One-Step Condensation and Hydrogenation of Furfural-Acetone Using Mixed and Single Catalyst Based on Ni/M-Oxide [M=Al; Mg]

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Abstract. Modification of furfural by condensation and hydrogenation reaction is a promising approach to produce higher alkane derivatives (C8-C13) as diesel fraction. This research investigated the catalytic activity of Ni/MgO as bifunctional catalyst compared with MgO-Ni/Al2O3 mixed catalyst for condensation-hydrogenation reaction. The Ni/MgO and Ni/Al2O3 with 20% Ni loading were prepared by wet impregnation methods using Ni(NO3)2·6H2O salt, calcined and reduced at 500°C. The catalyst performance was tested for one-step condensation-hydrogenation reaction using autoclave oil batch reactor. The reaction was conducted by reacting furfural and acetone in 1:1 ratio using water as solvent. Condensation reaction was performed at 100°C for 8 hours, followed by hydrogenation at 120 oC during 7 hours. Analysis by gas chromatography showed that C=C double bond of furfurylidene acetone were successfully hydrogenated. Using Ni/MgO catalyst at 120 oC, the products were identified as 1,5-bis-(2-furanyl)-1,4-penta-1-ene-3-one (2.68%) and 1,5-bis-(2-furanyl)-1,4-pentan-3-one (trace amount). On the other hand, reaction using mixed catalyst, MgO-Ni/Al2O3 showed better activity over bifunctional Ni/MgO at the same reaction temperature. The products were identified as 4-(2-furanyl)-3-butan-2-one (27.30%); 1,5-bis-(2-furanyl)-1,4-penta-1-ene-3-one (3.82%) and 1,5-bis-(2-furanyl)-1,4-pentan-3-one (1.11%). The impregnation of Ni on MgO decrease the physical properties of catalyst, confirmed by surface area analysis (SAA).

1. Introduction

Recently, alternative energy resources have been extensively explored due to the depletion of fossil fuels. Utilization of biomass as renewable material for bioenergy source has attracted considerable attention among other energy sources. The most potential candidate is furfural which derived from dehydration and hydrolysis of lignocellulosic biomass. Modification of furfural by condensation and hydrogenation reaction is a promising approach to produce higher alkane derivatives (C8-C13) as diesel fraction [1]. The aldol condensation of furfural with ketone/aldehyde would prolong the carbon chain and produces monomer/dimer of furanyl derivatives with carbon chain varied from C8-C15. The condensation adducts which contain ketonic C=O, aliphatic C=C, and furanic C=C bond can be converted into valuable liquid hydrocarbons through hydrogenation and followed by further deoxygenation reaction [2,3]. Combining the first-two reaction in one-step process is a big challenge.

The aldol condensation reaction is generally carried out in a homogeneous system using a strong base catalyst [4]. Homogeneous base catalysts such as NaOH and KOH have high reactivity and low cost production. However, there are several drawbacks such as the difficulty on the product separation, non-reusable and catalyzing side reactions such as oxidation and Cannizaro reactions [5]. Therefore,
the usage of heterogeneous catalyst e.g., MgO, CaO, Al₂O₃, and ZrO₂ give more advantages since it is reusable and easy to separate. MgO was reported as a good catalyst for aldol condensation reaction due to the high basic property [6].

On the other hand, the hydrogenation reaction use metal catalysts such as, copper (Cu), nickel (Ni), platinum (Pt), chromium (Cr) and palladium (Pd). Among different metal loading, the noble metal such as Pt and Pd have been revealed as suitable metals for hydrogenation reaction [7–9]. However, these noble metal are expensive and high cost for industrial scale. As a consequence, the development of non-precious metal catalyst seems more rational as economical alternatives. It was reported by Gandia (1993) [10], that Ni metal has high activity for the hydrogenation of aromatics, alkenes and carbonyl compounds. The usage of support also important to increase the activity of catalyst.

Presently, bifunctional catalyst has been widely developed. The bifunctional catalyst is a double function catalyst which make the reaction is possible to run more efficiently in one-step reaction. This catalyst has two active sides which can be used for two different reactions [3]. Combining Ni as a metal catalyst and MgO as the support material is expected effectively catalyze condensation-hydrogenation reaction. Herein, we investigated the catalytic activity of Ni/MgO as bifunctional catalyst compared with MgO-Ni/Al₂O₃ mixed catalyst for condensation and hydrogenation reaction in one-pot reaction. The usage of MgO-Ni/Al₂O₃ mixed catalyst is expected to be specific for each reaction. MgO catalysts in condensation reactions is capable for deprotonating acetone to form enolate ions, whereas Ni/Al₂O₃ catalysts are expected to be specific for hydrogenation reactions capable of weakening bonds between hydrogen atoms to reduce the C=C double bond alkene.

2. Experimental

2.1. Materials
Furfural (FUR) was obtained from Sigma-Aldrich Singapore with >98% purity and used without further purification. Analytical grade of Ni(NO₃)₂.6H₂O, Al₂O₃ (120-190 m²/g), methanol, and dichloromethane were bought from Merck Germany. Acetone was purchased from Smart Lab Tbk. Technical grade of MgO was obtained from the local vendor and calcined at 650°C for 2 hours under N₂ flowing before used. N₂ gas in >99.99% purity for calcination and condensation reaction, Ultra-High-Purity (UHP) H₂ gas for hydrogenation reaction from local vendor was used as received.

2.2. Methods

2.2.1. Preparation of Ni/Al₂O₃ and Ni/MgO
Ni/Al₂O₃ catalyst was prepared by wet impregnation method with 20 wt.% of Ni loading. Amount of Ni(NO₃)₂.6H₂O (9.9 g) was dissolved in 100 mL methanol added with 8 g of Al₂O₃ and stirred for 24 h at room temperature. After that, the excess of solvent was removed by rotary evaporator and the solid dried in the oven for a night. Ni/Al₂O₃ catalyst was obtained after calcination under N₂ gas and reduction using H₂ at 500°C for 4 h. The Ni/MgO catalyst was prepared with similar procedure by dissolved 20 wt.% of Ni equal to 12.38 g of Ni(NO₃)₂.6H₂O in 50 mL methanol added with 8.3 g of MgO and stirred for 24 h at room temperature. Calcination and reduction of Ni/MgO were conducted in similar condition.

2.2.2. Characterization
The catalysts obtained from previous methods were analyzed by X-ray diffraction (XRD) Pan Analytical Expert MPD. The measurements using Cu-Kα radiation at λ=1.5406 Å with the voltage and current held at 40 kV and 30 mA (2θ = 20-80°) at a scan rate of 1°/min. Scanning Electron Microscopy (SEM) was performed by Hitachi TM3000 connected with EDX Swift ED3000 to determine the surface morphology of the samples and qualitative calculation of metal loading in the catalyst. The surface area and pore volume of the catalyst are determined from BET adsorption isotherms using nitrogen at 77 K were measured by Quantrachrome NOVA1200 analyzer after degassed at 300°C. Conversion and selectivity of the products were analyzed using Gas
Chromatography Mass Spectrometer (GCMS) injected on GCMS QP2010S Shimadzu with FID detector and AGILENT HP 5MS column (30 m with ID = 0.25 mm)

2.2.3. Catalytic activity test
The condensation of furfural and acetone was performed by autoclave oil batch reactor. Prior to reaction, 0.2 gram catalysts (MgO-Ni/Al₂O₃ (1:1) as mixed catalysts; Ni/MgO as a single catalyst) were initially activated in situ in the autoclave at 150°C under N₂ atmosphere for 1 h. The ratio of the furfural and acetone is 1:1. Furthermore, the furfural of 1.16 g (0.012 mol; 1 mL) and acetone of 0.70 g (0.012 mol; 0.882 mL) were introduced into the autoclave under N₂ gas atmosphere. The condensation reaction was carried out for 8 h (Ni/MgO catalyst) and 6 h (MgO-Ni/Al₂O₃ catalyst) at 100°C under stirring condition [7]. After cooling down, N₂ gas was removed through the side valve and H₂ gas was introduced into autoclave. The hydrogenation reaction was carried out for 7 hours at temperature range of 120, 150 and 180°C under stirring condition. Then the autoclave was cooled to the room temperature, the liquid product was removed and filtered to separate the catalyst. The organic phase was separated by extraction using dichloromethane.

3. Results and discussion

3.1. Characterization of Ni/Al₂O₃ and Ni/MgO
Fig. 1 showed the morphology of the catalysts measured by Scanning Electron Microscopic (SEM). The particle size of the support material (MgO and Al₂O₃) is larger than after impregnation of Ni. It means that impregnation of nickel broke the support and resulted an irregular shape with smaller particle size. Agglomeration with irregular shapes is easily formed when impregnation method is used for the preparation of catalysts [11].

![SEM micrograph](image_url)

Figure 1. SEM micrograph of (a) Al₂O₃; (b) Ni/Al₂O₃; (c) MgO; (d) Ni/MgO (3000x optical zoom)

The crystal structure of Ni/Al₂O₃ and Ni/MgO were analyzed by X-ray diffraction (XRD) and the patterns were compared with the support material. The XRD spectra of the catalyst after reduced at 500 °C are shown in Fig. 2. The crystalline structure of Al₂O₃ and MgO were detected. This suggests that the impregnation of Ni does not change the crystalline structure of the support to an amorphous. The appearance of new peaks at 2θ = 44.27°, 51.59° and 75.89° are assigned for Ni metal formed from...
the reduction of Ni$^{2+}$ ions at 500°C under H$_2$ gas flow. The crystallinity index of Ni is identified for (111), (200) and (202).

Fig. 2(a) showed another peak at 2θ = 37.4°, 44.9° and 66.7° were subjected for NiAl$_2$O$_4$ phase from the defect spinel of Ni and Al$_2$O$_3$ according to the preparation methods of catalyst [12]. The NiO peaks at 2θ = 43° and 63° were not detected because it is easily reduced to produced Ni. In Fig. 2(b), the 42.8° peak is detected in high intensity representing the specific peaks of MgO and NiO [13]. In addition, it can be seen that the specific peak of MgO undergoes a shift to a larger number after impregnation of Ni metal. This shift is assumed due to a reaction between MgO and Ni formed a Ni$_{x}$Mg$_{1-x}$O solid as reported by Yamazaki et al. [14].

![Figure 2. XRD profile of (a) Al$_2$O$_3$ and Ni/Al$_2$O$_3$; (b) MgO and Ni/MgO](image)

| Catalyst      | $S_{BET}$ (m$^2$/g) | $V_{meso}$ (cc/g) | $D_{meso}$ (nm) | $D_{micro}$ (nm) |
|---------------|---------------------|-------------------|-----------------|-----------------|
| MgO           | 96.106              | 0.184             | 3.818           | 0.432           |
| Ni/MgO        | 1.984               | 0.014             | 3.838           | 0.821           |
| Al$_2$O$_3$   | 132.697             | 0.284             | 4.903           | 0.432           |
| Ni/Al$_2$O$_3$| 74.185              | 0.216             | 5.649           | 0.432           |

$S_{BET}$ (total surface area) by BET method; $V_{meso}$ (mesoporous volume), $D_{meso}$ (mesoporous diameter) by BJH method; $D_{micro}$ (microporous diameter) by HK method

Figure 3. Isotherms adsorption/desorption of (a) Ni/Al$_2$O$_3$ and (b) Ni/MgO

![Figure 3](image)
Fig. 3 showed the isotherms of Ni/Al₂O₃ and Ni/MgO with each support materials. Compared with Al₂O₃ and Ni/Al₂O₃, the impregnation of 20% Ni into MgO reduced the surface area (S_{BET}) significantly, from 96.106 m²/g to 1.984 m²/g. Likewise, the pore volume of MgO was drastically decreased from 0.184 cc/g to 0.014 cc/g after the impregnation (Table 1). On the other hand, the surface area of Al₂O₃ was not significantly reduced. The decreasing of the surface area of MgO might be due to the impregnation method which decreased the crystallinity of the support material and the pores were covered by the active metal [15]. Mesoporous diameter (D_{meso}) of Ni/MgO was increased by 0.02 pm compared with MgO, and microporous diameter (D_{micro}) increased after the impregnation process. It indicated that there is a strong interaction between Ni and MgO metals. Therefore, most of the MgO pores are blocked by Ni metal and produce microporous material [16].

3.2. Catalytic activity for condensation-hydrogenation reaction

Catalytic activity test of mixed (MgO-Ni/Al₂O₃) and single catalyst (Ni/MgO) for one-step condensation-hydrogenation reaction was carried out in the presence of water using autoclave oil batch reactor is depicted in Scheme 1. The condensation products were identified as monomer (I) and dimer (II). Since the obtained product from condensation is a liquid in room temperature making it possible for hydrogenation reaction without additional treatment [17]. The mixture of condensation product was directly hydrogenated using H₂ gas. GC-MS analysis showed that C=C double bond of monomer (I) and dimer (II) were successfully hydrogenated. The formation of hydrogenation product (III) can be elucidated from reduction of C=C exocyclic of monomer (I). Whereas, bis-furanyl derivatives (IV) and (V) should be hydrogenation product of dimer (II).

Scheme 1. One-step condensation-hydrogenation reaction of furfural-acetone

Fig. 4 showed the comparison yield of one-step condensation-hydrogenation reaction over MgO-Ni/Al₂O₃ mixed catalyst and Ni/MgO single catalyst. Using Ni/MgO catalyst at 120°C, the products were identified as 1,5-bis-(2-furanyl)-1,4-penta-1-ene-3-one (IV) (2.68%) and 1,5-bis-(2-furanyl)-1,4-pentan-3-one (V) (trace amount). On the other hand, reaction using MgO-Ni/γ-Al₂O₃ mixed catalyst, showed better activity over bifunctional Ni/MgO catalyst at same reaction temperature. The products were identified as 4-(2-furanyl)-3-butan-2-one (III) (27.30%); 1,5-bis-(2-furanyl)-1,4-penta-1-ene-3-one (IV) (3.82%) and 1,5-bis-(2-furanyl)-1,4-pentan-3-one (V) (1.11%).

Based on N₂ physisorption analysis, the impregnation of Ni on MgO decrease the physical properties of catalyst. The decreasing of the surface area and pore volume of MgO caused the condensation reaction does not proceed effectively. Yingxin and co-workers (2007) reported that there is a strong interaction between Ni metals and MgO making Ni²⁺ ions are totally stucked on the surface and cover MgO lattice [18]. Therefore, the conversion of furfural as starting material was lower on Ni/MgO catalyst than MgO-Ni/Al₂O₃. Mixed catalyst offer more advantages for one pot reaction,
since it has two specific active sites for each reaction. Further, reaction using Ni/MgO 10-15% Ni loading is under consideration.

![Figure 4. Condensation-hydrogenation reaction of furfural-acetone at 120°C](image)

3.3. Effect of reaction temperature on hydrogenation

MgO-Ni/Al₂O₃ showed better activity for one-step condensation-hydrogenation of furfural-acetone at 120°C. Therefore, it was needed to investigate effect of temperature on hydrogenation reaction using MgO-Ni/Al₂O₃ mixed catalyst. The conversion and selectivity of condensation-hydrogenation products are summarized in Table 2. Increasing temperature should only affect the hydrogenation products. The reaction at 150°C (entry 2) only gave hydrogenation product IV (2.07%). Increasing reaction temperature until 180°C (entry 3) produced the highest yield of hydrogenated monomer III (33.78%). Based on these results, hydrogenation reaction using MgO-Ni/Al₂O₃ mixed catalyst were not significantly influenced by the reaction temperature. However, it was reported by Sharma (2014) that higher hydrogenation reaction temperature would initiate the cracking of C-C bond [19].

| Entry | T (°C) | Conversion (%) | FUR  | I   | II  | III | IV  | V  |
|-------|--------|----------------|------|-----|-----|-----|-----|----|
| 1     | 120    | 84.79          | 15.21| 52.55| -   | 27.3| 3.82| 1.11|
| 2     | 150    | 89.60          | 10.40| 26.16| 61.37| -   | 2.07| -  |
| 3     | 180    | 56.09          | 43.91| 22.31| 33.78| -   | -   | -  |

*a Reaction condition: catalyst: MgO-Ni/Al₂O₃; condensation reaction during 6 h and hydrogenation reaction during 7 h, 40 psi H₂, water solvent

4. Conclusion

One-step condensation-hydrogenation reaction of furfural-acetone was successfully conducted using MgO-Ni/Al₂O₃ mixed catalyst and Ni/MgO single catalyst in autoclave batch reactor. MgO-Ni/Al₂O₃ mixed catalyst showed better activity over Ni/MgO catalyst at 120°C. The impregnation of Ni on MgO decrease the physical properties of catalyst, confirmed by SAA.
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