

VANILLIN CONVERSION BY ALDOL CONDENSATION USING HYDROTALCITE Mg-Al AND MODIFIED -Y ZEOLITE AS HETEROGENEOUS CATALYSTS[#]

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Abstract. Mg-Al hydrotalcite, MgO-Al₂O₃ mixed oxides, and modified-Y zeolite (sulfated Y zeolite and copper ion-exchanged Y zeolite) were prepared and characterized by XRD, EDX, and XRF techniques. These materials were used as heterogeneous catalysts in aldol condensation of vanillin and acetone. The obtained results showed that the heterogeneous acid catalysts as modified-Y zeolites were more effective than the heterogeneous base catalysts as hydrotalcite Mg-Al and MgO-Al₂O₃ mixed oxides in the aldol condensation reaction of vanillin. The highest conversion of vanillin was 95.5 % when the reaction was carried out at 120 °C in 5 hours, using sulfated Y zeolite. The catalytic activity of copper ion-exchanged Y zeolite is more stable than sulfated Y zeolite with the same reaction conditions.

Keywords: vanillin, aldol condensation, feruloyl methane, heterogeneous catalyst, modified-Y zeolite.

Classification numbers: 2.3.1.

1. INTRODUCTION

Vanillin (4-hydroxy -3-methoxy benzaldehyde) is a phenolic aldehyde. It could be obtained by synthesis, semi-synthesis, and isolation from natural materials. Vanillin is one of the most widely used flavor compounds in food, beverages, pharmaceuticals, and perfumes. In addition, vanillin is also used as a natural aldehyde to synthesize α , β -unsaturated ketones [1, 2], which have bioactivities. Feruloyl methane (vanillinacetone) is a product of vanillin conversion. It has bioactivities similar to curcumin, such as anti-inflammatory, antioxidant, immune-boosting, and antibacterial. Therefore, the study of vanillin conversion to valuable products is interesting, and improving vanillin converted performance is one of the most important factors.

[#]This paper is dedicated to the 40th anniversary of Institute for Tropical Technology if accepted for publication.

Aldol condensation is an important synthetic method widely used in organic synthesis. Many valuable products are produced by aldol condensation of carbonyl compounds, such as α,β -unsaturated carbonyl, or chiral β -hydroxy carbonyl compounds. These compounds are the building blocks for antibiotics, pheromones, and many biologically active compounds [1, 3]. In particular, the products obtained by aldol condensation with natural materials are preferred when they are used to produce flavor, cosmetics, pharmaceuticals, etc. [4-6]. This trend is increasingly being researched and invested to produce products that have a natural origin, good for human health.

The high conversion and product performance are important for carrying out chemical processes and one of the key conditions for high product performance in catalysis. Development of catalytic methods that avoid the production of stoichiometric by-products while maintain high levels of control available from stoichiometric processes. Indeed, numerous catalysts for the aldol condensation reaction have been reported in recent years, including enzymes, organometallic, organocatalysis, and the other catalysts.

Many papers about aldol condensation on acidic-basic homogeneous catalysts have been published. The traditional aldol reactions are generally performed using alkalis like NaOH and KOH in an organic solvent [1, 3, 5, 6]. The basic reagents are good catalysts for the aldol condensation as well as for the side reactions. The biggest problem of homogeneous catalytic processes is the difficulty of regenerating the catalyst and controlling the reaction. Therefore, many aldol condensation reactions using heterogeneous catalysis have been carried out [1, 4, 7 - 12]. For instance, Swagata Mandal and co-workers [1] have utilized solid base catalysts derived from hydrotalcite to achieve high yields and selectivities in the preparation of chalcones and flavanones of pharmacological interest, such as vestry. Similarly, Krittanun Deekomwong *et al.* [11] have investigated the aldol condensation of benzaldehyde and heptanal in the liquid phase on hydrotalcite transformed into basic solid with good yield. Walczyk *et al.* [7] have modified sepiolites by substituting a part of the Mg^{2+} located at the borders of its channels with alkaline ions to afford a strong base catalyst for the aldol condensation. Also Suttipat, Zhanling and some other authors have carried out the condensation of benzaldehyde with various active methylene compounds in the presence of zeolites as a solid acid catalyst [8 - 12].

In this work, aldol condensation reaction of vanillin which is a product of isoeugenol oxidation and acetone was carried out to produce feruloyl methane. Hydrotalcite Mg-Al, MgO-Al₂O₃ mixed oxides, and modified-Y zeolite (sulfated Y zeolite and copper ion-exchanged Y zeolite) materials were prepared, tested of catalytic activity in this reaction, and determined of conditions for high vanillin conversion. This is the new point of the article.

2. EXPERIMENTAL

2.1. Chemicals

Mg(NO₃)₂ · 2H₂O (Merck); Al(NO₃)₃ · 9H₂O (Merck), NaOH (PA, China), Na₂CO₃ (PA, China), Y zeolite (Netherlands), Cu(CH₃COO)₂ (Merck), Acetone (Aldric), and Vanillin (Product of oxidation of isoeugenol) were used.

2.2. Preparation of materials

Mg-Al hydrotalcite was prepared by the co-precipitate method according to reference [13], and notated as B1. MgO-Al₂O₃ mixed oxides were prepared by heating B1 at 500 °C for 5 hours. This material was notated as B2.

Modified-Y zeolite was prepared by copper ion-exchanged Y zeolite and sulfated Y zeolite. Copper ion-exchanged Y zeolite was prepared by the ion-exchange method. 2 g of Y zeolite (Si/Al~15) was added in a 250 ml flask which was filled with 100 ml of Cu(CH₃COO)₂ 0.1M solution. The mixture was stirred at 80 °C for 7 hours. Afterward, the solid material was filtered, washed with distilled water, dried at 100 °C for 12 hours. Then, the solid sample was heated at 500 °C for 4 hours. This material was notated as A1.

The sulfated Y zeolite was prepared by the incipient impregnation method. 50 ml of sulfuric acid solution (1M) was added in a glass beaker early filled with 2 g of Y zeolite (HY). The mixture was left for 1 hour at room temperature. Afterward, the samples were kept inside the fume cupboard to reduce the moisture content before transferring to the oven for 24 hours drying. The dried sample was treated in a furnace for 4 hours at 450 °C. The sample was notated as A2.

2.3. Methods

The material samples were characterized by analyses of: X-ray Diffraction (XRD) using XRD 202302, RigakuMiniflex 600/Japan, Scanning Electron Spectroscopy (SEM) - SEM-EDX 18701906, Hitachi TM 4000 Plus/Japan, and X-ray Fluorescence (XRF) - XRF EQ1510001830183, Jeol JSX-1000S/Japan, and N₂ adsorption/desorption isotherms NH₃ Temperature-Programmed Desorption (NH₃-TPD) technique. For the latest, N₂ adsorption /desorption isotherms were analyzed using MicroActive for TriStar II Plus Vision 2.03 and NH₃-TPD: MicroActive for AutoChem II 2920 Version 6.01. The catalytic activity of these materials was tested by the aldol condensation reaction of vanillin and acetone. Reactions were carried out into a Teflon-lined stainless-steel autoclave (25 mL) at 90 °C - 120 °C in 18 - 24 hours. GC-MS method was used to determine products of aldol condensation reaction (GC HP6890 – MS HP5973).

Vanillin conversion (%) and selectivity of feruloyl methane was calculated by the following equations:

$$\text{Conversion of vanillin (\%)} = \frac{(\text{Initial amount of vanillin} - \text{Residual amount of vanillin})}{\text{Initial amount of vanillin}} \times 100 \%$$

$$\begin{aligned} \text{Selectivity of feruloyl methane (\%)} &= \frac{\text{Amount of feruloyl methane}}{\text{Total amount of products}} \times 100\% \\ &= \frac{\text{Amount of feruloyl methane}}{\text{Conversion of vanillin}} \times 100\% \end{aligned}$$

3. RESULTS AND DISCUSSION

3.1. Characterization of catalytic materials

Figure 1 is the X-ray pattern of Mg-Al hydrotalcite (B1) and B2 sample in the 2θ range from 5 to 80°. The characteristic peaks of the hydrotalcite structure are shown on the XRD

pattern of B1 (at 2-theta: 11.7°; 23.5° and 34.9°, 48°; 60.8° and 62.0°) (Fig. 1a).

This proves that the B1 was hydrotalcite phase with high crystallinity. When B1 was heated at 500 °C for 5 hours, the structure of hydrotalcite was broken and MgO-Al₂O₃ mixed oxides (B2) were formed. XRD pattern of B2 (Fig. 1b) has two peaks at 2θ = 43° and 63° that were characteristic peaks of MgO crystals, while Al₂O₃ oxide was of amorphous type so there were no relevant peaks on the XRD pattern [4, 13 - 15]. Thus, the initial hydrotalcite structure of B1 has completely transformed into a mixture of MgO-Al₂O₃ oxides (B2). Because Mg and Al ions were arranged in order of the hydrotalcite structure, B1 after was heated at 500 °C to form an oxide mixture, the dispersion of MgO and Al₂O₃ oxides will be better.

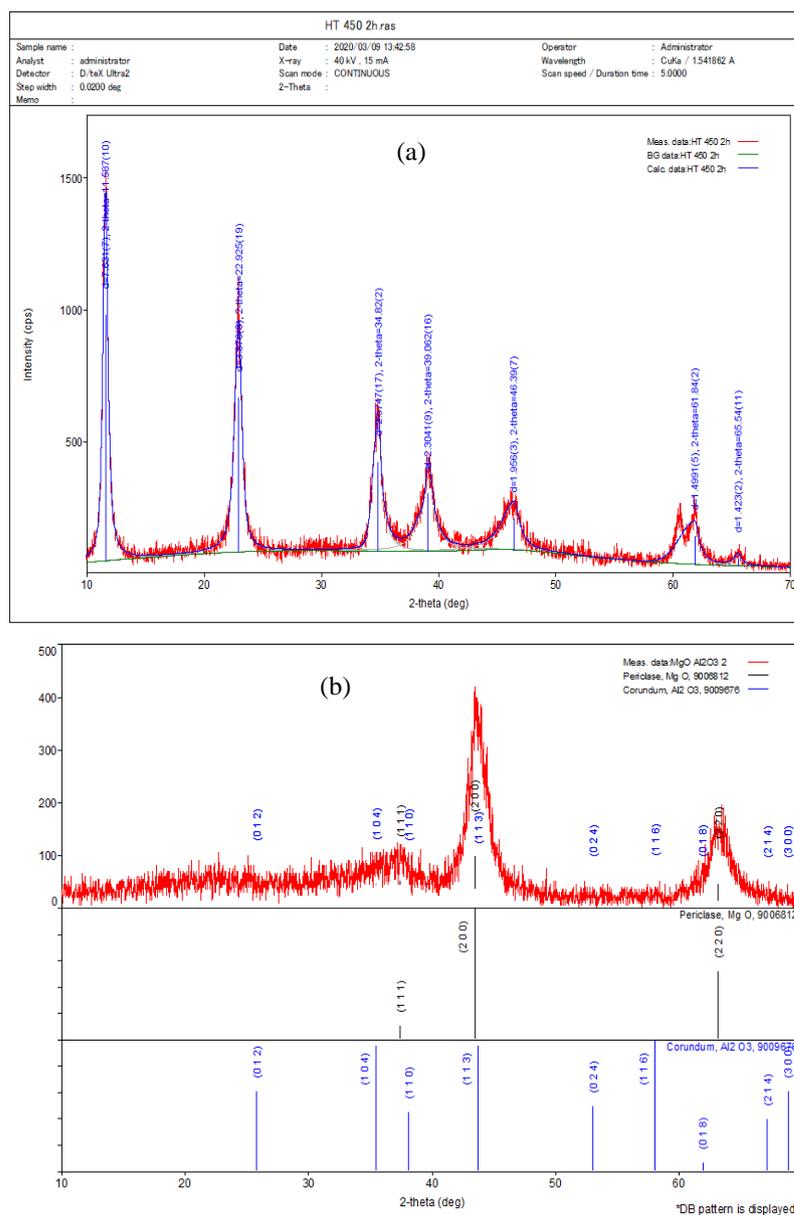


Figure 1. XRD diagram of B1 (a) and B2 (b) samples.

X-ray fluorescence spectroscopy (XRF) of B1 and B2 showed that the percentage in weight ratio Mg and Al (Mg/Al) was 54.9/43.1 with B1 and 55.3/43.2 with B2. The ratio of components in the sample of materials is similar when hydrotalcite type is transformed into a mixture of oxides.

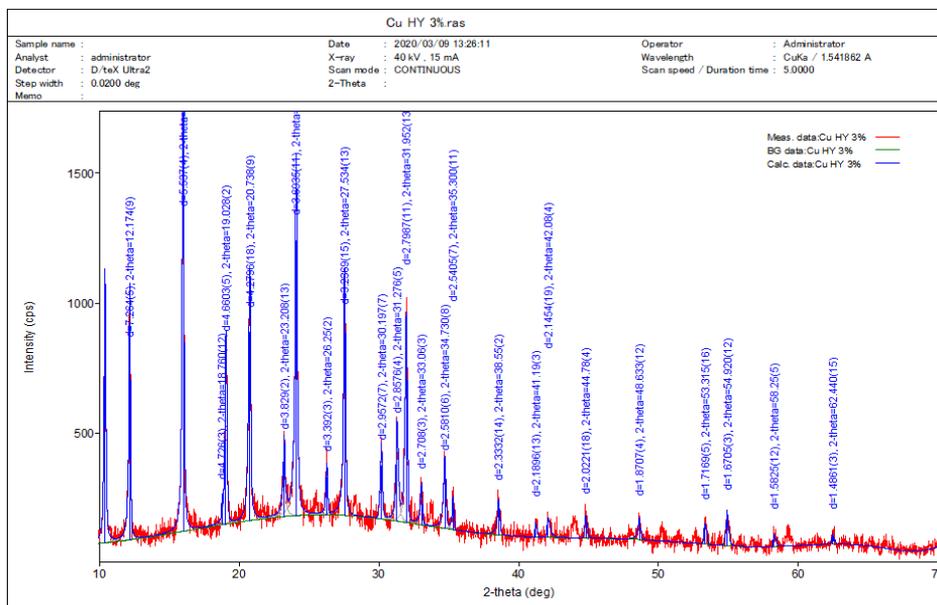


Figure 2. XRD diagram of copper ion-exchanged Y zeolite sample (A1).

Figure 2 presents the XRD pattern of the copper ion-exchanged Y zeolite (A1) at 2θ from 10° to 62° , which showed characteristic peaks of Y zeolite (at $2\theta = 18.5, 20.2, 23.5$ and 26.8) [10, 16]. In addition, X-ray diffractogram also exhibits diffraction signals of copper oxide at $2\theta = 36^\circ; 39^\circ; 49^\circ; 63^\circ$ [16 - 19]. However, these characteristic peaks are weak because the content of copper oxide is probably not high, so the crystallization of copper oxide is low. The original structure of the Y zeolite is not affected by the copper ion-exchanged process. It is possible that copper exists in both types to be copper ions in the zeolite Y network and partly in the type of CuO dispersed on the surface of zeolite Y [16, 19].

The XRD pattern of the reused typical A1 catalyst was also studied. The result showed structure of the Y zeolite is not changed (Fig. 3).

The amount of copper in the copper ion-exchanged Y zeolite (A1) materials determined by the Energy-dispersive X-ray (EDX) technique (Fig. 4). As seen, EDX spectrum exhibits characteristic peaks of Si, Al, O (in Y zeolite), and Cu (ion-exchanged) elements. The obtained result showed that the content of copper is 0.98 % in weight. In this case, the amount of exchanged copper is relatively low, the cause can be the difference in the atomic radius of the Cu (0.128 nm) and H (0.053 nm), so the exchange of H^+ ions with Cu^{2+} ions in the structural network of Y zeolite is relatively difficult. It is also possible that Y zeolite with a high Si/Al ratio (~ 15) was used, the number of H^+ sites that neutralizes the charge with the Al sites is low, so the amount of exchanged copper ions are not high [19].

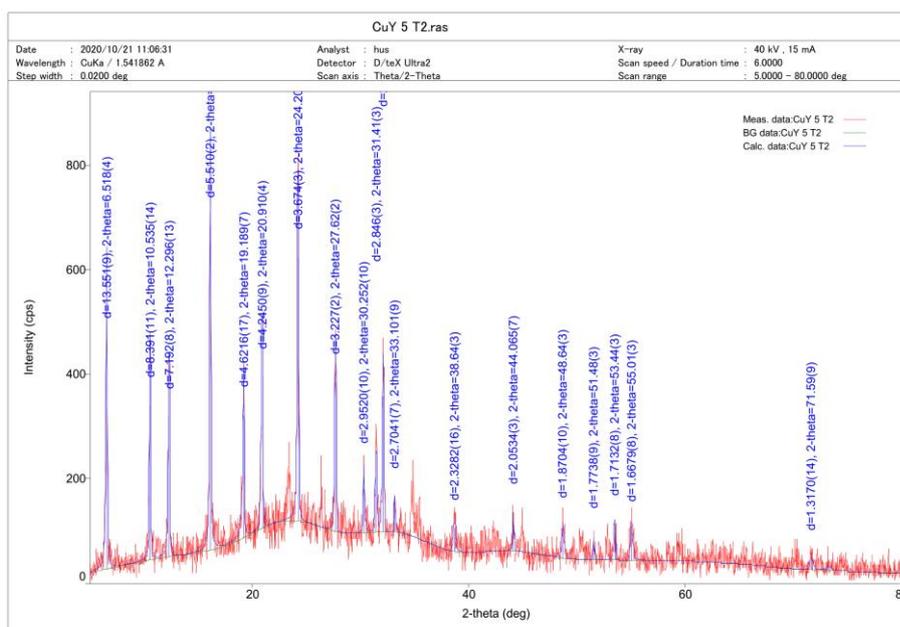
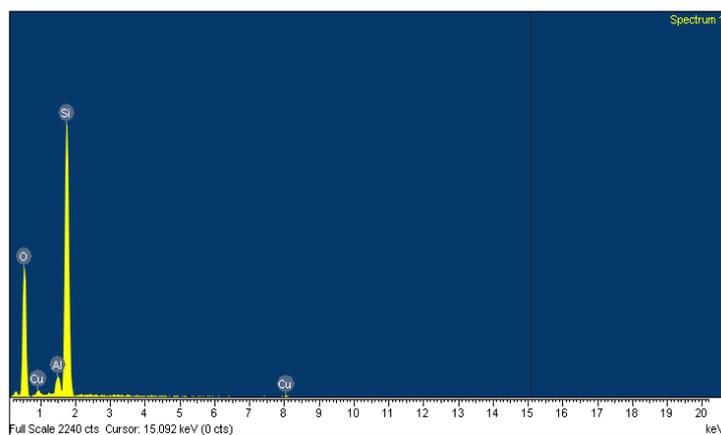


Figure 3. XRD diagram of copper ion-exchanged Y zeolite sample (reused catalyst).



Standard :
 O SiO₂ 1-Jun-1999 12:00 AM
 Al Al₂O₃ 1-Jun-1999 12:00 AM
 Si SiO₂ 1-Jun-1999 12:00 AM
 Cu Cu 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	60.56	73.17
Al K	2.26	1.62
Si K	36.20	24.91
Cu K	0.98	0.30
Totals	100.00	

Figure 4. EDX diagram and elemental content of copper ion-exchanged Y zeolite sample (A1).

The weight (%) of components in reused A1 catalyst has almost no change in comparison with that of fresh A1 catalyst. The weight of Cu in reused A1 catalyst is 0.91 %. So, a very small amount of Cu is decreased due to the leaching of CuO on surface of the catalyst after the reaction [16, 19].

The main purpose of preparation of sulfated Y zeolite (A2) is to graft SO₃H groups on the surface of Y zeolite to increase the acidity of Y, especially at temperatures lower than 150 °C [8, 10, 12, 20]. The SO₃ content of sulfated Y zeolite (A2) determined by XRF is 6.56 % (Table 1). This suggests that the SO₃H groups were successfully grafted on HY.

The reused catalyst was also investigated. The XRF results showed the weight (%) of SO₃ is greatly reduced in comparison with that of the fresh catalyst (Table 1). It might correspond to an amount of SO₃H groups leaching after the reaction [20].

Surface areas and pore size of catalytic samples were determined by the BET (Brunauer-Emmett-Teller) method from the nitrogen adsorption isotherm. The pore volume values were calculated from the nitrogen desorption isotherms using the BJH (Barrete-Joynere-Halenda) model. The results are presented in Table 2.

Table 1. The components of sulfated Y zeolite (A2-fresh and A2*-reused) determined by XRF.

Components	Weight %	
	(Fresh)	(Reused)
SiO ₂	90.97	93.15
Al ₂ O ₃	02.35	03.72
SO ₃	06.56	02.87
Others	00.22	00.26

Table 2. The nitrogen adsorption isotherm results of materials.

Sample	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Y zeolite	840.48	0.29	02.4
CuY	789.23	0.23	02.3
Cu-Hydrotalcite	049.33	0.42	32.7

The results showed that the surface areas, pore size and pore volume values decreased by metal oxide CuO loading. Y-zeolite and modified Y-zeolite (CuY) catalysts exhibited dominantly mesopore while that with Cu-hydrotalcite did mainly macropore structure.

Acidity of modified-Y zeolite samples (copper ion-exchanged Y zeolite and sulfated Y zeolite) were characterized by NH₃-TPD. Table 3 illustrates the results of ammonia temperature-programmed desorption of the samples.

Table 3. Acid properties of samples studied by NH₃-TPD.

Sample	Temperature at maximum (°C)	Acidity Amount (μmol/g)	Total Acidity (μmol/g)
Copper ion-exchanged Y zeolite	270,6	12,96	42,59
	355,8	8,88	
	554,8	20,75	
Sulfated Y zeolite	190,7	4,62	13,96
	385,0	14,68	
	564,1	7,66	

For NH₃-TPD (Table 3), the low temperature (≤ 300 °C) ammonia desorption corresponds to the weak acid sites, high temperature (≥ 400 °C) ammonia desorption corresponds to strong acid sites, and the intermediate temperature (300 °C - 400 °C) corresponds to medium acid sites. Both of the modified zeolite catalysts have weak, medium and strong acid sites. However, sulfated Y zeolite has predominant amount of medium acid sites, while the strong and weak acid sites is dominant with copper ion-exchanged Y zeolite. It can be seen that the amount of desorbed ammonia is higher in copper ion-exchanged Y zeolite sample than in sulfated Y zeolite sample.

3.2. Aldol condensation of vanillin and acetone on heterogeneous catalysts

The aldol condensation reaction of vanillin and acetone was carried out using B1, B2, A1, A2 materials as heterogeneous catalysts. The conditions of reaction as temperature or time were studied.

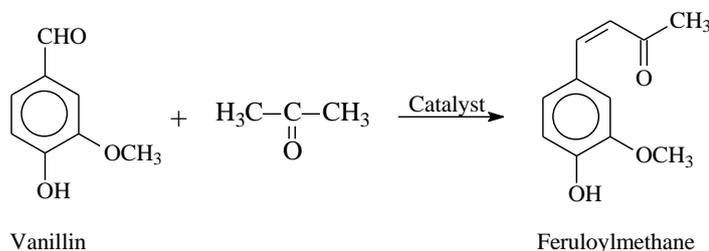


Figure 5. Aldol condensation reaction of vanillin and acetone.

**The effect of temperature*

Both acids and bases can be used as catalysts for aldol condensation reactions. Some reactions can be carried out using a basic catalyst such as condensation of benzaldehyde and acetone to form benzalacetone using the alkaline solution (10 %) as a homogeneous catalyst at room temperature, or aldol condensation reaction of citral and acetone using a mixture of MgO-Al₂O₃ as a basic heterogeneous catalyst at 110 °C [4 - 6, 13]. In this study, the aldol condensation reaction was initially investigated at different temperatures from 90 °C to 120 °C over B1 or B2 catalysts quantity of 5 wt% for 20 hours at 5:1 acetone/vanillin ratio. The result obtained (Table 4) revealed that the vanillin did not convert at 90 °C (Fig. 6a). Conversion of vanillin was 5.2 % and 11.1 % over B1 and B2 catalysts respectively at 110 °C (Fig. 6b). There was increasing in yield to 32.5 % upon increasing the temperature to 120 °C over the B2 catalyst. The yield improved as the reaction temperature increased because of the reaction rate as well as vanillin solubility in acetone increase with temperature increasing. Vanillin conversion over the B1 catalyst at 120 °C was 6.8 % lower than over B2 catalyst under the same reaction conditions.

Table 4. Results of aldol condensation of vanillin and acetone on based heterogeneous catalysts.

Catalyst	Temp. (°C)	Time (hour)	Conversion of vanillin (%)	The selectivity of feruloyl methane (%)
Hydrotalcite Mg-Al (B1)	90	20	-	-
	110	20	05.2	100
	120	20	06.8	100
MgO-Al ₂ O ₃ (B2)	90	20	-	-
	110	20	11.1	100
	120	20	32.5	100

(-)/Not defined or below the analytical limit

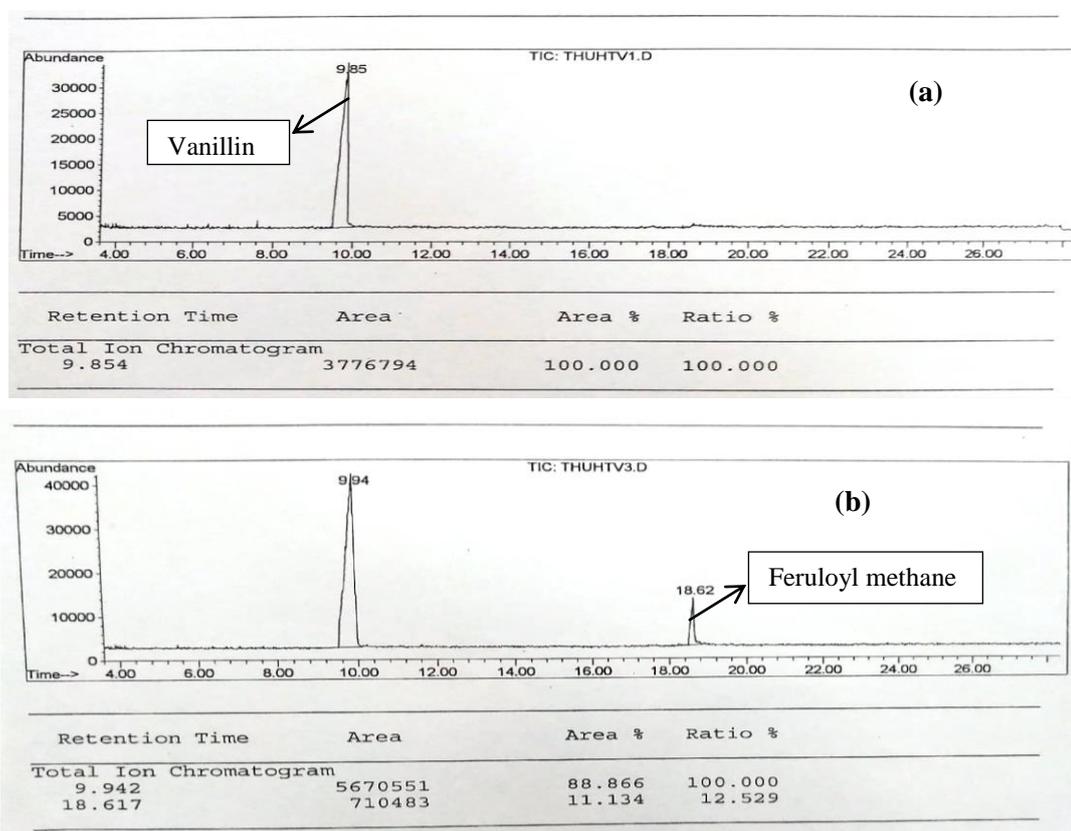


Figure 6. The GC chromatography diagrams for the mixture after reaction, at temperature of: 90 °C (a) and 120 °C (b), for 20 hours; B2 catalyst.

**Effect of reaction time*

The aldol condensation reaction was carried out for different reaction times from 18 to 24 hours at 110 °C using MgO-Al₂O₃ mixed oxides catalyst. The obtained results showed that vanillin conversion increased slightly with the increase of reaction time (Table 5). The conversion of vanillin was 16.2 % after 24 hours.

When the results of aldol condensation of vanillin were compared to other aldol condensation reactions under the same reaction conditions and on basic catalysts, such as the aldol condensation between citral and acetone [4 - 6, 13], the aldol condensation reaction of vanillin and acetone over a heterogeneous base catalyst (B1, B2) have a much lower yield. The reason is that the decomposition of feruloyl methane occurs strongly on the base catalyst to vanillin and acetone [2, 21]. The more basic the catalyst is the stronger the decomposition of feruloyl methane occurs. Therefore, the decomposition of feruloyl methane on Mg-Al hydrotalcite catalyst was stronger than on MgO-Al₂O₃ mixed oxides catalyst. On the other hand, Al₂O₃ oxide has Lewis acid sites, which also promote aldol condensation, so vanillin conversion on MgO-Al₂O₃ mixed oxides catalyst was higher than on hydrotalcite catalysts. Therefore, the aldol condensation reaction was chosen for further investigation on heterogeneous acid catalysts.

Table 5. Aldol condensation of vanillin and acetone for different reaction time over B2 catalyst.

Catalyst	Temp. (°C)	Time (hour)	Conversion of vanillin (%)	The selectivity of feruloyl methane (%)
MgO-Al ₂ O ₃	110	18	10.0	100
MgO-Al ₂ O ₃	110	20	11.1	100
MgO-Al ₂ O ₃	110	24	16.2	100

**The aldol condensation reaction on heterogeneous acid catalyst*

The aldol condensation reaction was investigated on the different heterogeneous acid catalysts as Y zeolite and modified-Y zeolite (copper ion-exchanged Y zeolite and sulfated Y zeolite). The reaction was carried out for 24 hours at 120 °C.

Table 6. The aldol condensation reaction on the heterogeneous acid catalyst.

Catalyst	Temp. (°C)	Time (hour)	Conversion of vanillin (%)	Selectivity of feruloyl methane (%)
Y zeolite (HY)	120	24	-	-
MgO-Al ₂ O ₃ (B1)	120	24	37.7	100.0
Copper ion-exchanged Y zeolite (A1)	120	24	51.6	93.3
Sulfated Y zeolite (A2)	120	24	95.5	86.3

(-)Not defined or below analytical limit

Results showed that there was a difference in the vanillin conversion when aldol condensation of vanillin and acetone was done on different heterogeneous acid catalysts. Although HY zeolite is a heterogeneous acid catalyst with strong acidity, however, the Lewis and Bronsted acid sites of HY zeolite were only activated at high temperatures (above 150 °C), so when the reaction was carried out at 120 °C on HY zeolite, vanillin conversion did not occur. There was a strong increase in yield when the modified-Y zeolite (copper ion-exchanged Y zeolite and sulfated Y zeolite) were used as acid catalysts for aldol condensation of vanillin because the decomposition of feruloyl methane did not occur on the acid catalyst. Conversion of vanillin was 51.6 % and 95.5 % over A1 and A2, respectively (Table 6), which are higher than those over alkaline solution in ethanol solvent [4 - 6, 13, 21]. The modification of Y zeolite by the copper ion exchange or the sulfation methods increased acidic sites (Lewis or Bronsted acid sites) of Y zeolite, especially, these acidic sites of the modified Y zeolite could be activated at much lower temperature than the unmodified Y zeolite [10, 20].

Active durability is also a very important factor in a catalyst. Active durability of A1 and A2 catalyst has been evaluated in aldol condensation reaction of vanillin. A1 and A2 catalysts were used for aldol condensation of vanillin and acetone (first time), then, these catalysts were filtered, washed, and dried for 12 hours at 90 °C and reused for subsequent reactions.

When the copper ion-exchanged Y zeolite was reused (second time) for aldol condensation reaction of vanillin, the obtained vanillin conversion was 47.2 %, compared to the first time it was down 6 % while the conversion was greatly reduced when sulfated Y zeolite (A2) was

reused (Table 7). The recycled catalyst results showed the conversion of vanillin was more than 3 times decreased in comparison with the sulfated Y zeolite catalyst (fresh). It might correspond to amount of SO₃H groups leaching after the reaction.

Table 7. Aldol condensation of vanillin and acetone on the reused catalyst.

Catalyst	Temp. (°C)	Time (hour)	Conversion of vanillin (%)
Copper ion-exchanged Y zeolite (fresh)	120	24	51.6
Copper ion-exchanged Y zeolite (reused)	120	24	47.2
Sulfated Y zeolite (fresh)	120	24	95.5
Sulfated Y zeolite (reused)	120	24	29.3

Thus, the copper ion-exchanged Y zeolite is more active durability than the sulfated Y-zeolite under the same conditions of the reaction. It is possible that in the reaction process, the sulfate groups grafted on the surface of zeolite Y to be unstable and were easily drafted at high temperature and for a long time of reaction.

4. CONCLUSIONS

Mg-Al hydrotalcite Mg-Al, MgO-Al₂O₃ mixed oxides, and modified-Y zeolite (sulfated Y zeolite and copper ion-exchanged Y zeolite) materials were prepared. The structure and components of materials were determined by XRD, EDX, XRF, and N₂ adsorption/desorption isotherms techniques.

The aldol condensation of vanillin and acetone was investigated on Mg-Al hydrotalcite Mg-Al, MgO-Al₂O₃ mixed oxides, and modified-Y zeolite (sulfated Y zeolite and copper ion-exchanged Y zeolite) as heterogeneous catalysts. The highest obtained conversion of vanillin was 95.5 % at 120 °C in 24 hours. These are the first reports of aldol condensation of vanillin on copper ion-exchanged Y zeolite and sulfated Y zeolite catalysts.

The copper ion-exchanged Y zeolite is of more active durability than the sulfated Y-zeolite under the same conditions of the aldol condensation reaction of vanillin and acetone.

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