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by Hartati Hartati

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Cyclic Acetalization of Furfural on Porous Aluminosilicate Acid Catalysts

Hartati^{1,2,3}, Didik Prasetyoko^{2,*}, and Mardi Santoso³

¹Department of Chemistry, Faculty of Science and Technology, Airlangga University, Kampus C UNAIR, Surabaya, 60115, Indonesia

²Laboratory of Material Chemistry and Energy, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sepuluh Nopember Institute of Technology (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia

³Laboratory of Natural Products and Chemical Synthesis, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sepuluh Nopember Institute of Technology (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia

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ABSTRACT

Porous aluminosilicate materials included microporous and mesoporous ZSM-5, hierarchical aluminosilicates, and mesoporous aluminosilicate were tested for acetalization of furfural (furan-2-carbaldehyde) with propylene glycol. The existing synthesis methods for aluminosilicate and ZSM-5 were modified to produce aluminosilicate material with hierarchical porous structure. Catalytic activity in acetalization of furfural by propylene glycol were conducted by refluxed of the mixture of furfural, propylene glycol and catalyst, using toluene as solvent and nitrobenzene as internal standard, at 106 °C for 4 h. The result showed that a combination of two structure directing agents, tetrapropylammonium hydroxide (TPAOH) and cetyltrimethylammonium bromide (CTAB) and modification of catalytic crystallization produced an active aluminosilicate framework that provides a wide access for a bulky reactants and strong acid sites to catalyze the reaction. The pore structure and the strength of the Brønsted acid sites were crucial for the high conversion of furfural to produce a cyclic acetal.

Keywords: acetalization; furfural; propylene glycol; porous aluminosilicates

ABSTRAK

Material aluminosilikat yang meliputi ZSM-5 mikropori dan mesopori, aluminosilikat berpori hirarkis, dan aluminosilikat mesopori diuji aktivitasnya untuk asetalisasi furfural (furan-2-karbalehida) dengan propilena glikol. Metode sintesis material aluminosilikat berpori dan ZSM-5 dimodifikasi untuk menghasilkan material aluminosilikat dengan struktur pori hirarkis. Reaksi katalitik katalis dalam asetalisasi furfural dilakukan dengan merefluks campuran furfural, propilena glikol, dan katalis, menggunakan toluena sebagai pelarut dan nitrobenzena sebagai standar internal, pada suhu 106 °C selama 4 jam. Hasil penelitian menunjukkan bahwa kombinasi dua agen pengarah struktur, tetrapropilamonium hidroksida (TPAOH) dan setiltrimetilamonium bromida (CTAB) dan modifikasi kondisi kristalisasi menghasilkan kerangka aluminosilikat yang dapat diakses oleh reaktan dan memiliki sisi asam yang kuat untuk reaksi katalisis. Struktur pori dan sisi asam Brønsted merupakan hal yang paling berpengaruh untuk mengkonversi furfural menjadi asetal siklis.

Kata Kunci: asetalisasi; furfural; propilena glikol; aluminosilikat berpori

INTRODUCTION

In general, acetalization is a viable method to protect carbonyl functionalities in organic compounds [1] and important process in industry and has been widely used to produce active additive in fragrances [2]. The industrial needs of acetal compound especially to be used as additive in fragrances has prompted this study to find alternative ways for designing a simpler synthesis approach and environmentally friendly catalysts [3].

Acetals include a number of 'amber' chemicals. These materials are so-called due to their resemblance

to *ambergris*, a material formed in the stomach of whales probably as a protection against intestinal damage by the 'shelly' parts of plankton. The material is occasionally found washed up on beaches, but the major source was the whaling industry. Unsurprisingly, this is now a rare and expensive material, driving the search for synthetic alternatives [4].

Furfural (furan-2-carboxaldehyde) is produced from plant residues which are rich in pentoses. This is one of important oxygen-containing heterocyclic aroma chemicals occurring in almost every type of food flavor and has a sweet caramel-like, nutty, baked bread,

* Corresponding author. Tel/Fax : +62-31-5943353/5928314
Email address : didikp@chem.its.ac.id

almond odor and flavor, and it is applied in cereal, roasted and meat flavorings [5].

Glycol/diol is the most widely used in the manufacture of acetal [2]. Jemi and Pandurangan [6] showed that propylene glycol is better used than ethylene glycol for acetalization, due to the addition of alkyl group in propylene glycol can increase the nucleophilic properties. The most researchers use glycerol/triol for acetalization [2,7-9].

Conventionally, syntheses of acetals are performed using protic acid catalyst such as hydrochloric acid, sulfuric acid, or *p*-toluenesulfonic acid (PTSA) [10]. Synthesis of acetal is generally done using a weak acid catalyst, whereas the synthesis of ketal using a strong acid, such as sulfuric acid or other catalyst PTSA and number. The methods mostly use reagents that can not be recycled, require neutralization process, and generate waste [2]. Solid acid catalysts, such as zeolites, molecular sieves, and related porous materials have many advantages in this respect [11]. The use of renewable feedstock is the one of 12 principles in green chemistry [12].

Zeolites [2] and molecular sieves [13-14] have been identified as a potential heterogeneous acid catalyst for such reaction. Aluminosilicate material was explored as active catalyst to drive the reaction where researches have been focused only on porous aluminosilicate catalysts [15]. However, the lack of interest in amorphous materials has prompted this study to explore a real potential of this material. We modify the existing recipe for preparation of ZSM-5 and aluminosilicate by combining two structure directing agents, reset mole ratio composition and crystallization conditions for the synthesis of catalysts to create a hierarchical material with high site acid strength. In this paper, we reported the result of our detailed investigations with respect to test of the porous aluminosilicate catalysts in acetalization of furfural with propylene glycol to produce cyclic acetal which is a vital ingredient in fragrances.

EXPERIMENTAL SECTION

Materials

All chemicals in the study were of analytical grade and used without further purification. Tetraethyl orthosilicate (TEOS, $\geq 99\%$), sodium aluminate (Al_2O_3 50–56%), sodium hydroxide ($\geq 98\%$), and tetrapropylammonium hydroxide (TPAOH, 1 L = 1.00 kg, 40 wt% solution in water), 3,4-dimethoxybenzaldehyde $\geq 98\%$, propylene glycol ($\geq 99\%$), toluene ($\geq 99.9\%$), and nitrobenzene ($\geq 99\%$) were purchased from Merck; hexadecyltrimethyl ammonium bromide (CTAB) were purchased from AppliChem, *p*-toluenesulfonic acid

(PTSA) from Sigma Aldric ($> 98.5\%$), while H-ZSM-5 standard from Zeolyst.

Instrumentation

The apparatus used in synthesis of catalysts consists of 250 mL stainless steel and polypropylene autoclaves, oven, porcelain crucible boat, centrifuge, tubular furnace, hot plate with magnetic stirrer, Leibig condenser, 50 mL two-necked round-bottom flask, and 100 °C thermometer.

X-ray diffraction patterns (XRD) were recorded on a Philips X'pert XRD instrument with Cu K α radiation with a step size of 0.02° and counting time of 10 sec. The samples were grinded in agate mortar before analysis. Data were recorded in the 2 θ range of 5–50°.

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Shimadzu 84005 spectrophotometer using the KBr pellet technique, in the range of 400–4000 cm^{-1} with a spectral resolution of 4 cm^{-1} , 45 scans, at 20 °C.

Specific surface areas (SSA) of the different materials were determined by N₂ adsorption-desorption measurements at 77 K by employing the Brunauer-Emmet-Teller (BET) method. Prior to N₂ adsorption, the sample was out gassed at 300 °C for 5 h to desorb moisture adsorbed on the surface and inside the porous network. Mesopore size distributions were calculated using the Barrett, Joyner, and Halenda (BJH) method on Quantachrome Nova version 10.01.

Spectra of pyridine adsorbed on the samples also were recorded on the same spectrometer for acidity study. Before measurement of pyridine adsorption, the samples were pressed to thin wafers (around 10 mg/cm^2) and placed into a sample holder. The sample disks were evacuated at 400 °C for 4 h in the N₂ and cooled to room temperature. Then 2 drops of pyridine was exposed near the disks at room temperature. After the adsorption at room temperature for 1 h the infrared spectra were recorded. The desorption procedure were conducted at 150 and 300 °C for 3 h in order to determine the acidity of Lewis and Brønsted acid sites by evaluating the amount of remaining adsorbed pyridine as temperature increases. The concentrations of Brønsted (B) and Lewis (L) acid sites were calculated from the peak areas of adsorbed pyridine at around 1540 and 1450 cm^{-1} , using $\epsilon(\text{B})$ and $\epsilon(\text{L})$ extinction coefficients of 1.88 and 1.42 $\text{cm} \cdot \text{mmol}^{-1}$, respectively [16].

The apparatus used in catalytic reaction are 50 mL three-necked round-bottom flask, Dean Stark apparatus, spiral condenser, 150 °C thermometer, hot plate with magnetic stirrer, syringe with 10 cm needle for sampling, and rubber stopper.

Procedure

Synthesis of catalysts

Microporous ZSM-5 (ZSM-5) was synthesized according to the procedures by Cheng et al. [17] and TPAB was used as structure-directing agents (SDA). Mesoporous ZSM-5 (ZSM-5-Me) and hierarchical aluminosilicates (Hie-AMS) were prepared by modification of the method for the synthesis of mesoporous ZSM-5 [18] and mesoporous titanosilicates [19], with a molar composition of $1\text{SiO}_2:\text{xAl}_2\text{O}_3:0.2\text{TPAOH}:38\text{H}_2\text{O}$ ($\text{x} = (\text{SiO}_2/\text{Al}_2\text{O}_3)^{-1}$). Sodium aluminate was dissolved in a solution of TEOS by stirring for 30 min. TPAOH and water were added into the reaction mixture and stirred for another 15 h at room temperature. The mixture was then transferred into a polypropylene autoclave and heated at 80 °C for 48 h for synthesis of ZSM-5-Me, while Hie-AMS (Hie-AMS-3, Hie-AMS-2, and Hie-AMS-1) were prepared by heated 80 °C for 24 h. In this research, CTAB was used as a mesophase forming agent (a molar ratio of $\text{SiO}_2/\text{CTAB} = 3.85$) was added after the reaction mixture was cooled at room temperature with a gentle stirred for 30 min. The mixture was then aged at room temperature for 3 h. The solid was separated from the supernatant by centrifugation and washed with distilled water until the pH of supernatant is 7. Finally, the solid was dried at 60 °C for 24 h and calcined at 550 °C for 1 h in N_2 and 6 h in air to remove any organic compounds. We were also prepared another type of amorphous mesoporous aluminosilicate (AAM) using the similar procedure, but TPAOH was replaced with NaOH. The final reactant compositions in molar ratio and hydrothermal conditions for all samples are summarized in Table 1.

All the synthesis products were treated with ammonium acetate solution (0.5 mol/L) at 60 °C for 3 h to produce hydrogen formed catalysts. The solids were centrifuged and washed thoroughly with distilled water before dried overnight at 110 °C and calcined at 550 °C for 1 h in N_2 and 6 h in air. The catalysts tested herein (Microporous ZSM-5, Hie-AMS-3, and AAM) were previously reported [20].

Catalytic performance

Catalytic reactions of the catalysts in acetalization of furfural by propylene glycol were carried out in 50 mL three-necked round-bottom flask [2], using a Dean Stark apparatus to remove the water formed during the reaction. Furfural (1.12 mmol), propylene glycol (2.15 mmol), nitrobenzene (100 μL , as internal standard for gas chromatography analysis), and dried catalyst (0.02 g) in toluene (20 mL) were refluxed by oil bath at around 106 °C for 4 h. Samples were taken at regular time periods and analyzed by Techcomp 7900

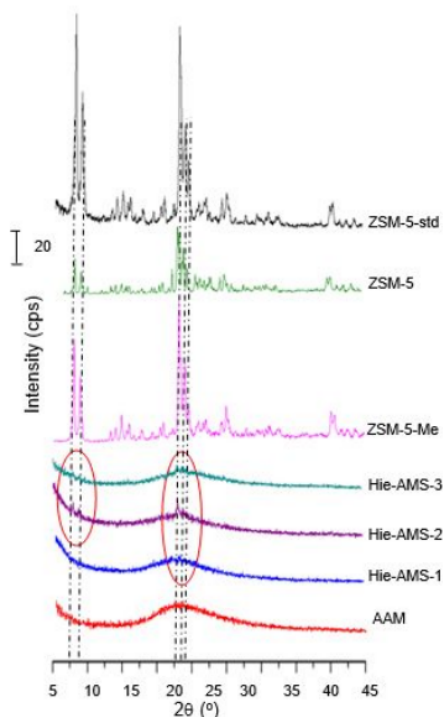


Fig 1. XRD patterns of the ZSM-5 [20], ZSM-5-Me, Hie-AMS-1, Hie-AMS-2, Hie-AMS-3 [20], and AAM [20], compared with XRD pattern of ZSM-5-std

Table 1. Molar ratio composition and crystallization conditions for the synthesis of catalysts

Catalysts	$\text{SiO}_2/\text{Al}_2\text{O}_3$ Mole Ratio ^a	Structure directing agents (SDA) ^b		Crystallization condition (°C; h)	Ref.
		1	2		
ZSM-5	12.87	TPAB	-	175; 24	20
ZSM-5-Me	43.17	TPAOH	CTAB	80; 48	-
Hie-AMS-3	39.42	TPAOH	CTAB	80; 24	-
Hie-AMS-2	34.13	TPAOH	CTAB	80; 24	-
Hie-AMS-1	11.39	TPAOH	CTAB	80; 24	20
AAM	49.24	-	CTAB	80; 24	20

^a) determined by EDX

^b) MFI structure template (1) and mesophase forming agent (2)

gas chromatography (GC) equipped with HP 88 column and FID detector. The products were also further identified using gas chromatography-mass spectrometer (GC-MS). The conversion of furfural and the selectivity of products were calculated based on equation by Pawar et al. [9] and Tayade, et al. [21], respectively. The results are also compared with *p*-toluenesulfonic acid as a homogeneous acid catalyst.

RESULT AND DISCUSSION

Characterization of the Catalysts

The catalysts were characterized by X-ray diffraction patterns (XRD), Fourier transform infrared spectroscopy (FTIR), N_2 adsorption-desorption, and pyridine adsorption - FTIR spectroscopy.

As illustrated in Fig. 1, microporous ZSM-5 (ZSM-5) and mesoporous ZSM-5 (ZSM-5-Me) obtained after the final hydrothermal treatment at 175 °C for 24 h and at 80 °C for 48 h, respectively, are highly crystalline as a standard of ZSM-5 (ZSM-5-std) that can be observed by X-ray diffraction pattern. For the materials prepared with the addition of TPAOH through crystallization conditions for the synthesis at 80 °C for 24 h, the sample Hie-AMS showed amorphous diffraction line although there is very small peak at around $2\theta = 7-8^\circ$ and 22° , may be suggesting the appearance of a crystalline ZSM-5 phase in the samples (Fig.1, circle). AAM only shows hump characteristic for amorphous phase and does not appear the typical MFI peaks at 2θ around $7-8^\circ$ and around 22° .

Fig. 2 shows the FTIR spectra all of materials in the range of 1400–400 cm^{-1} . Interpretations of these spectra were based on the assignment of the infrared bands of the structural groups in the material framework. The absorption at around 1222 cm^{-1} (external asymmetric stretching), 1000–1200 cm^{-1} (internal asymmetric stretching), 795 cm^{-1} (external symmetric stretching), and 445 cm^{-1} (T–O bending) are observed in the amorphous materials (Hie-AMS and AAM) and these characteristics are insensitive to the structural changes [21–22]. The infrared spectra of Hie-AMS and AAM also contained a shoulder band at around 980 cm^{-1} attributed to the terminal silanol group on the wall surface of the mesoporous materials [21]. The additional small band at around 545 cm^{-1} was only observed for the Hie-AMS samples. These bands are a characteristic of MFI type zeolite that arises from the double rings lattice vibration of the framework (Fig. 2, circle). Spectra FTIR of ZSM-5 and ZSM-5-Me exhibits a band at 550 cm^{-1} , which is commonly assigned to pentasil units in the MFI zeolite topology, while the band at around 1200 cm^{-1} is clearly resolved, indicating the high crystallinity of this material [23]. The bands at 550 cm^{-1} and 980 cm^{-1} in the spectra

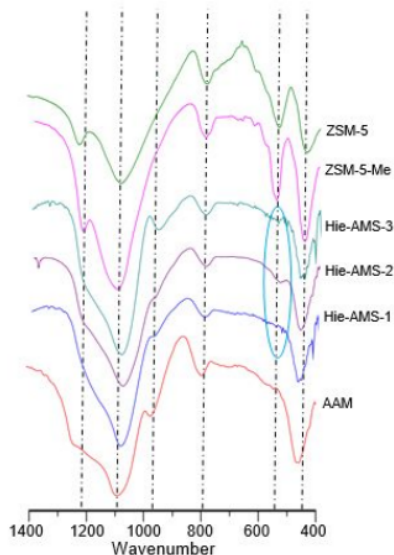


Fig 2. FTIR spectra of the ZSM-5 [20], ZSM-5-Me, Hie-AMS-1, Hie-AMS-2, Hie-AMS-3 [20], and AAM [20]

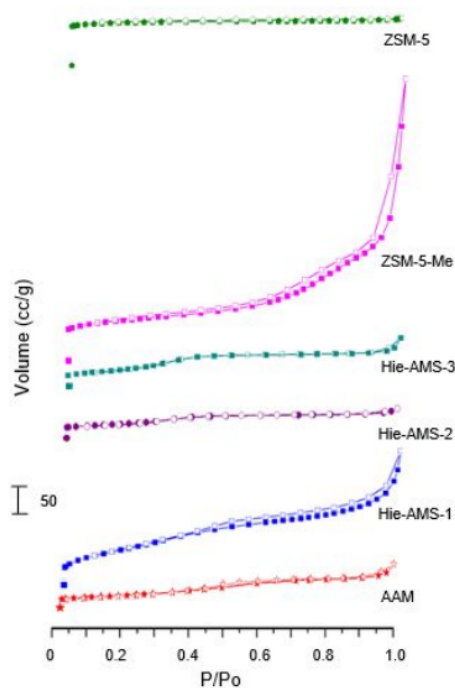


Fig 3. Nitrogen adsorption-desorption isotherm of the ZSM-5 [20], ZSM-5-Me, Hie-AMS-1, Hie-AMS-2, Hie-AMS-3 [20], and AAM [20]

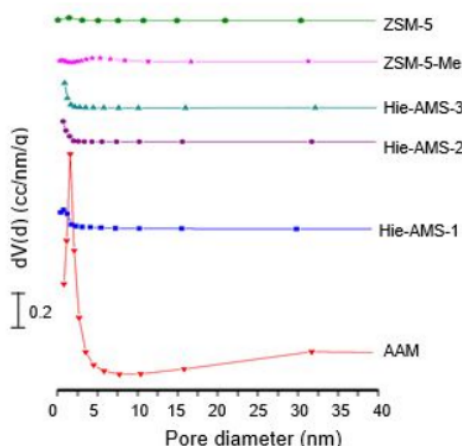
Table 2. Pore structure properties of catalysts

Catalysts	Surface Area		Pore Volume ^a (cm ³ /g)	Pore Diameter ^a (nm)	Ref.
	Mesoporous ^a (m ² /g)	Microporous ^b (m ² /g)			
ZSM-5	5.766	261.565	0.009	3.820	[20]
ZSM-5-Me	177.233	241.756	0.701	6.575	-
Hie-AMS-3	145.986	541.411	0.311	3.059	[20]
Hie-AMS-2	134.112	337.156	0.189	3.044	-
Hie-AMS-1	136.108	293.274	0.300	3.400	-
AAM	278.774	284.949	0.441	3.815	[20]

a. determined by BJH

b. determined by BET method at P/P₀ = 0.3**Table 3.** Acidity of catalysts

Catalysts	Acidity (mmol/g)				Ref.
	Brønsted		Lewis		
	150 °C	300 °C	150 °C	300 °C	
ZSM-5	1.53	1.24	0.95	0.84	[20]
ZSM-5-Me	0.72	0.67	1.16	1.15	-
Hie-AMS-3	1.29	0.78	1.19	1.00	[20]
Hie-AMS-2	0.83	0.58	1.24	0.88	-
Hie-AMS-1	0.96	0.00	1.47	1.37	-
AAM	0.00	0.00	1.05	0.87	[20]

**Fig 4.** Pore diameter of the ZSM-5 [20], ZSM-5-Me, Hie-AMS-1, Hie-AMS-2, Hie-AMS-3 [20], and AAM [20]

showed that Hie-AMS samples are hierarchical porous aluminosilicates.

The N₂ adsorption-desorption isotherm of the microporous ZSM-5 possesses a typical type I according to the IUPAC classification [24], as shown in Fig. 3. The characteristic of this type is shown with a very high adsorption at low relative pressure and an almost flat hysteresis loop appearing at P/P₀ > 0.10. The adsorption-desorption isotherms of the mesoporous ZSM-5 (ZSM-5-Me) is a typical type IV isotherm with capillary condensation at high relative pressure between 0.6 and 0.9, suggesting a relatively large mesoporous

size (Table 2). Hierarchical aluminosilicate (Hie-AMS) and amorphous aluminosilicate (AAM) also show a typical pattern of type IV structure. The hysteresis loop of Hie-AMS at relatively high pressure (0.85–0.95) is assigned to H4 hysteresis loop. Materials containing both microporous and mesoporous generally have H4 hysteresis loops [24]. Correspondingly, the sample mesoporous size distribution is estimated at about 3–6 nm by applying a BJH method (Fig. 4). Fig. 4 also shows that ZSM-5 and ZSM-5-Me have wide distribution with low peaks, while Hie-AMS and AAM show a narrow distribution with a sharper peaks.

The surface area of microporous structure of ZSM-5 is very high at around 260 m²/g (Table 2). However this material does not possess a mesoporous structure which can be seen by only 5.77 m²/g (2.2% of total surface area) and 0.01 cm³/g of mesoporous surface area and pore volume were detected. The mesoporous ZSM-5 showed the surface area more than 40% of total surface area, however the Hie-AMS and AAM contain both mesoporous and microporous structure. The surface areas of AAM and pore volume are around 278.77 m²/g (almost 50%) and 0.44 cm³/g, respectively. Meanwhile, the surface area of mesoporous Hie-AMS is less than 50% compared to microporous structure. It is interesting to note that the Hie-AMS also has a high pore volume (ca. 0.189–0.311 cm³/g). This finding proved that the Hie-AMS has hierarchical porous structure that will allow a good accessibility.

The acid sites of hydrogen formed catalysts were quantified by using FTIR spectra of adsorbed pyridine. FTIR spectra after pyridine desorption at 150 and 300 °C are shown in Fig. 5. The band at around 1444 cm⁻¹ corresponds to the chemisorption of pyridine (C–C stretching of a coordinative bonded pyridine complex) on Lewis (L) acid sites. The band at around 1544 cm⁻¹ is attributed to the C–C stretching vibration of the pyridinium ion and has been used to identify the presence of Brønsted (B) acid sites [25–26]. The intensity of these bands show a significant reduction when desorption temperature was increased up to 300 °C. This effect can be clearly seen on Brønsted acid

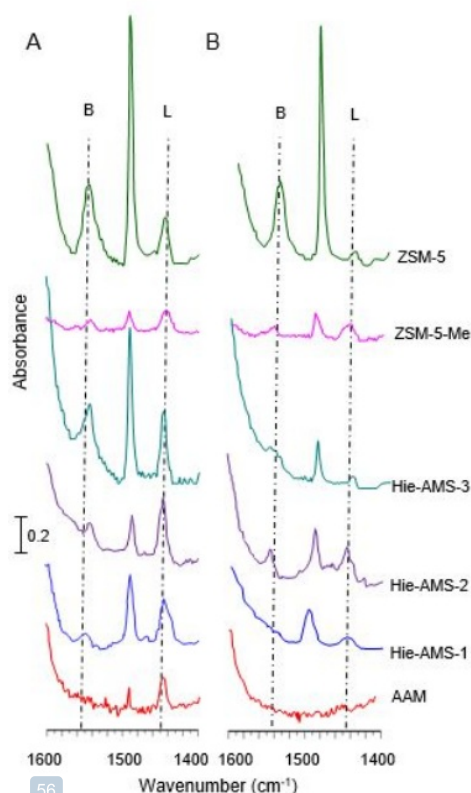


Fig 5. FTIR spectra of pyridine desorption on ZSM-5 [20], ZSM-5-Me, Hie-AMS-1, Hie-AMS-2, Hie-AMS-3 [20], and AAM [20], at 150 °C (A) and 300 °C (B)

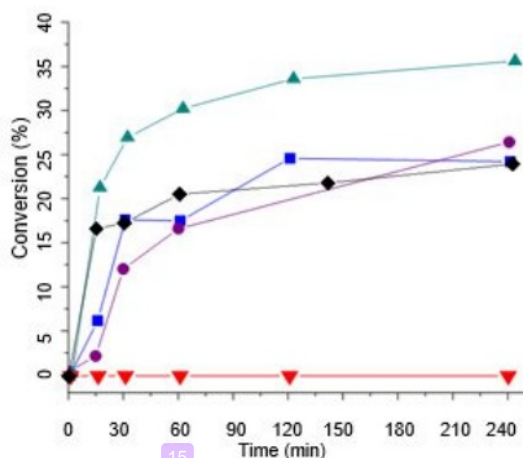


Fig 6. Conversion of furfural to acetal in the presence of H-Hie-AMS-3 (▲), H-Hie-AMS-2 (●), H-Hie-AMS-1 (■), H-AAM (▼), PTSA (◆) as catalyst

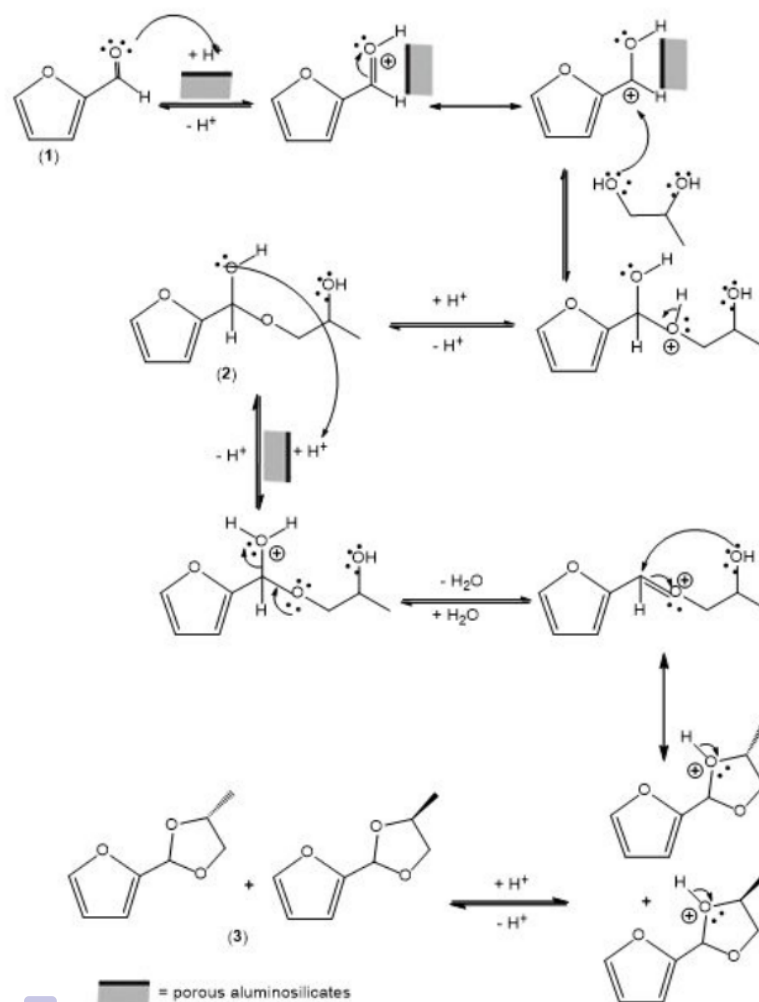
sites due to the interaction between pyridine and Brønsted acid sites are relatively weaker than Lewis acid sites (Table 3). The pyridine adsorption studies showed that H-Hie-AMS-3 has strong acid sites with both Lewis and Brønsted acid sites were observed in the structure. Different from H-ZSM-5 and H-Hie-AMS, H-AAM has no band observed at around 1544 cm^{-1} , indicating that the sample has a low acid strength.

Catalytic Activity

Acetalization of furfural with propylene glycol was done to evaluate the activity of the catalysts. The reaction was conducted at 106 °C using toluene as a solvent. This reaction requires a strong acid catalyst; and due to a bulky structure of chemical reactant, a large mesoporous channel is important to allow the reactant to reach the active acid site in the catalysts. The conversion of furfural for 4 h of reaction on H-ZSM-5, H-ZSM-5-Me, H-Hie-AMS, and H-AAM catalysts was shown in Fig. 6. Hie-AMS-3 is the most active catalysts with more than 20% of conversion within 15 min into the reaction. However, the conversion of furfural in the acetalization reaction with H-Hie-AMS-3 for 4 h is not up by 40% and in previous studies this catalyst were successfully used as catalysts in acetalization of 3,4-dimethoxy-benzaldehyde [20]. H-Hie-AMS-2 and H-Hie-AMS-1 catalysts which have mole ratio of Si/Al lower than H-Hie-AMS-3 catalyst (Table 1) showed slightly less active than H-Hie-AMS-3 catalyst. The Brønsted acid sites may play important role in the reaction, therefore H-Hie-AMS-3 more active than H-Hie-AMS-1 and H-Hie-AMS-2. The important of active acid sites for the reaction can be seen by no conversion of furfural by H-AAM catalysts. H-ZSM-5 and H-ZSM-5-Me was shown trace of conversion of furfural to acetal. Furfural propylene glycol acetal was observed as the only product from the reaction on the porous aluminosilicate catalysts as also shown on GC-MS spectra (100% selectivity). The result showed that the catalysts were highly selective for the synthesis of furfural propylene glycol acetal compared to PTSA that showed 94.7% selectivity.

Mechanism for Acetalization

Acetalization reaction in general is carried out by reacting aldehyde with an alcohol in the presence of an acid catalyst. The proposed reaction mechanism of furfural (1) with propylene glycol was shown in Scheme 1. In the first step of reaction, the formation of carbocation on the carbonyl group of furfural takes place over the Brønsted acid sites associated to tetrahedrally coordinated aluminium. Then, the carbocationic species were combined with nucleophilic



Scheme 1. Mechanism for the formation of furfural propylene glycol acetal

oxygen of propylene glycol. Hemiacetals (2) was formed after deprotonation, which then subsequently react with hydroxyl group on propylene glycol. This followed by the cyclodehydration to eliminate water molecule and produced 2-(furan-2-yl)-4-methyl-1,3-dioxolane (3) [15].

CONCLUSION

Improving the procedure for synthesizing mesoporous ZSM-5 has produced hierarchical aluminosilicate materials. The materials have strong acidic site. In addition, the material also has mesoporous structure beside still quite a lot of microporous structure. The use of hierarchical aluminosilicate materials for

catalysis in acetalization of furfural showed the acidity of the catalyst and the mesoporous structure of the aluminosilicate framework are crucial factor to ensure high conversion acetalization reaction. The reactivity of catalysts in acetalization of furfural especially influenced by pore structure and Brønsted acid sites. The mole ratio of Si/Al of the material catalyst also affects the reactivity of the hierarchical aluminosilicates as catalyst in acetalization. The activities of hierarchical porous aluminosilicates material in the acetalization of furfural with propylene glycol are better than PTSA based on conversion of furfural and selectivity.

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REFERENCES

1. Rubio-Caballero, J.M., Saravanamurugan, S., Maireles-Torres, P., and Riisager, A., 2014, *Catal. Today*, 234, 233–236.
2. Climent, M.J., Corma, A., and Velty A., 2004, *Appl. Catal., A*, 263 (2), 155–161.
3. Venkatachalam, K., Palanichamy, M., and Murugesan, V., 2010, *Catal. Commun.*, 12 (4), 299–303.
4. Rowe, D.J., 2005, "Aroma Chemicals I: C, H, O Compounds" in *Chemistry and Technology of Flavors and Fragrances*, Blackwell Publishing Ltd., Victoria, 72–73.
5. Zviely, M., 2005, "Aroma Chemicals II: Heterocycles" in *Chemistry and Technology of Flavors and Fragrances*, Blackwell Publishing Ltd., Victoria, 88–90.
6. Jermy, B.R., and Pandurangan, A., 2006, *J. Mol. Catal. A: Chem.*, 256 (1-2), 184–192.
7. Umbarkar, S.B., Kotbagi, T.V., Biradar, A.V., Pasricha, R., Chanale, J., Dongare, M.K., Mamede, A.S., Lancelot, C., and Payen, E., 2009, *J. Mol. Catal. A: Chem.*, 310, 150–158.
8. Khayoon, M.S., Abbas, A., Hameed, B.H., Triwahyono, S., Jalil, A.A., Haris, A.T., and Minett, A.I., 2014, *Catal. Lett.*, 144 (6), 1009–1015.
9. Pawar, R.R. Jadhav, S.V., and Bajaj, C.H., 2014, *Chem. Eng. J.*, 235, 61–66.
10. Bruckner, R., 2010, *Organic Mechanisms Reactions, Stereochemistry and Synthesis*, Springer-Verlag, Berlin Heidelberg, 373.
11. Sheldon, R., Arends, I.W.C.E., and Hanefeld, U., 2007, *Green Chemistry and Catalysis*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 10.
12. Sharma, S.K., and Mudhoo, A., 2011, *Green Chemistry for Environmental Sustainability*, NRC Press, Taylor and Francis Group, New York, 2.
13. Rodriguez, I., Climent, M.J., Iborra, S., Fornés, V., and Corma, A., 2000, *J. Catal.*, 192 (2), 441–447.
14. Liang, X.Z., Gao, S., Wang, W.J., Chen, W.P., and Yang, J.G., 2007, *Chin. Sci. Bull.*, 52 (13), 1780–1784.
15. Ajaikumar, S., and Pandurangan, A., 2008, *J. Mol. Catal. A: Chem.*, 290 (1-2), 35–43.
16. Emeis, C.A., 1993, *J. Catal.*, 141 (2), 347–354.
17. Cheng, Y., Wang, L.J., Li, J.S., Yang, Y.C., and Sun, X.Y., 2005, *Mater. Lett.*, 59 (27), 3427–3430.
18. Gonçalves, M.L., Dimitrov, L.D., Jordão, M.H., Wallau, M., and Urquieta-González, E.A., 2008, *Catal. Today*, 133-135, 69–79.
19. Eimer, G.A., Díaz, I., Sastre, E., Casuscelli, S.G., Crivello, M.E., Herrero, E.R., and Perez-Pariente, J., 2008, *Appl. Catal., A*, 343 (1-2), 77–86.
20. Hartati, Prasetyoko, D., Santoso, M., Bahruji, H., and Triwahyono, S., 2014, *Jurnal Teknologi*, 69 (5), 2180–3722.
21. Tayade, K.N., Mishra, M., Munusamy, K., and Somani, R.S., 2014, *J. Mol. Catal. A: Chem.*, 390, 91–96.
22. Meenakshi, S., Sahu, A.K., Bhat, S.D., Sridhar, P., Pitchumani, S., and Shukla, A.K., 2013, *Electrochim. Acta*, 89, 35–44.
23. Yang, J., Yu, S., Hu, H., Zhang, Y., Lu, J., Wang, J., and Yin, D., 2011, *Chem. Eng. J.*, 166 (3), 1083–1089.
24. Zhou, J., Hua, Z., Liu, Z., Wu, W., Zhu, Y., and Shi, J., 2011, *ACS Catal.*, 1, 287–291.
25. Thommes, M., 2010, *Chem. Ing. Tech.*, 82 (7), 1059–1073.
26. Jin, F., and Li, Y., 2009, *Catal. Today*, 145 (1-2), 101–107.
27. Hensen, E.J.M., Poduval, D.G., Degirmenci, V., Ligthart, D.A.J.M., Chen, W., Maugé, F., Rigutto, M.S., and van Veen, J.A.R., 2012, *J. Phys. Chem. C*, 116, 21416–21429.

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28 Zhang, Y.. "Mixed-matrix membranes composed of Matrimid[®] and mesoporous ZSM-5 nanoparticles", Journal of Membrane Science, 20081115

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32 data.epo.org

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36

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37

Zongtao Zhang, Yu Han, Lei Zhu, Runwei Wang, Yi Yu, Shilun Qiu, Dongyuan Zhao, Feng-Shou Xiao. "Strongly Acidic and High-Temperature Hydrothermally Stable Mesoporous Aluminosilicates with Ordered Hexagonal Structure", Angewandte Chemie International Edition, 2001

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