

CHAPTER III

EXPERIMENTS

3.1 Equipment and Apparatus

Ovens and Furnaces

Crystallization of SBA-15 support was performed at 100°C using a Memmert UM-500 oven as a heater. Organic template was removed from the SBA-15 support by calcination at 500°C using a Carbolite RHF 1600 muffle furnace with the programmable heating rate of 1°C/min.

X-ray Powder Diffractometer

Characteristic structure of synthesized support was identified using a Rigaku D/MAX 2200 Ultima⁺ X-ray Powder diffractometer equipped with a monochromator and a Cu-target X-ray tube.

Laser Raman Spectrometer

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

Nitrogen Adsorptometer

BET specific surface area and pore size distribution of SBA-15 support and WO₃/SBA-15 were measured using a Quantachrome Autosorb-1 nitrogen adsorptometer at Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang Campus.

Scanning Electron Microscope

Morphology of SBA-15 and WO₃/SBA-15 was investigated using JEOL JSM-5410LV scanning electron microscope at Scientific and Technological Research Equipment Center, Chulalongkorn University.

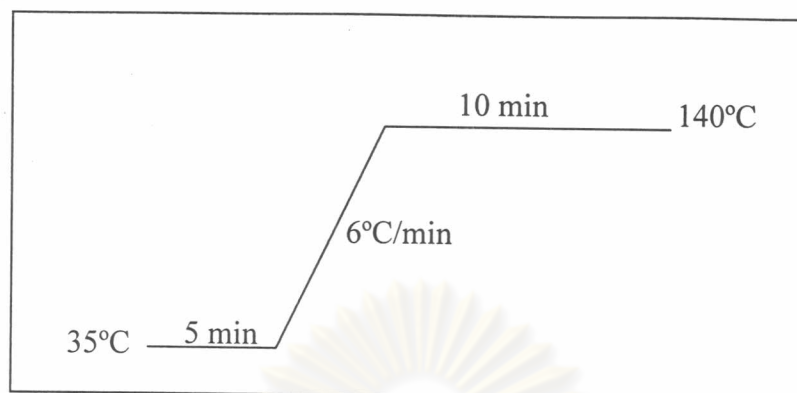
Distribution of tungsten species in catalysts was analyzed by the X-ray mapping using a JEOL JSM-6400 scanning electron microscope at Scientific and Technological Research Equipment Center, Chulalongkorn University.

DR-UV Spectrometer

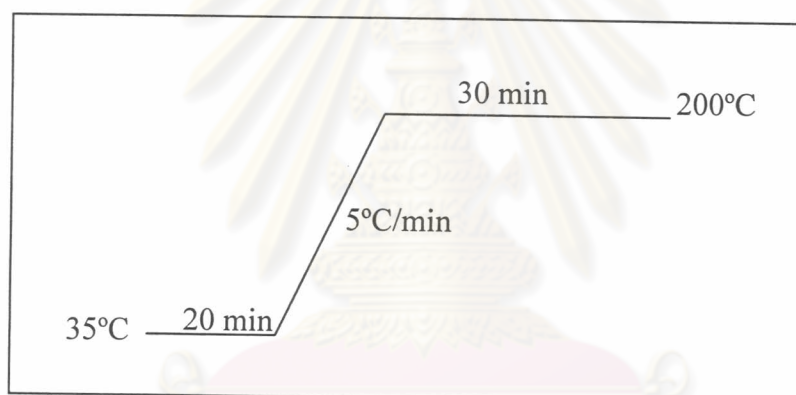
Tungsten coordination in catalysts was measured by the diffused reflectance-ultraviolet (DR-UV) spectrometer in the range of 200-400 nm using a Perkin Elmer LAMBDA 14 DR-UV-VIS spectrometer at Division of Institute of Analytical Chemistry Training, Ministry of Science and Technology.

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 30-m long and 0.32-mm outer diameter HP-5 (0.25 μm film thickness) column. The GC heating programs for gas and liquid analysis are shown in Scheme 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 laboratory-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.

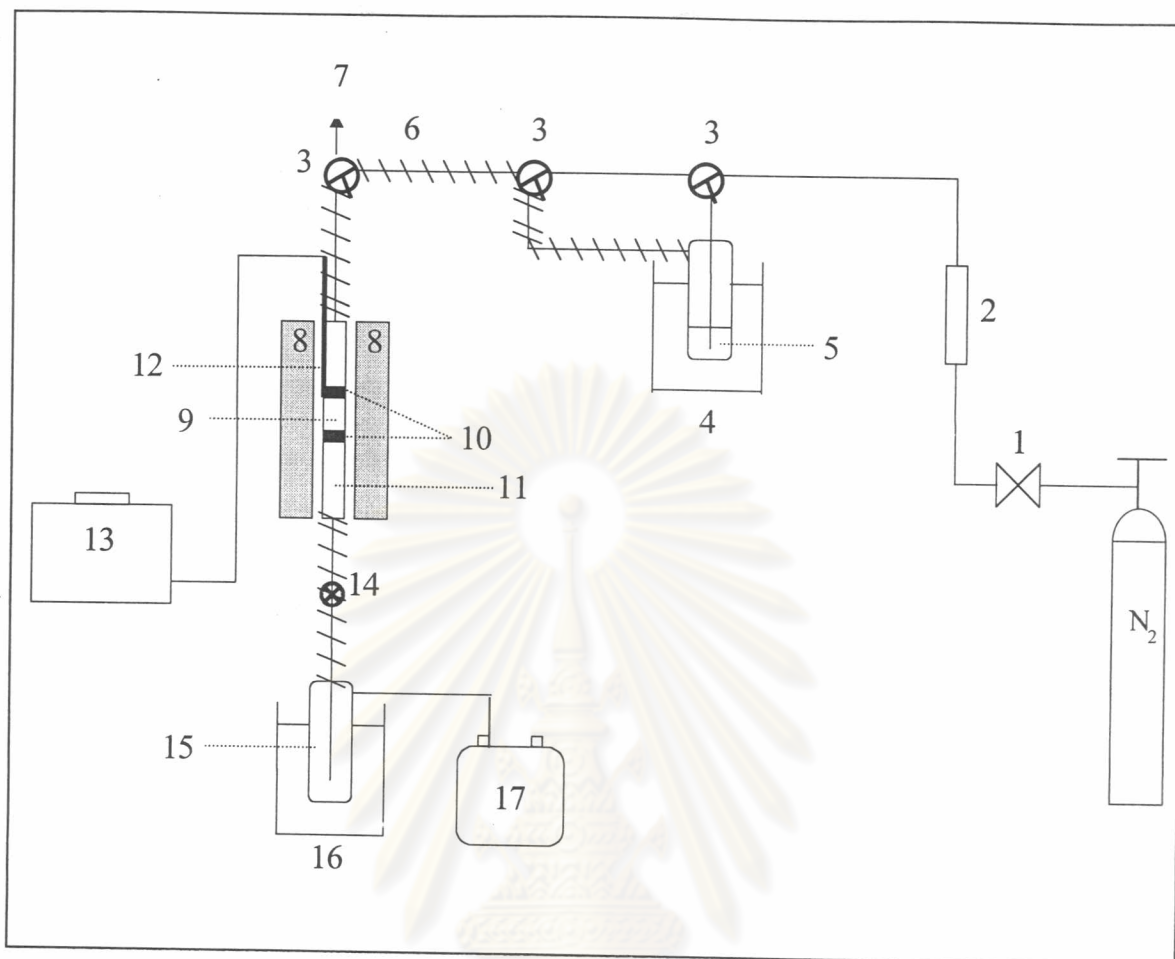


Figure 3.1 The apparatus for metathesis reaction

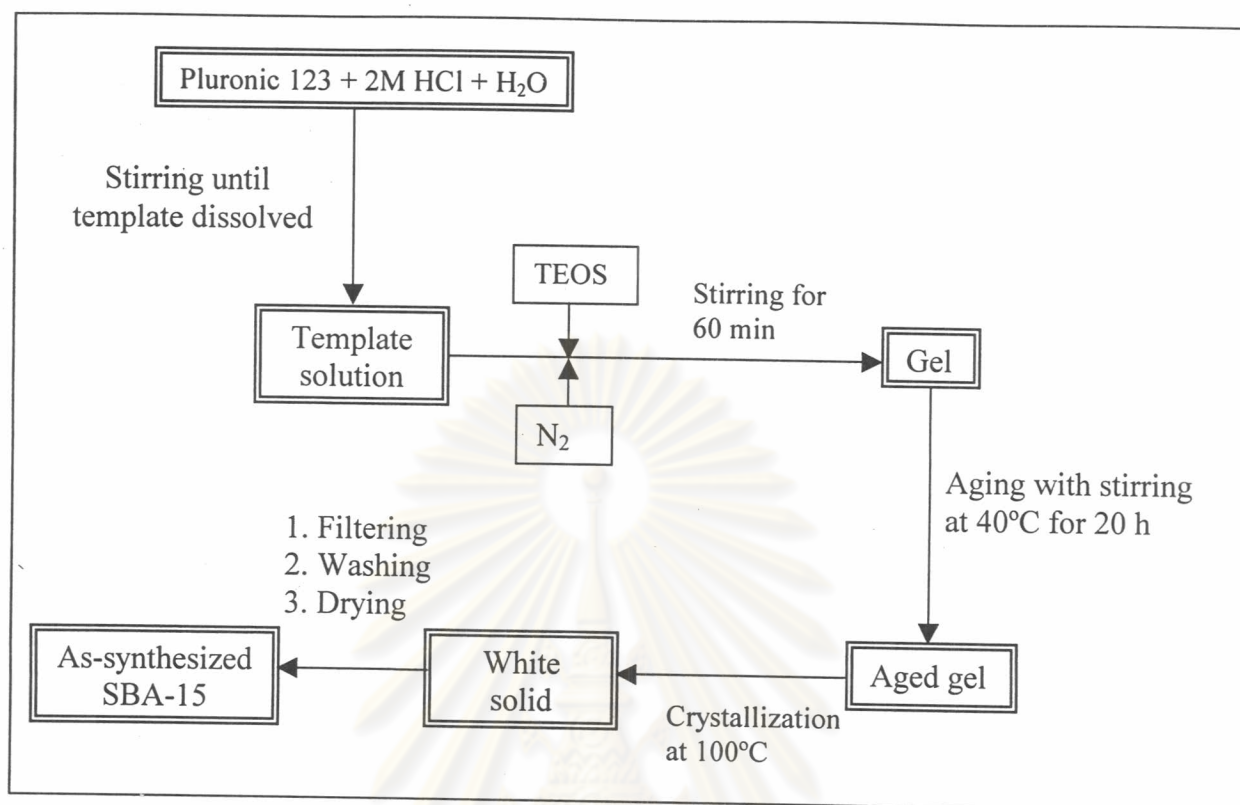
- | | |
|--------------------------|--------------------------------|
| (1) needle valve | (9) catalyst |
| (2) gas flow meter | (10) quartz wool |
| (3) three-way valve | (11) borosilicate tube reactor |
| (4) 1-hexene saturator | (12) thermocouple |
| (5) water bath | (13) temperature controller |
| (6) heating tape | (14) outlet sampling point |
| (7) inlet sampling point | (15) cold trap |
| (8) tube furnace | (16) dry ice-acetone bath |
| | (17) Tedlar bag |

3.2 Chemicals and Gases

Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, MW=5800) was supplied from Aldrich. Tetraethyl orthosilicate (98% TEOS) was commercially available from Fluka. 1-Hexene was supplied by Fluka. High purity 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 containing molecular sieve 4A. Standard gas mixture and liquid mixture for GC analysis were kindly provided by Thai Olefins. Other chemicals were purchased from BDH, Merck or Fluka, otherwise specifically identified.

3.3 Synthesis of SBA-15

SBA-15 silica was synthesized using a method reported by Stucky *et al.*⁵ using Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as pore directing agent. A 40 g of Pluronic P123 was dissolved in 30 g of water and 120 g of 2 M HCl solution in a 500-cm³ 4-neck round bottom flask. Then, 8.50 g of tetraethylorthosilane (TEOS) was added, and the resulting mixture was stirred for 1 h and then kept at 40°C for 24 h with stirring. The resulting gel was transferred into a Teflon bottle and heated at 100°C without stirring for 48 h. The Teflon bottle was taken from the oven and quenched with running tap water to room temperature. The solid was filtered, washed with deionized water and air dried by suction with a water aspirator for overnight. The white powder material was obtained. The procedure for preparing the SBA-15 support was shown in Scheme 3.2



Scheme 3.3 Preparation diagram for SBA-15 support

3.4 Organic Template Removal

Triblock copolymer, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, used in the preparation step of the pure-silica SBA-15 was removed from the pores at high temperature. The sample was calcined in a muffle furnace from room temperature to 500°C for 10 h.

3.5 Impregnation of WO_3 on SBA-15

The sample of $\text{WO}_3/\text{SBA-15}$ was prepared using an incipient wetness method and various loading amounts of WO_3 . A required amount of readily soluble sodium tungstate $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ as shown in Table 3.1 was dissolved in 1 g of deionized water. In a 120-

cm³ plastic bottle, the clear solution of sodium tungstate was added dropwise on the calcined SBA-15 support with shaking vigorously. The tungstate-loaded sample was shaken vigorously for another 20 min to disperse tungsten on the support uniformly. After thoroughly mixing, the loaded sample was air dried by suction with a water aspirator for 3 h. The sample was calcined in air at 500°C for 10 h to convert the tungstate ions to the activated tungsten (VI) oxide form.

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	0.0142	1.00
3	0.0427	1.00
5	0.0713	1.00
7	0.0998	1.00
10	0.1420	1.00

3.6 Catalytic Activity Test of WO₃/SBA-15 for Metathesis of 1-Hexene

The calcined catalyst (ca. 0.35 g) was pressed into a wafer using a hydraulic press of pressure 0.5 tons for 5 min and then it was 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 was held in place by a plug of quartz wool. The height of the

loaded catalyst was 3.00 cm and resulted 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 500°C for 1 h under nitrogen flow at 12.7 cm³/min. The feed of 30.5% of 1-hexene vapor in nitrogen was passed from the top through the catalyst at the reaction temperature at a certain gas-hourly space velocity (GHSV). After time on stream of 30 min, a 1- μ l portion of the gas products was withdrawn by a gas tight syringe from the catalytic line at the septum point below the catalyst location and was analyzed for 1-hexene remained using GC equipped with the alumina-PLOT column. At the same time the products were separated into liquid in a cold trap sunk in a dry ice/acetone bath and into gas collected in a Tedlar bag. The gas and liquid products were analyzed using GC equipped with the alumina-PLOT column and HP-5 column, respectively.

3.6.1 Effect of Temperature on Catalytic Activity

1-Hexene conversion in metathesis reaction was tested using WO₃/SBA-15 as a catalyst to select the optimal temperature. The 5% WO₃/SBA-15 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 100, 200, 300, 400 and 500°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 WO₃/SBA-15 catalyst with various loadings of tungsten oxides (1, 3, 5, 7 or 10%) 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 and at the selected temperatures. After 30 min, the gas and liquid products were collected and analyzed by GC.



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย