

CHAPTER III

EXPERIMENTS

3.1 Instruments and Apparatuses

Ovens and Furnaces

During the synthesis course, crystallization of ZSM-5 support was performed using a Memmert UM-500 oven as a heater. Organic templates were removed by calcination at 550-600°C using a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C. The calcination temperature was depended on types of support.

XRD

Characteristic structure of synthesized supports were identified using a Rigaku D/MAX-2200 X-ray diffractometer (XRD) at Petroleum and Petrochemical College, Chulalongkorn University with nickel filtered Cu K_{α} radiation (40 kV, 30 mA) at an angle of 2θ ranged from 1.2 to 10° for Al-HMS samples and 5 to 40° for ZSM-5 samples. In case of Al-HMS, the scan speed was 2°/min while that of 5°/min was applied for ZSM-5. The scan step was fixed at 0.02°. The three slits setting (scattering, divergent and receiving slits) for Al-HMS were fixed at 0.5°, 0.5° and 0.15 mm, respectively and value of 0.5°, 0.5°, 0.30 mm were applied for ZSM-5.

ICP

Aluminum contents in synthesized supports were analyzed using a Perkin Elmer PLASMA-1000 inductively coupled plasma (ICP) spectrometer at the Scientific and Technology Research Equipment Center of Chulalongkorn University.

DR-UV Spectrometer

Tungsten coordination in catalysts was measured by the diffused reflectance-ultraviolet-visible (DR-UV-Vis) spectrometer in the range of 200-600 nm using a Perkin Elmer LAMBDA 14 DR-UV-VIS spectrometer at Institute of Analytical Chemistry Training, Ministry of Science and Technology.

Laser Raman Spectrometer

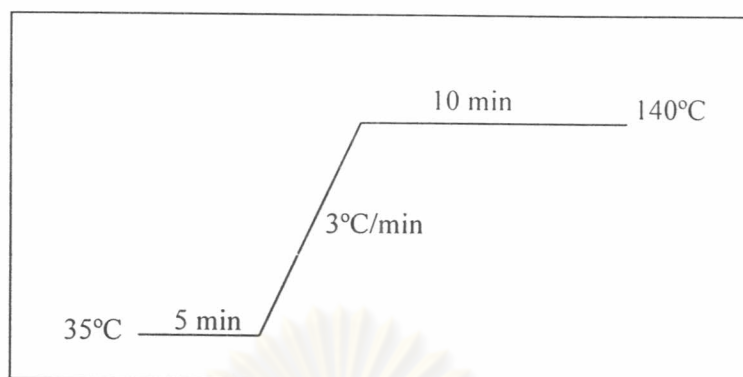
Tungsten phases in the catalysts were characterized using a Renishaw 1000 Laser Raman spectrometer at the Gem and Jewelry Institute of Thailand (GIT), Chulalongkorn University.

Nitrogen Adsorptometer

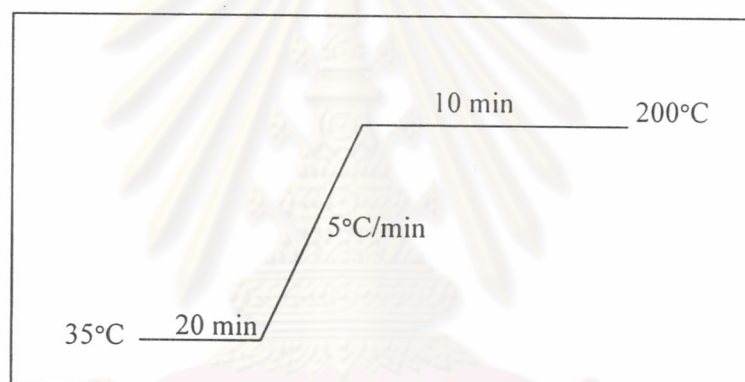
The values of BET specific surface area of catalysts were measured using a Quantachrome Autosorb-1 nitrogen adsorptometer at Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang Campus and National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency.

Gas Chromatograph

Hydrocarbon gases were analyzed using a Shimadzu GC-9A gas chromatograph equipped with a 30-m long and 0.53-mm outer diameter Alumina-PLOT column. Liquid samples were analyzed using a Shimadzu GC-14A gas chromatograph equipped with a 30-m long and 0.25-mm outer diameter HP-5 (0.25 μm film thickness) column. All GC detectors are flame ionization detector (FID). The GC heating programs for a 15- μl portion of gas and a portion of 0.10- μl liquid analysis are shown in Schemes 3.1 and 3.2, respectively.



Scheme 3.1 The GC heating program for gas analysis.



Scheme 3.2 The GC heating program for liquid analysis.

Catalytic Apparatus

The catalytic apparatus for metathesis of 1-hexene assembled in our laboratory comprises of a borosilicate tube reactor of a 0.54-cm internal diameter, our own-made split-tube furnace, a K-type thermocouple connected to the temperature programming assembly, a gas manifold, a gas-liquid saturator and a nitrogen gas cylinder. The catalytic apparatus is shown in Figure 3.1.

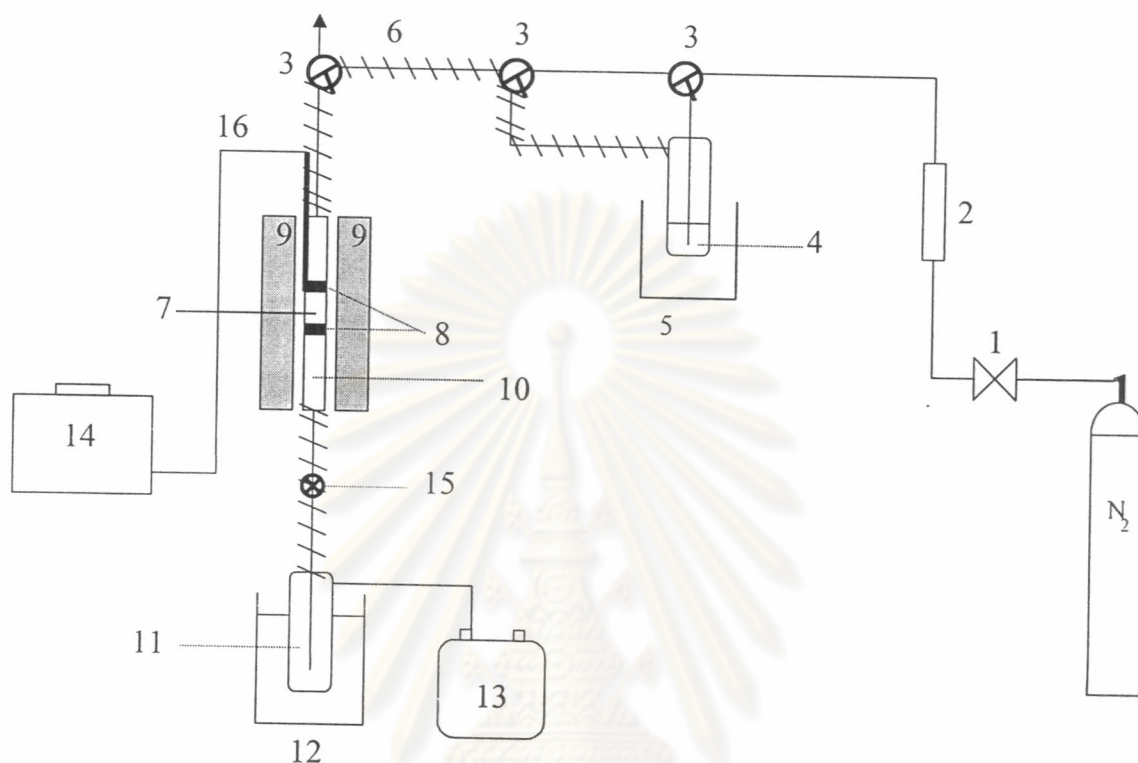


Figure 3.1 The apparatus for metathesis reaction.

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|--------------------------------|----------------------------|---------------------|
| (1) needle valve | (2) gas flow meter | (3) three way valve |
| (4) 1-hexene saturator | (5) water bath | (6) heating tape |
| (7) catalyst | (8) quartz wool | (9) tube furnace |
| (10) borosilicate tube reactor | (11) cooling trap | |
| (12) dry ice-acetone bath | (13) Tedlar bag | |
| (14) temperature controller | (15) outlet sampling point | |
| (16) thermocouple | | |

3.2 Chemicals and Gases

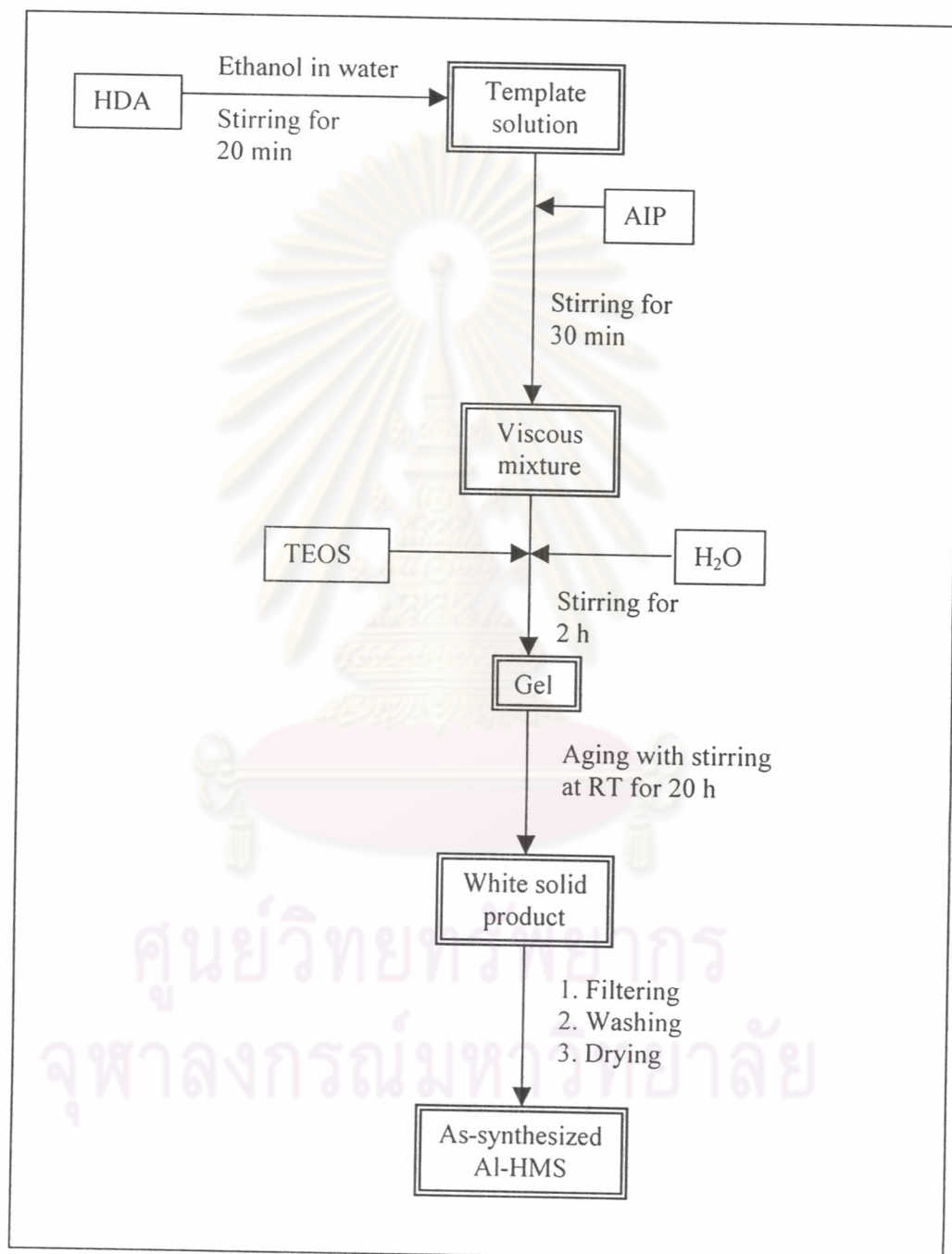
Tetraethyl orthosilicate (98% TEOS) was commercially available from Fluka. Colloidal silica (Ludox AS 40%), alumina (activated, acidic), and silica-alumina catalyst support were purchased from Aldrich. Hexadecylamine (HDA) and Aluminum isopropoxide (AIP) were obtained from TCI Japan. 1-Hexene was supplied by Fluka. Highly pure grade nitrogen was purchased from Thai Industrial Gases (TIG) and a trace amount of moisture in gas was removed by passing through a 40 cm x 2.5 cm tube of molecular sieve 4A. Standard gas mixture and liquid mixture for GC analysis were kindly provided by Thai Olefins. Other chemicals were purchased from Merck or Fluka, otherwise specifically identified.

3.3 Synthesis of Supporting materials

3.3.1 Synthesis of Al-HMS with a Si/Al Ratio in Gel of 40

Synthesis of Al-HMS was performed by modifying the procedures reported by Tuel *et al.*²³ and Rao *et al.*⁴⁶ The gel molar composition of $1.0\text{SiO}_2 : 0.0125\text{Al}_2\text{O}_3 : 0.25\text{HDA} : 8.30\text{EtOH} : 100 \text{H}_2\text{O}$ was prepared by dissolving 4.02 g of hexadecylamine (HDA) in the mixed solvent of ethanol and water (25.49 g of ethanol and 66.13 g of water) in a 250-cm³ beaker. The mixture was stirred for 20 min until homogeneous solution was obtained. Then 0.34 g of aluminum isopropoxide (AIP) was added to the mixture under vigorous stirring for 30 min. A portion of 14.17 g of tetraethyl orthosilicate (TEOS) and a portion of 54.0 g of water were then added dropwise in sequence into the mixture with stirring for 2 h. After aging with stirring the resulting gel for 20 h, the white solid product was filtered and washed several times until pH equal to 7. The solid was air-dried for 1 day. A yield of 6.74 g as-synthesized Al-HMS was obtained.

The hexadecylamine template was removed by calcination of the sample at the temperature of 550°C for 10 h. The procedure for preparing the Al-HMS support was shown in Scheme 3.3



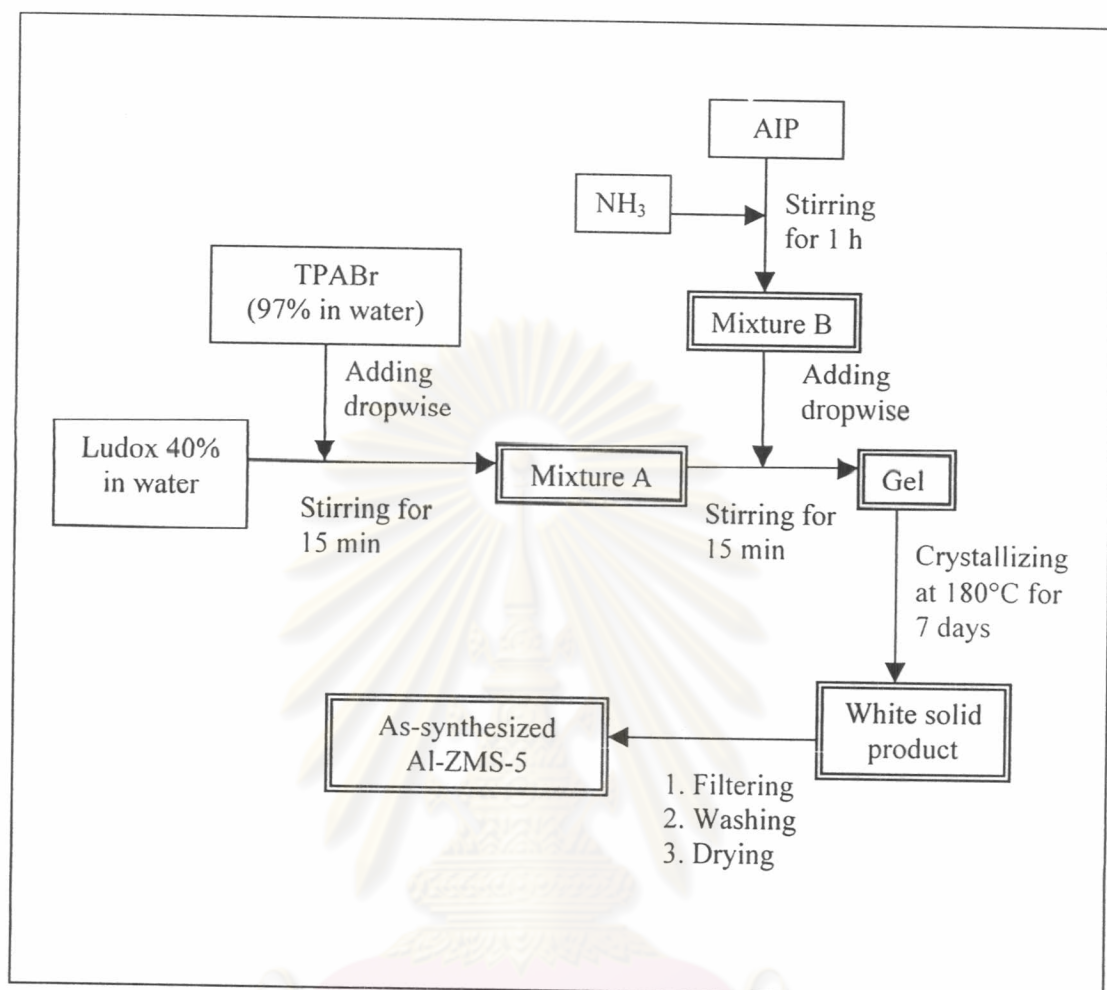
Scheme 3.3 Preparation diagram for Al-HMS support.

3.3.2 Synthesis of Pure Silica HMS

Pure silica HMS was also synthesized using the procedure described in section 3.3.1 but no aluminum isopropoxide was added. A yield of 7.75 g as-synthesized white solid product was obtained. The template removal process was carried out similarly to the case of Al-HMS.

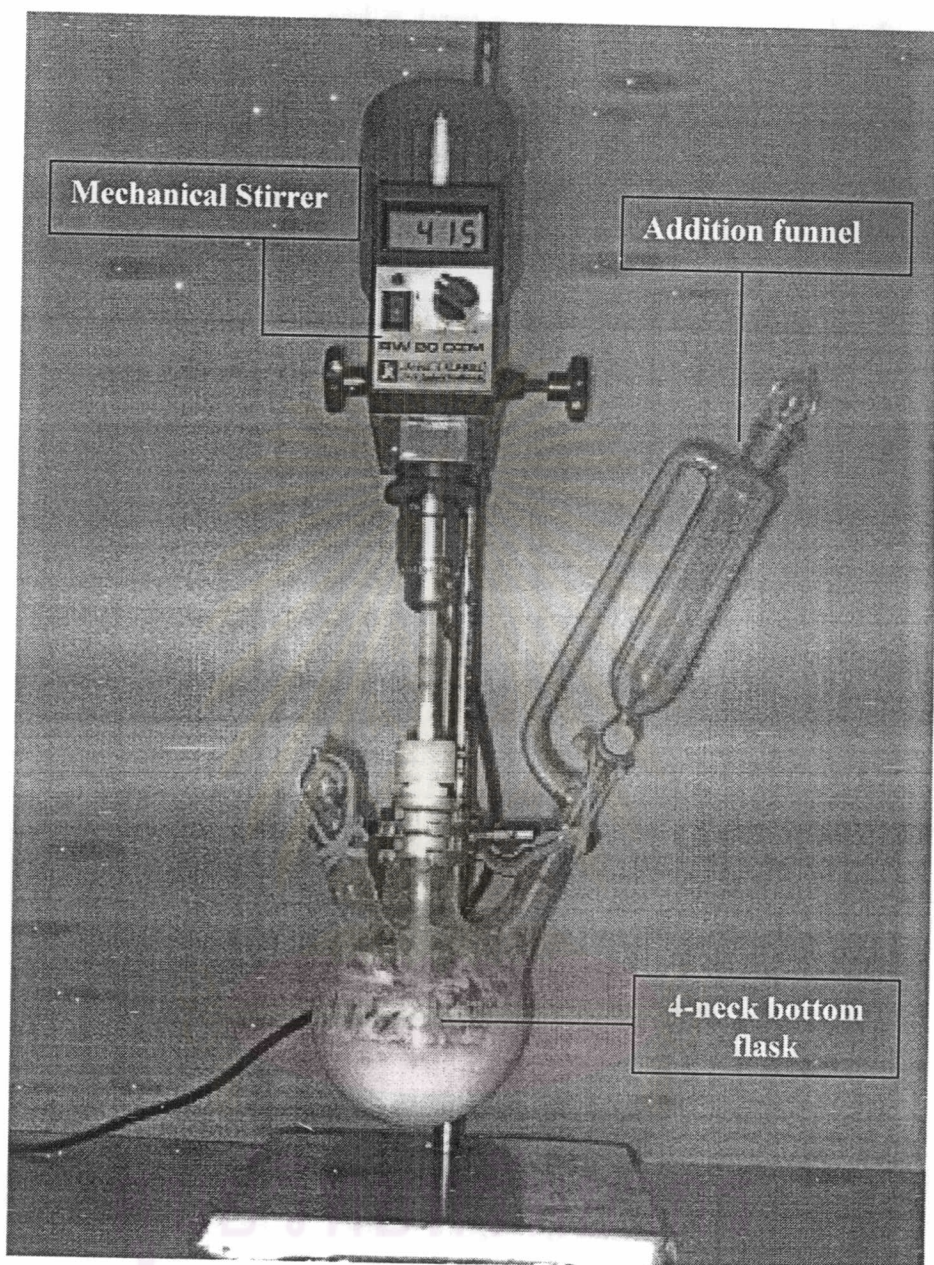
3.3.3 Synthesis of ZSM-5 with a Si/Al ratio in Gel of 40

ZSM-5 was synthesized in basic condition using a gel composition of $1.0\text{SiO}_2 : 0.0125\text{Al}_2\text{O}_3 : 0.27\text{TPABr} : 4.67\text{NH}_3 : 26\text{H}_2\text{O}$ by following the recipe reported by Böhlmann.⁵⁶ Template solution was prepared by dissolving 5.13 g of tetrapropylammonium bromide (TPABr) in 5.00 g of water. It was then added into solution containing 10.73 g of colloidal silica (Ludox) in a 500-cm³ 4-neck round bottom flask with continuous stirring for 15 min yielding mixture A. Mixture B was obtained by mixing 0.365 g of aluminum isopropoxide (AIP) in 22.68 g of 25wt% ammonia solution under vigorous stirring for 1 h. After that, mixture B was added dropwise to the mixture A under vigorous stirring for another 15 min. The resulting gel with a pH value of 11.7 was transferred to a Teflon-lined stainless steel autoclave and was crystallized at 180°C for 7 days. After that white solid product was filtered and washed until no base. The solid was dried overnight at 100°C, giving the white crystalline product weights of 7.88 g. The product was calcined in air at the temperature of 600°C for 10 h in order to remove the TPABr template. The procedure was illustrated in Scheme 3.4 and apparatus for gel preparation was shown in Figure 3.2



Scheme 3.4 Preparation diagram for ZSM-5 support.

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Figure 3.2 Apparatus for gel preparation of ZSM-5.

3.4 Sample Preparation for ICP Analysis

In a 100-cm³ Teflon beaker, 0.0400 g of a calcined support was soaked with 20 cm³ of 6M HCl and subsequently 20 cm³ of 48% HF was added dropwise to remove silica in the form of volatile SiF₄ species. The sample was gently heated until dryness on a hot plate and the fluoride treatment was repeated twice more before 10 cm³ of a mixture of 6M HCl : 6M HNO₃ at the ratio of 1 : 3 was added slowly and warmed until dryness again. After that the 10-cm³ of water was added. Then the solution was warmed until complete dissolution. The solution was transferred to a 50-cm³ polypropylene volumetric flask and made to the volume with deionized water. The flask was capped and shaken thoroughly before transferred to a plastic bottle with a threaded cap lined under with a polyethylene seal.

3.5 Preparation of Supported Tungsten Catalysts

Alumina, silica-alumina, Al-HMS, pure silica HMS and ZSM-5 were studied as supporting materials. Various supported tungsten catalysts were prepared using an incipient-wetness impregnation method and the loading amount of tungsten was varied. A required amount of Na₂WO₄·2H₂O as shown in Table 3.1 was dissolved in 0.5 g of deionized water. In case of ZSM-5 support, the amount of water was reduced to 0.25 to prevent a state of slurry mixture. The clear solution of sodium tungstate was dropped to 1.00 g of a calcined support with vigorously shaking for 20 min to disperse tungsten on the support uniformly. The loaded sample was air-dried by suction with a water aspirator for 3 h and was calcined in air at 500°C for 5 h to convert the tungstate ions (WO₄²⁻) to the tungsten oxide form (WO₃). In case of using commercial Alumina and Silica-Alumina as supports, the moisture was removed by calcination of the sample at the temperature of 450°C for 2 h before impregnation.

Table 3.1 The amount of sodium tungstate impregnated on various supports.

% Loading of WO ₃ on support	Corresponding impregnated amount of Na ₂ WO ₄ ·2H ₂ O (g)	Weight of support (g)
1.00	0.0142	1.00
3.00	0.0427	1.00
6.00	0.0853	1.00
9.00	0.1307	1.00

3.6 Catalytic Activity Test of Supported Tungsten Catalysts for Metathesis of 1-Hexene

Five supported tungsten catalysts were denoted as WO₃/alumina, WO₃/silica-alumina, WO₃/HMS, WO₃/Al-HMS and WO₃/ZSM-5 were studied both at the high loading of 9wt% WO₃ and the low loading of 1wt% at the reaction temperature of 500°C. Before a catalytic activity test was performed, the catalyst (ca. 0.1 g) was pressed in to a pellet using a hydraulic press at the pressure of 0.5 tons for 5 min and crushed to tiny pieces. A 0.35-g portion of the catalyst was loaded into the middle of a borosilicate tubular reactor, with the inner diameter of 0.54 cm and hold in place by a plug of quartz wool. The height of a catalyst was 3 cm resulting in the volume of 0.69 cm³. The catalysis was carried out using apparatus shown in Figure 3.1. The catalyst was then activated in the tubular reactor at the temperature of 500°C for 1 h under nitrogen flow at a rate of 12.7 cm³/min. The feed of 30.5% 1-hexene vapor in nitrogen was passed from top through the catalyst at the reaction temperature and at a certain gas-hourly space velocity (GHSV). After time on stream of 30 min, a 1-μl portion of the gas products was

withdrawn from the catalytic line by a gas tight syringe at the septum point below the catalyst location, and was analyzed for 1-hexene remained using the GC equipped with the alumina-PLOT column. At the same time the products were collected either as liquid in a cold trap sunk in a dry ice/acetone bath or into gas collected in a Tedlar bag. The liquid and gas products were analyzed by GC.

3.6.1 Effect of Temperature on Catalytic Activity

To investigate the effect of the temperature on 1-hexene conversion in pure metathesis reaction, the WO_3/HMS was used as a catalyst due to prevent competitive reaction such as cracking reaction. The 1wt % WO_3/HMS catalyst was introduced into the tubular reactor. After the catalyst was activated at 500°C , the feed of 30.5% 1-hexene vapor in nitrogen was passed through the catalyst at a GHSV of 500 h^{-1} and at various temperatures of 500, 300 and 200°C . After 30 min the gas and liquid products were collected and analyzed by GC.

3.6.2 Effect of Tungsten content on Catalytic Activity

The WO_3/HMS catalyst with various percentage loading of tungsten oxides (1, 3, 6 or 9%) was introduced into the tubular reactor. After the catalyst was activated at the temperature of 500°C , the feed of 30.5% 1-hexene vapor in nitrogen was passed through the catalyst at a GHSV of 500 h^{-1} at the two different temperatures of 500°C and 300°C . After 30 min the gas and liquid products were collected and analyzed by GC.