

CHAPTER III

EXPERIMENTAL SECTION

3.1 Studied Catalysts

The bimetallic Pt-Sn/Al₂O₃ catalysts used in this work were prepared at the University of Michigan by co-impregnation of Degussa nonporous fumed alumina having a BET surface area of 90 m²/g. The precursors, H₂PtCl₆(Aldrich) and SnCl₂ (Aldrich) were dissolved in acetone. One of the bimetallic catalysts was prepared from the nonacidic, chlorine-free precursors tetraamineplatinum (II) hydroxide hydrate(STREM) and tin(II)tartrate to lower the chlorine content. After impregnation, the catalysts were dried at 393 K followed by calcination in air for 2 hours at 773 K. After calcination, the catalysts were reduced for 5 hours in flowing hydrogen at 673 K. The metal content and level of chlorine of the samples were determined by neutron activation analysis. The analytical results of the prepared catalysts are summarized in Table 3.1. The catalysts were further characterized by chemisorption of CO, H₂, and O₂, and the surface composition was determined by XPS (Balakrishnan and Schwank, 1991).

Table 3.1 Metal loading and chlorine level of catalyst samples

Catalyst sample	%wt. of Pt	%wt. of Sn	%wt. of Cl
5.0Pt/Al ₂ O ₃	5.0	0.0	n/a
1.0Pt-0.1Sn/Al ₂ O ₃	0.96	0.14	0.97
1.0Pt-0.5Sn/Al ₂ O ₃ ⁱⁱ (L.C.)	0.92	0.58	0.38

ⁱ n/a = not available

ⁱⁱ L.C. = Low Chloride

3.2 Studied Gases and Volatile Organic Compounds (VOCs)

Ultra high purified (UHP) hydrogen, helium and nitrogen were commercially obtained from Thai Industrial Gases Public Co., Ltd (TIG). The solvents used were methyl alcohol (CH_3OH), acetone ($(\text{CH}_3)_2\text{CO}$), and ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) procured as AR grade from J.T. Baker.

3.3 Experimental Apparatus

The Micromeritics TPD/TPR 2900 was employed as an analyzer for both pulse chemisorption and Temperature-Programmed Desorption. The temperatures of thermal conductivity detector (TCD), valve and loop were maintained at 100°C , 100°C , 75°C , respectively. UHP nitrogen was selected as a carrier gas with a flow rate of 50 ml/min. The detector current was set at 55 mA. The schematic diagram of the experimental system is shown in Figure 3.1. It consists of three gas lines. The first line is for the preparation gas, the second line is for carrier and reference gas and the last line is for the loop gas used for carrying the solvent vapor to the loop injection.

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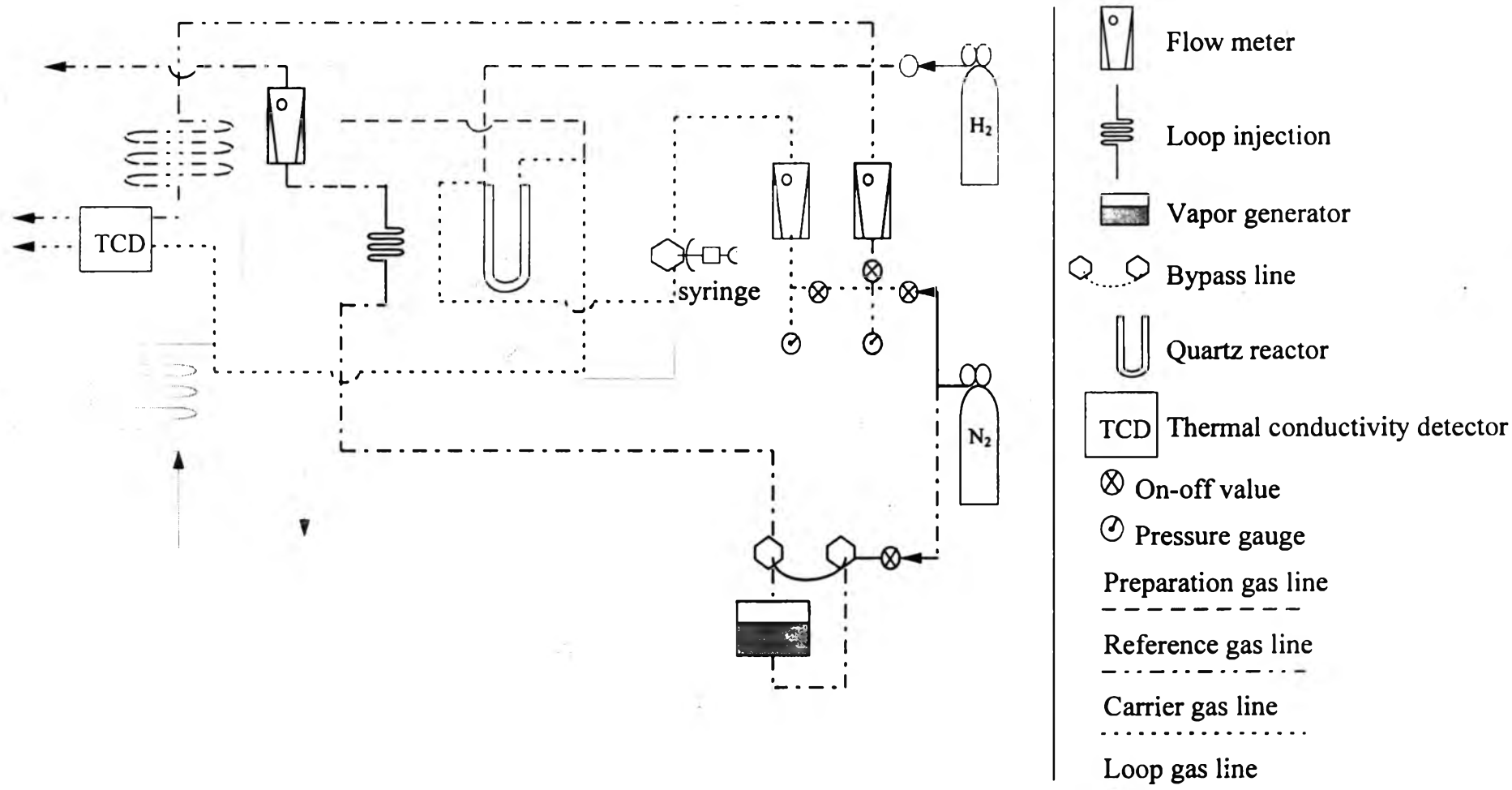


Figure 3.1 Schematic flow diagram of the Micromeritics TPD/TPR 2900.

3.4 Experimental Procedures

A catalyst sample of 0.05 g was placed into a quartz tube reactor which was externally heated by a tube furnace. Prior to chemisorption and temperature-programmed desorption (TPD), the catalyst sample was reduced for 2 hours at 673 K with a stream of UHP hydrogen at an approximately flow rate of 25 ml/min. After completing the reduction step, the catalyst was then cooled down to a room temperature by introducing a stream of UHP nitrogen. Then, pulse chemisorption and TPD experiments were performed using the Micromeritics TPD/TPR 2900 with the following adsorbates: methyl alcohol, acetone, and ethyl acetate. There were 3 different catalyst samples to be studied.

3.3.1 Pulse Chemisorption

After the catalyst sample was cooled down to a room temperature in a stream of nitrogen, UHP nitrogen was then switched to the loop gas line through the vapor generator where the adsorbate was vaporized at a desired temperature. Vapor injection was made in 5-minute intervals until no further vapor uptake by the catalyst was observed. The total amount of adsorption could be calculated by summarizing the vapor uptake observed in the series of injections until saturation was reached.

3.3.2 Temperature-Programmed Desorption (TPD)

Once the adsorption process was completed, the furnace controller was set to ramp the furnace temperature up to 800°C at a linear ramp rate of 10°C/min. As the temperature increased, a surface species began to desorb and the signal of the desorbed species from the thermal conductivity detector was displayed as a function of temperature. Graphically, the TPD/TPR 2900 data were represented as peaks in signal versus time plots and temperature versus time plots. The location of peaks on the temperature axis depicts the strength of adsorption. For simple adsorbates that do not undergo decomposition during TPD, the number of peaks can indicate the number of

energetically distinct surface sites. The higher the temperature required to break the chemisorption bond, the stronger the active site is. The area under each peak represents the quantity of adsorbed species on a given type of surface sites. The adsorbates used in this study, however, are likely to undergo decomposition at elevated temperatures, and this can lead to additional peaks in the TPD spectrum.