CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 <u>Hydrogenation of Tetralin</u>

3.1.1.1 Catalyst Preparation

1. Gamma-alumina (γ-Al_2O_3, from Saint-Gobian NorPro Corporation)
2. $Ni(NO_3)_2.6H_2O$ (from AnalaR Co. Ltd.)
3. $Pt(NH_3)_4(NO_3)_2$ (from Aldrich Co. Ltd.)
4. $Pd(NO_3)_2.xH_2O$ (from Aldrich Co. Ltd.)
5. Deionized water

3.1.1.2 Reactants for Catalytic Activity Testing

1. 1,2,3,4-Tetrahydro-naphthalene (97+%tetralin; from Fluka Co. Ltd.,)
2. Decahydronapthalene (decalin, 99%, a mixture of trans- and cis-decalin at a 60/40 molar ratio; from Fluka, Co. Ltd.)
3. Hydrogen (H_2, UHP)

3.1.2 <u>Ring Opening of 1,3-Dimethylcyclohexane</u>

3.1.2.1 Catalyst Preparation

1. Gamma-alumina (γ-Al_2O_3; from Sasol Co. Ltd.)
2. Silica (HiSil-210; from PPG Co. Ltd.)
3. $IrCl_3.3\,H_2O$ (from Alfa-Aesar Co. Ltd.)
4. $NiCl_2.xH_2O$ (from Alfa-Aesar Co. Ltd.)
5. K_2CO_3 (from Alfa-Aesar Co. Ltd.)
6. Deionized water

3.1.2.2 Reactants for Catalytic Activity Testing

1. 1,3-Dimethylcyclohexane (from Sigma-Aldrich Co. Ltd.)
2. Hydrogen (H_2, UHP)

3.2 Catalyst Preparation

3.2.1 Catalysts for Hydrogenation Reaction

Commercial gamma-alumina support (γ-Al_2O_3, Saint-Gobian NorPro Corp, surface area 252 m^2/g) was ground and sieved to 40-60 mesh to avoid internal mass transfer limitation. Pt, Pd and Ni metals were loaded on gamma-alumina using conventional incipient wetness impregnation technique with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ (Aldrich), $Pd(NO_3)_2.xH_2O$ (Aldrich) andt $Ni(NO_3)_2.6H_2O$ (AnalaR), respectively. The concentration of the precursor solution was adjusted according to the target metal loading. In this study, 1 wt.%Pt, 1 wt.%Pd, and 5 wt.%Ni loading catalysts were prepared. After the impregnation the samples were dried under an ambient temperature for 4 h, then dried overnight at 110 °C, and finally calcined in an oven for 2 h at 300 °C for Pt and Pd catalyst samples and at 400 °C for Ni sample.

3.2.2 Catalysts for Ring Opening Reaction

Gamma-alumina (γ-Al_2O_3, HP-140 from Sasol) and silica (HiSil-210; PPG) were used as supports for the various catalysts investigated. All catalysts were prepared by incipient wetness impregnation (co-impregnation) with aqueous solutions of $IrCl_3.3H_2O$ (Alfa-Aesar), $NiCl_2.xH_2O$ (Alfa-Aesar), and K_2CO_3 (Alfa-Aesar). In each case, the concentration of the precursor solution was adjusted to the desired metal loading. In this study, a fixed metal loading of 0.9 wt.% Ir was used in the monometallic catalysts supported on Al_2O_3 and SiO_2. For the bimetallic Ir-Ni catalysts, 0.3 and 0.1 wt.% Ni loadings were used in combination with 0.9 wt.% Ir on the Al_2O_3 support to obtain a Ni:Ir molar ratio of 1.0 and 0.3, respectively. The catalysts thus obtained are denoted as $IrNi1.0/Al_2O_3$ and $IrNi0.3/Al_2O_3$, respectively. In addition, sequential (two-step) impregnation was used to prepare a $IrNi0.3/Al_2O_3$ catalyst; in this case, a calcined monometallic 0.1wt % Ni/Al_2O_3 sample was further impregnated with the solution of the Ir precursor. For the K-promoted catalysts, 0.5 wt.% K was impregnated on Al_2O_3, before the impregnation with Ir, using a K concentration adjusted to obtain a K:Ir molar ratio equal 2.5 ($0.9Ir$-$0.5K/Al_2O_3$). After impregnation the samples were kept at ambient temperature for 4 h, then dried at 110 °C overnight, and finally calcined in air at 300 °C for the Ir and Ir-K catalysts, while a temperature of 400°C was used for the Ir-Ni catalysts.

3.3 Catalytic Activity Testing

3.3.1 Hydrogenation Reaction

The catalytic activity measurements were carried out in a continuous fixed bed stainless steel 3/4" O.D. reactor, equipped with a thermowell to insert the thermocouple into the center of the catalyst bed. The reaction was conducted in the gas phase at 548 K and 3540 kPa; the H_2/HC molar ratio was kept at 25. Space velocities were systematically varied by independently changing the catalyst amount or the hydrocarbon flow rate. The catalyst was firstly reduced under flowing H_2 at 3540 kPa for 1.5 h at 573 K for Pt and Pd, and 723 K for Ni. After this reduction treatment, the reactor was cooled down in flowing H_2 to 548 K. Then, the liquid reactant was introduced to the reactor using a high-pressure pump at a rate of 3.6 ml/h. Two different hydrocarbon compounds, 1,2,3,4-tetrahydro-naphthalene (tetralin, Fluka, 97+%) and decahydronapthalene (decalin, Fluka, 99%, a mixture of trans- and cis-decalin at a 60/40 molar ratio) were used as pure feeds. When a mixed feed was used, tetralin was mixed with decalin, keeping a 20/80 ratio. The products were analyzed online in a HP6890 gas chromatograph, equipped with an FID detector and an HP-5 column. Different amounts of catalyst were tested to obtain the evolution of products as a function of space time, expressed as W/F, where W is the mass of catalysts (g) and F is the flow rate of hydrocarbon feed (mol/h). In all cases, the product distribution was compared after 6 h on stream (TOS = 6 h), using a fresh catalyst sample in each individual run. Under the conditions used in this study no catalyst deactivation was observed.

3.3.2 Ring Opening Reaction

The reactions of ring opening of 1,3-dimethylcyclohexane (1,3-DMCH, Sigma-Aldrich) and hydrogenolysis of two of the primary products (2,4-dimethylhexane, 2,4- DMC6, and 2-methlyheptane, 2-MC7, from Sigma-Aldrich) were carried out on a fixed bed reactor (1/2" OD stainless steel tube), equipped with a thermowell in the center of the catalysts bed to insert the thermocouple. The catalytic activity measurements were conducted in the gas phase at 603 K, a H_2/HC molar ratio of 30, and a total pressure of 3540 kPa. The catalyst was first reduced for 1.5 h under flowing H_2 at 3540 kPa and 723 K. After the pretreatment, the reactor was cooled down in flowing H_2. Then, the liquid reactant was introduced in the reactor using an Isco LC-500 high-pressure pump. The products were collected in a dry-ice in acetone bath (at a temperature of 197 K to capture all the products) and were analyzed in HP5890 and GC-MS.

Schematic flow diagram and experimental apparatus are shown in Figures 3.1 and 3.2, respectively.

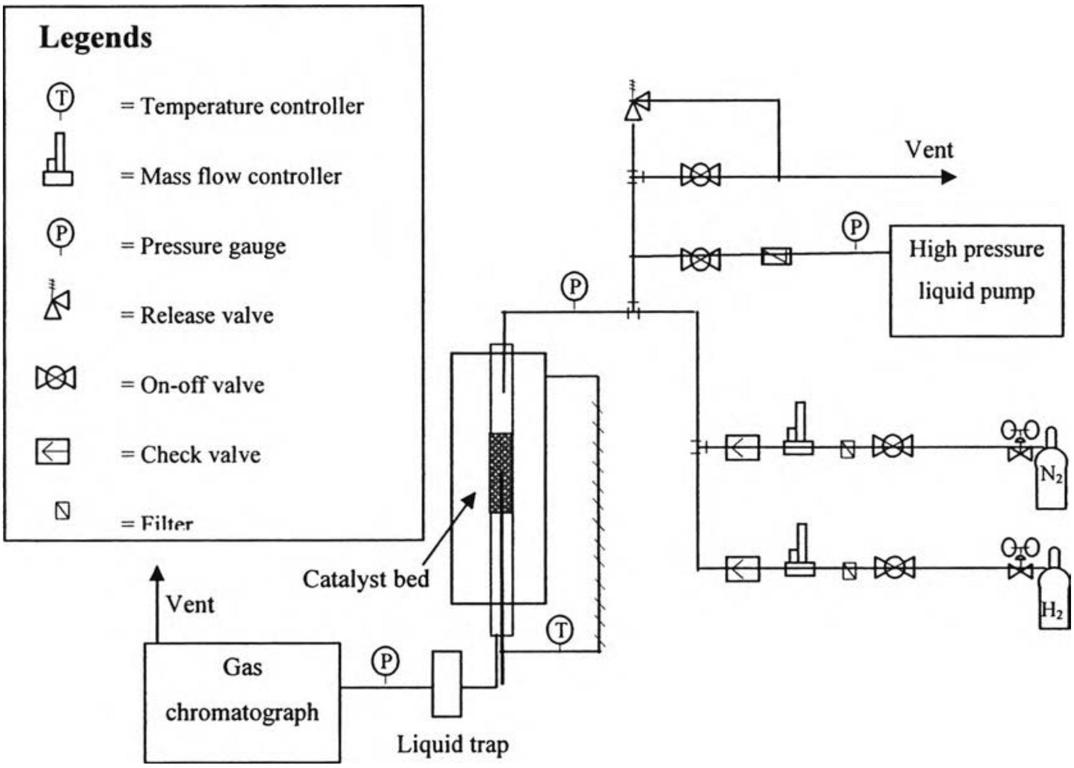

Figure 3.1 Schematic diagram of the experimental set up for hydrogenation and ring opening reaction.

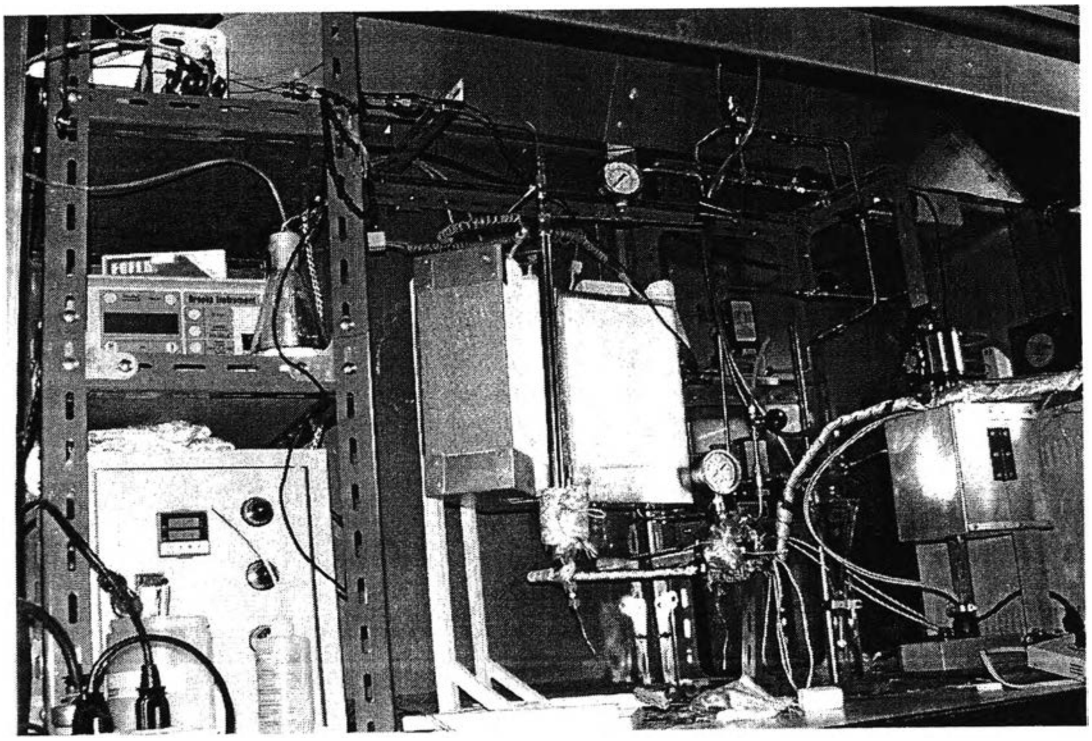

Figure 3.2 A photograph of the experimental apparatus.