

CHAPTER III

EXPERIMENTAL

3.1 Instruments and Apparatus

Ovens and Furnaces

During the synthesis course, crystallization was performed using a Memmert UM-500 oven as a heater. Heating of any solid sample at 100°C was carried out using the same oven. Calcination of the solid catalysts at 540°C was achieved in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C.

XRD

Synthesized samples were identified for the structure using a Rigaku D/MAX-22000 X-ray diffractometer (XRD) at the Petroleum and Petrochemical College, Chulalongkorn University with nickel filtered Cu K α radiation (30 kV, 30mA) at an angle of 2θ range from 1.5 to 10°. The scan speed was 2°/min and the scan step was 0.02°. The three slits (scattering, divergent and receiving slits) were fixed at 0.5°, 0.5° and 0.15 mm, respectively.

ICP-AES

Tungsten contents in the catalysts were analyzed using the Perkin Elmer PLASMA-1000 inductively coupled plasma-atomic emission (ICP-AES) spectrometer at the Scientific and Technological Research Equipment Center of Chulalongkorn University.

Nitrogen Adsorptometer

Characterization of catalyst porosity in terms of nitrogen adsorption-desorption

isotherms, BET specific surface area, and pore size distribution of the catalysts was carried out using a Bel Japan BELSORP 28 SA adsorptometer at Professor T. Tatsumi's Laboratory, Yokohama National University, Japan.

FTIR Spectrometer

Vibration of metal-oxygen bonds in the catalysts were measured in the wave number range from 600 to 1500 cm^{-1} using a Nicolet Impact 410 Fourier transformed infrared (FTIR) spectrometer with the KBr pellet technique at Department of Chemistry, Faculty of Science, Chulalongkorn University.

Laser Raman Spectrometer

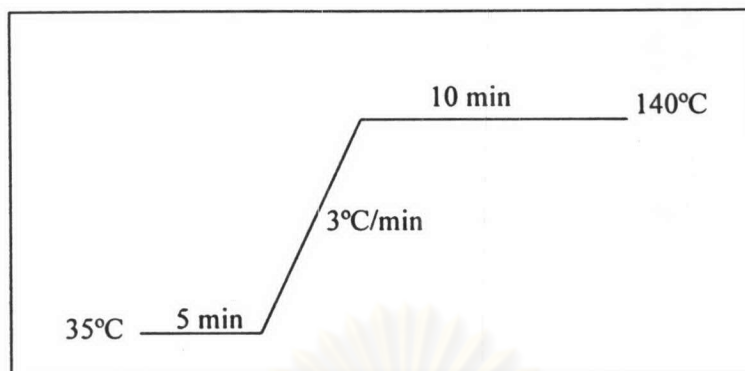
The catalysts were characterized for tungsten phase using a Renishaw 1000 Laser Raman spectrometer at the National Research Institute of Gems and Jewelry, Chulalongkorn University.

DR-UV-Vis spectrometer

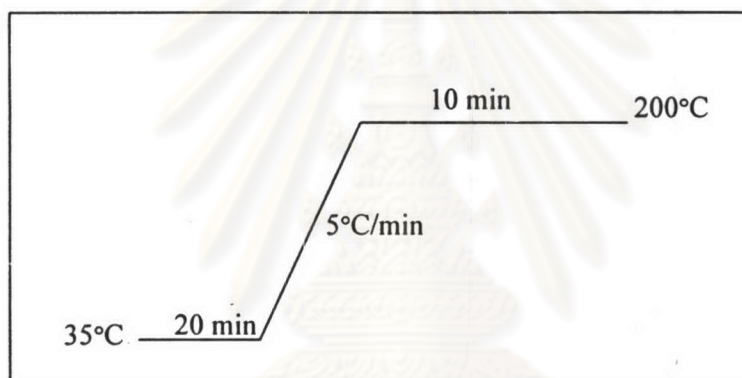
The diffused reflectance-ultraviolet-visible (DR-UV-VIS) spectra of the catalysts was measured in the range of 200-600 nm using a Cary 5E ultraviolet-visible spectrophotometer at Professor T. Tatsumi's Laboratory, Yokohama National University, Japan.

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-17A gas chromatograph equipped with a 30-m long and 0.25-mm outer diameter DB-1 (0.25 μm film thickness) column and a Shimadzu GC-14A gas chromatograph equipped with a 30-m long and 0.25-mm outer diameter Carbowax (0.25 μm film thickness) column. All GC detectors are flame ionization detector (FID). The GC heating programs for 0.20- cm^3 gas and 0.20- 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.

The 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 temperature programming assembly, a gas manifold, a gas-liquid saturator and a nitrogen gas cylinder. The catalytic apparatus is shown in Figure 3.1.

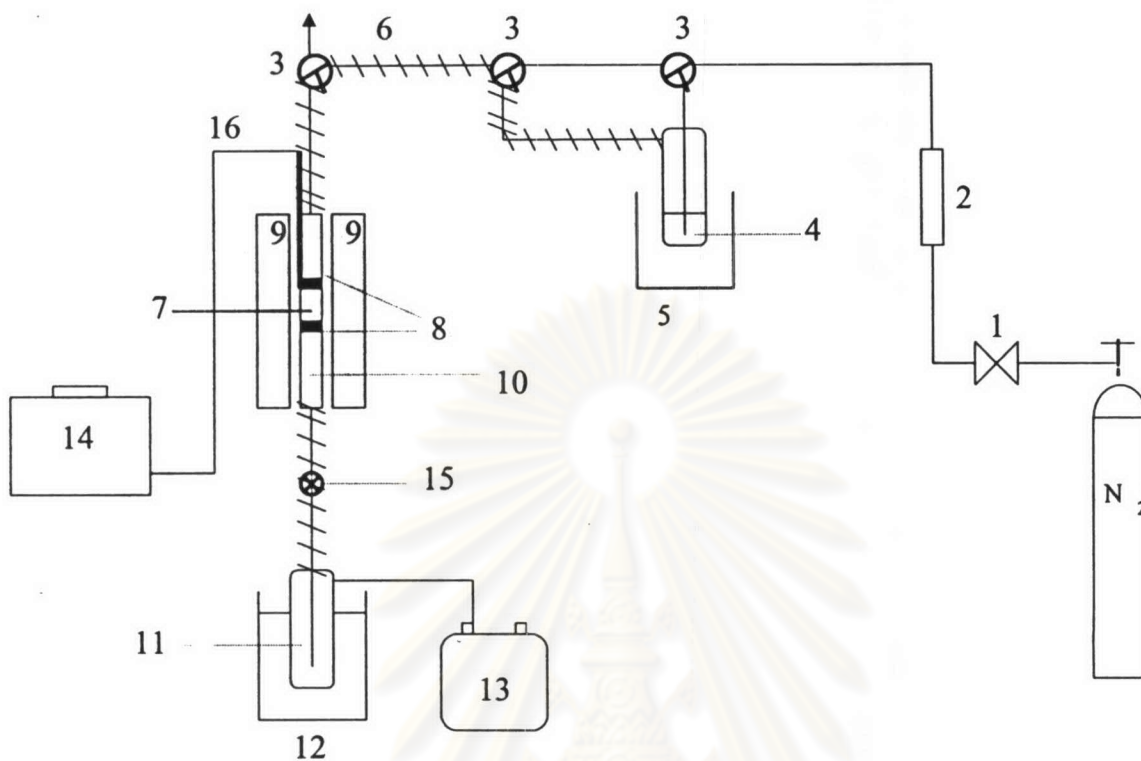


Figure 3.1 The apparatus for metathesis reaction.

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

3.2 Chemicals and Gases

To remove a trace amount of moisture nitrogen, highly pure grade purchased from Thai Industrial Gases (TIG) was passed through a 40 cm x 2.5 cm tube of the molecular sieve 4A. Tetraethyl orthosilicate (98% TEOS) was commercially available from Fluka. Colloidal silica (Ludox AS 40%), cetylpyridinium (CPBr) and ammonium tungstate (99.99% $(\text{NH}_4)_2\text{WO}_4$) were purchased from Aldrich. Cetyltrimethylammonium bromide (CTABr) was from TCI, Japan. 1-Hexene supplied from BDH was used without any treatment. Standard gas mixture and liquid mixture for GC analysis was kindly obtained from Thai Olefins. Other chemicals were from Merck or Fluka, otherwise specifically identified.

3.3 Direct Synthesis of W-MCM-41

3.3.1 Synthesis of W-MCM-41 with the Si/W Ratio in Gel of 100 in Acidic Condition

Following the procedure reported by Zhang *et al.*⁵⁰ a gel with a molar composition of $\text{SiO}_2 : 0.01 \text{ WO}_3 : 0.3 \text{ CPBr} : 6 \text{ HCl} : 6 \text{ H}_2\text{O}$ was prepared. Solution A was prepared by dissolving 0.1419 g of ammonium tungstate in 3.33 cm³ of deionized water. Solution B was prepared by dissolving 5.77 g of cetylpyridinium bromide (CPBr) in 60 cm³ of 5 M HCl. Into a 500-cm³ 4-neck round bottom flask containing Solution B, 10.63 g of TEOS and Solution A were simultaneously added dropwise under a vigorous stirring. The resulted gel of 81.5 g was crystallized in the flask at 50°C under gentle stirring for 22 h. Apparatus for the gel preparation was shown in Figure 3.2. The white solid product was obtained at a yield of 4.13 g.

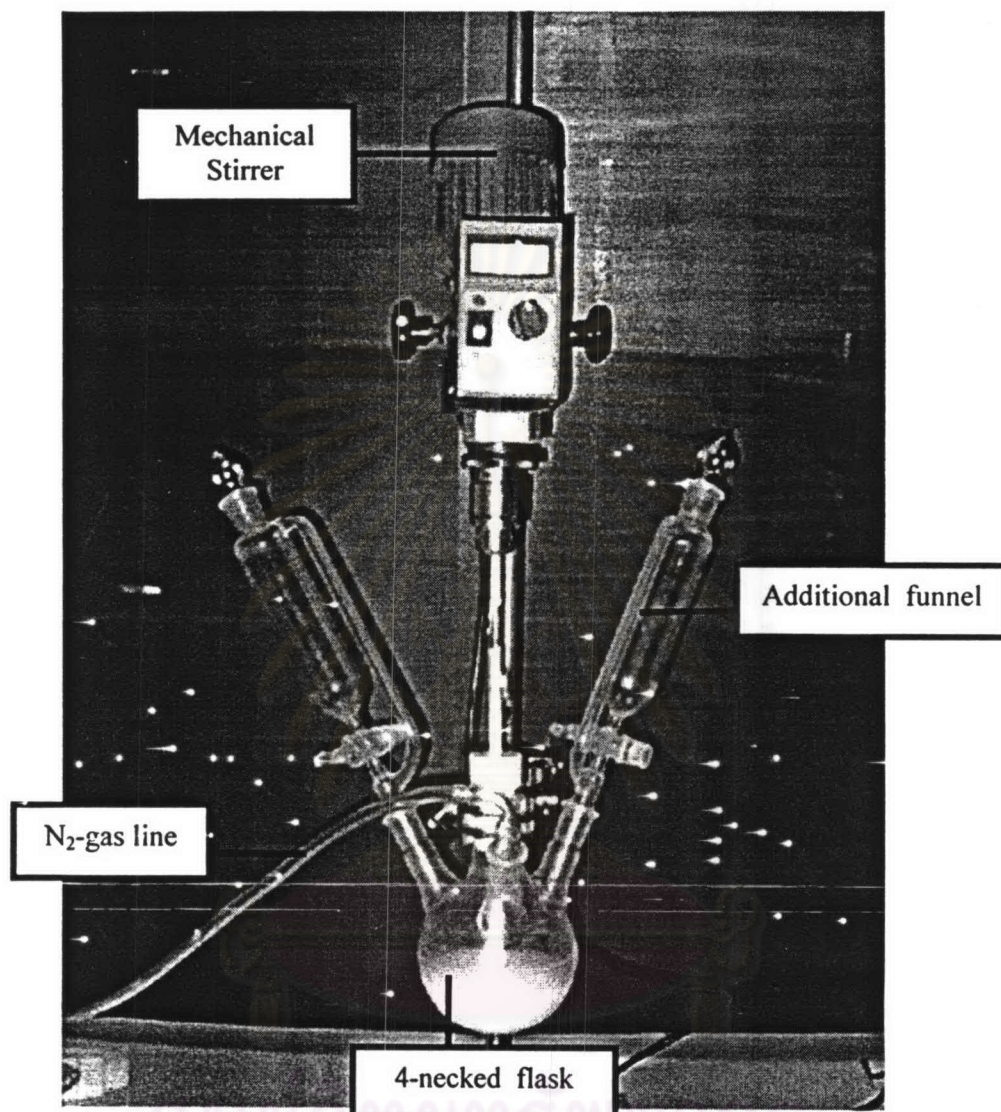


Figure 3.2 The apparatus of gel preparation

3.3.2 Synthesis of W-MCM-41 with the Si/W Ratio in Gel of 100 in Basic Condition

Referring to the method reported by Cho *et al.*^{63,64} a gel with a molar composition of CTABr : 0.3 NH₃ : 4 SiO₂ : Na₂O : 0.04 WO₃ : 200 H₂O was prepared. Solution A was obtained by mixing 20.03 g of Ludox with 22.67 g of 11.78% sodium hydroxide solution (2.67 g of NaOH in 20 g of H₂O). Solution B containing 25% CTABr was prepared by dissolving 12.15 g of CTABr in 36.45 g of deionized water. Into a 500-cm³ 4-neck round bottom flask containing Solution B and 0.40 g of an aqueous solution of 25% NH₃ was added. Then Solution A was added to the basic solution in the flask. The mixture was stirred vigorously using a mechanical stirrer for 30 min. A solution of 0.3786 g of ammonium tungstate ((NH₄)₂WO₄) in water was added dropwise into the mixture with continuous stirring. The mixture was further stirred for another 30 min. The resulted gel of 141.9 g was transferred into a stainless steel bomb lined up with Teflon. The bomb was tightly capped and heated at 100°C without stirring for 24 h. The bomb was taken off and quenched with running tap water to room temperature. The pH of the gel was adjusted to 10.2 using 30% acetic acid. The bomb was recapped and heated at 100°C for another 24 h. The adjustment of the gel pH was carried out everyday. After the total crystallization period was spent for 5 days, the white solid product was filtered and washed several times until no base. The solid was dried in an oven at 100°C for 16 h. The white crystalline material was obtained at a yield of 7.18 g.

3.3.3 Synthesis of W-MCM-41 Using Sodium Tungstate as a Tungsten Source

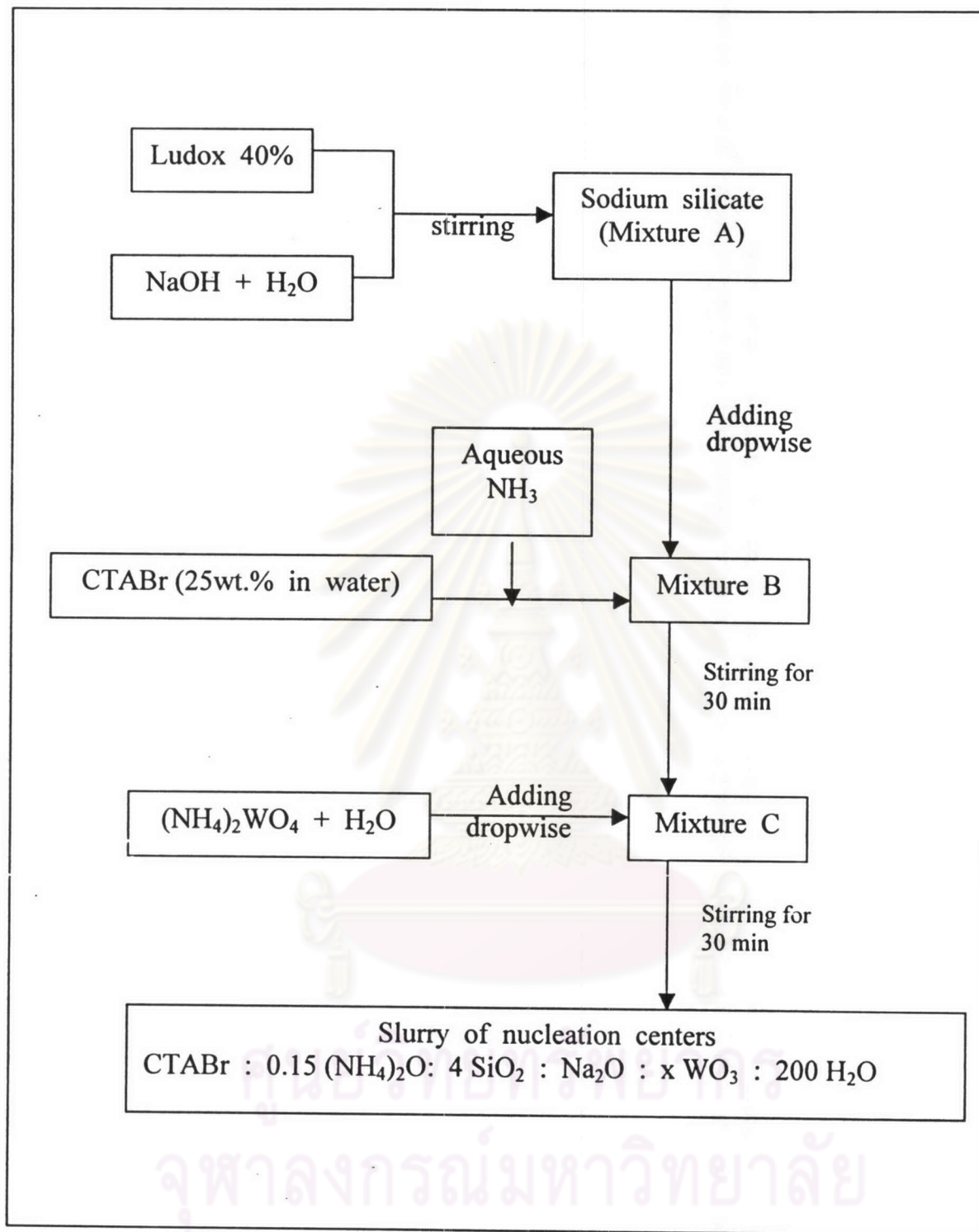
To study the effect of tungsten sources on the up-taken amount of tungsten from the starting gel, another W-MCM-41 sample was prepared in a similar way as described in Section 3.3.2 except that $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was used instead of $(\text{NH}_4)_2\text{WO}_4$.

3.3.4 Synthesis of W-MCM-41 with Various Si/W Ratios

To obtain the maximum loading of W in the catalysts, W-MCM-41 samples with the Si/W ratio in gel of 120, 100, 80, 60, 50, 8 and 4 were synthesized using the method in basic condition as described in Section 3.3.2. The schematic diagram for the gel preparation with various Si/W ratios was illustrated in Scheme 3.3. The amount of ammonium tungstate required for each preparation of W-MCM-41 with various Si/W ratios in gel was compiled in Table 3.1.

Table 3.1 Amount of ammonium tungstate required for each preparation of W-MCM-41 with various Si/W ratios in gel.

Si/W (in gel)	Weight of $(\text{NH}_4)_2\text{WO}_4$ (g)
120	0.3152
100	0.3785
80	0.4732
60	0.6313
50	0.7572
8	4.7320
4	9.4640



Scheme 3.3 Preparation diagram of the gel mixture with various Si/W ratios in the synthesis of W-MCM-41

3.4 Sample Preparation for ICP Analysis

In a 100-cm³ Teflon beaker 0.0400 g of a calcined catalyst was soaked with 20 cm³ of 6 M HCl and subsequently 20 cm³ of 48% HF was added dropwise to get rid of silica in the form of volatile SiF₄ species. The sample was heated but not boiled until dryness on a hot plate and the fluoride treatment was repeated once more before 10 cm³ of a mixture of 6 M HCl : 6 M HNO₃ at a ratio of 1:3 was added slowly and warmed until dryness again. Then 20 cm³ of 20% sodium hydroxide solution was added and the solution was warmed up for 1 h to 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 shaken thoroughly. The solution was transferred into a plastic bottle with a treaded cap lined under with a polyethylene seal. The standard solution of 1000-ppm tungsten in HNO₃ (from BDH) was diluted to 1, 2, 4, 5, 10 and 20 ppm to construct a calibration curve.

3.5 Impregnation of WO₃ on MCM-41

3.5.1 Preparation of MCM-41 as a Catalyst Support

The pure-silica MCM-41 was prepared using the method described in Section 3.3.2 but no ammonium tungstate was added. A yield of 12 g of an as-synthesized white solid product was obtained. The sample was then calcined in air at 540°C for 6 h in order to remove the CTABr template from the pores. The loss on ignition is about 50% by weight.

3.5.2 Preparation of WO₃/MCM-41

The sample of WO₃/MCM-41 was prepared using an incipient wetness method and various loading amounts of W corresponding to those in the W-MCM-41 samples

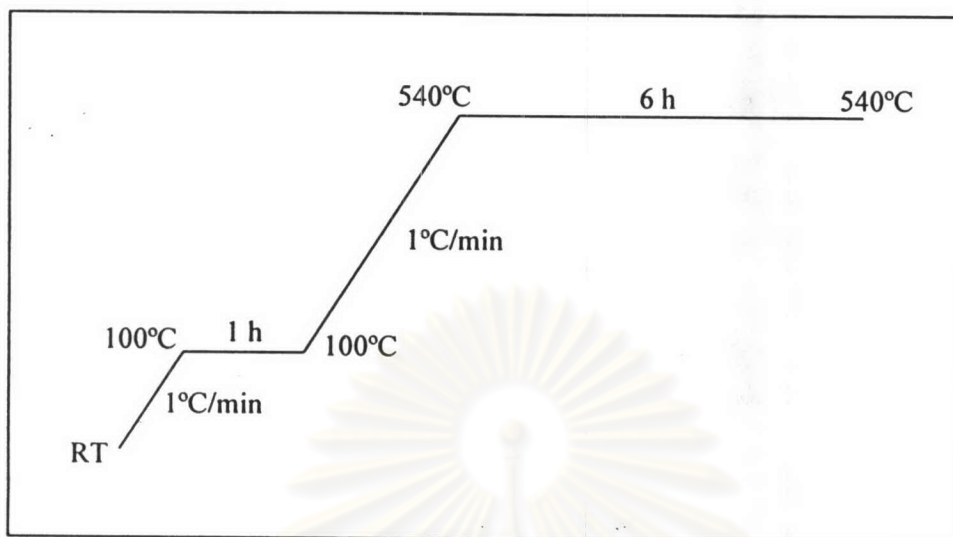
prepared by direct synthesis as follows. A required amount of readily soluble $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ as shown in Table 3.2 was dissolved in 1 g of deionized water. In a 120-cm³ plastic bottle the clear solution of sodium tungstate was dropped by portion on the calcined MCM-41 support with alternate shaking vigorously. The tungsten-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 white solid was calcined in air at 500°C for 5 h to convert the tungstate ions to the activated tungsten(III) oxide form. The final products have the color ranging from white to green with increasing the tungsten-loading amount.

Table 3.2 The amount of sodium tungstate impregnated on MCM-41

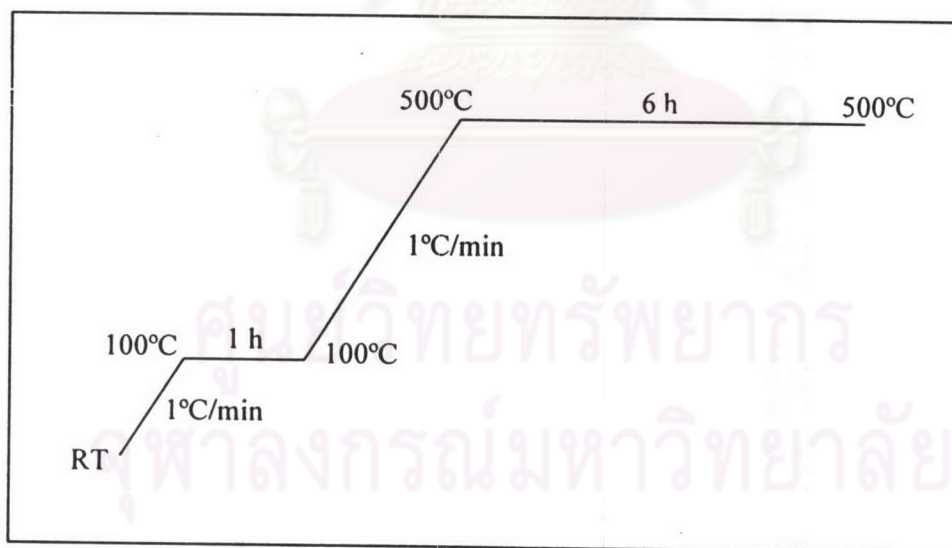
Molar ratio of Si/W in catalyst	% Loading of WO_3 on MCM-41	Corresponding impregnated amount of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (g)	Weight of the MCM-41 support
1637	0.2329	0.0033	1.00
383	1.0075	0.0143	1.00
84	4.5928	0.0653	1.00

3.6 Organic Template Removal

An organic template, either CPBr or CTABr used in the preparation step of the catalysts was removed from the catalyst pores by converting to carbon dioxide at high temperature. The as-synthesized W-MCM-41 samples were calcined in crucible dishes from room temperature to 540°C for 6 h in a muffle furnace using a heating program shown in Scheme 3.4. The impregnated $\text{WO}_3/\text{MCM-41}$ samples were calcined at 500°C using the heating program shown in Scheme 3.5.



Scheme 3.4 The heating program for calcination of the W-MCM-41 catalysts (RT = room temperature)



Scheme 3.5 The heating program for calcination of the impregnated $\text{WO}_3/\text{MCM-41}$ catalysts (RT = room temperature)

3.7 Catalytic Activity Test of W-MCM-41 and WO₃/MCM-41 Catalysts for Metathesis of 1-Hexene

Both W-MCM-41 and impregnated WO₃/MCM-41 catalysts were freshly calcined at 540°C and 500°C, respectively before a catalytic test was performed. The calcined catalyst (ca. 0.1 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 0.30-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 the loaded catalyst was 3 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 the GC equipped with a 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 liquid products were analyzed using the GC equipped with the DB-1 coated column (1% dimethyl polysiloxane). The gas products were analyzed using the GC equipped with the carbowax coated column.

3.7.1 Study of Effect of Temperature on Catalytic Activities

The W-MCM-41 catalyst with the Si/W ratio in product of 84, was loaded into the tubular reactor. The catalyst was activated under nitrogen flow at the temperature of 500°C. Subsequently, the feed of 30.5% 1-hexene balanced with nitrogen was passed through

the catalyst at a GHSV of 500 h^{-1} and at the different catalyst temperatures of 300, 400 and 500°C . After 30 min the gas and liquid products were collected and analyzed by GC.

3.7.2 Study of Effect of Si/W Ratio on Catalytic Activities

The tiny-pellet W-MCM-41 with various Si/W ratios in product of 84, 334 and 1613 was introduced into the tubular reactor. After the catalyst deactivation 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} at the reaction temperature of 500°C . After 30 min the gas and liquid products were collected and analyzed by GC.

3.7.3 Catalytic Activity of $\text{WO}_3/\text{MCM-41}$ for 1-Hexene Metathesis

Similarly, the metathesis of 1-hexene was tested over the impregnated $\text{WO}_3/\text{MCM-41}$ catalysts with the Si/W ratios of 84, 383 and 1613 at a GHSV of 500 h^{-1} , the reaction temperature of 500°C , and time on stream of 30 min. The results are compared to those using the W-MCM-41 with the equal amount of tungsten loading.

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย