Article

Catalytic Synthesis of Methacrolein via the Condensation of Formaldehyde and Propionaldehyde with L-Proline Intercalated Layered Double Hydroxides

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Abstract: Aldol condensation reactions are very important C–C coupling reactions in organic chemistry. In this study, the catalytic performance of layered double hydroxides (LDHs) in the aldol condensation reaction of formaldehyde (FA) and propionaldehyde (PA) was investigated. The M_xAl -LDHs (denoted as re- M_xAl -LDHs; $M = Ca$ and Mg ; $X = 2-4$), as heterogeneous basic catalysts toward the aldol condensation reaction, were prepared via a two-step procedure. The catalyst exhibited a high PA conversion (82.59%), but the methacrolein (MAL) selectivity was only 36.01% due to the limitation of the alkali-catalyzed mechanism. On this basis, the direct intercalation of L-proline into LDHs also has been investigated. The influences of several operating conditions, including the temperature, reaction time, and substrate content, on the reaction results were systematically studied, and the optimized reaction conditions were obtained. The optimized Mg_3Al -Pro-LDHs catalyst exhibited a much higher MAL selectivity than those of re- Mg_xAl -LDHs.

Keywords: layered double hydroxides; L-proline; aldol condensation reaction

Citation: Ju, L.; Li, G.; Luo, H.

Catalytic Synthesis of Methacrolein via the Condensation of Formaldehyde and Propionaldehyde with L-Proline Intercalated Layered Double Hydroxides. *Catalysts* **2022**, *12*, 42. <https://doi.org/10.3390/catal12010042>

Received: 13 December 2021

Accepted: 29 December 2021

Published: 31 December 2021

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1. Introduction

Methacrolein (MAL) is an important chemical intermediate for the preparation of methyl methacrylate, thermoplastic monomers, and various fragrances and pharmaceuticals [1–4]. The synthesis of MAL mainly includes the following processes: acetone cyanohydrin process, isobutene direct oxidation process, and formaldehyde (FA) and propionaldehyde (PA) condensation processes. The aldol condensation process using FA and PA can occur under mild conditions with relatively high yield. It can be carried out in two ways, i.e., the direct aldol condensation pathway and the Mannich reaction pathway. The catalysts used in the two reaction pathways are completely different. Direct aldol condensation uses bases such as NaOH, KOH, or triethylamine as catalysts [5–7]. Although this method has a high conversion of PA, the selectivity of the target product is unsatisfactory. The main side reactions are the self-condensation of the reactants and the Cannizzaro reaction [8]. The Mannich reaction, also known as amine methylation reaction, is one of the important organic reactions and has a good effect of the directional extension of the carbon chain [9,10]. The secondary amine/carboxylic acid combination is generally used as a catalyst for this reaction. Lei et al. used different secondary amine compounds to catalyze the reaction of FA and PA to synthesize MAL. The result showed that the catalytic performance of diethylamine is the highest among different secondary amines, and the yield of MAL can reach 94% [11]. Yu et al. found that L-proline is the optimal catalyst for the Mannich synthesis of MAL among the various amino acid compounds, with a conversion of 97% and a yield of 94% [12]. Unfortunately, the industrial application of this catalyst is challenged due to the cost and the subsequent separation. To overcome this issue, L-proline is introduced into different carriers, such as silica materials, metal-organic frameworks (MOFs) and layered double hydroxides (LDHs), and a good yield and a high

enantioselectivity are obtained in an asymmetric aldol condensation [13–15]. So far, there have been few reports on heterogeneous catalysts for the Mannich reaction of FA and PA to produce MAL.

LDHs are a type of two-dimensional anionic interlayer material, also known as aluminum hydroxide-like compounds. Brucite-like metal cations layers are formed by the octahedral coordination of metal cations and lattice hydroxyl groups. The divalent cations can be replaced by trivalent cations, resulting in a partial positive charge density in the layered architecture. The layers are then maintained by organic or inorganic anions to balance the positive charge of the metal cations layers, making the LDHs material electrically neutral [16–18]. Amino acids are a common amphoteric compound, and their charged properties can be adjusted by the pH of the aqueous solution. It is precisely because of the adjustable charging properties of amino acids that make them an ideal choice for intercalation [19–21]. In recent years, based on the concepts of intercalation assembly, many insights on the structure–property correlation have been obtained from the work in the characterization of layered structures, the establishment of structural models, and the functional development of intercalation assemblies [22–26]. In particular, the powerful materials that can be assembled through intercalation have attracted the attention of researchers from all over the world, and they have shown broad application prospects in the field of catalysis [27–29].

In this work, active M_xAl -LDHs catalysts with OH^- interlayer anions (denoted as re- M_xAl -LDHs; $M = Ca$ and Mg ; $X = 2-4$) were obtained and used in the aldol condensation reaction of FA with PA to produce MAL. Then, based on the amphotericity of amino acids, L-proline was successfully intercalated into the layers by coprecipitation or rehydration and characterized by XRD and FTIR. The catalytic performances of these materials in aldol condensation were also studied.

2. Results and Discussion

2.1. Re- Mg_xAl -LDHs and Re- Ca_xAl -LDHs

2.1.1. Powder X-ray Diffractometry (XRD)

In this paper, re- M_xAl -LDHs were prepared by calcination and subsequently rehydration, and the XRD patterns are shown in Figures 1 and 2. Figure 1A represents the XRD patterns of the prepared Mg_xAl -LDHs precursors with various Mg/Al ratios. It can be seen that the series of Mg_xAl -LDHs had obvious characteristic peaks at 2θ of 11.20° (003), 22.56° (006), 34.28° (009), and 60.22° (110) and the peaks were relatively symmetrical and sharp, which showed that the pure-phase and good-quality precursors were successfully obtained by the co-precipitation method [30–32]. The position of the characteristic peak (003) showed that the interlayer of the M_xAl -LDHs precursors was mainly NO_3^- and CO_3^{2-} . From the XRD patterns of Ca_xAl -LDHs, it can be seen that when the ratio of Ca/Al was 2, the characteristic diffraction peak had a strong intensity and there were no other impurity peaks. With the increase of the Ca content, in addition to the decrease in the intensity of the characteristic diffraction peaks of the LDHs phase, the $Ca(OH)_2$ phase diffraction peaks with a lower intensity gradually appeared (centered at $\sim 18.06^\circ$ and $\sim 34.26^\circ$). The excessive Ca in the sample prepared by the above co-precipitation method did not enter the layers and appeared in the form of the $Ca(OH)_2$ phase, which in turn led to the poor crystallinity of the sample. Because of the large ion radius of Ca^{2+} , it was easy to cause the octahedral structure distortion and increase the sample disorder after entering LDHs layers. Figure 1B represents the XRD patterns of the prepared Mg_xAl -composite metal oxides (MMOs) with various Mg/Al ratios. After the calcination of Mg_xAl -LDHs precursors, the characteristic diffraction peak of the original LDHs materials disappeared. The peaks at 34.98° , 43.01° , and 62.46° are attributed to the MgO phase. Since Al_2O_3 exists in the amorphous phase, its characteristic diffraction peaks were not observed. The trace amounts of $CaCO_3$ ($\sim 29.72^\circ$) were found in Ca_xAl -MMOs, which may be caused by the insufficient calcination or the introduction of CO_2 in the synthesis process. Figure 1C represents the XRD patterns of the re- Mg_xAl -LDHs. The Mg_xAl -MMOs were placed in an

alkaline solution for structural restoration, and re-Mg_xAl-LDHs with the interlayer anions replaced by OH[−] were obtained, due to the structural memory effect of LDHs materials.

Figure 1. XRD patterns of Mg_xAl-layered double hydroxides (LDHs) (A), Mg_xAl-composite metal oxides (MMOs) (B), and re-Mg_xAl-LDHs (C), where a, b, and c represent samples with Mg/Al ratios of 2:1, 3:1, and 4:1, respectively.

Figure 2. XRD patterns of Ca_xAl-LDHs (A), Ca_xAl-MMOs (B), and re-Ca_xAl-LDHs (C), where a, b, and c represent samples with Ca/Al ratios of 2:1, 3:1, and 4:1, respectively.

2.1.2. Evaluation of the Catalytic Performance

It can be seen from Table 1 that the solid base catalysts (re-M_xAl-LDHs) with OH[−] interlayer anions prepared through the process of calcination and subsequently rehydration showed high alkali catalytic activity in the aldol condensation of FA and PA. The effects of different metals and ratios of re-M_xAl-LDHs on aldol condensation were investigated. After the calcination and rehydration of Mg_xAl-LDHs precursors, the layered structure was replaced with OH[−] as an interlayer anion. The obtained re-M_xAl-LDHs sample introduced a large number of OH[−] anionic basic groups between the layers, which was likely to increase the number of Brønsted basic sites. Moreover, the disorder degree of the sample structure also increased significantly via a two-step procedure, and its relatively incomplete crystal form (surface defect) led to a fuller exposure of Brønsted basic sites on the surface. For the calcium-based LDHs catalyst, the conversion of PA and the selectivity of MAL increased gradually with the increase of the Ca/Al ratio. For the magnesium-based LDHs catalyst, the conversion of PA and the selectivity of MAL increased first and then decreased with the increase of the Mg/Al ratio. The magnesium-based catalyst re-Mg₃Al-LDHs achieved the optimal catalytic performance in the aldol condensation process (PA conversion: 82.59%; MAL selectivity: 36.01%).

Table 1. Results of the aldol condensation reaction with re-M_xAl-LDHs catalysts.

Catalyst	PA Conversion (%)	MAL Selectivity (%)
re-Ca ₂ Al-LDHs	73.61	17.93
re-Ca ₃ Al-LDHs	79.30	18.22
re-Ca ₄ Al-LDHs	84.56	24.85
re-Mg ₂ Al-LDHs	80.18	21.25
re-Mg ₃ Al-LDHs	82.59	36.01
re-Mg ₄ Al-LDHs	43.95	22.31

Reaction conditions: 0.2 g catalyst; 15 mL dimethyl sulfoxide (DMSO); 3.8 mL formaldehyde (FA); 3.7 mL propionaldehyde (PA); 60 °C; 4 h.

The product distribution using re-Mg_xAl-LDHs is shown in Figure 3. Apart from the cross-condensation of FA and PA to produce MAL, other possible reactions in this system included the self-condensation of PA (2-methyl-2-pentenal (MP)), the isomerization of β -hydroxyaldehyde (cis-2-butene-1,4-diol (BED)), and the Cannizzaro reaction (1,1,1-Tris(hydroxymethyl)ethane (TME)). All the reactions can be carried out under the condition of the base catalysis. After changing the metal ion and ratio of the LDHs material, the selectivity of MAL was still not satisfactory. For this defect, we further intercalated L-proline, which had a high selectivity for the cross-condensation reaction into LDHs.

Figure 3. Results of the aldol condensation reaction with re-Mg_xAl-LDHs catalysts.

2.2. Re-Mg₃Al-Pro-LDHs and Mg₃Al-Pro-LDHs

2.2.1. XRD

Re-Mg₃Al-Pro-LDHs and Mg₃Al-Pro-LDHs were prepared by the rehydration and co-precipitation method, and the XRD patterns are shown in Figure 4. For the Mg₃Al-LDHs sample, the main characteristic diffraction peaks appeared at 11.20° (003), 22.56° (006), 34.28° (009), and 60.22° (110). The re-Mg₃Al-Pro-LDHs and Mg₃Al-Pro-LDHs showed the similar diffraction peaks, which indicated that the L-proline intercalation by both methods did not affect the original layered structure. According to Bragg's law, the corresponding crystalline spacing can be obtained. For example, the crystalline spacing of the (003) peak in Mg₃Al-LDHs was 0.78 nm. After L-proline intercalation, the characteristic peaks (003) of re-Mg₃Al-Pro-LDHs and Mg₃Al-Pro-LDHs shifted to a lower 2 θ (10.20°/9.80°), and the crystalline spacings increased to 0.86 nm and 0.90 nm, respectively. This is consistent with the literature reports of L-proline intercalation materials, and it can also prove that the L-proline molecules were successfully intercalated into the interlayer of LDHs materials [33,34].

Figure 4. XRD patterns of re-Mg₃Al-Pro-LDHs (a), Mg₃Al-Pro-LDHs (b), and Mg₃Al-LDHs (c).

The metal atoms on the layer of the LDHs material were connected by covalent bonds, and the host layer and the guest were connected by the electrostatic force, the hydrogen bond, and other forces. Previous studies have shown that the long axis length of L-proline is 0.64 nm and the short axis length is 0.30 nm. According to the data in Table 2, subtracting the thickness of the layer of 0.21 nm and the hydrogen bond space of 0.27 nm [35,36], the gallery heights of the intercalated materials were 0.42 nm and 0.38 nm, respectively. Its value was less than the length of the long axis of the L-proline molecule and greater than the length of its short axis. Therefore, it can be considered that the carboxyl group of L-proline was connected with the metal cations layers and arranged between the layered structures in an inclined manner. The structural model of the intercalation material is shown in Figure 5. Furthermore, the interlayer anions led to the difference of the spacing between the intercalated materials prepared by co-precipitation and rehydration methods. Except for L-proline, the interlayer anion in co-precipitation process was mainly NO₃[−], while the interlayer anion in the rehydration process was mainly OH[−], and the size of NO₃[−] was larger than that of OH[−].

Table 2. XRD data of the diffraction peaks of Mg₃Al-LDHs, Mg₃Al-Pro-LDHs, and re-Mg₃Al-Pro-LDHs.

Diffraction Peaks	Mg ₃ Al-LDHs		Mg ₃ Al-Pro-LDHs		re-Mg ₃ Al-Pro-LDHs	
	2θ (°)	d (nm)	2θ (°)	d (nm)	2θ (°)	d (nm)
003	11.20	0.78	9.80	0.90	10.20	0.86
006	22.56	0.39	19.80	0.45	20.02	0.44
009	34.28	0.26	34.50	0.26	34.82	0.26
110	60.22	0.15	60.78	0.15	60.94	0.15

Figure 5. Structural model of L-proline-intercalated LDHs.

2.2.2. FTIR

The successful intercalation of L-proline in magnesium-based LDHs was also confirmed by FTIR. The results are shown in Figure 6. The samples showed a broad absorption peak at 3450 cm^{-1} , which is mainly due to the water molecules between the layers of LDHs and the stretching vibration of hydroxyl groups. The absorption peak moved to a lower wavenumber than the characteristic peak of free hydroxyl (appeared at 3600 cm^{-1}), which was caused by the hydrogen bond between the interlayer water molecules and the hydroxyl in the laminate. The characteristic peaks of L-proline samples at 2985 cm^{-1} and 2742 cm^{-1} belonged to the asymmetric stretching vibration and bending vibration of the N–H bond and the C–H bond [37–39]. The $\text{Mg}_3\text{Al-Pro-LDHs}$ sample also showed the corresponding characteristic peaks, and the peaks were sharp and obvious, but these peaks did not appear in the spectrum of the $\text{Mg}_3\text{Al-LDHs}$ sample, which indicated that the L-proline molecules successfully entered the LDHs interlayer. The characteristic peaks of $\text{Mg}_3\text{Al-Pro-LDHs}$ samples at 1624 cm^{-1} and 1384 cm^{-1} are attributed to the asymmetric bending vibration of the carboxyl group in the L-proline molecule. The above LDHs materials showed obvious characteristic peaks at 827 cm^{-1} and 677 cm^{-1} , which are mainly attributed to the lattice vibration of the Mg–O and Al–O bonds and the tensile and flexural vibrations of M–O–M and O–M–O ($\text{M} = \text{Mg}^{2+}$ or Al^{3+}), indicating that the layered structure was maintained well [40–42].

Figure 6. FTIR patterns of re- $\text{Mg}_3\text{Al-Pro-LDHs}$ (a), $\text{Mg}_3\text{Al-Pro-LDHs}$ (b), L-proline (c), and $\text{Mg}_3\text{Al-LDHs}$ (d).

2.2.3. Evaluation of the Catalytic Performance

It can be seen from Table 3 that the catalytic performance using the L-proline intercalation materials was investigated in the aldol condensation reaction of FA and PA. Compared with re- $\text{M}_x\text{Al-LDHs}$, the MAL selectivity was greatly improved. Presumably, after the intercalation of L-proline, the active site was replaced or partially replaced with L-proline molecules, allowing the reaction to proceed by the mechanism of the Mannich reaction [43–45]. As shown in Figure 7, under the action of hydrogen ions in the solution, FA and the secondary amine group of L-proline underwent a nucleophilic addition to produce iminium ions, and one molecule of water was released. Then, PA reacted with the iminium ions to form the Mannich base, which later dissociated to MAL. Since the LDHs provided a certain amount of basic sites, other side reactions cannot be completely prohibited. The catalytic performance of the L-proline-intercalated LDHs catalyst synthesized by rehydration was lower than that by co-precipitation. After the calcination of the $\text{Mg}_3\text{Al-LDHs}$ precursor, the structure of the composite metal oxide remained, and the steric hindrance of L-proline molecule was large, which was not conducive to the intercalation assembly of the L-proline group. The density of active sites was lower than that by the co-precipitation method, which led to the reduction of the catalytic activity.

Table 3. Results of the aldol condensation using LDHs with L-proline intercalation.

Catalyst	PA Conversion (%)	MAL Selectivity (%)
Mg ₃ Al-Pro-LDHs	21.09	94.58
re-Mg ₃ Al-Pro-LDHs	19.50	64.72

Reaction conditions: 0.2 g catalyst; 15 mL DMSO; 3.8 mL FA; 3.7 mL PA; 60 °C; 4 h.

Figure 7. Proposed catalytic cycle for the aldol condensation reaction with the Mannich pathway.

It can be seen from Table 4 that the result of the aldol condensation reaction was closely related to the amount of the substrate. With the increase of the amount of the substrate, the conversion of PA gradually decreased, and the selectivity of MAL increased. In Figure 8, the result indicated that the temperature and the reaction time had impacts on the aldol condensation reaction. Under the optimal operating conditions (substrate amount: 5 mmol; temperature: 60 °C; reaction time: 30 min), the PA conversion was 91.39%, and the MAL selectivity was 51.48%. In Figure 9, the reusability test showed that the MAL selectivity remained unchanged and the catalytic activity decreased after four recycling, which was caused by the leaching of L-proline species and the loss of the catalyst during the separation process. Although L-proline was an effective catalyst for the aldol condensation to produce MAL via the Mannich pathway, the inherent defects (large amount of catalyst, difficult to separate, etc.) led to a challenge for industrial applications. In this work, L-proline was intercalated into LDHs, and the catalytic effect was evaluated in the target reaction. Generally, this catalyst has three advantages as following: (i) facilely and inexpensively synthesizing the catalyst; (ii) making up for the defection of large L-proline consumption; (iii) reducing the cost of product separation. LDHs as a “molecular container” is a fascinating field of research which directly bridges homogenous and heterogeneous catalysis.

Table 4. Results of the aldol condensation reaction with Mg₃Al-Pro-LDHs catalysts at different substrate amounts.

Substrate Amount (mmol)	PA Conversion (%)	MAL Selectivity (%)
5	97.67	32.97
25	41.72	45.25
50	20.89	96.82

Reaction conditions: 0.2 g catalyst; 15 mL DMSO; FA:PA molar ratio = 1:1; 60 °C; 4 h.

Figure 8. Results of the aldol condensation reaction of Mg₃Al-Pro-LDHs under different temperatures (A) and different reaction times (B).

Figure 9. Reusability test results for Mg₃Al-Pro-LDHs.

3. Materials and Methods

3.1. Reagents and Instruments

Mg(NO₃)₂·6H₂O (99%; Sinopharm Chemical Reagent Co., Ltd., Beijing, China), Ca(NO₃)₂·4H₂O (99%; Aladdin Biochemical Technology Co., Shanghai, China), Al(NO₃)₃·9H₂O (99%; Xilong Chemical Co., Ltd., Shanghai, China), NaOH (99%; Tianda Chemical Reagent Factory, Tianjin, China), PA (99%; Aladdin Biochemical Technology Co., Shanghai, China), FA (37–40%; Liaoning Quanrui Chemical Reagent Factory, Liaoning, China), ethanol (99.7%; Tianjin Damao Chemical Reagent Factory, Tianjin, China), MAL (99%; Aladdin Biochemical Technology Co., Shanghai, China), MP (99%; Aladdin Biochemical Technology Co., Shanghai, China), BED (99%; Aladdin Biochemical Technology Co., Shanghai, China), TME (99%; Aladdin Biochemical Technology Co., Shanghai, China), dimethyl sulfoxide (DMSO; 99%; Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China), L-proline (99%; Aladdin Biochemical Technology Co., Shanghai, China) were purchased and used without further purification. Decarbonated deionized water was used in all the experimental processes.

XRD patterns were performed at a scanning speed of 10°/min on a Smart Lab 9 diffractometer equipped with Cu K α radiation (λ : 1.5406 Å; voltage: 45 kV; current: 200 mA) in the range of 5–85° with a step of 0.01°. The XRD data can be used to obtain the information on the crystallinity and layer spacing of the prepared catalyst.

FTIR spectra were obtained using a Bruker EQUINOX55 spectrometer from 400 cm^{−1} to 4000 cm^{−1} by the standard KBr disk method, which was used to determine whether the guest compound entered the interlayer of the LDHs material.

3.2. Catalysts Preparation

Preparation of $M_x\text{Al-LDHs}$ precursors: $M_x\text{Al-LDHs}$ precursors with different M/Al molar ratios were prepared by the co-precipitation method, and the typical preparation process was as follows. Solution A was mixed solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with various Ca/Al molar ratios (from 2 to 4); solution B was an aqueous sodium hydroxide solution with $[\text{NaOH}] = 1.1 \text{ M}$. Then, solutions A and B were uniformly poured into a 250 mL three-neck flask, with a controlled stirring speed of 100 rpm for 6 h. The whole process was carried out in a nitrogen-protected atmosphere. The white emulsion obtained was centrifuged at 3000 rpm for 3 min, washed three times with deionized water and ethanol and dried in an oven at 60°C for 24 h to obtain the $\text{Ca}_x\text{Al-LDHs}$ precursor. Meanwhile, different molar ratios of $\text{Mg}_x\text{Al-LDHs}$ precursors were synthesized by the same method using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. An additional crystallization process was required for the preparation of $\text{Mg}_x\text{Al-LDHs}$ samples (crystallization temperature: 110°C ; crystallization time: 12 h).

Preparation of composite metal oxides: A certain mass of $\text{Mg}_x\text{Al-LDHs}$ or $\text{Ca}_x\text{Al-LDHs}$ series precursors were fully ground with a quartz mortar and evenly placed in a quartz boat. The precursors were then placed in an atmospheric tube furnace protected by nitrogen and calcined at 450°C for 4 h. The product was naturally cooled to room temperature, namely $\text{Ca}_x\text{Al-MMOs}$ or $\text{Mg}_x\text{Al-MMOs}$.

Preparation of re- $M_x\text{Al-LDHs}$: A certain mass of $\text{Ca}_x\text{Al-MMOs}$ or $\text{Mg}_x\text{Al-MMOs}$ was placed in a three-neck flask and protected by nitrogen. An aqueous sodium hydroxide solution with $[\text{NaOH}] = 1.1 \text{ M}$ was added to the flask and stirred at 30°C for 2 h, then centrifuged and separated. The obtained product was washed three times with deionized water and ethanol and placed in a vacuum-drying oven for 24 h to obtain a structurally restored solid base catalyst, namely re- $\text{Mg}_x\text{Al-LDHs}$ or re- $\text{Ca}_x\text{Al-LDHs}$.

Preparation of $\text{Mg}_3\text{Al-Pro-LDHs}$: The L-proline-intercalated LDHs catalyst was prepared by the co-precipitation method. Firstly, 100 mL of solutions A and B were prepared. Solution A was mixed solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.6 M) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.2 M); solution B was a mixed solution of L-proline and NaOH with an equal concentration (1.1 M). Solutions A and B were diverted into a 250 mL three-neck flask and reacted for 6 h at room temperature. All the above processes were carried out under nitrogen protection. The slurry obtained was washed three times with deionized water and then placed in a vacuum-drying oven for 24 h, namely $\text{Mg}_3\text{Al-Pro-LDHs}$.

Preparation of re- $\text{Mg}_3\text{Al-Pro-LDHs}$: The preparation method is similar to that used to prepare the re- $M_x\text{Al-LDHs}$ catalysts. L-proline was dissolved in a newly prepared NaOH solution with an equal concentration (0.06 M) and mixed with a certain mass of composite metal oxides, and the resulting slurry was reacted at room temperature for 24 h. All the above processes were carried out under nitrogen protection. The product was fully washed until it was approximately neutral and placed in a vacuum-drying oven for 24 h, namely re- $\text{Mg}_3\text{Al-Pro-LDHs}$.

3.3. Synthesis of MAL from FA and PA

The FA and PA condensation reaction was carried out in a 100 mL stainless steel reactor. The solid-phase catalyst was mixed with a solvent (DMSO) and added into the reactor. FA, PA, and internal standard ethanol were added sequentially, and the reaction began. After the reaction, the liquid-phase products were separated by centrifugation and analyzed by gas chromatography.

The catalytic performances of the catalysts were evaluated based on the conversion of PA and the selectivity of MAL. The corresponding expressions are as follows.

The conversion of PA was written as:

$$X_{\text{PA}} = \frac{n_{\text{PA},\text{in}} - n_{\text{PA},\text{out}}}{n_{\text{PA},\text{in}}} \times 100\%,$$

The selectivity of MAL was written as:

$$S_{MAL} = \frac{n_{MAL,out}}{n_{PA,in} - n_{PA,out}} \times 100\%,$$

The selectivity of MP was written as:

$$S_{MP} = \frac{n_{MP,out}}{n_{PA,in} - n_{PA,out}} \times 100\%,$$

The selectivity of BED was written as:

$$S_{BED} = \frac{n_{BED,out}}{n_{PA,in} - n_{PA,out}} \times 100\%,$$

The selectivity of TME was written as:

$$S_{TME} = \frac{n_{TME,out}}{n_{PA,in} - n_{PA,out}} \times 100\%,$$

where $n_{PA,in}$ and $n_{PA,out}$ are the moles of PA in the system before and after the reaction, respectively, and $n_{MAL,out}$, $n_{MP,out}$, $n_{BED,out}$, and $n_{TME,out}$ are the obtained moles of MAL, MP, BED, and TME.

4. Conclusions

Due to the defects of homogeneous catalysts and difficult separation, it is urgent to develop heterogeneous catalysts with excellent catalytic performance in the aldol condensation reaction of FA and PA. In this paper, based on its so-called memory effect, the interlayer anion in LDHs was successfully replaced by OH^- after calcination and rehydration processes. The rehydrated LDHs as unselective solid-base catalysts presented high catalytic activity and low MAL selectivity. Then, L-proline was successfully intercalated and assembled in LDHs, which was confirmed by XRD and FTIR. The latter showed higher MAL selectivity. The reusability test showed that the selectivity of the target product remained unchanged after the catalyst was recycled four times. The leaching of L-proline species into the solution and the loss of the catalyst during the separation process resulted in a gradual decrease in the catalytic activity. This work provides a facile and cost-effective approach to the preparation of L-proline-intercalated LDHs, which can be used as a heterogeneous catalyst in the green catalysis of aldol condensation reactions.

Author Contributions: Data curation, L.J. and G.L.; Investigation, L.J., G.L. and H.L.; Methodology, L.J. and G.L.; Software, L.J.; Supervision, G.L.; Validation, L.J.; Writing—original draft, L.J.; Writing—review & editing, G.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors acknowledge the financial support from Sanlibennuo Chemical Industry Co., Weifang, China.

Conflicts of Interest: The authors declare no conflict of interest.

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