



CHAPTER 3

EXPERIMENT

Materials

1. As-received Rice husk (from Rajaburi)
2. Tetrapropylammonium bromide ($C_{12}H_{26}BrN$; TPABr), Lab grade (Merck)
3. Sodium hydroxide (NaOH), Lab grade (Merck)
4. Sodium aluminate ($NaAlO_2$), Lab grade (Riedel-de Haën)
5. Hydrochloric acid 37% (HCl), Lab grade (Merck)
6. Nitric acid 1 mol/L (HNO_3), Lab grade (AnalaR)
7. Barium chloride dihydrate ($BaCl_2 \cdot H_2O$), Lab grade (Merck)
8. Titanium oxysulfate hydrate ($TiOSO_4 \cdot xH_2O$), Lab grade (Riedel-de Haën)
9. Methylene blue ($C_{16}H_{18}ClN_3S$; MB), Lab grade (Fluka)

Preparation of amorphous silica from rice husk

Rice husk (RH) obtained from the local agricultural resource, Rajaburi, was firstly washed with distilled water to remove residual dirt and clay particles, and then dried at 80 °C for 12 h. The dried rice husk was subjected to acid treatment. Acid leaching was carried out by boiling 50 g of rice husk in 500 ml of 1 mol/L HCl solution for 2 h. After leaching, the RH was neutralized by thorough washing with distilled water, filtered, and then dried at 80 °C for 12 h. To obtain rice husk ash (RHA) silica, 30 g of acid leached rice husk was placed in a separating sagger (size 20x20x1cm) and introduced into a muffle furnace to burn at 400-900 °C for 3 h. The burning was performed in air at a heating rate of 15 °C/min. The preparation of RHA silica from RH is presented as a flow chart in Fig. 3.1.

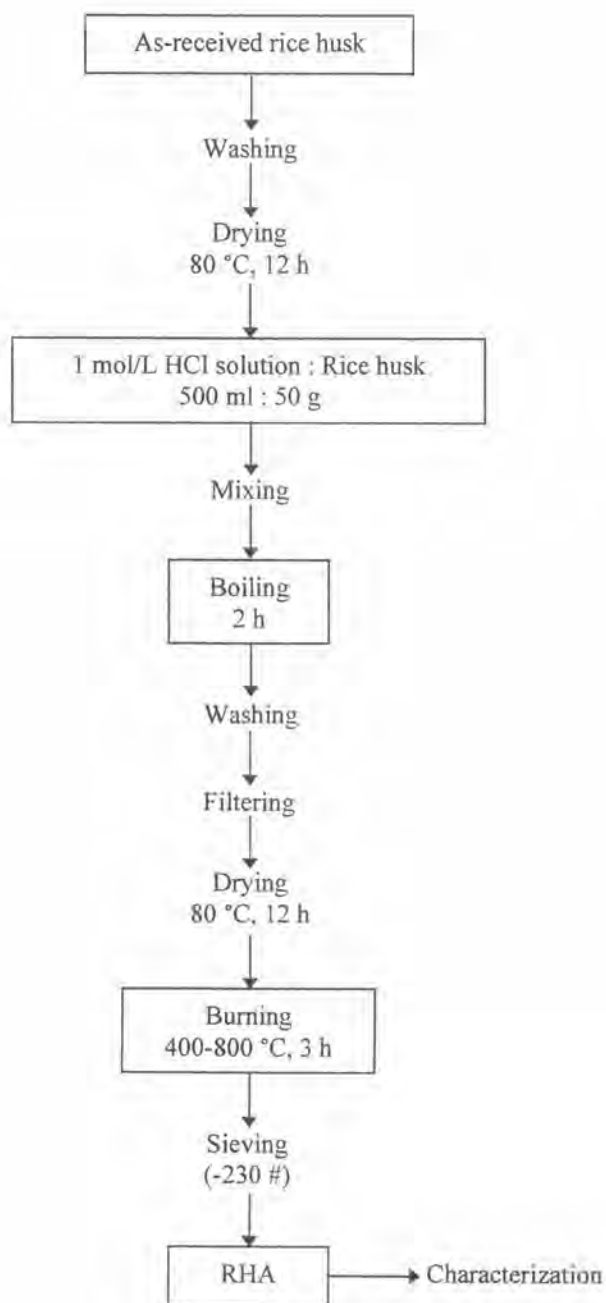


Fig. 3.1 Flow chart for the preparation of silica from rice husk.

Synthesis of ZSM-5 zeolite

The hydrothermal synthesis of ZSM-5 zeolite was performed in a stainless steel bomb lined with PTFE under autogenous pressure using different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar

ratios, from the as-prepared ground RHA silica, under hydrolysis at 150 °C for 2-120 h, using a low concentration of TPABr as the organic template. The preparation of the precursor gels was performed by a modification to that of Mohamed et al^[6]. Briefly; two grams finely ground RHA silica and 0.18 mol/L TPABr solution were mixed with 0.27 mol/L NaOH solution in a final volume of 50 ml and the resultant suspension was stirred for 30 min at room temperature. An aqueous solution of sodium aluminate was prepared separately by mixing a calculated proportion of sodium aluminate powder and 0.27 mol/L NaOH solution to obtain the gel with a desired SiO₂/Al₂O₃ molar ratio (Table 3.1). The sodium aluminate solution was then added to the suspension with stirring for 1 h at room temperature. The pH of the gel was adjusted to about 11 by the addition of 1 mol/L HNO₃ acid before hydrothermal treatment at 150 °C. After each time interval, the obtained product was separated by centrifugation, washed with distilled water, dried at 80 °C for 12 h, calcined in air 550 °C for 5 h to remove the organic template, cooled in a desiccator and then weighed to four decimal places. The weight obtained based on the weight of the ground RHA silica plus Al₂O₃ (in the NaAlO₂ powder), was taken as the product yield (w%)^[7],

Table 3.1 Initial chemical compositions of the precursor gel

SiO ₂ /Al ₂ O ₃	Na ₂ O*/SiO ₂	NaAlO ₂ (mg)	H ₂ O (g)	NaOH (mg)	TPABr (g)	RHA (g)
30	0.212	209.8	49.2	424	0.5	2
50	0.194	124.7	49.2	424	0.5	2
80	0.182	76.8	49.2	424	0.5	2
100	0.177	60.8	49.2	424	0.5	2
200	0.169	28.9	49.2	424	0.5	2
400	0.165	13.1	49.2	424	0.5	2
800	0.163	4.9	49.2	424	0.5	2
1000	0.162	3.3	49.2	424	0.5	2
2075	0.160	-	49.2	424	0.5	2

* Total Na₂O

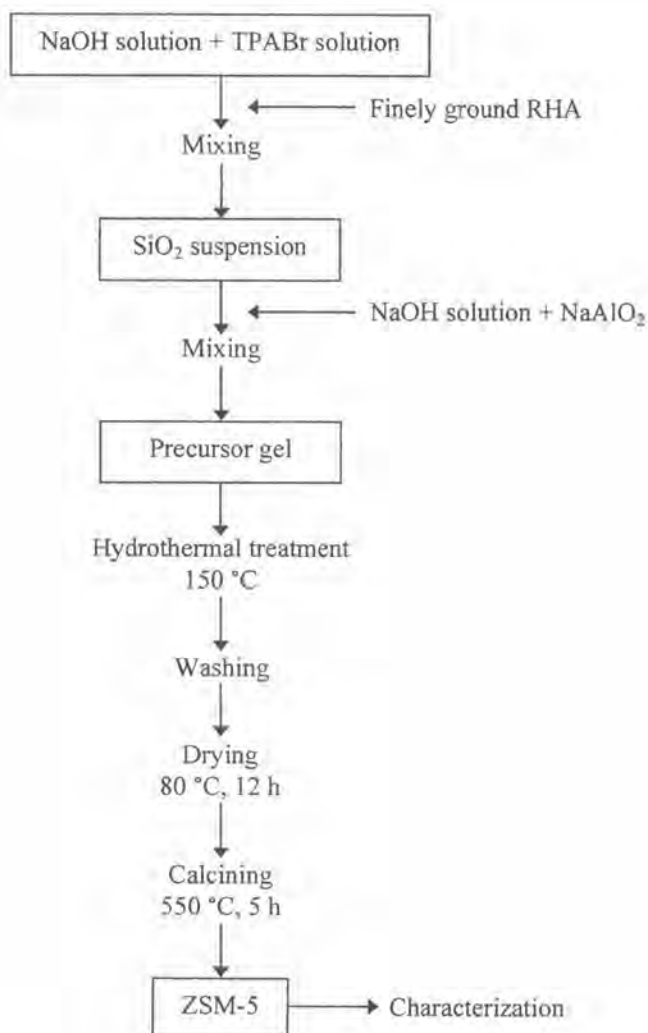


Fig. 3.2. Flow chart for the synthesis of ZSM-5 zeolite from RHA silica.

Preparation of TiO₂/ZSM-5 composite

TiO₂/ZSM-5 composites were prepared by impregnation method, using TiOSO₄ and NaOH as the sources of TiO₂ and the hydrolysis agent, respectively. The preparation of SO₄²⁻-containing TiO₂ sol was performed by a modification to that of Sakthivel et al.^[75] Firstly, 20 ml of 0.1 mol/L TiOSO₄ solution was adjusted by 1.25 mol/L NaOH solution while stirring magnetically to obtain TiO₂ sol of pH 6. After stirring for 1 h, a

required amount of synthesized ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 80) was added to each TiO_2 sol to get 1:20, 1:10, 1:5, 1:2.5 and 1:1 weight ratio of $\text{TiO}_2/\text{ZSM-5}$. The mixture was then stirred for 1 h at room temperature, filtered, dried at $80\text{ }^\circ\text{C}$ for 12 h, crushed and calcined in air at $400\text{-}800\text{ }^\circ\text{C}$ for 4 h. In order to quantify the SO_4^{2-} ion retained in the samples, the washed solution was added by dropping BaCl_2 solution of 0.5 mol/L until there is no white precipitate. The content of SO_4^{2-} ion in the samples was taken via the weight of BaSO_4 precipitates (calcined at $900\text{ }^\circ\text{C}$) in the washed solution. The preparation of $\text{TiO}_2/\text{ZSM-5}$ composite is presented as a flow chart in Fig. 3.3.

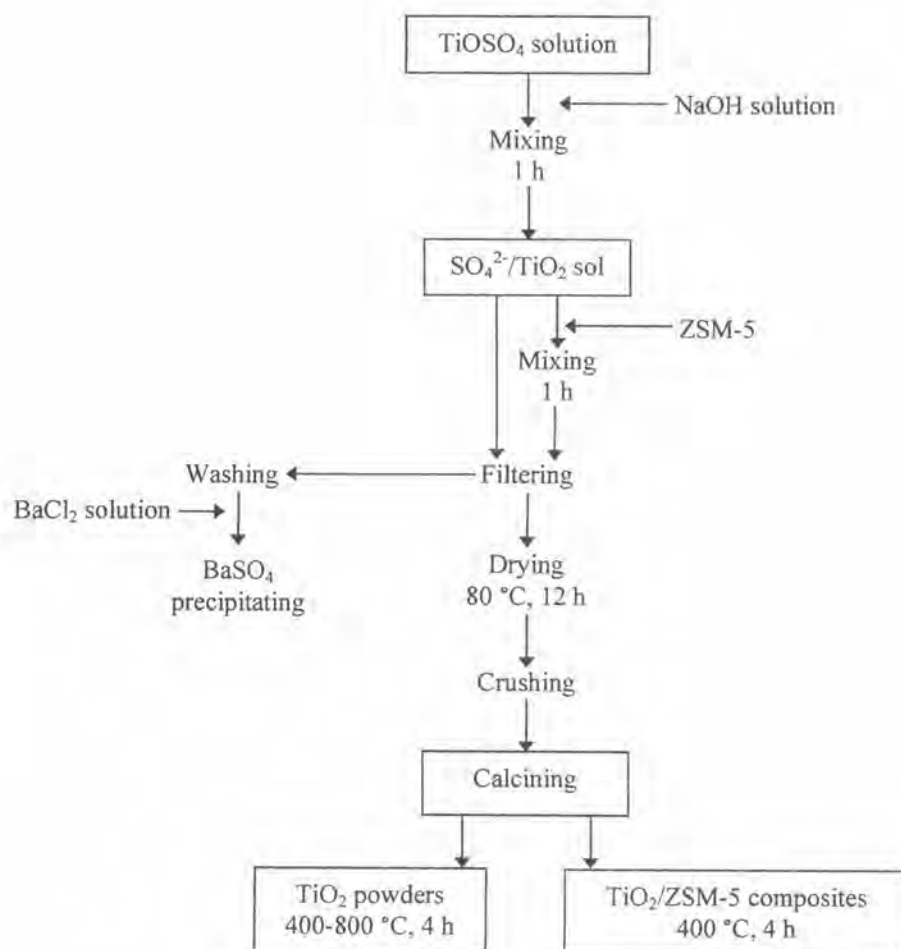


Fig. 3.3. Flow chart for the preparation $\text{TiO}_2/\text{ZSM-5}$ composite.

Characterization

The chemical analysis of the RHA silica was performed by X-ray fluorescence (XRF) with a Philips PW 1480 spectrometer. The RHA silica and the obtained ZSM-5, silicalite, TiO₂ and composite were characterized for phase analysis and morphology by X-ray diffraction (XRD) using Bruker, D8 Advance and scanning electron microscopy (SEM) using a JEOL JSM 6400, respectively. The contents of SiO₂ and Al₂O₃ in the zeolite were determined by the EDAX technique. The BET specific surface area and the BJH pore size distribution were measured using a Coulter SA 3100. The FT-IR spectra were recorded using a PerkinElmer (Spectrum One) spectrometer. The value of zeta potential of ZSM-5 and the obtained SO₄²⁻-containing TiO₂ in aqueous solution were determined by zetasizer (Malvern, Nano ZS) at pH 5.8 (It was found to be -7 mV for TiO₂ and -17 mV for ZSM-5, hence explaining the adsorption of the cationic MB dye).

Photocatalytic activity measurement

The photocatalytic activity was evaluated by the oxidation of methylene blue (MB) dye under UV irradiation. The experiment was performed at pH 5.8 which was the natural pH of the methylene blue dye solution. The catalyst of 0.01 g was dispersed in 20 ml of 0.02 mmol/L aqueous dye solution. The suspension was then magnetically stirred in the dark for 3 h to reach adsorption equilibrium at room temperature. Subsequently, the suspension was irradiated by UV lamps (using 10 W black light at 300-400 nm) with intensity of 2 mW/cm². At specific time intervals (0.5 h), the suspension was centrifuged at 2000 rpm to separate the catalyst from dye solution. Change in the concentration of MB dye solution was determined by measuring the absorbance at 644 nm using spectrophotometer (PerkinElmer Lambda 35).