

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Support Preparation Materials

- Fumed silica (SiO_2) with surface area $473.5 \text{ m}^2/\text{g}$, of 99.8% purity, was obtained from Sigma Chemical Co., Ltd.
- Aluminium hydroxide hydrate $[\text{Al}(\text{OH})_3]$ with surface area $50.77 \text{ m}^2/\text{g}$ was obtained from Sigma Chemical Co., Ltd.
- Triethanolamine, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ was obtained from Carlo Erba Reagenti.
- Triisopropanolamine (AG), $\text{N}(\text{CH}_2\text{CH}(\text{CH}_3)\text{OH})_3$, of 95% purity, was obtained from Fluka Chemical Co., Ltd.
- Ethylene glycol (EG: $\text{HOCH}_2\text{CH}_2\text{OH}$) was obtained from J.T. Baker Inc.
- Acetonitrile (CH_3CN) was obtained from Lab-Scan Co., Ltd.
- Potassium hydroxide pellets (KOH) of 85% purity was obtained from Carlo Erba Reagenti.
- Silicone oil was obtained from Lab-Scan Co., Ltd.
- Nickle (II) nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ of 98% purity was obtained from Fluka Chemical Co., Ltd.

3.1.2 Gases

- Nitrogen of 99.99% purity used as purge gas to prevent zeolite precursors degradation and used for driving the auto-sampling valve was supplied from Thai Industrial Gas Public Co., Ltd.
- Hydrogen of 99.99% purity used for catalyst reduction was supplied from Thai Industrial Gas Public Co., Ltd.
- Helium of 99.99% purity used as the balanced gas in the feed stream and carrier gas of gas chromatograph was supplied from Thai Industrial Gas Public Co., Ltd.

- Methane of 99.99% purity used as a reactant gas was supplied from Thai Industrial Gas Public Co., Ltd.

- Carbon dioxide of 20% purity in Helium used as a reactant gas was supplied from Praxair (Thailand) Co., Ltd.

3.2 KH Zeolite Preparation

Preparation of KH zeolite was started from precursors synthesis following by hydrothermal treatment associated with microwave technique according to Wongkasemjit's method (Sathupanya *et al.*, 2004). Silatrane and alumatrane used as precursors were obtained from the reaction of silica and alumina with triethanolamine via sol-gel process.

3.2.1 Silatrane Synthesis (Si-TEA)

Silatrane was synthesized by mixing silicon dioxide 0.1 mol and triethanolamine 0.125 mol in a simple distillation set using 100 ml ethylene glycol as a solvent. The reaction was performed at the boiling point of ethylene glycol under nitrogen atmosphere for 12 hrs to remove water as a by-product and ethylene glycol from the system. Subsequently, the rest of ethylene glycol was removed under vacuum at 110°C. The brownish white solid was washed with dried acetonitrile for three times. The white powder product was characterized by using FTIR and TGA techniques.

3.2.2 Alumatrane Synthesis (Al-TIS)

Alumatrane synthesis was performed by mixing 0.1 mol aluminium hydroxide and 0.125 mol triisopropanolamine in a simple distillation set and using 100 ml ethylene glycol as a solvent. The reaction was carried out at the boiling point of ethylene glycol under flow nitrogen atmosphere to remove the by-product water and ethylene glycol from the system. The reaction was carried out for 10 hrs and the rest of ethylene glycol was removed by heating at 110°C under vacuum. The crude product was washed with dried acetonitrile for four times to remove undesired organic residues and characterized by using FTIR and TGA techniques.

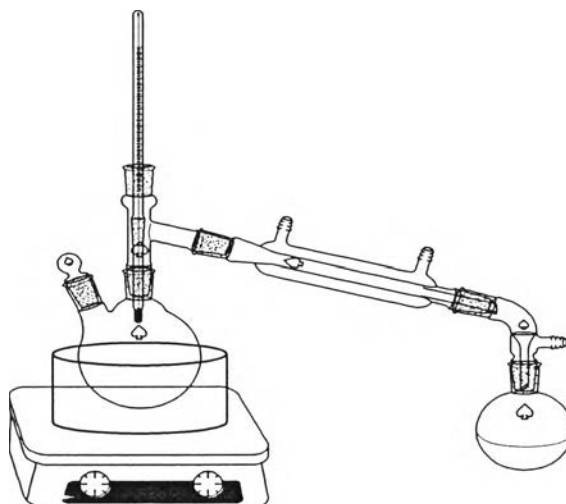


Figure 3.1 The simple distillation set for silatrane and alumatrane synthesis.

3.2.3 Precursors Characterizations

The thermal stability and ceramic yield of precursors, Si-TEA and Al-TIS, were obtained by using a Perkin Elmer TG/DTA, Pyris Diamond Model. Approximately 5-20 mg of sample was placed into a platinum pan and heated in air with heating rate of 20°C/min and 10 ml/min of oxygen flow rate. The functional group of transformed gel was measured by using a Thermo Nicolet, Nexus (NEXUS 670 FT-IR) with a resolution of 4 cm⁻¹. The solid samples were mixed and palletized with dried KBr.

3.2.4 KH Zeolite Synthesis

Potassium aluminosilicate gel was prepared by the sol-gel process using Si-TEA and Al-TIS as precursors and KOH as the hydrolytic agent. The Si-TEA and Al-TIS was mixed with KOH solution at room temperature. Gel formation was studied at a molar ratio of SiO₂: 0.1Al₂O₃: 3K₂O: 410H₂O. The solution mixture was aged for 12 hrs before transferring to Teflon lined vessel (100 ml) sealed with a Teflon cap contained in a microwave oven model MSP1000, CEM Corporation (Spec. 1000 W and 2450 MHz), for hydrothermal microwave treatment. Temperature measurement was conducted by inserting a fiber optic temperature probe inside the vessel. The probe was immersed into the solution mixture to control

the temperature of the solution inside the vessel. The mixture was heated at 150°C for 5 hrs. The obtained white precipitates were washed with distilled water until its pH equals 7 and were finally dried overnight at 75°C. The notations for all synthesized KH zeolites were given in the below table.

Table 3.1 Notation for the single batch KH zeolite: $\text{SiO}_2: 0.1\text{Al}_2\text{O}_3: 3\text{K}_2\text{O}: 410\text{H}_2\text{O}$

Notation	$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{K}_2\text{O}:\text{H}_2\text{O}$	Notation	$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{K}_2\text{O}:\text{H}_2\text{O}$
KH8	1 : 0.1 : 3 : 410	KH18	1 : 0.1 : 3 : 410
KH9	1 : 0.1 : 3 : 410	KH24	1 : 0.1 : 3 : 410
KH10	1 : 0.1 : 3 : 410	KH25	1 : 0.1 : 3 : 410
KH11	1 : 0.1 : 3 : 410	KH26	1 : 0.1 : 3 : 410
KH12	1 : 0.1 : 3 : 410	KH27	1 : 0.1 : 3 : 410
KH14	1 : 0.1 : 2.5 : 410	KH28	1 : 0.1 : 3 : 410
KH15	1 : 0.1 : 2 : 410	KH29	1 : 0.1 : 3 : 410
KH16	1 : 0.1 : 1.5 : 410	KH32	1 : 0.1 : 3 : 410
KH17	1 : 0.1 : 3 : 410	KH33	1 : 0.1 : 3 : 410

Since the obtained product from this procedure is around 0.1 g, that not enough to use as a catalyst support in carbon dioxide reforming of methane, the attempts on up scalings were performed in KH zeolite synthesis part. The notations for all upscale batches were given in the below table.

Table 3.2 Notation for the double batches KH zeolite: $2(\text{SiO}_2: 0.1\text{Al}_2\text{O}_3: 3\text{K}_2\text{O}: 410\text{H}_2\text{O})$

Notation	$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{K}_2\text{O}:\text{H}_2\text{O}$
KH13	2(1 : 0.1 : 3 : 410)
KH19	2(1 : 0.1 : 3 : 410)

Table 3.3 Notation for the triple batches KH zeolite: 3(SiO₂: 0.1Al₂O₃: 3K₂O: 410H₂O)

Notation	SiO ₂ :Al ₂ O ₃ :K ₂ O:H ₂ O
KH20	3(1 : 0.1 : 3 : 410)
KH22	3(1 : 0.1 : 3 : 410)
KH30	3(1 : 0.1 : 3 : 410)

Table 3.4 Notation for the quadruple batches KH zeolite: 4(SiO₂: 0.1Al₂O₃: 3K₂O: 410H₂O)

Notation	SiO ₂ :Al ₂ O ₃ :K ₂ O:H ₂ O
KH21	4(1 : 0.1 : 3 : 410)
KH23	4(1 : 0.1 : 3 : 410)
KH31	4(1 : 0.1 : 3 : 410)

3.3 KH Zeolite Characterizations

The crystallinity of aluminosilicate products was characterized by using a Rigaku X-Ray diffractometer at a scanning speed of 5°/sec, CuK_α as a source and CuK_β as a filter. The working range was $2\theta = 5$ to 60° . The morphology of the aluminosilicate products were observed by using a JEOL 5200-2AE scanning electron microscope (SEM) with 1500 to 5000 magnifications.

3.4 Catalysts Preparation

Ni supported catalysts were prepared by incipient wetness impregnation using Ni(NO₃)₂.6H₂O as the metal precursors. First, the synthesized KH zeolite was calcined in air at 500°C for 5 hrs before being impregnated with Ni(NO₃)₂.6H₂O to

get a 8% of Ni loading amount. The catalyst was then dried at 110°C for 24 hrs and calcined again in air at 500°C for 5 hrs to complete the decomposition of precursors.

3.5 Catalytic Activity

The prepared catalysts were carried out in the carbon dioxide reforming of methane to study the activity and stability of the catalysts. The reaction was performed in a stainless steel tube reactor, which was connected to the gas flow controller and gas chromatograph. Before testing catalytic activity, 0.1 g of fresh catalysts were packed in the stainless steel tube reactor and then reduced under hydrogen atmosphere at 600°C for 1 hrs. After that, the reduced catalysts were flushed under a stream of helium at the reaction temperature for 20 min. Then, the methane and carbon dioxide (molar ratio of CH₄:CO₂ = 1:1) were introduced to the reactor at 700°C, 1 atmospheric pressure with a space velocity of total gas mixture (GHSV) of 30000 mL h⁻¹ g⁻¹. The concentration of input reactants and output products were analyzed by using a Hewlett Packard 5890 Series II gas chromatograph. The packed column used for the separation was Carbosphere column, 80/100 mesh, and 1/8-inch stainless steel. Each cycle of GC analysis took 18 min to complete before starting the next injection. The conditions of GC are shown as follows:

Injection Temperature:	110°C
Oven Temperature:	110°C
Detector Temperature:	175°C
Carrier Gas:	He (99.99% purity)