

# CHARACTERIZATION OF AlMCM-41 SYNTHESIZED WITH RICE HUSK SILICA AND UTILIZATION AS SUPPORTS FOR PLATINUM- IRON CATALYSTS

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**Abstract** - RH-MCM-41 was synthesized by using silica from rice husk and further modified to increase acidity by adding Al with grafting method with Si/Al ratio of 75 and 25. The resulting materials were referred to as RH-AlMCM-41(75) and RH-AlMCM-41(25). The XRD spectra of all RH-AlMCM-41 confirmed a mesoporous structure of MCM-41. Surface areas of all RH-AlMCM-41 were in the range of 700-800 m<sup>2</sup>/g, lower than that of the parent RH-MCM-41, which was 1230 m<sup>2</sup>/g. After Al addition the Si/Al ratios of RH-AlMCM-41(75) and RH-AlMCM-41(25) were higher than that of the parent RH-MCM-41. The RH-AlMCM-41 materials were used as supports for bimetallic platinum-iron catalysts, denoted as Pt-Fe/RH-AlMCM-41, with Pt and Fe amounts of 0.5 and 5.0% by weight, respectively. Results from TPR indicated that the presence of Al might assist the interaction between Pt and Fe as the reduction temperature of iron oxides shifted to a lower value. All catalysts were active for phenol hydroxylation using H<sub>2</sub>O<sub>2</sub> as an oxidant, for which the highest conversions were observed on the RH-MCM-41 material with the highest surface area. The acidity of the supports did not present a significant role in improving the catalytic performance.

**Keywords:** RH-AlMCM-41; Rice husk; Phenol hydroxylation; Pt-Fe/RH-AlMCM-41.

## INTRODUCTION

Rice husk is a by-product from rice milling and could be considered as an agricultural waste (Huang et al., 2001). Its major components are organic compounds such as cellulose and lignin; and amorphous silica. Silica with high purity can be obtained from rice husk by leaching it with mineral acid before calcination (Krishnarao et al., 2001). The rice husk silica can be used as a silica source for the synthesis of porous materials such as zeolite X and Y and MCM-41 (Khemthong et al., 2007; Wittayakun et al., 2008; Grisdanurak et al., 2003). This work focused on continuation of using rice husk

silica as a source for the synthesis of MCM-41, which was further modified with Al.

Mesoporous MCM-41 is amorphous silica with a regular mesopore system (pore size 2-50 nm) which consists of an array of unidimensional and hexagonally shaped mesopores. MCM-41 has attracted considerable interest as a model substance for gas adsorption and catalyst support (Matsumoto et al., 1999). However, it has relatively low surface acidity and a modification to increase acidity is necessary for the applications of MCM-41 for acid-catalyzed reactions such as cracking, isomerization, alkylation and hydroxylation (Matsumoto et al., 1999; Shylesh et al., 2004; Park et al., 2002).

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Brønsted acid sites on surface of MCM-41 could be generated through isomorphous substitution of Si by Al. There are two methods to introduce Al to MCM-41: direct sol-gel method (Pre) and post-synthetic grafting method (Post). Modification of MCM-41 by the sol-gel method was reported to result in unfavorable hydrothermal structural deterioration and relatively low concentration and strength of Brønsted acid sites even at high aluminum content (Park et al., 2002). Therefore, post-synthesis modifications have been developed to maintain structural stability and to incorporate various metal elements into siliceous MCM-41 support. In this work, MCM-41 synthesized with rice husk silica was modified to increase acidity by adding Al with grafting method with Si/Al ratio of 75 and 25. They will be referred to as RH-*Al*MCM-41. The products were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM) and N<sub>2</sub> adsorption-desorption (BET method). They were further used as catalyst supports for platinum and iron, which were tested for phenol hydroxylation.

The phenol hydroxylation to produce dihydroxybenzenes is an important selective oxidation reaction in which the products, 1,2-dihydroxybenzene or catechol and 1,3-dihydroxybenzene or hydroquinone, are used in various applications such as photographic chemicals, antioxidants, flavoring agents, polymerization inhibitors and pharmaceuticals (Kannan et al., 2005). The process of phenol hydroxylation with 30% H<sub>2</sub>O<sub>2</sub> could be a useful process in the future because of its simplicity and lack of pollution. Redox molecular sieves, which are promising materials for transformations of large organic molecules in liquid phase reactions, have emerged recently by incorporating various transition metal species such as platinum and iron (Kannan et al., 2005; Choi et al., 2006; Kuznetsova et al., 2005; Masende et al., 2006). In this work, the catalysts consisting of bimetallic platinum/iron supported on RH-*Al*MCM-41 were tested for the hydroxylation of phenol. The percent conversions of phenol at different reaction times were determined.

## EXPERIMENTAL

### Extraction of Silica from Rice Husk and Preparation of RH-*Al*MCM-41

The rice husk silica (RHS) was prepared by a procedure similar to our previous work (Khemthong et al., 2007; Wittayakun et al., 2008). Its phase was

amorphous and the purity of silica from XRF was 98 wt%. The rice husk silica also contained 0.56 wt% of Al<sub>2</sub>O<sub>3</sub>.

The parent RH-MCM-41 was synthesized by a method from the literature with modifications (Park et al., 2002). Briefly, a starting gel with a molar composition of 4 SiO<sub>2</sub> : 1 CTMABr : 0.29 H<sub>2</sub>SO<sub>4</sub> : 400 H<sub>2</sub>O (CTMABr = cetyltrimethylammonium bromide) was prepared and the gel pH was adjusted to 11 with H<sub>2</sub>SO<sub>4</sub>. The crystallization was done in a Teflon-lined autoclave at 100°C in static conditions for 3 days. The RH-MCM-41 powder was separated by centrifugation, washed with distilled water, dried and calcined at 540°C for 6 h to remove the CTMABr template.

RH-*Al*MCM-41 supports with Si/Al ratio of 75 and 25 were prepared from the parent RH-MCM-41 and NaAlO<sub>2</sub> by the grafting method by a procedure from the literature (Park et al., 2002). The starting materials (0.5 g) were mixed with an aqueous NaAlO<sub>2</sub> solution of 25 ml with Si/Al ratio of 75 and 25 in a polypropylene bottle and stirred vigorously for 30 min. Then the solid powder was separated by centrifugation, dried at 100°C overnight and calcined at 300°C for 2 h. The RH-*Al*MCM-41 with Si/Al ratio of 75 and 25 were referred to as RH-*Al*MCM-41(75) and RH-*Al*MCM-41(25) throughout this article.

### Characterization of RH-*Al*MCM-41

All supports were characterized by XRF (EDS Oxford Instrument ED 2000), powder XRD (Bruker axs D5005 with Cu K $\alpha$  radiation), TEM (JEOL JEM 2010) and N<sub>2</sub> adsorption-desorption (BET method, Micromeritics Analyzer ASAP 2010).

The samples and synthetic calibration standards for XRF analysis were prepared by borate-fusion technique (Buurman et al., 1996). The flat sample disks were bombarded with X-rays generated with a high voltage of 40 kV and current of 30 mA. The quantities of oxides of silicon and aluminum were determined by a standard procedure and the acidities were calculated based on XRF measurements.

The samples for TEM studies were dispersed in absolute ethanol by sonication, dropped on a copper carbon only grid and dried at 70°C with UV lamp. The voltage for electron acceleration in the TEM was 120 kV.

Physical characteristics of the sample were obtained from N<sub>2</sub> adsorption-desorption isotherm at -196°C. Before measurement, each sample was degassed under vacuum at 300°C for 3 h. The BET surface area was obtained from the N<sub>2</sub> adsorption data in the relative pressure range of 0.01-0.3. The

pore size and pore volumes were calculated from the desorption branches of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

### Preparation of 0.5Pt5Fe/RH-AIMCM-41

The 0.5 wt% of platinum and 5 wt% of iron catalysts supported on RH-AIMCM-41 were prepared by co-impregnation with 0.45 M of  $\text{FeCl}_3$  and  $4.8 \times 10^{-3}$  M of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . The materials were dried at  $100^\circ\text{C}$  overnight and calcined at  $300^\circ\text{C}$  for 2 h, with a heating rate of  $10^\circ\text{C}/\text{min}$ . The catalysts obtained were 0.5Pt5Fe/RH-MCM-41, 0.5Pt5Fe/RH-AIMCM-41(75) and 0.5Pt5Fe/RH-AIMCM-41(25).

### Catalyst Characterization by Temperature-Programmed Reduction (TPR)

In each measurement, a catalyst sample of approximately 50 mg was packed in a quartz tube, pretreated by heating from room temperature to  $300^\circ\text{C}$  in helium flow (flow rate 20 mL/min and ramp rate of  $10^\circ\text{C}/\text{min}$ ) and held for 1 h to remove water. After cooling down to room temperature, a gas mixture containing 5%  $\text{H}_2$  in He was introduced with flow rate of 2 mL/min and the temperature was ramped again at the rate of  $5^\circ\text{C}/\text{min}$  from room temperature to  $600^\circ\text{C}$ . The water from reduction was detected continuously by a mass spectrometer (Balzer QME200) and plotted with temperature.

### Catalytic Testing for Phenol Hydroxylation

The catalytic testing for phenol hydroxylation, the catalyst, phenol and  $\text{H}_2\text{O}_2$  solution (30% w/v) were mixed (phenol/ $\text{H}_2\text{O}_2$  mole ratio = 2/3) in a two-necked round bottle (250 ml) equipped with a magnetic stirrer and a reflux condenser. The reaction was carried out at  $70^\circ\text{C}$  for 4 h and the catalyst was separated by centrifugation. The product was sampled every hour and analyzed by gas chromatography (Shimadzu GC14-A) with a capillary column (ID-BP1 3.0  $\mu\text{m}$ , 30 m  $\times$  0.53 mm), a flame ionization detector (FID); the injector and column temperatures were  $250^\circ\text{C}$  and  $190^\circ\text{C}$ , respectively.

## RESULTS AND DISCUSSION

### Characterization of RH-AIMCM-41

Because the aluminum was added to RH-MCM-41 by grafting, in which the support was mixed with

a solution of  $\text{NaAlO}_2$  and stirred vigorously, some aluminum might remain in the solution. Thus, it was necessary to determine the actual amount of aluminum deposited on RH-MCM-41 by XRF. The obtained Si/Al ratios and calculated acidities of RH-MCM-41 and RH-AIMCM-41s are displayed in Table 1. The Si/Al ratios were slightly lower than the calculated values because there was some aluminum present in the rice husk silica source. The amount of Al added to the parent RH-MCM-41 was significant enough to change the Si/Al ratio and calculated acidity.

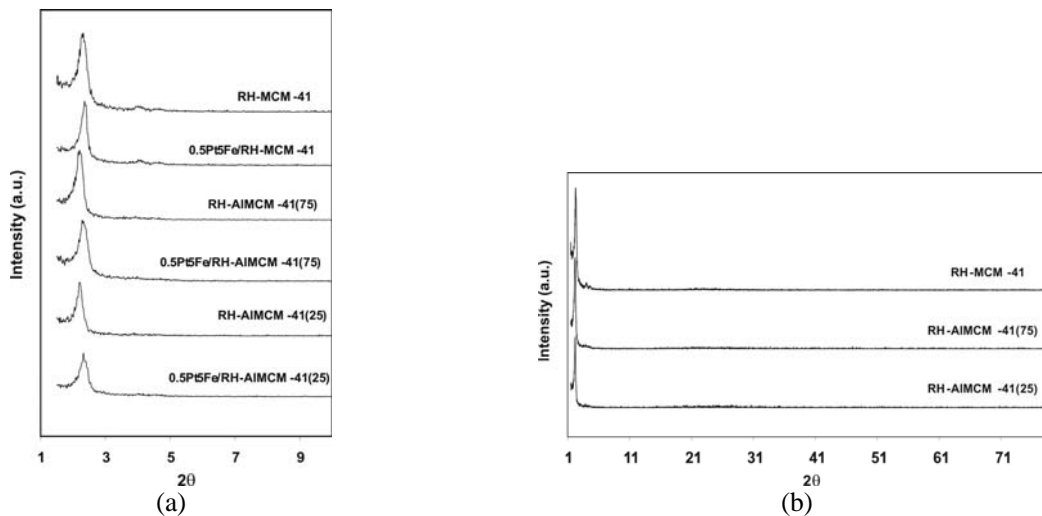
The XRD patterns of the calcined supports and catalysts are displayed in Fig. 1 a. The RH-MCM-41 showed a strong peak at 2.5 and small peaks at 4, and 4.5  $^\circ 2\theta$  corresponding to the 100, 110 and 200 planes of a hexagonal lattice, respectively, and distances of 35, 22 and 19  $\text{Å}$ , respectively. All RH-AIMCM-41 had only the main peak of the 100 plane with lower intensity than that of the parent RH-MCM-41, indicating the decrease of crystallinity after Al grafting. The relative crystallinity of each RH-AIMCM-41 compared to the parent RH-MCM-41 was calculated from area of the main peak. The results are shown in Table 2. After grafting, aluminium could in principle be found as isolated atoms or as aggregates of alumina. The peaks of alumina in RH-AIMCM-41(75) and RH-AIMCM-41(25) samples were not detected by XRD (see Fig. 1b), indicating that aluminum was well dispersed on the MCM-41 framework.

The  $\text{N}_2$  adsorption isotherms of RH-MCM-41, RH-AIMCM-41(75) and RH-AIMCM-41(25) samples are shown in Fig 2. All isotherms corresponded to a mixture of type IV and type I, which are typical isotherms of mesoporous materials. At low  $P/P_0$ , the adsorbed amount increased quickly due to adsorption to form a monolayer. The adsorbed amounts of all RH-AIMCM-41 samples were lower than that of RH-MCM-41 indicating that their surface areas decreased after Al grafting (see Table 2). The  $\text{N}_2$  adsorption increased again before reaching a nearly constant volume. This range corresponded to nitrogen adsorption in the mesopores of RH-MCM-41, RH-AIMCM-41(75) and RH-AIMCM-41(25). However, the adsorption in this range for RH-AIMCM-41 did not increase sharply as in RH-MCM-41, indicating that some mesopores might collapse during the Al-grafting. It was possible that the surface area decreased because the pores of RH-AIMCM-41 were blocked by alumina particles.

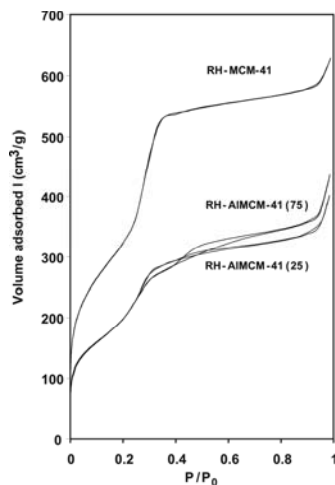
The TEM images of RH-MCM-41, RH-AIMCM-41(75) and RH-AIMCM-41(25) are shown in Fig. 3. All samples displayed well-ordered structures.

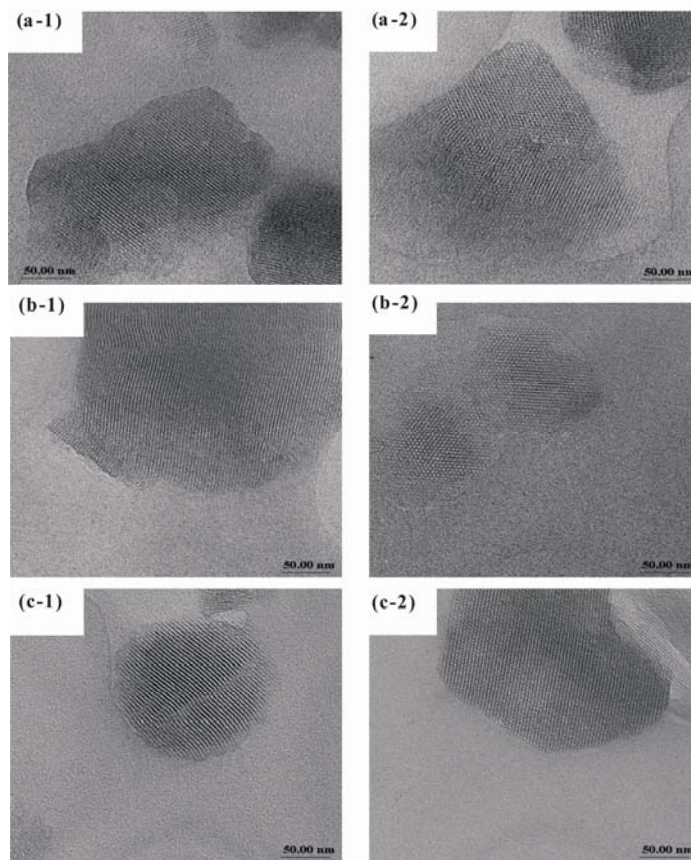
**Table 1: Si/Al ratio of RH-MCM-41 and RH-AIMCM-41**

Sample	Si/Al ratio from preparation	Si/Al ratio from XRF	Calculated acidity <sup>b</sup> (mmol/g)
RH-MCM-41	-	118.3 <sup>a</sup>	0.29
RH-AIMCM-41(75)	75.0	67.7	0.52
RH-AIMCM-41(25)	25.0	23.6	1.40

<sup>a</sup>rice husk silica contained 0.56wt% of Al<sub>2</sub>O<sub>3</sub><sup>b</sup>based on XRF**Figure 1:** (a) XRD patterns at small angles of all supports and catalysts (b) XRD patterns of RH-MCM-41, RH-AIMCM-41(75) and RH-AIMCM-41(25) at large angles.**Table 2: Relative crystallinity and surface area of samples prepared in this work.**

Sample	Relative crystallinity (%)	Surface area (m <sup>2</sup> /g)
RH-MCM-41	100	1231
0.5Pt5Fe /RH-MCM-41	78	-
RH-AIMCM-41(75)	89	741
0.5Pt5Fe /RH-AIMCM-41(75)	79	-
RH-AIMCM-41(25)	68	746
0.5Pt5Fe /RH-AIMCM-41(25)	57	-

**Figure 2:** N<sub>2</sub> adsorption isotherm of RH-AIMCM-41

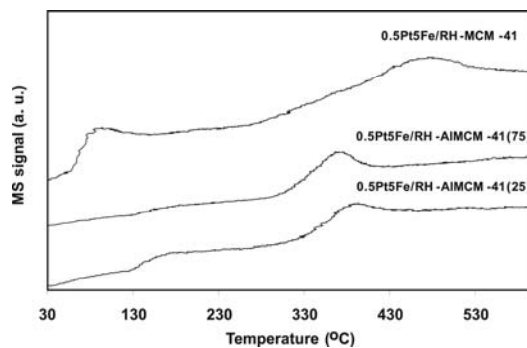


**Figure 3:** TEM micrograph of (a) RH-MCM-41, (b) RH-Al-MCM-41(75) and (c) RH-Al-MCM-41(25)

#### Characterization of Pt-Fe/MCM-41 by TPR

The TPR results for bimetallic Pt-Fe catalysts supported on RH-MCM-41, RH-AIMCM-41(75) and RH-AIMCM-41(25) are shown in Figure 4. For 0.5Pt5Fe/RH-MCM-41, there were two peaks; the first peak around 100°C was assigned to the reduction of platinum and the second around 480°C was assigned to the reduction of iron. The assignment was based on the fact that platinum oxides are more easily reduced than iron (Jia et al., 1999). For the 0.5Pt5Fe/RH-AIMCM-41(75) and

0.5Pt5Fe/RH-AIMCM-41(25), the reduction peaks of iron in all catalysts shifted to lower temperature with maximum around 380°C. It was possible that iron on these supports is located near platinum. After platinum oxide was reduced, it may become the adsorption site for hydrogen and the reducer could easily migrate to reduce iron oxides, resulting in lower reduction temperature. Because this behavior was not observed for the bimetallic catalyst on RH-MCM-41, it was possible that the presence of Al on RH-MCM-41 created an ion exchange site where Pt(IV) and Fe(III) clustered.



**Figure 4:** Water produced from temperature-programmed reduction of catalysts

**Table 3: Pt-Fe bimetallic catalysts on RH-AIMCM-41 for phenol hydroxylation (phenol/H<sub>2</sub>O<sub>2</sub>=3/1, 70°C and amount of catalyst 0.05 g)**

Catalysts	Time (h)	%Conversion of phenol	Selectivity of catechol	Selectivity of hydroquinone
0.5Pt5Fe /RH-MCM-41	1	26.39	49.73	50.27
	2	28.61	48.63	51.36
	3	29.54	50.32	49.67
	4	30.30	48.97	51.03
0.5Pt5Fe /RH-AIMCM-41(75)	1	7.47	71.33	28.66
	2	19.36	49.55	50.44
	3	22.36	48.58	51.42
	4	22.56	48.20	51.79
0.5Pt5Fe /RH-AIMCM-41(25)	1	25.87	48.13	51.87
	2	23.10	49.92	50.08
	3	22.46	47.62	52.38
	4	25.43	46.53	53.47

### Catalytic Testing of Pt-Fe/MCM-41 for Phenol Hydroxylation

Table 3 shows the performance of the Pt-Fe bimetallic catalysts for the phenol hydroxylation reaction. After the first hour, all catalysts showed conversion of phenol: the highest of 28 % was over 0.5Pt5Fe/RH-MCM-41, probably because the support presented the highest surface area. After the second hour, all catalysts showed increased conversion and seemed to approach steady state with a slight increase of conversion. As the conversions on 0.5Pt5Fe/RH-AIMCM-41(75) and 0.5Pt5Fe/RH-AIMCM-41(25) were not significantly different, the increase of support acidity did not have a significant influence on the catalytic performance.

### CONCLUSIONS

RH-MCM-41 was prepared successfully with rice husk silica source and its calculated acidity was improved by adding aluminum via grafting method. However, the aluminum addition caused a decrease in the surface area of RH-AIMCM-41(75) and RH-AIMCM-41(25). The prepared RH-AIMCM-41 materials were used as supports for bimetallic Pt-Fe catalysts and tested for hydroxylation of phenol. However, 5Fe0.5Pt/RH-MCM-41 showed the highest phenol conversion because the RH-MCM-41 support had significantly higher surface area.

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