to suppress higher harmonics. The data in the EXAFS region were collected with an even grid of 0.07 k (k is the wave vector) and with a constant integration time. Some samples contained 1.0 wt% Re, and each of these was scanned at least four times. One sample contained only 0.1 wt% Re, and it was scanned 10 times. The average collection time per scan was 30 min.

4.2.11 Analysis of EXAFS Spectra

Data reduction and analysis were carried out with the average of all the scans taken for each sample, by use of the software XDAP.⁵¹ The data were fitted to multiple-shell models with a difference file technique, with fitting done in both R - (distance) and k -space [52]. The objective function used for the least-squares fitting of the data is reported elsewhere [52]. Both the magnitude and the imaginary part of the Fourier-

transformed data were fitted with k^1 , k^2 , and k^3 weightings of the data until the fit was optimized.

The software FEFF7 [53] was used to determine amplitude- and phase-shift functions by theoretical calculations for reference materials with known crystal structures, except that experimental EXAFS results were used as a reference for Re–O contributions characterized by multiple scattering. The reference compounds used for each EXAFS contribution are summarized in Supporting Information.

The presence of low-Z scatterers at distances of approximately 3.0 Å from Re is an indication of carbonyl oxygen atoms (which are characterized by collinear multiple scattering with the carbonyl carbon atom). To distinguish such contributions from single-scattering contributions, phase- and amplitude-correction was used [52]. The identities of the other contributions were also confirmed by using phase and amplitude correction.

To estimate the value of the amplitude reduction factor in the EXAFS equation, S_0^2 [52], the EXAFS spectra characterizing the precursor $\text{H}_3\text{Re}_3(\text{CO})_{12}$ were analyzed by fixing the values of interatomic distances and coordination numbers to those determined by crystallography [54] and allowing the values of S_0^2 to vary. The values of the inner potential correction, ΔE_0 , and the Debye-Waller factor, $\Delta\sigma^2$, with respect to the reference material were also allowed to vary for each contribution in the determination of the value of S_0^2 . A satisfactory value of S_0^2 of 0.91 was obtained [55].

The number of fitted parameters for each model was statistically justified according to the criterion of the Nyquist theorem (Tables 6–8) [56]. To estimate the statistical error associated with the $\chi(k)$ values for each data set (used in the estimation of precisions), the averaged data were Fourier filtered by using a k -window larger than that used for the data fitting and an R -range of 0–10 Å. The filtered data were then subtracted from the raw data to obtain an estimate of the error at each point. The root mean square error was calculated and used for calculation of precisions and the goodness of fit.

The precisions reported for each of the parameters in the EXAFS models were calculated on the basis of the objective function of the fitting routine [52]. The values of goodness of fit and of the $(\Delta\chi)^2$ function (recommended by the International XAFS Society [57]) are included with each fit. Details of calculation and Fourier transformation of the EXAFS data are given in Appendix D.

4.3 Reactivity measurements

4.3.1 Photocatalytic reaction

The apparatus and experimental procedures employed to evaluate the performance of various photocatalysts were described in this section.

4.3.1.1 Materials

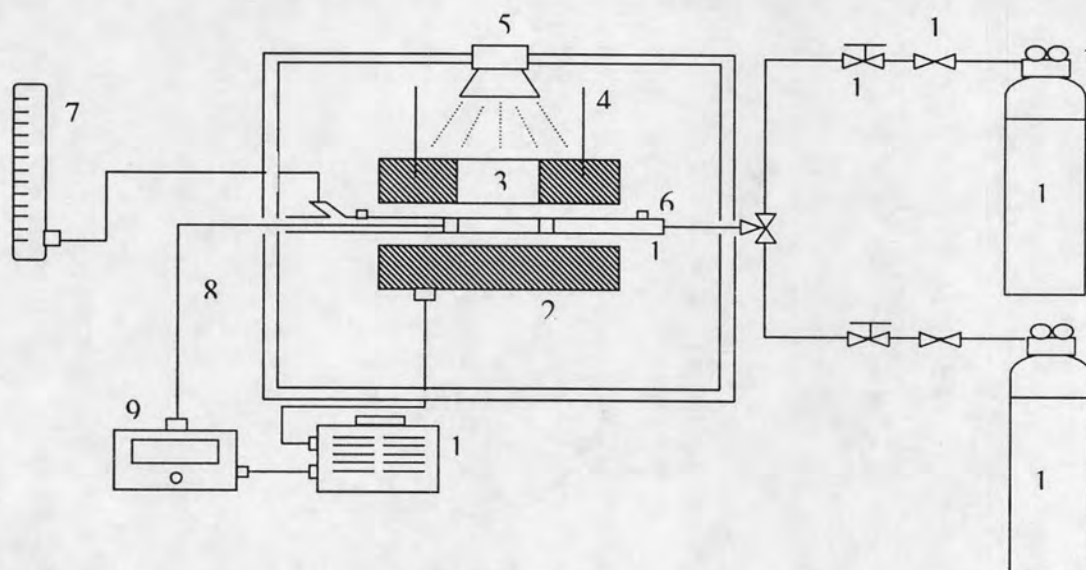
The reactant gas used for this study was ethylene in air as supplied by Thai Industrial Gas Limited. The gas mixture contained 0.1 vol % ethylene in balance air. Total flow rate of gas in the experiments was 15 ml/min.

4.3.1.2 Apparatus

Photoreactor system consists of a photoreactor and a gas controlling system.

4.3.1.2.1 Photoreactor

The photoreactor (see Figure 4.1) had two main components: an ultraviolet light source and the tubular packed bed reactor. The reactor was made from a Pyrex glass tube with a diameter of 5 mm and a length of 27 cm. The stainless steel tube is 1.5" in length and 3/8" in diameter connected to the both ends of the reactor. Two sampling points were located on the left and right of catalyst bed. Photocatalyst was packed between two quartz wool layers.



- | | | |
|---------------------------------|----------------------------------|------------------|
| 1. Reactor regulator | 6. Sampling port | 11. Pressure |
| 2. Furnace | 7. Bubble flow meter | 12. On-off valve |
| 3. Window for irradiation valve | 8. Thermocouple | 13. Metering |
| 4. Aluminium plate | 9. Temperature controller | 14. Air tank |
| 5. Source of light tank | 10. Variable voltage transformer | 15. Ethylene |

Figure 4.1: Photoreactor for experiments

UV light sources were black light blue fluorescent bulbs (8 Watts). Four light bulbs were located 1.5 cm away from the reactor in square configuration. The photoreactor was covered with two layers of aluminum foil to minimize radiation losses from the system.

4.3.1.2.2 Gas Controlling System

Each feed line reactant was equipped with a pressure gauge and a ball valve. Flow rate of gas was adjusted using a metering valve and was measured using a bubble flow meter.

4.3.1.3 Experimental procedure for determining the activity of the photocatalyst

The photocatalytic activity was performed over 0.4 g of catalyst, which was packed in the reactor. The photoreactor was incorporated into the reactor system. Prior to each experiment, the reactor was supplied with air at a flow rate of 15 ml/min. The photocatalyst was illuminated by ultraviolet light sources for one hour in order to remove any organic compounds that might remain from previous experiments from the surface of the catalyst. After one hour, the reactant, 0.1% (v/v) ethylene in air, was fed to the reactor at a flow rate of 15 ml/min. The temperature of the reactor under illumination was about 90°C, as measured using a K-type thermocouple. The flow rate of each gas was measured using a bubble flow meter. The diagram of the flow reactor system in order to test the photocatalysts was shown in Figure 4.2.

The effluent gas was sampled to measure the concentration of ethylene using GC-14B gas chromatograph (Shimadzu), equipped with a flame ionization detector. The operating conditions for the instrument were listed in Table 4.2. The composition was measured every 20 minutes until steady state was achieved (as indicated by constant peak areas in the gas chromatograms).

Table 4.2: Operating conditions for gas chromatography

Gas Chromagraph	SHIMADZU GC-14B
Detector	FID
Column	VZ10
Carrier gas	H ₂ (99.999%)
Carrier gas flow (ml/min)	30 cc/min
Column temperature	
- initial (°C)	70
- final (°C)	70
Injector temperature (°C)	100
Detector temperature (°C)	150
Current (Ma)	-
Analysed gas	Hydrocarbon C ₁ -C ₄

The photocatalytic reactor was set up as shown in Figure 1. The catalysts were packed into a 1 cm diameter horizontal quartz tube. Illumination was provided by 500 W mercury lamps, located above the horizontal quartz tube. The reactant was 0.1% (v/v) ethylene in air. Reactor effluent samples were taken at 30 min intervals and analyzed by GC. The composition of hydrocarbons in the feed and product stream was analyzed by a Shimadzu GC14B (VZ10) gas chromatograph equipped with a flame ionization detector. In all case, steady state was reached within 4 h.

4.3.2 CO-hydrogenation reaction

4.3.2.1 Materials

The reactant gas used for the reaction study was the carbon monoxide in hydrogen feed stream as supplied by Thai Industrial Gas Limited (TIG). The gas mixture contained 9.73 vol% Co in H₂. The total flow rate was 30 ml/min with the H₂/CO ratio of 10/1. Ultra high purity hydrogen and high purity argon manufactured by Thai Industrial Gas Limited (TIG) were used for reduction and balanced flow rate.

4.3.2.2 Apparatus

Flow diagram of CO hydrogenation system is shown in Figure 4.1. The system consists of reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.3.2.2.1 Reactor

The reactor was made from a stainless steel tube (O.D. 3/8"). Two sampling points were provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

4.3.2.2.2 Automation Temperature Controller

This unit consisted of a magnetic switch connected to a variable voltage transformer and a solid state relay temperature controller model no. SS2425DZ connected to a thermocouple. Reactor temperature was measured at the bottom of the catalyst bed in the reactor. The temperature control set point is adjustable within the range of 0-800⁰C at the maximum voltage output of 220 volt.

4.3.2.2.3 Electrical Furnace

The furnace supplied heat to the reactor for CO hydrogenation. The reactor could be operated from temperature up to 800⁰C at the maximum voltage of 220 volt.

4.3.2.2.4 Gas Controlling System

Reactant for the system was each equipped with a pressure regulator and an on-off valve and the gas flow rates were adjusted by using metering valves.

4.3.2.2.5 Gas Chromatograph

The composition of hydrocarbons in the product stream was analyzed by a Shimadzu GC-14B(VZ-10) gas chromatograph equipped with a flame ionization detector. A Shimadzu GC-8A (molecular sieve 5A) gas chromatograph equipped with a thermal conductivity detector was used to analyze CO and H₂ in the feed and product streams. The operating conditions for each instrument are shown in the Table 4.3.

Table 4.3 Operating condition for gas chromatograph

Gas Chromatograph	SHIMADZU GC-8A	SHIMADZU GC-14B
Detector	TCD	FID
Column	Molecular sieve 5	VZ10
- Column material	SUS	-
- Length	2 m	-
- Outer diameter	4 mm	-
- Inner diameter	3 mm	-
- Mesh range	60/80	60/80
- Maximum temperature	350 ⁰ C	80 ⁰ C
Carrier gas	He(99.999%)	N ₂ (99.999%)
Carrier gas flow(ml/min)	30 ml./min	30 ml./min
Column temperature		
- initial(⁰ C)	60	70
- final (⁰ C)	60	70
Injector temperature (⁰ C)	100	100
Detector temperature (⁰ C)	100	150
Current (Ma)	80	-
Analysed gas	Ar,CO,H ₂	Hydrocarbon C ₁ - C ₄

4.3.2.3 Procedures

CO hydrogenation was performed using 0.2 g of catalyst was packed in the middle of the stainless steel microreactor, which located in the electrical furnace. The total flow rate was 30 ml/min with the H₂/CO ratio of 10/1. The catalyst sample was re-reduced *in situ* in flowing H₂ at 350⁰C for 10 h prior to CO hydrogenation. CO hydrogenation was carried out at 220⁰C and 1 atm total pressure. The product streams were analyzed by gas chromatography (GC). In all cases, steady-state was reached within 5 h.

The effluent gases were sampled to analyse the concentration of hydrocarbon (C1-C4) using GC-14 B equipped with a VZ10 column , whereas carbonmonoxide concentration was analyzed by GC-8A equipped with a Molecular sieve 5A column. Details of calculation for CO conversion and activity are given in Appendix E.