UNIVERSITI TEKNOLOGI MARA

CATALYTIC SYNTHESIS OF 5-ARYLIDENE MELDRUM'S ACID DERIVATIVES USING MGAL HYDROTALCITE AND MIXED OXIDE

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ABSTRACT

MgAl hydrotalcites, known as layered double hydroxide (LDH), serve as valuable catalysts in organic reactions due to their distinct properties. The catalyst can enhance the catalytic performance of Knoevenagel condensation due to the presence of Bronsted basic sites. However, there are no reported studies on the synthesis of 5-arylidene Meldrum's acid derivatives in the presence of MgAl hydrotalcite in Knoevenagel condensation reactions. Furthermore, 5-arylidene Meldrum's acid derivatives have been found to possess great biological activities, including antimicrobial, antifungal, anticancer, antibacterial, antioxidant, and anti-malarial. Consequently, this study investigates the catalytic capabilities of MgAl hydrotalcite (MgAl HT) and MgAl mixed oxide (MgAl MO), with ratio Mg/Al 4:1, applied in the Knoevenagel condensation reaction obtaining 5-arylidene Meldrum's acid derivatives. This research aims to synthesize MgAl hydrotalcite through an alkali-free co-precipitation method, followed by calcination to obtain mixed oxide. The textural and physicochemical properties of the synthesized catalysts were effectively characterized using TGA, PXRD, BET, FTIR and FESEM. MgAl hydrotalcite exhibited a sharp crystalline layered structure and lower specific surface areas compared to calcined catalyst, which displayed broad diffraction peaks in PXRD, thus indicating high specific surface areas due to decomposition of the interlayer space of MgAl hydrotalcite. The second part of the research involves chemical studies synthesizing derivatives of Meldrum's acid **7-21** using Meldrum's acid **1** as the starting material with different substituted aldehydes **2-6** and amines **12-16** to afford derivatives **7-11** in 12-99 % yields and **17-21** in 58-69% respectively in the absence of catalysts. The third aim is to evaluate the catalytic performance of MgAl hydrotalcite and MgAl mixed oxide in Knoevenagel condensation, which gave different results, providing new insights into their catalytic activities. The presence of catalysts in a model reaction involving aldehydes had a significant effect on the reaction, yielding **MgAl HT** – **7-11** in 50-99% and **MgAl MO** – **7-11** in 60-100%. The performance of the catalyzed Knoevenagel reaction was much better compared to the uncatalyzed reaction in terms of high yield and shorter time. The absence of a catalyst significantly extended the reaction time, emphasizing the catalytic role of MgAl hydrotalcite and MgAl mixed oxide, known for their distinctive structural properties, in accelerating the reaction and ultimately improving the yield of the desired products. Both catalysts exhibited good performance, yielding **MgAl HT** – **17-21** in 23-81% and **MgAl MO** – **17-21** in 17-84%. The structures of all synthesized Meldrum's acid derivatives were confirmed by NMR, FTIR and GCMS spectroscopy.

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CHAPTER 1
INTRODUCTION

1.1 The Importance of MgAl Hydrotalcite

MgAl hydrotalcites, known as layered double hydroxide (LDH) have emerged as significant catalyst in organic reactions due to its unique properties and versatility in facilitating various organic transformations. They serve as solid bases that exhibit potential catalytic activity and good stability under required reaction conditions (Zulkifli *et* al. 2022). The use of MgAl hydrotalcites is essential in various applications, including the pharmaceutical industry, plastic processing as a stabilizer, catalysis, ion-exchange and adsorption (López-Martínez & Melián-Cabrera, 2021). Their general formula represents as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}.mH_2O]$; where M^{2+} is a divalent metal cation while M^{3+} is a trivalent metal cation and A^{n-} is an anion that compensates in the interlayer region. Modifying metal cations and anionic species with different ions can enhance the catalytic activity and selectivity.

Hydrotalcite is classified as a heterogeneous catalyst with numerous advantages over homogeneous catalyst such as catalyst reusability, high purity by-products and good separation and purification (Nur Fazira Edlina *et* al., 2020). The catalysts that work under homogeneous conditions comes with several drawbacks such as difficulty in catalyst recovery, the requirement for high reaction temperatures, difficulties in separating products, and the use of excess solvents that leads to a significant amount of waste, resulting in environmental pollution (Appaturi *et* al., 2021). Consequently, heterogeneous catalyst has been proved to offer several significant benefits compared to homogeneous catalyst (Opanasenko *et* al., 2013). In this context, MgAl hydrotalcite as heterogeneous catalyst was introduced in both condensation reaction due to their unique properties. Therefore, the exploration of MgAl hydrotalcite as the catalyst in both condensation reaction involving aldehydes and amines has been examined based on its catalytic activity.