

CHAPTER III

EXPERIMENTAL SECTION

3.1 Chemicals

Hydrogen tetra chloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) used in this research was A.C.S grade obtained from Aldrich.

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) used was purum p.a. grade obtained from Fluka.

Manganese (II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) used was purum p.a. grade with ≥ 97 percent purity obtained from Fluka.

Yttrium (III) nitrate tetrahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$) used was R&D grade with 99.99 % purity obtained from Aldrich.

Nickel (II) oxide (NiO) used was A.C.S grade obtained from Aldrich.

Manganese (IV) oxide (MnO_2) and Yttrium (III) oxide (Y_2O_3) used were R&D grade with 99.99 percent purity obtained from Aldrich.

30 % Ammonium hydroxide solution used was RPE grade provided by Carlo Erba.

3.2 Catalyst Preparation

In this research, both the coprecipitation and deposition-precipitation methods were used to prepare for the gold-doped oxide catalysts at different weight ratios ($\text{Au}/(\text{Au}+\text{MO}_x) = 0.5/100, 1/100$ and $1.5/100$).

3.2.1 Coprecipitation Method

A mixture of nickel (II) nitrate hexahydrate and hydrogen tetrachloroaurate trihydrate at three different ratios (0.5wt.%Au, 1.0wt.%Au, and 1.5wt.%Au) was dissolved in distilled water and the solution was heated

to 60-70°C. 1 M ammonium hydroxide solution was added drop-wise to the stirred solution until a pH of 8 was reached. The precipitate was left at 60-70°C for 1 h to allow precipitation. The precipitate was filtrated, washed with hot distilled water, dried at 120°C, ground into a fine powder, and finally calcined in air at three different temperatures (300, 400, and 500°C) for 4 h.

3.2.2 Deposition-precipitation Method

After the pH of an aqueous solution of hydrogen tetrachloroaurate trihydrate was adjusted to a fixed point in the range of 6-10 (pH about 8 in this experiment) and the solution was then heated to 60-70°C, a metal oxide was immersed in the solution. Three types of metal oxides (NiO, MnO₂ and Y₂O₃) were used in this preparation. Aging for about 1 hour, this allowed the deposition of Au(OH)₃ on the surface of the metal oxide. The solution was treated in the same manner as described in the coprecipitation method.

3.3 Catalyst Characterization

The characteristics of the gold-doped oxide catalysts prepared was determined with regard to their physical and chemical properties using atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), BET surface area analyzer, TPD/TPR analyzer, and transmission electron microscopy (TEM).

3.3.1 Atomic Absorption Spectroscopy (AAS)

The actual contents of gold loaded in the catalysts prepared were determined by an atomic absorption spectroscopy, VARIAN Model 300/400. The standard solutions used in this work manufactured by Merck had 1000 ppm of gold. Firstly, a known weight around 0.02 g of catalysts was completely dissolved in a mixture solution of hydrochloric acid and nitric acid.

The solution was then diluted to the measuring range. The concentration of gold was obtained by comparing its absorbance with the calibration curve of the standard solution.

3.3.2 X-ray Diffraction (XRD)

X-ray diffraction is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. Comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

X-ray diffraction patterns of all catalyst samples were obtained by using a Phillips PW 1830/00 No. DY 1241 diffractometer equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 Å). The sample was first ground to fine homogeneous powder with using a mortar. The powder was then spread on a glass slide specimen holder, and examined between 5-90° 2θ at a scan rate of 1.5° 2θ/min in 0.02° 2θ increments. CuKα (λ = 0.154 nm) radiation was used as an X-ray source and operated at 40 kV, and 30 mA. The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to an online microcomputer for storage and subsequent data and analysis by PC-APD version 3.5B. Peak positions were compared with the standard JCPDS files to identify crystalline phases.

The XRD patterns were used for average particle diameter estimation by line broadening measurements in the Debye-Scherrer equation,

$$t = K\lambda/\beta\cos\theta \quad (3.1)$$

where

- λ = the wavelength (nm);
- K = the Debye-Scherrer constant which to some degree depends on the shape of peak (assume equal to 0.9);
- β = the full width at half maximum (FWHM) of the broadened peak;
- θ = the Bragg angle of the reflection (degree); and
- t = the thickness of the crystal (nm)

3.3.3 BET Surface Area Measurements

The surface areas of all catalysts prepared were determined by measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature below the critical temperature of the adsorbate. An adsorption or desorption occurs the changing in the pressure in the sample cell until equilibrium is established. This volume-pressure data can be calculated for the BET surface area. The BET surface area measurement was done by using Quantachrome Corporation Autosorb I. The catalyst sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum (150°C, 6 hours) before starting analysis to determine its surface area. Autosorb ANYGAS Version 2.10 is used to analyze the results.

The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1) P}{V_m c P_0} \quad (3.2)$$

where

- V = the volume of gas adsorbed;
- P = the pressure of gas;

P_0 = the saturated vapor pressure of the liquid at the operating temperature;

V_m = the volume equivalent to an adsorbed monolayer;

c = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction which is given by

$$c = \exp\left(\frac{H_1 - H_L}{RT}\right) \quad (3.3)$$

where

H_1 = the fixed heat of adsorption;

H_L = the latent heat of evaporation;

R = the gas constant; and

T = the temperature

The surface area can be determined by using the following equation:

$$S_g = \frac{V_m}{0.0224} (6.02 \times 10^{23}) (A) \quad (3.4)$$

where

S_g = the specific surface area (m^2/g); and

A = the area occupied by each adsorbate molecule (m^2)

3.3.4 Temperature Programmed Desorption (TPD)

Temperature-Programmed Desorption (TPD) analyses were employed to determine the number, type, and strength of active sites available on the surface of catalyst samples. It can be done by measuring the amount of gas desorbed at various temperatures. After the sample had been outgassed,

reduced, or otherwise prepared, a steady stream of analysis gas was allowed to flow over the sample and reacted with the active sites. The programmed desorption began by raising the temperature linearly with time while a constant stream of inert carrier gas was still passing over the sample. As it has been known that at a particular temperature, the heat will overcome the activation energy; therefore, the bond between the adsorbate and adsorbent will break and the adsorbed species will desorb. If different active metals are present, they usually will desorb the reacted species at different temperatures. The desorbed molecules enter the stream of inert carrier gas and are swept to the detector which measures the gas concentrations. The volume of desorbed species combined with stoichiometry factor, and the temperature at which pre-adsorbed species desorb, yields the number and strength of active sites.

TPD of oxygen was operated by flowing a steady stream of 5% oxygen balanced with helium gas at temperature of 200°C about one hour after that cooling down to room temperature, and then heating up to 700°C.

3.3.5 Transmission Electron Microscopy (TEM)

The catalysts were ultrasonically dispersed in ethanol for minutes. The suspended composites were dropped onto copper grid coated with polyvinyl desiccate. Transmission electron micrographs. JEOL 2000 CX atomic resolution transmission electron microscope was employed to observe the morphology of all catalyst samples.