CONDENSATION OF INDOLE WITH ISATIN OVER $AlCl_3$/MESOPOROUS ALUMINOSILICATE

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ABSTRACT

Aluminium chloride immobilized on mesoporous aluminosilicate was investigated as catalysts in the condensation of isatin with indole. $AlCl_3$/mesoporous aluminosilicate ($AlCl_3$/AM) catalysts were prepared by impregnation of 1, 5, 10 and 15 wt% $AlCl_3$ on the surface of mesoporous aluminosilicate. A maximum conversion of isatin was achieved using 15% $AlCl_3$/AM catalyst whereas the highest selectivity of 68.97% towards trisindoline was obtained using pure AM. The activity of the catalysts was depended on their acid site number and surface area. The number of Brønsted acid and the surface area affected to the conversion of isatin while the total acidity and the number of Lewis acid influenced the selectivity.

Keywords: *$AlCl_3$; mesoporous aluminosilicate; impregnation; condensation; indole; isatin*

ABSTRAK

Aluminium klorida terimobilisasi pada permukaan aluminosilikat mesopori telah dipelajari sebagai katalis pada kondensasi indola dengan isatin. Katalis $AlCl_3$/aluminosilikat mesopori ($AlCl_3$/AM) disiapkan dengan metode impregnasi $AlCl_3$ sebanyak 1, 5, 10, dan 15 %(b/b) pada permukaan aluminosilikat mesopori. Konversi maksimum isatin diperoleh dengan katalis $AlCl_3$/AM 15%, sedangkan selektivitas tertinggi terhadap trisindolin diperoleh menggunakan AM murni sebesar 68,97%. Aktivitas katalitik bergantung pada jumlah sisi asam dan luas permukaan. Jumlah sisi Brønsted dan luas permukaan berpengaruh pada konversi isatin sedangkan total keasaman dan jumlah sisi Lewis berpengaruh pada selektivitas.

Kata Kunci: *$AlCl_3$; aluminosilikat mesopori; impregnasi; kondensasi; indola; isatin*

INTRODUCTION

A derivative compound of indole such as trisindoline or 3,3-Bis(indole-3-yl) oxindole can be produced by condensation reaction through electrophilic substitution between C-3 of indole and the carbonyl group of ketone or aldehyde (e.g. activated isatin). Trisindoline has a high antibiotic activity against *E. Coli*, *Bacillus subtilis*, and *Staphylococcus aureus* [1]. Besides, it can be used as an anticancer agent against uterus sarcoma cells in humans (MES-SA and MES-SA/DX5), *colorectal adenocarcinoma*cell (HTC15) [2].

Various acid catalysts have been used to activate the carbonyl group of isatin to form a suitable intermediate for the reaction with indole. Wang and Ji [3] reported the use of cerium (IV) ammonium nitrate (CAN) in the condensation of indole with isatin in methanol carried out using ultrasonic wave resulting in 96% yield of trisindoline. In another research, the condensation of indole with isatin was carried out in two steps using copper (II) bromide and silver (I) carbonate [4]. Recently, Kamal et al. [5] reported the high activity of $FeCl_3$ in the indole condensation giving 93% of trisindoline yield.

$AlCl_3$ also can be used in the condensation of indole with isatin. The previous research indicated that $AlCl_3$ is an active catalyst for this reaction [6]. However, as a homogeneous catalyst, $AlCl_3$ suffers from the common problems involving product separation and reusability. These drawbacks can be solved by heterogenization of the homogeneous catalyst to produce a heterogeneous catalyst which has high

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activity and selectivity. This process can be done by immobilization of the homogeneous catalyst on the heterogeneous catalyst surface through impregnation or encapsulation [7]. $AlCl_3$ catalyst has been previously impregnated on the MCM-41. The addition of 15 wt% $AlCl_3$ enhanced the activity of NaX zeolite catalyst in benzene reaction. Among other acid catalysts such as $FeCl_3$, $ZnCl_2$, $NiCl_2$, and $CuCl_2$, $AlCl_3$ was the best catalyst to be immobilized onto MCM-41 surface resulting in a fast reaction rate and high conversion of benzyl chloride [8].

As an amorphous porous material with high surface area and large pore size, mesoporous aluminosilicate is a promising heterogeneous catalyst used to immobilize $AlCl_3$ resulting in easier separation process in catalytic reaction. Mesoporous aluminosilicate contains Brønsted and Lewis acids on its structure due to the incorporation of trivalen aluminium atoms into the framework of tetrahedral silica [9]. The presence of hydrogen ion balancing the negative charge due to the presence of $[AlO_4]^{5-}$ in the framework of zeolites results in Brønsted acid. Heating process at a high temperature (500 °C) leads to the addition of water in ZSM-5 crystal which reacts with Al cations forming a cluster of Al-OH acid. Hence, water will come out leading to the formation of coordinated Al_3 ion (strong Lewis acid) [10]. Nur et al. [11] reported the existence of the relation between Brønsted and Lewis acids on zeolite beta in the selectivity of Friedel-Crafts alkylation reaction.

In this study, $AlCl_3$/mesoporous aluminosilicate catalyst was used in the condensation of indole with isatin. The effect of $AlCl_3$ loading on the catalyst activity was investigated.

EXPERIMENTAL SECTION

Materials

Starting materials of samples were commercial tetrapropylammonium hydroxide (TPAOH; Merck, 40%), hexadecyltrimethylammonium bromide (CTABr; Applichem, 99%), tetraethyl orthosilicate (TEOS; Merck 99%), sodium aluminate (Sigma-Aldrich, 50-56% Al_2O_3), ammonium acetate (>98%, Merck), aluminium chloride anhydrous ($AlCl_3$), indole (Merck, >99%), isatin (Sigma-Aldrich, 98%), pyridine (Merck, 99.5%), deionized water, sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), ethyl acetate, ethanol (Merck, 99%), acetonitrile (Merck, >99.9%), N_2 gas.

Instrumentation

The crystalline structure of the catalysts was determined by an X-ray diffractometer (XRD, Phillips Expert). The IR spectrum was recorded using Fourier Transform Infrared spectroscopy (FTIR, Shimadzu Instrument Spectrum One 8400S) through KBr pellet method. The acidity of samples was determined by infrared spectroscopy technique using pyridine as probe molecule. The wafer of the sample (10-12 mg) was locked in the cell equipped and evacuated at 400 °C, continued by adsorption of pyridine at room temperature. After evacuation at 150 °C for 3 h, infrared spectra of the sample were recorded at room temperature in the region of 1400-1700 cm^{-1}. To analyze the pore structure of the catalysts, nitrogen sorption Quantachrome Instruments was used. 0.4 g catalysts was preheated at 250 °C for 2.5 h and cooled prior to the measurements at a temperature of -196 °C. Leaching test was carried out by mixing 0.05 g catalysts with 10 mL acetonitrile. The mixture was then stirred for 2.5 h at room temperature and filtered to remove the solid phase. The solution was evaporated to get a concentrate solution and diluted with distilled water to a 10 mL volume for being tested in ICP measurement to measure the aluminium content.

Procedure

Preparation of mesoporous aluminosilicate

Mesoporous aluminosilicate was prepared by modifying Goncalves et al. [12] and Eimer et al. [13] methods. Sodium aluminate (50-56% Al_2O_3, Sigma Aldrich,) was completely dissolved in tetraethyl orthosilicate (TEOS, 99%, Merck). The solution was mixed with tetrapropylammonium hydroxide (TPAOH, 40%, Merck,) and distilled water resulting in a mixture with mole ratio of 1 SiO_2:0.05 Al_2O_3:0.2 TPAOH:38 H_2O. The mixture was stirred for 15 h and settled at 80 °C for 24 h. Cetyltrimethylammonium bromide (CTAB, 99%, Applichem) was then added and stirred until perfectly mixed for 30 min to give SiO_2 to CTAB molar ratio of 3.85. The mixture was then aged for 3 h. The solid product was recovered by filtration, followed by washing with distilled water until the pH was neutral and drying at 60 °C for 24 h. The dried solid was calcined at 550 °C for 1 h and 6 h with the presence and the absence of N_2 flow, respectively to obtain mesoporous aluminosilicate.

The mesoporous aluminosilicate was then placed in ion exchange process. 7.708 g ammonium acetate was dissolved in 100 ml distilled water and added with 10 g mesoporous aluminosilicate. The mixture was refluxed at 60 °C for 3 h, filtered and dried at 100 °C. The solid product was calcined at 550 °C for 1 h and 6 h with the presence and the absence of N_2 flow, respectively to achieve mesoporous aluminosilicate with high acidity known as AM.

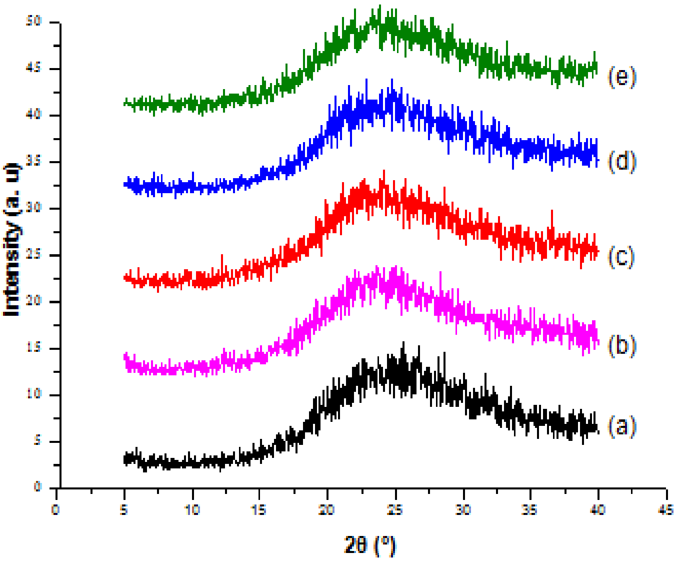

Fig 1. XRD patterns of catalysts: (a) AM; (b) 1% $AlCl_3$/AM; (c) 5% $AlCl_3$/AM; (d) 10% $AlCl_3$/AM; (e) 15% $AlCl_3$/AM

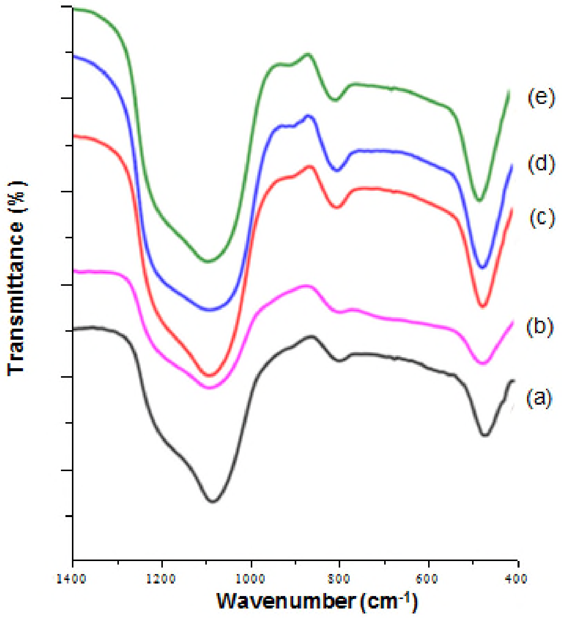

Fig 2. FTIR spectra: (a) AM; (b) 1% $AlCl_3$/AM; (c) 5% $AlCl_3$/AM; (d) 10% $AlCl_3$/AM; (e) 15% $AlCl_3$/AM

Preparation of $AlCl_3$/mesoporous aluminosilicate

$AlCl_3$/mesoporous aluminosilicate was prepared using impregnation method. Mesoporous aluminosilicate was refluxed with $AlCl_3$ anhydrate (Merck) in 5 mL ethanol (99%, Merck) at 65 °C for 4 h [14]. The mixture was evaporated to eliminate the alcohol, dried at 100 °C for 6 h and calcined at 350 °C for 6 h to obtain the product. The amounts of $AlCl_3$ loading on AM were varied at 1, 5, 10, and 15 wt% toward $AlCl_3$ weight ratio.

Activity of the catalysts

The activity of the catalyst was tested in the condensation reaction of indole with isatin. The reaction was performed in 50 mL round flask connected with a reflux condenser and stirrer plate. A mixture composed of 0.5 mmol isatin (98%, Sigma Aldrich), 1 mmol indole (>99%, Merck), 0.5 g catalyst and 10 mL acetonitrile (>99.9%, Merck) was stirred at room temperature for 2.5 h and saturated with 5 mL sodium bicarbonate ($NaHCO_3$). The mixture was extracted with 3 mL ethyl acetate three times, washed with distilled water, added with sodium sulfate (Na_2SO_4) and then filtered. The amount of unreacted isatin and the obtained trisindoline was measured using a densitometer based on the comparison of their color density intensity with the standard. The wavenumber was set at 443 nm using silica gel 60 F_{254} as a stationary phase and dichloromethane-ethyl acetate (10:1) as a mobile phase. The volume spotting were 5 µL and 2 µL for isatin and trisindoline, respectively. The retention factors were set at 0.43 and 0.21 for isatin and trisindoline, respectively.

RESULT AND DISCUSSION

Characterization of the Catalysts

X-ray diffraction

The X-ray diffraction patterns of the obtained $AlCl_3$/mesoporous aluminosilicates are given in Fig. 1. It can be clearly seen that all samples were amorphous solid where a broad peak was observed from 15° to 35°. This result was similar to the XRD pattern of silica [15] which also presented in amorphous phase.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the catalysts showing the effect of $AlCl_3$ impregnation on mesoporous aluminosilicate are presented in Fig. 2 while the vibrational assignments are given in Table 1. Vibrational bands at 1080, 794 and 466 cm^{-1} on mesoporous aluminosilicate spectra are the lattice vibrational modes associated with internal bonding of tetrahedral AlO_4 or SiO_4 [16]. The appearance of peaks at 1080 and 794 cm^{-1} indicate the presence of asymmetric vibration and symmetric vibration of T-O-T, respectively where T represents Si or Al. Furthermore, a broad peak at 466 cm^{-1} shows T-O bending vibration [17].

The impregnation of $AlCl_3$ on mesoporous aluminosilicate resulted in a new peak formation around 900 cm^{-1} representing Si-OH or Al-OH or Si-OM vibration where M is metal [18]. The presence of this peak confirms that the catalysts are amorphous solid containing hydroxyl groups as found in the mesoporous

Table 1. Wavenumber of FTIR spectra of the catalysts

Sample	Stretching TO_4		Bending T-O	Vibration Si-OH/Si-O-M
	Asymmetric	Symmetric		
AM	1080.17	794.70	466.79	-
1% $AlCl_3$/AM	1083.99	794.54	466.93	-
5% $AlCl_3$/AM	1087.89	798.56	466.79	893.26
10% $AlCl_3$/AM	1087.89	794.70	466.79	895.00
15% $AlCl_3$/AM	1087.89	794.70	466.79	898.86

Table 2. Brønsted and Lewis acidities of the catalysts

Sample	Acidity, mmol/g		Total acid, mmol/g	L/B
	Brønsted (B)	Lewis (L)		
AM	0.017	0.027	0.044	1.605
1% $AlCl_3$/AM	0.028	0.024	0.052	0.859
5% $AlCl_3$/AM	0.027	0.025	0.052	0.908
10% $AlCl_3$/AM	0.014	0.038	0.052	2.745
15% $AlCl_3$/AM	0.011	0.051	0.062	4.605

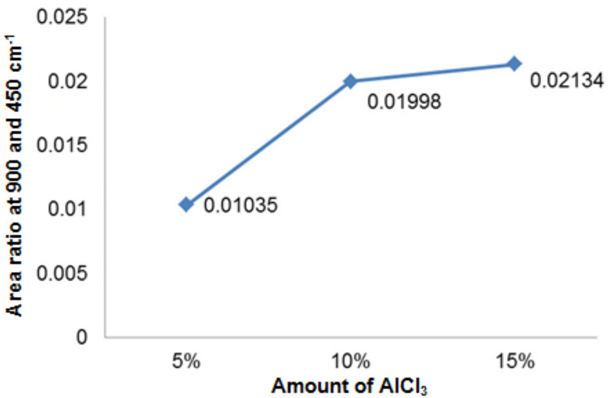

Fig 3. The effect of $AlCl_3$ amount to the area ratio at 900 and 450 cm^{-1}

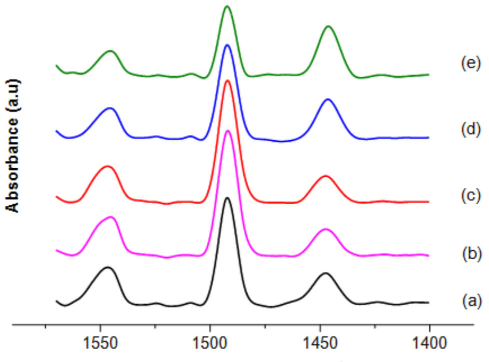

Fig 4. FTIR spectra of catalysts after being used in pyridine adsorption: (a) AM; (b) 1% $AlCl_3$/AM; (c) 5% $AlCl_3$/AM; (d) 10% $AlCl_3$/AM; (e) 15% $AlCl_3$/AM

MCM-41 [19]. However, this peak was absence in 1 wt% $AlCl_3$/AM catalyst due to the lack of $AlCl_3$ loading. Moreover, the incorporation of $AlCl_3$ in the silica framework gave a shifting to the asymmetric TO_4 peak towards a higher wavenumber by an increasing in $AlCl_3$ loading.

Fig. 3 gives the relationship between the amount of impregnated $AlCl_3$ and the ratio of peak area at 900 and 450 cm^{-1}. The ratio of peak area was found to increase with an increasing in amount of $AlCl_3$ indicating the interaction of $AlCl_3$ in mesoporous aluminosilicate framework.

Analysis of pyridine adsorption

The results of acidity test are presented in Fig. 4 in which all catalysts possessed both of Lewis and Brønsted acids indicated by the presence of peaks at 1445 and 1545 cm^{-1}. The addition of $AlCl_3$ content increased the total acidity as given in Table 2. However, the impregnation of 1, 5 and 10% $AlCl_3$ had a same effect to the total acidity. Among other catalysts, 15% $AlCl_3$/AM catalyst exhibited the highest total acidity.

Leaching test

Leaching test was performed to see the success of $AlCl_3$ heterogenization process as the results are shown in Table 3. The aluminium content in unbound $AlCl_3$ with mesoporous aluminosilicate was measured using ICP based on facts that $AlCl_3$ as homogeneous catalysts is soluble in acetonitrile while mesoporous aluminosilicate is insoluble in it. The amount of leached $AlCl_3$ was achieved by converting the Al amount from ICP measurement to $AlCl_3$ amount using their relative mass ratio. The results show that leaching process only happened to 15% $AlCl_3$/AM catalyst due to the excess of $AlCl_3$ loading. $AlCl_3$ is not completely bound to the mesoporous aluminosilicate surface at this condition causing the catalyst still acts as a homogeneous catalyst. The leached catalyst will dominate the catalysis reaction even though in very small amount resulting in many problems related with homogeneous catalysis process [20]. Therefore, the impregnation of $AlCl_3$ on mesoporous aluminosilicate can be only done at maximum 10 wt% loading.

Table 3. Leaching test results of $AlCl_3$/AM catalyst

Sample	Amount of Al[a]		Amount of leached $AlCl_3$ (mg)	Amount of $AlCl_3$ at 0,05 g catalyst (mg)[b]	wt% Leaching
	ppm	mg			
1% $AlCl_3$/AM	-	-	-	0.5	-
5% $AlCl_3$/AM	-	-	-	2.5	-
10% $AlCl_3$/AM	-	-	-	5	-
15% $AlCl_3$/AM	0.448	0.00448	0.022	7.5	0.293

[a] Result of ICP measurement
[b] Result of theoretical calculation

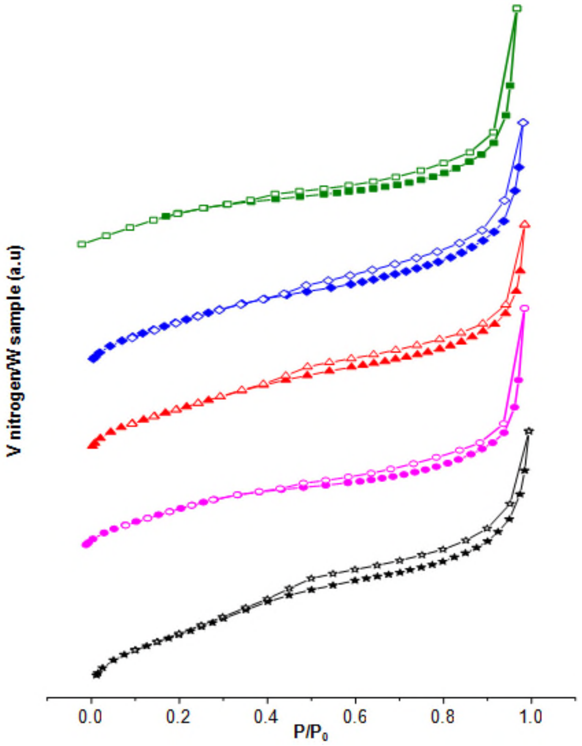

Fig 5. Nitrogen adsorption-desorption isotherms of the catalysts: (☆) AM; (○) 1% $AlCl_3$/AM; (Δ) 5% $AlCl_3$/AM; (◊) 10% $AlCl_3$/AM; (□) 15% $AlCl_3$/AM. Adsorption (closed), desorption (open)

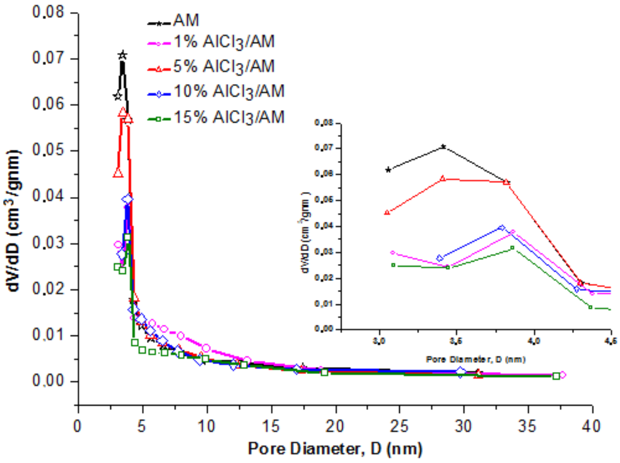

Fig 6. Pore size distribution (BJH desorption) of the catalyst

Adsorption-desorption of nitrogen

Nitrogen adsorption-desorption experiment was carried out to determine the pore distribution and total surface area of the catalysts. Fig. 5 depicts the nitrogen adsorption-desorption isotherms of AM and $AlCl_3$/AM catalysts. All isotherms show a hysteresis loop in the middle of the area, which can be ascribed as Type IV isotherms as adsorption type of mesoporous solids with pore diameter of 2-50 nm [21]. The isotherms of the composite granules have hysteresis loops in the similar relative pressure from 0.55 to 0.8, showing almost identical pore size distributions in the range of 3 to 6 nm with the same average pore size of 4.4 nm [22].

The pore size distributions presented in Fig. 6 show that the pore diameter of the catalysts is more than 2 nm (about 3-4 nm). These results confirm that the catalysts are mesoporous solids with a hysteresis loop in their nitrogen adsorption-desorption isotherms. The impregnated mesoporous aluminosilicates have less pores than their pure state leading to a conclusion that $AlCl_3$ was distributed in the pores of mesoporous aluminosilicate due to the impregnation process. This fact is consistent with a study observed by Khodakov et al. [23] where cobalt nitrate was distributed in the pores of MCM-41 and SBA-15 through an impregnation process.

The impregnation process also had an effect to the total surface area which the value was tended to decrease with an addition of $AlCl_3$ as given in Table 4. The impregnated $AlCl_3$ covered the surface of mesoporous aluminosilicate leading to the reduction in surface area. A similar result was conducted by Chen et al. [24] where impregnated S-ZrO_2 was uniformly dispersed on the MCM-41 surface lowering the surface area. 1% $AlCl_3$/AM catalyst had similar surface area with pure AM since the impregnated $AlCl_3$ was in very small amount resulting in negligible effect to the surface area. However, 15% $AlCl_3$/AM catalyst possessed a high total surface area as a result of a new surface formation due to the excess amount of $AlCl_3$. This fact could be connected with leaching phenomenon happened to this catalyst. Reddy et al. [25] reported that the addition of excess silica to SBA-15 could produce a thin wall causing the expansion of the SBA-15 surface. Unlike the surface area, the pore diameter of the catalysts was not affected by the addition

Table 4. Pore diameter and total surface area of the catalysts

Catalysts	Pore Diameter (nm)	Total Surface Area (m^2/g)
AM	3-4	293
1% $AlCl_3$/AM	3-4	307
5% $AlCl_3$/AM	3-4	278
10% $AlCl_3$/AM	3-4	236
15% $AlCl_3$/AM	3-4	289

Table 5. Activity of the catalysts in the condensation reaction of indole with isatin

Catalyst	Unreacted isatin (%)	Reacted isatin[a] (%)	Obtained trisindoline (%)	Conversion of isatin[c] (%)	Selectivity of trisindoline[d] (%)
AM	2.68	36.06	24.87	93.08	68.97
1% $AlCl_3$/AM	2.39	36.35	13.2	93.83	36.31
5% $AlCl_3$/AM	1.49	37.25	14.65	96.15	39.33
10% $AlCl_3$/AM	6.74	32	21.75	82.60	67.97
15% $AlCl_3$/AM	0[b]	38.74	11.72	100.00[b]	30.25

[a] Difference between amount of initial and unreacted isatin (amount of initial isatin = 38.74%)
[b] Not detected on densitometer because limited detection of 21.23 ng or 424 ppb (thus the value considered as 0)
[c] Conversion = (Amount of reacted isatin/amount of initial isatin) x 100%
[d] Selectivity = (Amount of obtained trisindoline/amount of reacted isatin) x 100%

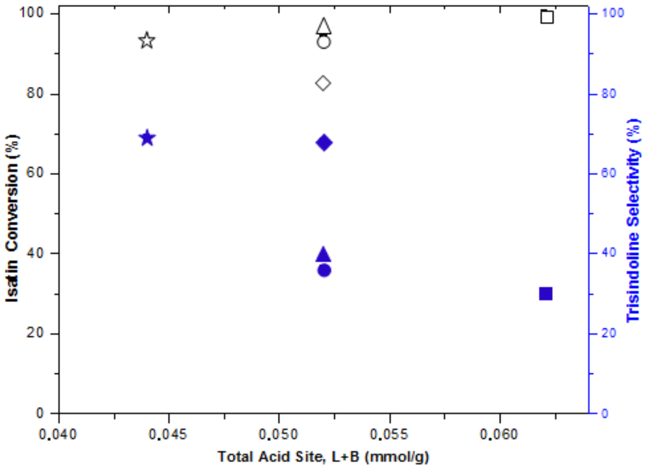

Fig 7. The relationship between the total acid sites on AM (☆), 1% $AlCl_3$/AM (○), 5% $AlCl_3$/AM (Δ), 10% $AlCl_3$/AM (◊) and 15% $AlCl_3$/AM (□)and the conversion of isatin (open) and trisindoline selectivity (closed)

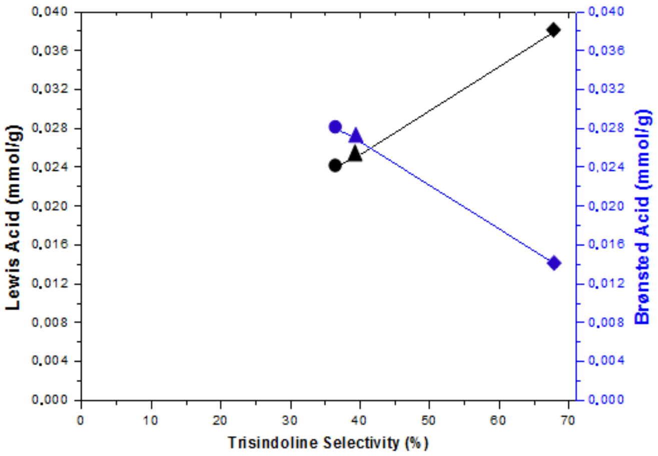

Fig 8. Relationship between selectivity towards trisindoline and the number of acid site: Lewis acid (black) and Brønsted acid (blue) on the catalyst 1% $AlCl_3$/AM (O), 5% $AlCl_3$/AM (Δ), and 10% $AlCl_3$/ AM (◊)

of $AlCl_3$ because of the similar size.

Activity of the Catalysts

The activity of the catalysts was evaluated in the condensation reaction of indole with isatin. As shown in Table 5, mesoporous aluminosilicate is the most active catalyst for the reaction giving a trisindoline selectivity of 68.97%. An impregnation of 15% $AlCl_3$ on AM surface resulted in a maximum conversion of isatin even though the obtained selectivity towards trisindoline was very low. We found the presence of 0.293% leached $AlCl_3$ in this catalyst which may affect significantly to the catalyst activity. The catalysis reaction may be performed by both of 15% $AlCl_3$/AM catalyst and the leached $AlCl_3$ as homogeneous catalyst.

The catalyst activity is influenced by the acidity of the catalysts. The conversion of isatin and the selectivity towards trisindoline are inversely proportional to the number of acid site as shown in Fig. 7. 15% $AlCl_3$/AM catalyst exhibits the most obvious trend due its low selectivity with its high acidity.

Even though they had a same acid site number, but the catalysts with 1, 5 and 10% of $AlCl_3$ loading catalyzed the reaction with different conversion. We tried to relate the number of Brønsted acid with the catalyst activity since we believed that the catalysis of isatin condensation reaction is strongly depended on

Table 6. Effect of the amount of the Brønsted acid and the surface area of the catalyst conversion of isatin at 1% $AlCl_3$/AM, 5% $AlCl_3$/AM, and 10% $AlCl_3$/AM.

Catalyst	Brønsted (mmol/g)	Surface Area (m^2/g)	Brønsted/Surface Area (mmol/m^2)	Conversion of Isatin (%)
1% $AlCl_3$/AM	0.028	307.44	9.1 x 10^{-5}	93.83
5% $AlCl_3$/AM	0.027	278.05	9.7 x 10^{-5}	96.15
10% $AlCl_3$/AM	0.014	235.55	5.9 x 10^{-5}	82.60

Brønsted acid type. Based on Table 6, 5% $AlCl_3$/AM catalyst possesses the highest Brønsted acid site per area resulting in the highest conversion also. Hence, the catalyst activity in converting isatin was influenced not only by the number of Brønsted acid, but also the surface area of the catalysts. A research reported by Firoozi et al. [26] showed that the activity of ZSM-5 was also depended on its large surface.

It is interesting to note that catalysts with a high number of Lewis acid possess a high selectivity towards trisindoline formation as shown in Fig. 8. Weingarten et al. [27] obtained a similar result in xylose dehydration reaction where the presence of Lewis acid in the catalyst enhanced the rate of humin formation instead furfural. The catalyst accelerated the reaction with a high conversion and a low selectivity towards furfural since the Lewis acid adsorbed the produced furfural and converted it directly into humin, a more complex compound as a by-product. In this study, it could be assumed that the Brønsted acid adsorbed the produced trisindoline and turned it into another product reducing the selectivity.

CONCLUSION

$AlCl_3$/mesoporous aluminosilicates catalysts with a variety of $AlCl_3$ loading amount have been synthesized. The synthesized catalysts were in amorphous phase with their pore diameter of 3-4 nm. Impregnation of $AlCl_3$ on the surface of mesoporous aluminosilicates increased the number of Lewis acid and total acid. The impregnation of $AlCl_3$ on mesoporous aluminosilicate could be only done at maximum 10 wt% loading due to the leaching process happened in 15% $AlCl_3$/AM catalyst. 15% $AlCl_3$/AM catalyst possessed the highest isatin conversion while the pure AM catalyzed the reaction with the highest selectivity towards trisindoline. The conversion of isatin was influenced by the total acid number of the Brønsted acid and the surface area while the selectivity depended on the total amount of the acid and the Lewis acid.

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