

CHAPTER III

EXPERIMENTAL

3.1 Materials

Zeolite Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$) was obtained from Zeolyst International Co. Ltd., USA. The structure of zeolite was confirmed by a JEOL (model JDX-8030) X-ray powder diffractometer. Nitrogen and hydrogen (99.99% purity) was obtained from Praxair Ltd. All reagents were analytical grades as listed in Table 3.1.

Table 3.1 Chemicals and suppliers

Chemicals	Suppliers
Acetone	Reagent Chemical Industry Ltd, Thailand
Aluminum oxide	Fluka Chemie A.G., Switzerland
Ammonium hydroxide	Merck, Germany
Ethylene glycolethylether	Fluka Chemie A.G., Switzerland
Gallium (III) nitrate hydrate	Aldrich Chemical Company, Inc., USA
<i>n</i> -Hexane	Merck, Germany
Magnesium nitrate hexahydrate	Fluka Chemies A.G., Switzerland
Mordenite	Zeolyst International Co., Ltd., USA.
MCM-41	Donated by JAIST (Japan Advanced Institute of Science and Technology, Japan)
Bentonite	Donated by JAIST (Japan Advanced Institute of Science and Technology, Japan)
Palladium (II) acetate	Fluka Chemie A.G., Switzerland
Potassium carbonate	Ajax chemicals, Australia
Potassium chloride	Ajax chemicals, Australia
Silver nitrate	Merck, Germany
Tetraamine platinum (II) chloride hydrate	Aldrich Chemical Company, Inc., USA
Ultra high purity nitrogen gas (99.99%)	Thai Industrial Gas Co., Ltd., Thailand

3.2 Equipment and apparatus

Oven and furnace

The catalysts were preliminary dried at 100°C in a Memmert UM-500 oven and further at 350°C in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C.min⁻¹.

The catalytic apparatus (in Figure 3.1) comprises a quartz tubular reactor of 10-mm. inner diameter. *n*-Hexane was fed as liquid using syringe a pump (No.15). When heated, it became gas and was carried by the nitrogen through a catalyst bed (No.7) in side a catalytic reactor (No.5).

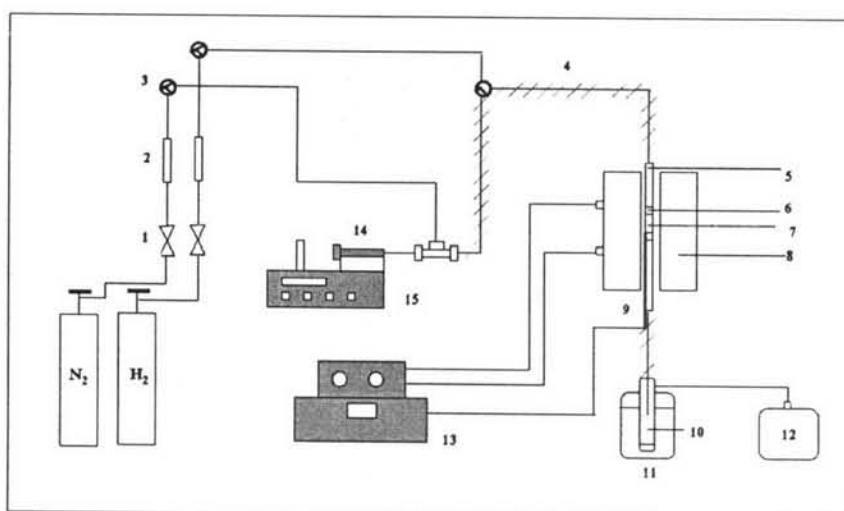


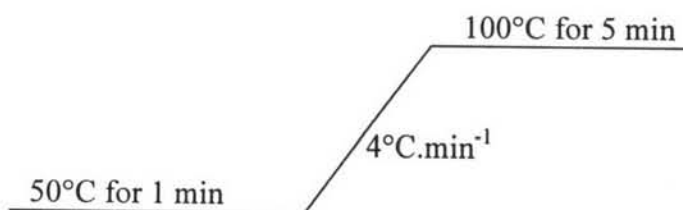
Figure 3.1 schematic diagrams of the reaction apparatus.

- | | | |
|---|----------------------------|--------------------|
| 1 = needle valve, | 2 = flow controller, | 3 = two-way valve, |
| 4 = heater cable, | 5 = tubular reactor, | 6 = quartz, |
| 7 = catalyst, | 8 = electric furnace, | 9 = thermostat, |
| 10 = cold trap, | 11 = dry ice-acetone bath, | 12 = Tedlar bag, |
| 13 = temperature programmed controller, | | |
| 14 = syringe, | 15 = syringe pump. | |

Gas Chromatography

Hydrocarbon liquid was analyzed using a Shimadzu GC-9A gas chromatograph equipped with a 50-m long and 0.53-mm diameter Alumina-PLOT column. Liquid products were analyzed using a Shimadzu GC-8A gas chromatograph equipped with a 30-m long and 0.32-mm diameter DB-1 column. The condition used for the determination of %conversion of *n*-hexane is as follows:

Carrier gas	: Nitrogen
Carrier gas pressure	: 40 kPa
Detector temperature	: 220°C
Injection temperature	: 220°C
Programmed temperature	:



3.3 Preparation of metal loaded catalysts

In this work, two different methods are used for the loading of metal onto the mordenite.

A. Preparation of catalysts using impregnation method

A1. Monometallic, x%Pt (or Pd)/HM

A predetermined amount of tetraammine platinum (II) chloride hydrate or palladium nitrate was dissolved in 3 ml of deionized water, the solution was dropped onto mordenite (6.8801g) and the mixture was shaken for 30 min, then dried in oven at 100 °C and calcined in muffle furnace at 350 °C for 5h.

The catalysts prepared were designed as follows: x%Pt/HM and x%Pd/HM for catalysts impregnated x% by weight (based on total weight of catalyst) of Pt and Pd, respectively.

A2. Bimetallic, x%Pt (or Pd) y%Ga (or Zn)/HM

A predetermined amount of tetraammine platinum (II) chloride hydrate or palladium nitrate was dissolved in 3 ml of deionized water, the solution was dropped onto mordenite (6.8801g) and the mixture was shaken for 30 min, and then dried in oven at 100 °C. After that a predetermined amount of gallium (III) nitrate hydrate or zinc chloride dissolved in deionized water was added and stirred for another 30 min. The mixture was dried in oven at 100°C and calcined in muffle furnace at 350°C 5h.

A3. Bimetallic and loaded with K, x%Pt y%Ga 1%K/HM

K salt solution was dropped onto the x%Pt (or Pd) y%Ga/HM catalyst prepared in A2 above (1%K based on total weight of catalyst). The mixture was shaken for 30 min. Finally it was dried at 100°C and calcined in muffle furnace at 350°C 5h. The catalysts were coded as x%Pt (or Pd) y%Ga 1%K/HM.

B. Preparation of catalysts using ion exchange method

Hydrogen over OH group of acid form mordenite was exchanged with potassium by ion-exchange method.

B1. Loading K via ion exchange

H-MOR (5.0 g) and 80 ml of 8.0 M of K salt solution (ACL or K₂CO₃) were added to the round bottom flask and heated by using an oil bath at 80°C for 24 h. The solids were separated from solution by filtration and washed several times with deionized water until no chloride observed. The resulting solid was dried at 100°C and then calcined in a muffle furnace at 350°C for 5 h.

The catalysts which were loaded with KCl or K₂CO₃ by ion-exchange were coded as KCl-M and K₂CO₃-M, respectively. These were further modified in B2 below.

B2. Bimetallic, x%Pt y%Ga/K-M

KCl-M and K₂CO₃-M (prepared from B1 above) was introduced Pt and Ga by impregnation as the same procedure with bimetallic catalysts (see A2, x%Pt y%Ga/HM). These catalysts were designated as x%Pt y%Ga/K-M.

B3. Loading Pt or Pd via ion exchange, x%Pt (or Pd)-M

Tetraammine platinum (II) chlorides hydrate 0.1803g (or palladium nitrate 0.1202g) was dissolved in deionized water 40 ml. Mordenite (5.0g) was suspended in this solution and stirred at 80°C for 24 h. The solids were separated from solution by filtration and washed several times with deionized water until no chloride was observed. The resulting solid was dried at 100°C and then calcined in a muffle furnace at 350°C for 5 h. These catalysts were designated as x%Pt (or Pd)-HM. The metal content was determined by XRF.

In this work, the prepared catalysts are given following codes:

<u>Impregnation method</u>	<u>Ion exchange method</u>
x%Pt/HM	x%Pt -M
x%Pd/HM	x%Pd-M
x%Pty%Ga /HM	x%Pty%Ga/KM
x%Pdy%Ga /HM	
x%Pty%Zn /HM	
x%Pdy%Zn /HM	
x%Pty%Ga 1%K/HM	
x%Pdy%Ga 1%K/HM	

3.4 Preparation of pellet catalysts

The catalysts were pressed towards a 0.7 millimeter. thick self-supporting wafer using a stainless steel of a 13 millimeter. inner diameter. The hydraulic press with pressing force of 5 tons was held on the catalyst wafer for 5 min. The catalyst wafer was crushed into tiny pellets of approximate size of $2 \times 2 \times 0.7 \text{ mm}^3$.

3.5 Characterization methods

X-ray powder diffractometer

XRD measurement was performed using a Rigaku D/Max-2200 X-ray powder diffractometer at Department of Chemistry, Chulalongkorn University, with nickel filtered CuK_α radiation (30kV, 30mA) at an angle of 2θ ranged from 5 to 40° . The scan speed was $5^\circ\text{C}\cdot\text{min}^{-1}$, and the scan step was 0.02° . Scattering, divergent and receiving slits were fixed at 0.5° , 0.5° and 0.3 mm, respectively.

X-ray fluorescence spectrometer

Metal contents were analyzed using a SISON instrument ARL 8410 X-ray fluorescence spectrometer at the Scientific and Technology Research Equipment Center, Chulalongkorn University.

Temperature program desorption ammonia (TPD)

The concentration of acid sites was measured by ammonia TPD. 90 mg of sample was evacuated at 400°C for 1 h (heating rate of $10^\circ\text{C min}^{-1}$) after that, samples was pretreated by He for 1 h at 400°C . After cooling to room temperature ammonia was adsorbed for 1 h with a partial pressure of 10 mbar. Physisorbed ammonia was removed by heating the sample to 100°C for 1 h. TPD was performed up to 700°C with a heating rate of $10^\circ\text{C min}^{-1}$. A thermal conducting detector was used to detect the desorbing molecules.

Surface Area Analyzer

Specific surface area of a catalyst was determined using a micromeritics adsorptometer, model Flowsorb 2300. The principle is adsorption of particular molecular species from gas N₂ onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample.

3.6 Catalytic activity tests

The catalysis was carried out in an apparatus shown in Figure 3.1. The catalyst (1.0 g) was loaded into a quartz tubular reactor and held in place by a plug of quartz wool, the catalyst portion was covered with small amount of quartz wool. The gas lines were stainless steel tubing wrapped in the heating tape. The height of the catalyst portion was 25 mm. The catalyst was activated by flowing N₂ (20 ml/min) and reduced by flowing H₂ (20 ml.min⁻¹ at 500°C for 1 h). *n*-Hexane was fed using syringe pump to mix with nitrogen at a constant WHSV of 1.0 h⁻¹ (which was corresponded to a gas flow of 10.0 ml.min⁻¹). The feed was passed from the top through the catalyst. After a given time, the gaseous products were collected into a Tedlar bag and analyzed for hydrocarbon components using GC. For the liquid products, they were trapped in a Dewar cooled with dry ice/acetone.

In this work, a blank test was performed without catalyst in the reactor, at the same condition used in this work. The result showed that liquid trapped in the Dewar contained only *n*-hexane.

-Effect of Pt and Pd metal

The catalytic activity of 1%Pt1%Ga/HM and 1%Pd1%Ga/HM catalysts were determined and compared at the same reaction condition.

Condition: N₂ flow rate 10 ml/min, WHSV 1 h⁻¹, reaction temperature 400°C, 1.0 cm³.min⁻¹ *n*-hexane feeding rate.

-Effect of bimetallic

0.5%Pt1%Ga/HM, 0.5%Pt2%Ga/HM, 1%Pt1%Ga/HM, 0.5%Pt1%Zn/HM and 0.5%Pt2%Zn/HM catalysts were determined and compared at the same condition.

Condition: N₂ flow rate 10 ml.min⁻¹, WHSV 1 h⁻¹, reaction temperature 400°C, 1.0 cm³.min⁻¹ *n*-hexane feeding rate.

-Effect of metal loading method

Two series of catalysts were compared under the same reaction condition.

1%Pt/HM vs. 0.95%Pt-M catalysts

1%Pd/HM vs. 1.12%Pd/HM catalysts

Condition: N₂ flow rate 10 ml/min, WHSV 1 h⁻¹, reaction temperature 400°C, 1.0 cm³.min⁻¹ *n*-hexane feeding rate.

-Effect of potassium

1%Pt1%Ga/HM and 1%Pt1%Ga1%K/HM catalysts were determined and compared at the same condition.

Condition: N₂ flow rate 10 ml/min, WHSV 1 h⁻¹, reaction temperature 400°C, 1.0 cm³.min⁻¹ *n*-hexane feeding rate.

-Effect of time on stream

The catalysts chosen for this study are 0.5%Pt1%Ga/HM and 1%Pt1%Ga/HM catalysts. Reactions were determined in 3, 5 and 8 h and compared at the same condition.

Condition: N₂ flow rate 10 ml/min, WHSV 1 h⁻¹, reaction temperature 400°C, 1.0 cm³.min⁻¹ *n*-hexane feeding rate.

-Effect of admixture

Many materials were mixed with the chosen catalyst, 1%Pt1%Ga/HM by physical method in 1:1 weight ratio.

Condition: N₂ flow rate 10 ml/min, WHSV 1 h⁻¹, reaction temperature 400°C, 1.0 cm³.min⁻¹ *n*-hexane feed rate.

The materials chosen for the study are follows:

ZrO₂

MgO

MCM-41

Hydrotalcite

Bentonite and K-bentonite

Ga/Al₂O₃

The preparative procedures of all materials are presented in Appendices (B).

Regeneration of the catalysts

After use, the catalyst was reduced by flowing H₂ at the rate of 20 ml.min⁻¹ for 3 h. and tested activity at the same condition with the fresh catalyst.