

ORIGINAL ARTICLES

Reaction Efficiency of Crossed-Aldol Condensation between Acetone and Benzaldehyde over ZrO_2 and ZrO_2 -Montmorillonite Catalyst

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ABSTRACT

A homogeneous catalyst is commonly utilized in benzalacetone synthesis via crossed-aldol condensation reaction from benzaldehyde and acetone. The reaction generally occurs in low efficiency caused by the presence of $H\alpha$ which tends to direct double crossed-aldol condensation and produced dibenzalacetone as a side product. The aim of this research is to find an eco-friendly synthesis process by using a heterogeneous catalyst. In the present research, heterogeneous catalysts of ZrO_2 and ZrO_2 supported montmorillonite (ZrO_2 -montmorillonite) were evaluated in the improvement of reaction activity. In this case, the reaction yield (% yield) was used as the parameter for comparing the efficiency. As suggested by the general mechanism of the heterogeneous catalysis, the obtained result showed increased reaction yields in both ZrO_2 -montmorillonite and ZrO_2 catalyzed reactions, however, ZrO_2 -montmorillonite results were superior. Quantitatively increased efficiency was obtained in that ZrO_2 -montmorillonite catalyzed reaction was 29.16–436.77 % compared to the uncatalyzed reaction.

Key words: crossed aldol condensation, heterogeneous catalyst, ZrO_2 -montmorillonite

Introduction

Synthesis of dibenzalacetone and benzalacetone derivatives by using crossed-aldol condensation reaction has been reported using either homogeneous acid catalyst or homogeneous base catalyst. Acid catalysts reportedly used for crossed-aldol condensation reaction include the use of sulphuric acid and hydrochloric acid (Pudjono and Widada, 2001; Sardjiman, 2000). In another aldol condensation experiment, Lewis acid was also reported as catalyst (Yamano *et al.*, 2007; Kabalka *et al.*, 1999; Gill *et al.*, 2011). The base catalysts that are generally used on dibenzalacetone and its derivatives are sodium hydroxide and potassium hydroxide (Handayani and Arty, 2008; Guofeng *et al.*, 2004). In these reactions the yield of benzalacetone synthesis is commonly lower compared to dibenzalacetone (Handayani, 2009). The low result was caused by the formation of undesired side products. The main reason for side product formation in the synthesis is because the product of the reaction has $H\alpha$ potential to be further reacted to produce dibenzalacetone. Furthermore, the self-aldol condensation is probably occurring between acetone as a side product.

Previous researchers have reported on the aldol condensation reaction in the presence of different heterogeneous base catalysts. The heterogeneous form of the catalyst was attempted to achieve a more selective, thermally stable and feasibly renewable catalyst. Another advantage is related to the eco-friendly properties of heterogeneous catalysts due to their regeneratable and reusable properties (Chari *et al.*, 2007). Among these kinds of catalyst, hydrotalcite is perhaps the most popular due to its high surface area, simple preparation and regeneratable properties (Cavani *et al.*, 1991). Since available anionic sites are created from its layered double hydroxide basic structure, aldol condensation over hydrotalcite was reported to be effective (Ibrahim and Lwin, 2010; Bhaumik *et al.*, 2004; Yasin *et al.*, 2010; Cavani *et al.*, 1991; Perez *et al.*, 2004). Starting from these researches, the goal of heterogeneous catalysis is hypothesized to be preferable, providing more advantages and eliminating the problems surrounding the utilization of a homogeneous catalyst while producing a significant result. The development of a heterogeneous catalyst for aldol condensation application is becoming both interesting and important. In the present work, zirconia (ZrO_2), in its dispersed form, in a clay host was analyzed as a heterogeneous catalyst for benzalacetone synthesis. The selection of zirconia materials was based on its surface activity and chemical stability in various conditions. In an effort to increase the surface activity, ZrO_2 was dispersed in montmorillonite in the form of ZrO_2 pillared montmorillonite (ZrO_2 -montmorillonite). As an abundant material in Indonesia, the use of natural montmorillonite as support for catalysts is widely developed

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as reported from previous researches (Fatimah *et al.*, 2009b; Fatimah and Huda, 2012; Wibowo *et al.*, 2011). High surface area and modifiable properties are the most important characteristics of montmorillonite as an inorganic support of metal or metal oxide catalysts (Ghribi and Chlendi, 2011). Montmorillonite is characterized as a silicate-alumina sheet structure with a 2:1 ratio and contains exchangeable cations in interlayer spaces which can be exchanged by metal or metal precursors. After ion exchange process, the stable metal or metal oxide in rigid structure will be produced (Fan *et al.*, 2006; Bendani *et al.*, 2008). Referring to the basic concept of kinetics theory, the success of reaction is affected by specific reaction conditions such as: synthetic technique, temperature, time and solvent. Therefore, the optimization of these parameters are important to study.

Materials and Methods

Synthesis of benzalacetone was performed by crossed-aldol condensation between 0.02 mol of acetone and 0.01 mol of NaOH in a solvent for three hours. To study the optimum condition, reaction condition was varied. The success of reaction was evaluated by determination of percentage yield. The percentage yield was measured by chromatographic method using a thin layer chromatography-densitometry scanner based on the formula

$$\text{yield} = \frac{\text{product weight} \times \text{concentration (TLC Scanner)}}{\text{theoretic weight}} \times 100\%$$

The functional group of the products was identified by using Fourier transform infra-red (FTIR), whereas amount, type and proton position were analyzed by using H-NMR 500 MHz.

Fig. 1 shows the pattern of FTIR spectrum result obtained from reaction. Band at region of 3060–3028 cm^{-1} is associated with C-H aromatic bond, and aliphatic C-H is showed by the absorbance at 2918 cm^{-1} . C=O carbonyl bond is appeared at 1651 cm^{-1} and aromatic C-C bond is identified by several absorbance at around 1602–1450 cm^{-1} .

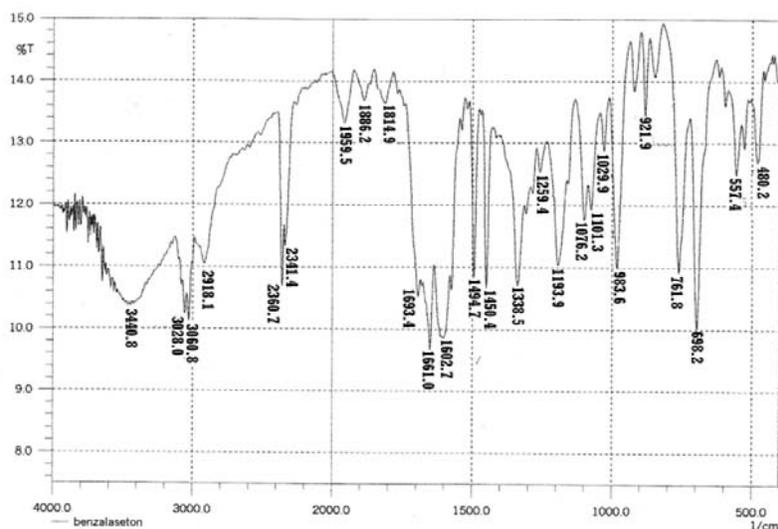


Fig. 1: FTIR Spectrum of synthesis result

There are six proton peaks in the H-NMR spectrum. The first singlet peak is three methyl protons at 2.3 ppm, α and β protons are depicted in a doublet band at 6.3 and 6.6 ppm. Proton appeared at 7.4 ppm (2H, triplet), 7.3 ppm (2H, triplet) and 6.8 ppm (1H, triplet) showed ortho, meta and para proton of aromatic functional group. From these results of FTIR and H-NMR it can be certainly noted that the compound analyzed is benzalacetone. The products were analyzed by comparing Rf value from TLC-scanner of each compound that was previously analyzed using FTIR and H-NMR.

As the first step, synthesis technique, solvent and reaction temperature were optimized. For the optimization stage of synthesis technique, two different sequences of nucleophile formation were varied. In method 1; self-aldol condensation was avoided by reacting acetone after benzaldehyde was added in the reaction system. As a counterpart, in method 2, nucleophile was initially formed by reacting base catalyst with acetone that has a $\text{H}\alpha$. Different polarity of solvent was obtained from the variation of methanol and ethanol:water 1:1, and for temperature variation, the condition were at 10 $^{\circ}\text{C}$ (ice bath), 28 $^{\circ}\text{C}$ (room temperature) and reflux was evaluated. The best condition from this optimization step was selected for further testing.

The improvement of synthesis method was studied by comparing the efficiency of homogeneous and heterogeneous catalysts by varying the addition of NaOH, NaOH+ZrO₂-montmorillonite, NaOH+ZrO₂, ZrO₂-montmorillonite and pure ZrO₂. NaOH catalysis was done by addition of 0.03 mol and for zirconia catalysis 0.1 g of ZrO₂ powder was added. Catalysts that were examined in this study are ZrO₂ and ZrO₂-montmorillonite. ZrO₂ was prepared by sol-gel reaction of Zr-isopropoxide in alkaline environment followed by calcinations at 500 °C. ZrO₂-montmorillonite used in this reaction was obtained by pillarization process into Indonesian montmorillonite by using ZrOCl₂ as precursor and calcination temperature of 400 °C as was reported by Fatimah *et al.* (2008). For advanced study, reaction time was varied at 1, 2, 3, 4 and 5 hours. Improvement of reaction efficiency is another important evaluation study conducted by several concentrations of NaOH used in the reaction system.

Results and Discussion.

Efforts to improve reaction efficiency through the selection of appropriate synthesis methods of benzalacetone synthesis were completed by comparing the sequence of formation of nucleophiles. Nucleophile formation occurs through the attack of base on H_α owned by acetone. The nucleophile formed then attacked the carbonyl carbon of benzaldehyde. The nucleophile can also attack the carbonyl carbon of acetone and produce the self-aldol condensation. This condition can be prevented by reacting base to benzaldehyde first. The results shown in Figure 2 indicate that the benzaldehyde previously added into the reaction system first (method 1) gave better results compared to the acetone first (method 2).

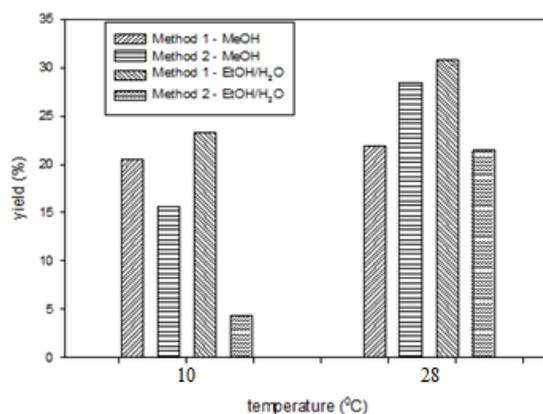


Fig. 2: Yield of reaction by varied benzalacetone synthesis method

Aldol condensation can be engaged at 100 °C, 28 °C and reflux condition (Handayani *et al.*, 2010; Handayani and Arty, 2008; Salehi *et al.*, 2002). In this research, the best condition was obtained at room temperature (28 °C). In contrast, at reflux condition, the aldol condensation did not occur as indicated by unchanged composition during the reflux. In the whole study, it is noted that the optimum result was found in ethanol-water solvent and under room temperature. This condition was used to investigate the efficiency of heterogeneous catalyst utilization depicted in Figure 3.

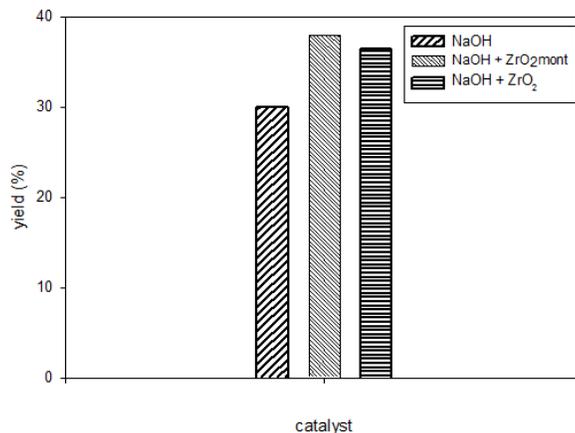


Fig. 3: Efficiency of heterogeneous catalyst utilization

Aldol condensation reaction over an only heterogeneous catalyst: ZrO_2 and ZrO_2 -montmorillonite showed no result. This is presumably because the zirconia is acidic. The use of acid catalysts in cross-aldol condensation reaction will follow the enol mechanism. Because the stability of the enol form of acetone is lower than its keto form, the aldol condensation over acid catalyst is more difficult (Mourgues *et al.*, 2001).

The results showed that the use of NaOH and acid catalyst (ZrO_2 and ZrO_2 -montmorillonite) simultaneously gives better results than the use of only acid or base catalyst alone. Zirconia as an acid can bind to the free electrons of the carbonyl oxygen in benzaldehyde resulting in the polarization of the carbonyl C-O bond because the carbonyl carbon became more positive. This condition leads nucleophile formed by O-H attack on bases easier in condensation with the polarized C carbonyl of benzaldehyde (Figure 4). The use of acid and alkaline catalysts in a cooperative system in this study appears to increase the selectivity of the reaction yielding more products. This is consistent with the results of Climent *et al.* (2002).

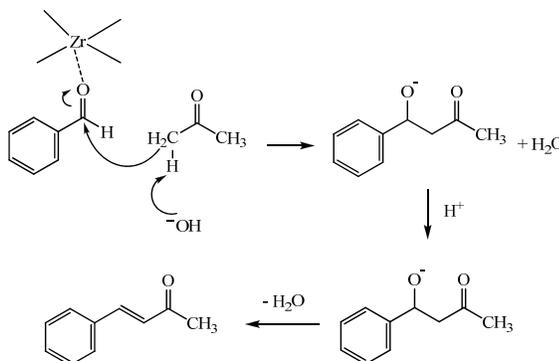


Fig. 4: Mechanism of crossed aldol-condensation reaction catalyzed by ZrO_2 -montmorillonite

From Figure 4, it is seen that the result of the synthesis using ZrO_2 -montmorillonite is superior to using ZrO_2 . The porous structure of ZrO_2 -montmorillonite is feasible for reactants being adsorbed and delocalized for further surface reaction producing the product. This is due to the surface reaction mechanism that will be followed by elevated reaction rate. Interpretation of catalyst activity can be measured by reaction yield in that as the reaction rate is higher at the time of analysis the yield will be increased (Santen, 2010; Fatimah, 2009).

Table 1: Specific surface area, surface acidity and acid distribution of ZrO_2 -montmorillonite compared to montmorillonite

| Sample | Specific surface area (m ² /g) | Solid acidity (mmole pyridine/gram) | Brönsted to Lewis acid ratio |
|--------------------------|---|-------------------------------------|------------------------------|
| ZrO_2 -montmorillonite | 45.90 | 0.59 | 1.14 |
| ZrO_2 | 19.56 | 0.21 | 0.96 |
| Montmorillonite | 96.75 | 0.65 | 1.24 |

The role of ZrO_2 -montmorillonite in the improvement of catalytic activity is confirmed by specific surface area data, FTIR spectrum of ZrO_2 -montmorillonite in the analysis of solid surface acidity (Figure 5) and the solid distribution listed in Table 1. The data of surface acidity was measured by butylamine titration and for acid distribution, Brönsted to Lewis acid ratio was evaluated by an equation utilized and previously reported (Fatimah *et al.*, 2009a; Fatimah, 2009). FTIR spectrum depicted the adsorption interaction of pyridine with surface which ammine-surface and aromatics functional group correspond to Brönsted and Lewis acid sites respectively.

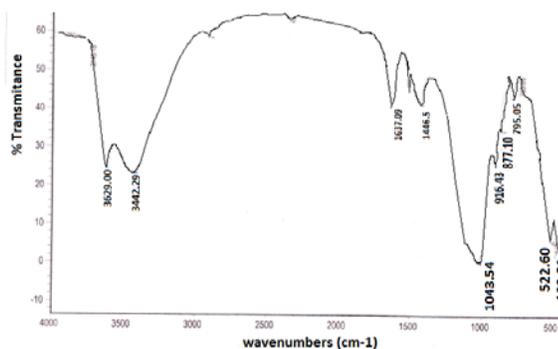


Fig. 5: FTIR spectrum of pyridine adsorbed ZrO_2 -montmorillonit

From Figure 5, spectrum at 1446.5 cm^{-1} and 1543.6 cm^{-1} are responsible for pyridine adsorbed in material and from the absorbance value resulting from the Brönsted to Lewis acid ratio of 1.14. The bands localized at $1545\text{--}1555\text{ cm}^{-1}$ is assigned to pyridine adsorbed on Brönsted acid sites and the band at $1445\text{--}1455\text{ cm}^{-1}$ is attributed to pyridine adsorbed on Lewis acid sites. Decreased Brönsted to Lewis acid ratio in ZrO_2 -montmorillonite is attributed to the presence of Zr incorporated in material. Another possible reason is increased specific surface area by ZrO_2 attachment which contributed to improve reactant diffusion during solid mechanism. This similar pattern in the role of acid and surface area to the mechanism is consistent with the report by Garro *et al.* (2005).

Furthermore, both reactions at various times of reaction were compared, and the results are depicted in Figure 6 and Figure 7. From both pictures it is noted that during the reaction dibenzalacetone is always produced as a side product between acetone and benzaldehyde. This is due to the fact that the product still contains $\text{H}\alpha$ to undergo double crossed aldol condensation forming dibenzalacetone. Thus, generally dibenzalacetone is more easily produced than benzalacetone. The best results were obtained under the condition of the combination of NaOH catalyst NaOH + ZrO_2 -montmorillonite for four hours.

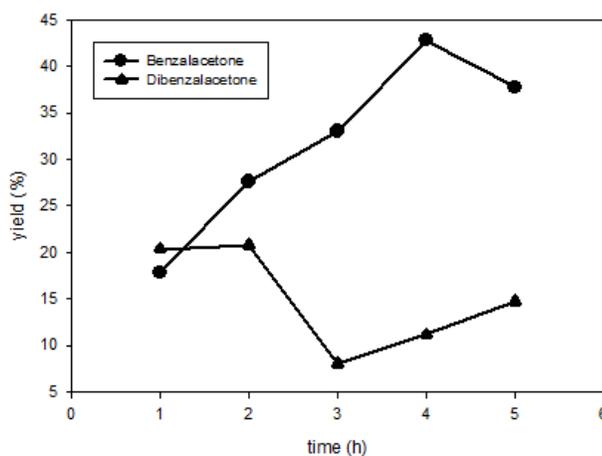


Fig. 6: Crossed aldol condensation between benzaldehyde and acetone with ZrO_2 -montmorillonite as catalyst

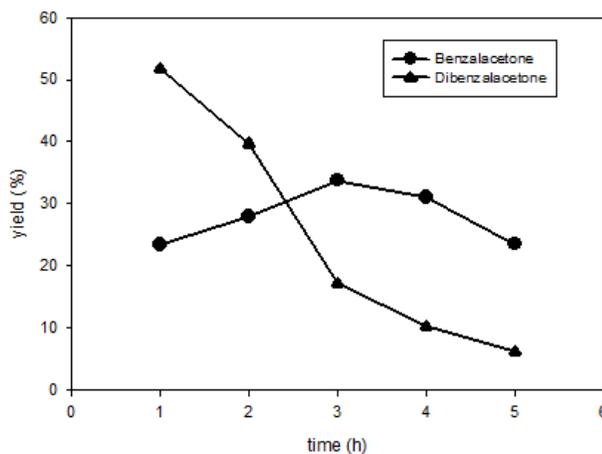


Fig. 7: Crossed aldol condensation between benzaldehyde and acetone catalyzed by ZrO_2

The use of zirconia as a heterogeneous acidic catalyst together with NaOH produces higher reaction efficiency. This suggests that condensation reactions may still be running even though the concentration of alkali is reduced. The advantage likely gained by reducing base concentration is that the reaction is both low-cost and also supports a green chemistry program. Therefore, the concentration of base needs to be optimized. The results of the reaction by varying the concentration of NaOH base is presented in Figure 8.

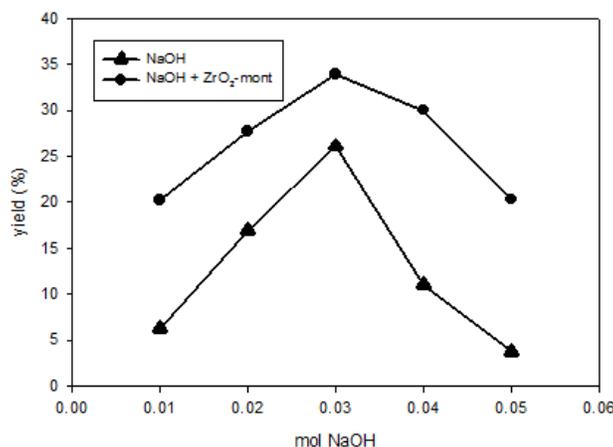


Fig. 8: % Yield of benzalacetone at varied NaOH concentration

The use of zirconia catalyst and NaOH at the same time give better results than the use of base catalyst alone even at any concentration variation (Figure 8). As seen from the highest percentage of increase listed in Table 2, the best results was obtained by reacting NaOH 0.05 mol producing 436.77% yield.

Table 2: Yield of reaction using cooperative NaOH/ZrO₂-montmorillonite catalyst

| No | NaOH (mol) | Yield(%) | | Increase (%) |
|----|------------|----------|--|--------------|
| | | NaOH | NaOH/ZrO ₂ -montmorillonite | |
| 1 | 0.01 | 6.27 | 20.20 | 222.16 |
| 2 | 0.02 | 16.94 | 27.71 | 63.73 |
| 3 | 0.03 | 26.09 | 33.87 | 29.83 |
| 4 | 0.04 | 11.06 | 29.98 | 171.06 |
| 5 | 0.05 | 3.78 | 20.29 | 436.77 |

The production gained by using NaOH 0.01 mol was not-significant compared to the NaOH 0.05mol method. Therefore, the use of lower concentration (0.01 mol) provides more efficiency. These results support the green chemistry program well because it uses only a small concentration of NaOH. The best results were gained at the NaOH concentration of 0.03 moles and this reinforces the reason suggested that the combination of the use of both NaOH catalyst and ZrO₂-montmorillonite is effective in the cross-aldol condensation reaction.

Conclusion:

Results showed that the best condition for benzalacetone synthesis is method 1, in that benzaldehyde was added initially before acetone addition and under ethanol-water over NaOH-ZrO₂-montmorillonite for four hours at room temperature. From the obtained results, it can be concluded that the use of combined catalyst of NaOH and ZrO₂-montmorillonite is a very promising method of increasing reaction efficiency of crossed aldol condensation between benzaldehyde and acetone.

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