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Solvent-Free Synthesis of Jasminaldehyde in a Fixed-Bed Flow Reactor over Mg-Al Mixed Oxide

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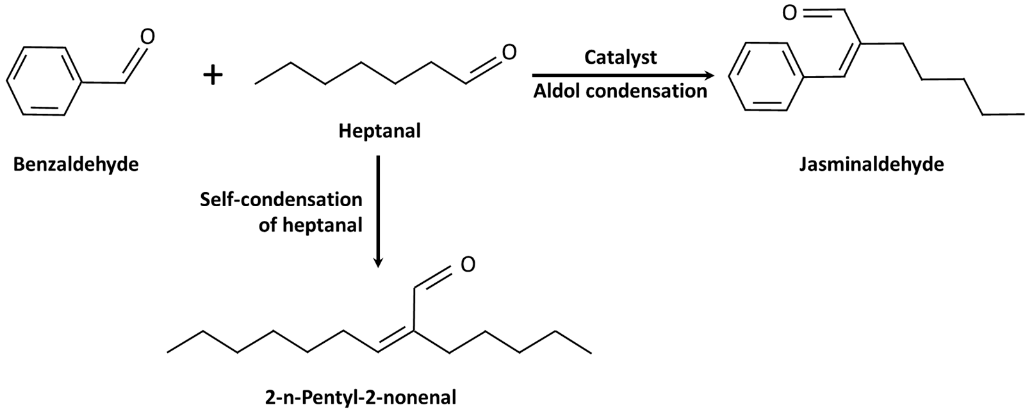
Abstract: In spite of the rapid developments in synthesis methodologies in different fields, the traditional methods are still used for the synthesis of organic compounds, and regardless of the type of chemistry, these reactions are typically performed in standardized glassware. The high-throughput chemical synthesis of organic compounds such as fragrant molecules, with more economic benefits, is of interest to investigate and develop a process that is more economical and industrially favorable. In this research, the catalytic activity of Mg-Al catalyst derived from hydrotalcite-like precursors with the Mg/Al molar ratio of 3 was investigated for the solvent-free synthesis of jasminaldehyde via aldol condensation of benzaldehyde and heptanal. The reaction was carried out in a fixed-bed flow reactor, at 1 MPa, and at different temperatures. Both Brønsted and Lewis (O^{2-} anions) base sites, and Lewis acid sites exist on the surface of the Mg-Al catalyst, which can improve the catalytic performance. Increasing the reaction temperature from 100 °C to 140 °C enhanced both heptanal conversion and selectivity to jasminaldehyde. After 78 h of reaction at 140 °C, the selectivity to jasminaldehyde reached 41% at the heptanal conversion 36%. Self-condensation of heptanal also resulted in the formation of 2-n-pentyl-2-n-nonenal. The presence of weak Lewis acid sites creates a positive charge on the carbonyl group of benzaldehyde, and makes it more prone to attack by the carbanion of heptanal. Heptanal, is an aliphatic aldehyde, with higher activity than benzaldehyde. Therefore, the possibility of activated heptanal reacting with other heptanal molecules is higher than its reaction with the positively charged benzaldehyde molecule, especially at a low molar ratio of benzaldehyde to heptanal.

Keywords: Mg-Al hydrotalcite; aldol condensation; jasminaldehyde; benzaldehyde; heptanal; fixed-bed flow reactor

1. Introduction

Jasminaldehyde, which also known as α-amylcinnamaldehyde, is a traditional perfumery chemical with a violet scent. Before the 20th century, perfumes were mainly dependent on natural sources for their ingredients, and due to the limitations in supply, they were expensive to produce [1]. According to the reports, natural sources are used for the production of less than 5% of perfumery molecules [2]. Owing to the lower price of synthetic materials, their higher stability in acidic, basic, and even oxidizing media, these compounds became more attractive to be used in the synthesis of perfumery chemicals [2]. Jasminaldehyde can be synthesized via the cross aldol condensation of heptanal ($C_7H_{14}O$) and benzaldehyde (C_7H_6O) (Scheme 1), and this process has been intensively studied by researchers to enhance the yield of jasminaldehyde [3–10]. In addition to jasminaldehyde, the self-condensation of heptanal resulted in the formation of 2-n-pentyl-2-n-nonenal ($C_{14}H_{26}O$) as the main by-product of this reaction. A high molar ratio of benzaldehyde to heptanal is required during the reaction to reduce the possibility of a self-condensation reaction. Though, the high concentration of benzaldehyde also may result in the presence of some unreacted benzaldehyde in the product mixture [2,3,8,11]. Other methods such as stepwise addition of heptanal, or addition of methanol to the reaction mixture to react with the excess heptanal, are suggested to reduce the formation of by-product (2-n-pentyl-2-n-nonenal) [2].



Scheme 1. Aldol condensation of heptanal and benzaldehyde.

In the conventional industrial process, homogeneous inorganic hydroxides such as NaOH and KOH are used for the production of jasminaldehyde. However, the use of theses homogeneous hydroxide-based catalysts has several drawbacks, such as lack of reusability of catalyst, employing a corrosive mixtures, formation of a large amount of liquid waste, separation and disposal of effluent containing sodium or potassium hydroxides [3,5,12–14]. Thus, it is necessary to develop solid base heterogeneous catalysts for the synthesis of jasminaldehyde to provide an industrial process with easy product separation, lower corrosion of the reactor, the possibility of regeneration and reuse of catalysts, and the formation of the product with higher selectivity to jasminaldehyde. The higher reaction rate is achieved using base catalysts, while acid catalysts give slower rates [1]. Different types of heterogeneous catalyst have been used for the synthesis of jasminaldehyde by Wong et al. [15], and a microwave reactor was used for the evaluation of the catalyst performance in batch mode, at 180 °C. It has been reported that the nanocrystalline aluminosilicate F-type zeolite prepared from rice husk ash silica source, was used as a heterogeneous catalyst in microwave-enhanced aldol condensation for the synthesis of jasminaldehyde. The heptanal conversion of 77.1% and jasminaldehyde selectivity of 69.5% was obtained over this catalyst at 180 °C, 40 min, benzaldehyde to heptanal ratio of 5, and 40 min of microwave irradiation time. The reaction was also evaluated in the presence of several types of solvents with different polarity (in E_T^N scale), including dichloromethane, acetonitrile, dimethyl sulfoxide, ethanol, and water, with the polarities of 0.309, 0.444, 0.460, 0.654, and 1.000, respectively. It was observed that the polar solvents resulted in better conversion of heptanal, while the selectivity to jasminaldehyde was found to be independent of the type of solvent. However, compared with the solvent-containing reactions, the solvent-free reaction showed a better catalytic performance. The prepared nanocatalysts also showed excellent reusability, and after five consecutive reaction cycles, there was not a significant loss in their activity and selectivity.

Hamza and Nagaraju [7] investigated the synthesis of jasminaldehyde using the amorphous metal-aluminophosphate catalysts (MAlPs), where M is 2.5 mol.% Cu, Fe, Zr, Cr, Zn, or Ce. The aldol condensation reaction was performed in a three-necked round bottom flask with the benzaldehyde to heptanal ratio of 5. The FeAlP catalyst showed the highest catalytic activity (75%) as well as the highest selectivity to jasminaldehyde (71%) after 4 h of reaction at 140 °C. The good catalytic performance of this catalyst could be ascribed to the cooperative role of the optimal amount of acidic and basic sites with weaker strength. In general, because of its monobasic property and the low selectivity to jasminaldehyde, magnesium oxide is not an appropriate catalyst for the synthesis of jasminaldehyde. Therefore, Fan [3], prepared the acid-base bi-functional magnesium oxide catalysts ($MgO-NO_3-H_2O_2$)

using a simple hydrogen peroxide reflux calcination procedure. The catalytic activity of the catalysts for aldol condensation reactor was evaluated in a two-necked round bottom flask placed in an oil bath. Before addition of catalyst to the reactor, the proper amount of benzaldehyde and heptanal with the benzaldehyde to heptanal ratio of 5 was mixed and the mixture heated up to 140 °C. The prepared catalysts showed a high selectivity of 88% and heptanal conversion of 99% after 5.5 h of reaction at 140 °C. By increasing the benzaldehyde to heptanal ratio to 15, the jasminaldehyde selectivity increased to 94%, while the conversion remained unchanged (99%). The investigation of reaction mechanism over this catalyst indicated that this bi-functional magnesium oxide catalyst favored adsorption of benzaldehyde over heptanal, which resulted in a higher ratio of benzaldehyde to heptanal on the surface of the catalyst. Furthermore, the existence of weak Lewis acid sites on the surface of the catalyst caused a partial positive charge on carbonyl group of benzaldehyde, makes it more prone to a nucleophilic attack by the heptanal carbanion. Results revealed that the acid-base bifunctional catalysts are the desired types of catalyst for aldol condensation reaction with high selectivity to jasminaldehyde.

Hydrotalcites (HTCs) are found to be a promising catalyst for this reaction. The chemical composition of hydrotalcites can be shown with the general formula of $\left(M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right)^{x+}\left(A^{n-}_{x/n}\right)^{x-}.mH_2O$, where M^{2+} (e.g., Cu^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}) is the divalent metal cation, and M^{3+} is the trivalent cation (e.g., Fe^{3+}, Al^{3+}, Mn^{3+}, Cr^{3+}), and A^{n-} is a n-valent anion (e.g., NO_3^-, CO_3^{2-}, SO_4^{2-}, OH^-). The partial metal cation M^{2+}/M^{3+} replacement take place, and the additional positive charge is counterbalanced by anions A^{n-} existing in interlayers, along with the water molecules. The x parameter is the surface charge determined by the ratio of two metal cations ($x = M^{3+}/(M^{2+} + M^{3+})$), and its value is reported to be in the range of 0.1 to 0.5, however for the pure phases, it is reported to be in the range of $0.2 < x < 0.33$ [16–18]. Thermal treatment of hydrotalcites could convert them into the well-dispersed mixed metal oxides (MMOs) with a lot of Lewis base sites, high surface areas, and a large number of defects formed as a result of the incorporation of Al^{3+} ions into the Mg^{2+} lattice [16,17]. Subsequently, rehydration of MMOs, in the absence of carbon dioxide, converts them to the layered structure with hydroxyl anions incorporated in the interlayer area and forming activated HTCs with rich Brønsted-type basic sites [16,17].

The nature and strength of the basic and acidic sites of the hydrotalcites can be tuned by variation of these parameters: (a) nature of the substituting cations in the structures of hydrotalcite, (b) nature of anions existed in interlayer regions, (c) characteristic M^{2+}/M^{3+} molar ratio, and (d) thermal treatment and activation of layered materials [19,20]. Sharma et al. [8,12] used the Mg-Al hydrotalcite catalyst with the Mg/Al molar ratio of 2.0 to 3.5 via the coprecipitation method. The highest jasminaldehyde selectivity of 86% and heptanal conversion of 98% was obtained for the Mg/Al ratio of 3.5, after 8 h of reaction at 125 °C, and heptanal to benzaldehyde molar ratio of 5. They also studied the effect of reconstruction of Mg-Al hydrotalcite on its performance in the synthesis of jasminaldehyde. The reconstruction was undertaken by stirring the calcined hydrotalcite sample in de-carbonated deionized water under the nitrogen atmosphere, resulted in the reinstatement of the original layered structure of hydrotalcite containing hydroxyl groups as the main compensation anions in the interlayer space instead of carbonate anions [12]. Results revealed that the conversion of heptanal increased to 96% for the reconstructed hydrotalcite, which is higher than those of as-synthesized (51%) and calcined (60%) hydrotalcites. High conversion of almost 96% with the selectivity of 65% to jasminaldehyde obtained at benzaldehyde to heptanal ratio of 3, at 130 °C and 120 min of reaction. The selectivity increased to about 84% by raising the benzaldehyde to heptanal ratio to 10. In another study by Yadav and Aduri [13], the Mg-Al calcined hydrotalcite (CHT) supported on hexagonal mesoporous silica (HMS) (CHT/HMS = 20% (*w*/*w*)), was used for the synthesis of jasminaldehyde. The catalyst showed an excellent activity and selectivity in this reaction, at 150 °C and the benzaldehyde to heptanal ratio of 5. The results were ascribed to the bi-functional character of the CHT/HMS catalyst, where the weak acid sites are responsible for the activation of benzaldehyde by protonation of the carbonyl groups, which favors the attack of enolate heptanal intermediate formed on the basic sites of the CHT/HMS catalyst.

Vrbková et al. [6] synthesized several layered double hydrotalcite catalysts, with the Mg/Al molar ratio of 2.0 to 4.0, and their activity in aldol condensation reaction was investigated. After 4 h of reaction, conversion of at least 90% was achieved with all catalysts, however, in general, catalysts with Mg/Al ratio of 3 and 4 showed higher activity and selectivity in the solvent-free reaction at 100 °C, and benzaldehyde to heptanal ration of 2. The reaction also studied in the presence of N,N′-dimethylformamide (DMF) as the solvent, and it was found that the DMF is not a suitable solvent for this reaction, and resulted in lower reaction rate and selectivity. One of the reasons for the lower activity in the presence of a solvent might be its basicity. The aldehydic hydrogen in benzaldehyde is a bit more acidic than that of heptanal; thus, it could preferentially interact with DMF, and it is less available to react with heptanal. Another reason might be that the different compounds are competing for the same active sites, where solvent also can be adsorbed on both acidic and basic sites. Therefore, the presence of solvent could decrease the possibility of adsorption of reactant molecules. Later, the same research group [5], studied the synthesis of jasminaldehyde over the zinc modified Mg-Al mixed oxide at 80–120 °C, 7 h, and the benzaldehyde to heptanal mole ratio of 2. Comparison of the activity of Mg-Al oxide and the zinc-modified Mg-Al oxides catalysts under the same reaction conditions revealed that the zinc-modified Mg-Al catalysts yielding 15–20% higher jasminaldehyde than Mg-Al catalyst. The higher reaction temperature led to a higher reaction rate as well as a higher selectivity to jasminaldehyde. The presence of DMF solvent was also found to have a negative impact on the reaction rate and selectivity to jasminaldehyde, but it can be suitable for reducing the viscosity of the mixture, which is preferred for the reaction in a flow reactor.

Even though during the last decades, there are rapid developments in synthesis methodologies in different fields, but organic synthesis is still being performed in a very traditional way. These reactions are typically carried out in standardized glassware, and regardless of the type of chemistry, compounds are synthesized in batch-wise. Due to its direct application to the synthesis of organic chemicals such as fragrant molecules, the high-throughput chemical synthesis has been a major field of interest in the past decade, and efforts were made to make them more economical than natural products. Using the continuous-flow processes, in addition to improving the catalytic performance and optimizing the reaction conditions, are considered to be a universal lever to make the process more economical and industrially favorable. Therefore, in the current study, a continuous flow fixed-bed reactor is used for the aldol condensation reaction over Mg-Al hydrotalcite catalyst with the Mg/Al ratio of 3. The Mg-Al hydrotalcite catalysts prepared by the coprecipitation method and their physicochemical properties were characterized through different characterization methods.

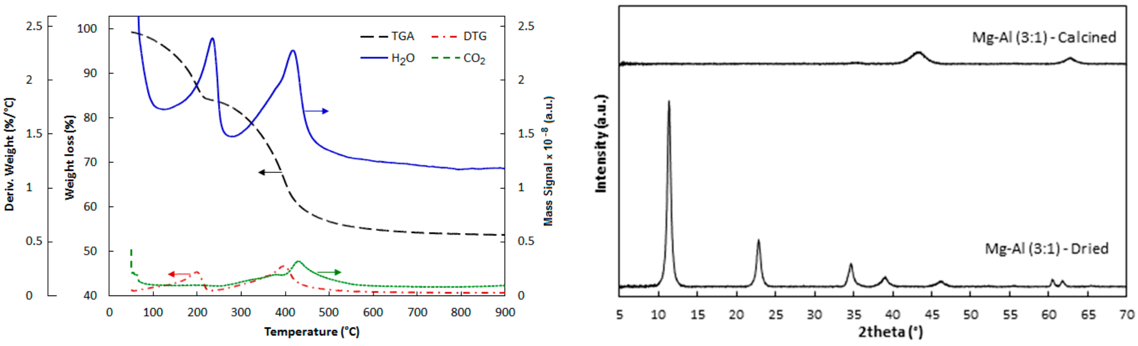
2. Results and Discussion

2.1. Catalyst Characterization

The chemical composition of the prepared Mg-Al hydrotalcite was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). It was found that the Mg/Al ratio of the prepared hydrotalcite was higher than the targeted ratio. The weight percentage of Mg and Al were 25 wt.% and 8 wt.%, respectively, with the Mg/Al molar ratio of 3.45. The differences between the targeted and obtained Mg/Al ratio could be attributed to the use of hydrated nitrate precursors for the synthesis of the catalyst, where the amount of bonded water molecules can vary. Also, there could be some losses during the washing of precipitated solids, which caused some changes in the actual obtained ratio.

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis were performed to investigate the transformation process of hydrotalcite layered structure into the mixed oxide. As can be seen in Figure 1a, several phases of weight loss observed for the prepared Mg-Al hydrotalcite, which could be attributed to the thermal decomposition of the catalyst. The 25% weight loss at low temperature (up to 280 °C) and the DTG peak at 200 °C was due to the evaporation of the physically adsorbed and interlayer water molecules. The second phase of weight loss (up to 45%)

at a higher temperature range (280–550 °C) and the DTG peak at around 400 °C were attributed to the removal of the carbonate anions and hydroxyl from the interlayer space, together with interlayer water. These findings are in good accordance with the mass spectroscopy results, where two peaks were observed for the released water at around 240 °C and 420 °C. During the thermal treatment of hydrotalcites, dehydroxylation and decarbonization are overlapped; therefore, performing the mass spectroscopy analysis following TGA could help to identify both reactions. The interlayer carbonate of the hydrotalcite structure was released as CO_2 simultaneously with water around 440 °C. The TG analysis of the synthesized Mg-Al hydrotalcite is in line with the results observed by Kloproggea et al. [21], and the TGA-MS (mass spectrometry) of Mg-Al hydrotalcites confirmed a major loss of H_2O (dehydroxylation) and CO_2 at around 410 °C.



(**a**) (**b**)

Figure 1. (**a**) Thermogravimetric analysis-mass spectrometry (TGA-MS) analysis of the dried Mg-Al catalyst, (**b**) X-ray diffraction (XRD) patterns of the dried and calcined Mg-Al catalysts.

The X-ray diffraction (XRD) patterns of the Mg-Al mixed oxide catalysts are exhibited in Figure 1b. The dried catalyst had the hydrotalcite crystallized structure, with the corresponding peaks at 11.4°, 22.8°, 34.7°, 39.1°, 46.3°, 60.5° and 61.8°, corresponded to the (0 0 3), (0 0 6), (0 0 9), (0 1 5), (0 1 8), (1 1 0), and (1 1 3) planes (JCPDS #70-2151) [22–24]. After calcination at 450 °C under air atmosphere, the hydrotalcite structure of the sample is decomposed and converted into the mixed oxides of MgO and Al_2O_3. The peaks corresponding to the MgO phase are observed at 43.2° and 62.7° (JCPDS 77-2179). The diffraction peaks corresponding to the AlO_x phase were not observed in the XRD pattern of the calcined catalysts. It could be due to the insertion of Al^{3+} into the MgO lattice without any phase separation in the calcined samples [23,25].

The scanning electron microscope (SEM) images of the dried Mg-Al hydrotalcite is displayed in Figure 2. A well-developed layered hydrotalcite structure with visible edge and thin flat crystals observed for this sample, which is in good agreement with the XRD result, where a very clear hydrotalcite crystallized structure was observed for this sample. After calcination of the Mg-Al hydrotalcite at 450 °C, the nanoplates-like feature can still be discriminated, which indicated that the thermal decomposition of the interlayer anions occurred without any phase segregation and sintering, which could be occurred at higher calcination temperature [25].

Nitrogen adsorption-desorption isotherms analysis was carried out to determine the textural properties of the prepared Mg-Al catalysts (Figure 3a). The type IV isotherm and the H3 hysteresis loop was observed for both samples. The characteristic features of type IV isotherm are attributed to its hysteresis loop, which is attributed to the capillary condensation occurring in mesopores, and the limiting uptake over a range of high P/P_0. Hysteresis appearing in the multilayer range of physisorption isotherms is generally related to the capillary condensation in the mesopore structures. Generally, the shapes of hysteresis loops have been recognized with the specific pore structures. Type H3 hysteresis loop, which does not show any limiting adsorption at high P/P_0, is usually identified with agglomerates or aggregates of plate-like particles giving rise to slit-shaped pores [26]. The isotherm for these catalysts at a relative pressure of 0.45 to 1.0 demonstrated the typical hysteresis loop of mesoporous materials with a wide pore size distribution. The Mg-Al dried sample showed a wide pore size distribution varied from 5 nm to about 30 nm, while the calcined sample showed a narrower size distribution, mainly less than 20 nm (Figure 3b). As summarized in Table 1, the specific surface area and pore volume of the sample increased from 73.3 to 241.9 m^2/g after calcination at 450 °C. These findings are also confirmed by other researchers [16,17], who reported that the calcination of Mg-Al hydrotalcite converted them into well-dispersed mixed oxides with high surface areas, and a large number of defects formed as a result of the incorporation of Al^{3+} ions into the Mg^{2+} lattice.

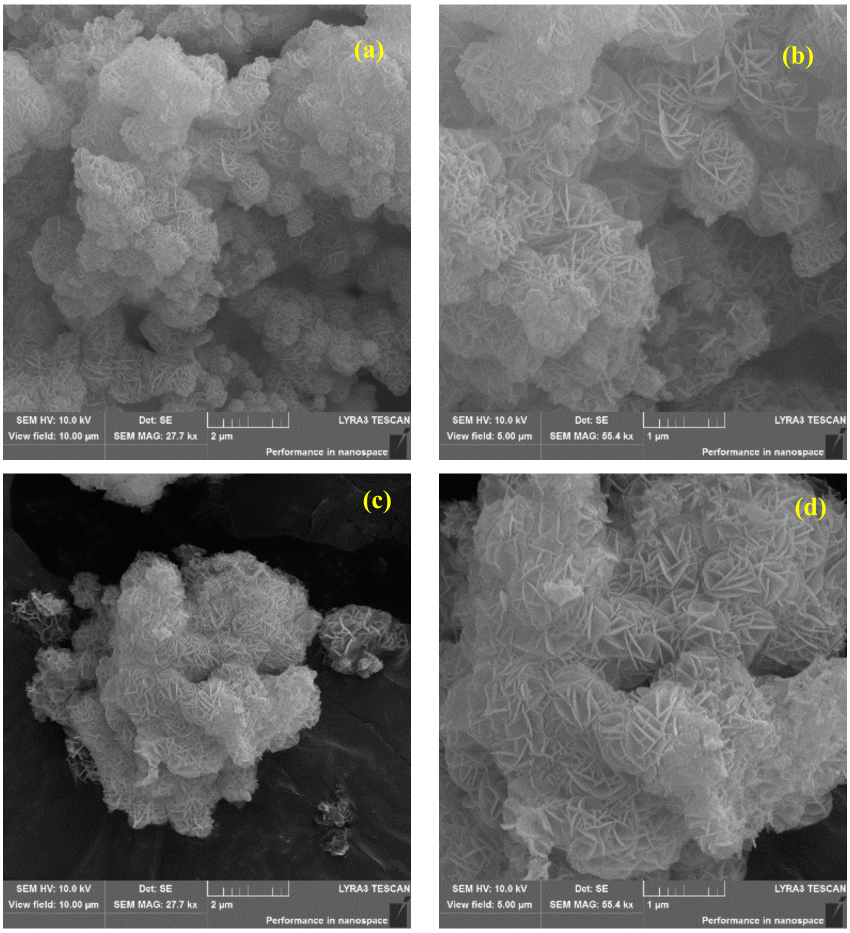
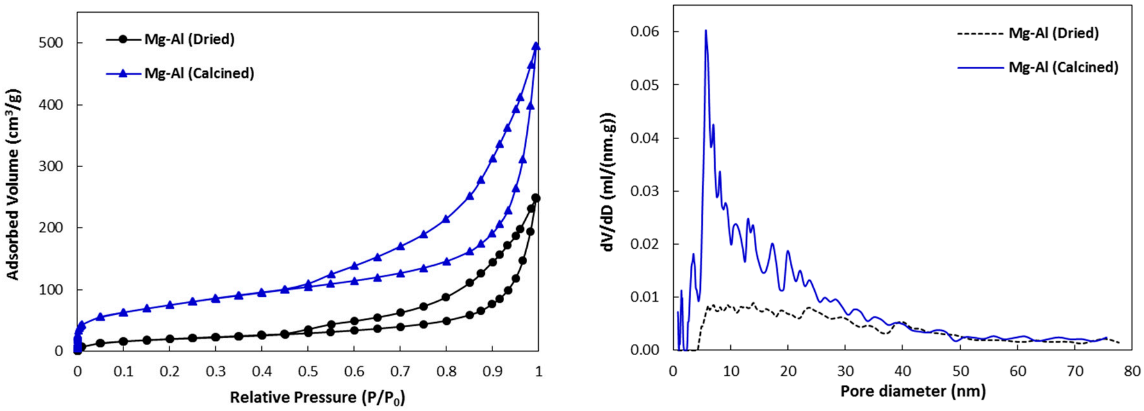


Figure 2. Scanning electron microscope (SEM) images of the (**a**,**b**) dried, and (**c**,**d**) calcined Mg-Al catalysts.



(**a**) (**b**)

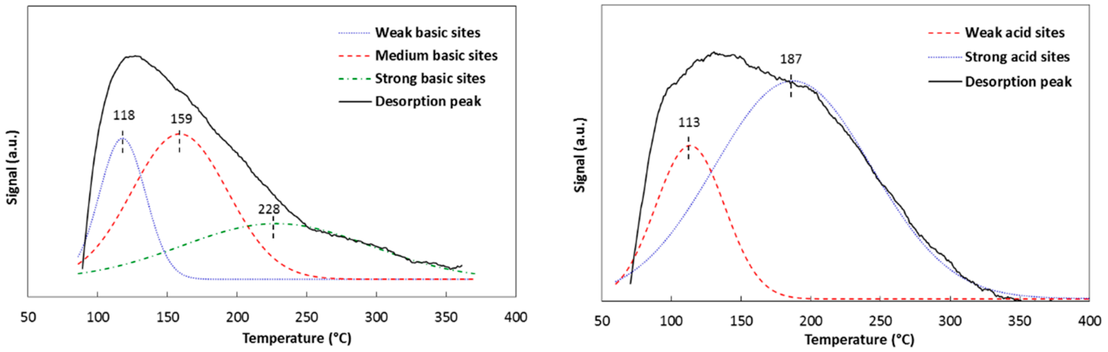
Figure 3. (**a**) N_2 physisorption isotherms, and (**b**) pore distribution of Mg-Al catalysts.

Table 1. Textural properties of Mg-Al catalysts.

Sample	Isotherm Type	Hysteresis	Specific Surface Area (m^2/g)	Total Pore Volume (cm^3/g)
Mg-Al (Dried)	IV	H3	73.3	0.308
Mg-Al (Calcined)	IV	H3	241.9	0.654

The CO_2 temperature-programmed desorption (CO_2-TPD) analysis was used for determination of the strength and amount of the basic sites of the calcined sample. The asymmetric CO_2 desorption peak is centered at around 100–130 °C, together with two shoulders at 150–180 °C and 200–250 °C, corresponding to three types of basic sites including the weak Brønsted OH groups, medium-strength metal-oxygen Lewis pairs, and strong Lewis basic sites-oxygen anions, respectively [27]. The basicity of hydrotalcite-derived mixed oxides is affected by the precursor composition, including the type of anions in the interlayers and the cations in brucite-like layers. The total basicity of the Mg-Al catalyst was calculated through the integration of the CO_2 desorption profile, which was deconvoluted into three Gaussian contributions corresponding to each type of weak, medium, and strong basic sites. The total basicity of the sample was found to be 1193 µmol/g, where the concentration of the weak, medium, and strong basic sites were 22.8%, 50.0%, and 27.2% of total basicity respectively. It has been reported that the higher basic sites with medium and strong strength could be beneficial for aldol condensation of benzaldehyde with heptanal [5]; therefore, the active basic sites in this reaction are mainly $M^{n+} - O^{2-}$ pairs.

The strength and density of the acid sites were determined using ammonia temperature-programmed desorption (NH_3-TPD) analysis (Figure 4b). The NH_3-TPD profile has two overlapping curves, where the first peak at around 110 °C could be due to the desorption of residual NH_3 weakly bonded to the surface of the catalyst, and could be attributed to the existence of Brønsted acid sites on the surface of catalysts, created by the existence of OH^- groups [28]; and the second peak at around 190 °C, might be caused by further desorption of stronger bonded NH_3 species from the Lewis acid sites ascribed to the presence of $Al^{3+} - O^{2-} - Mg^{2+}$ species in the structure of the mixed oxides and containing the Al^{3+} cations mainly in octahedral sites [28,29].



(**a**) (**b**)

Figure 4. (**a**) CO_2-TPD, and (**b**) NH_3-TPD of calcined Mg-Al catalyst.

2.2. *Catalytic Performance for the Aldol Condensation Reaction*

The catalytic activity for aldol condensation of benzaldehyde with heptanal was investigated in a fixed-bed flow reactor under solvent-free condition with the benzaldehyde to heptanal ratio of 2, at two different reaction temperatures (100 °C, 140 °C), at the reaction pressure of 1 MPa (Figure 5). The results of the reaction at 100 °C (Figure 5a) showed that after 10 h of reaction the heptanal conversion was around 30%, and after 20 h of reaction, the conversion started to decrease and reached around 16% after 44 h of reaction and then remained constant. In contrast, longer reaction time is favored to the formation of jasminaldehyde and 2-n-pentyl-2-n-nonenal. The jasminaldehyde selectivity was almost

27% after 32 h of reaction, and reached 40% after 44 h of reaction and remained almost constant until the end of the reaction (68 h). The selectivity to 2-n-pentyl-2-n-nonenal also followed the same trend and increased from 35% after 30 h to 52% after 68 h of the reaction.

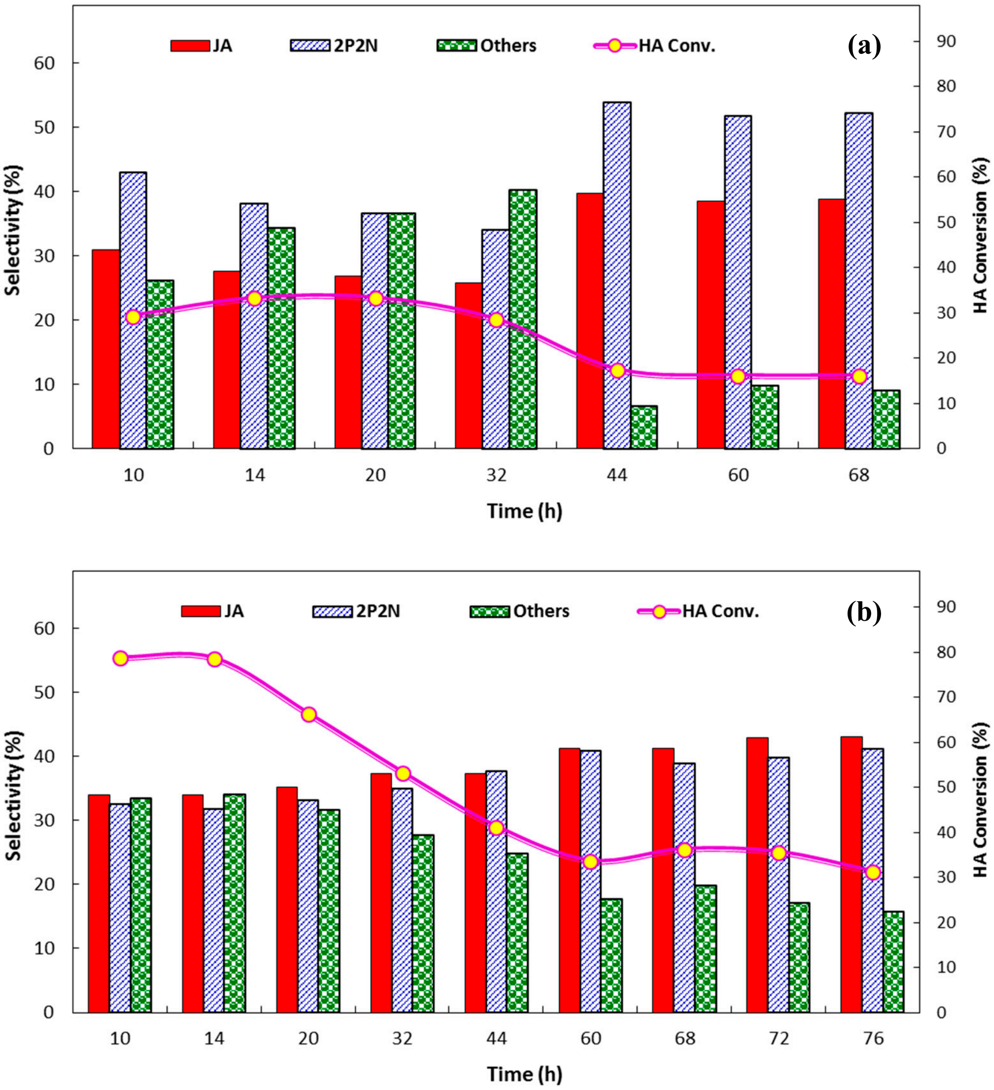


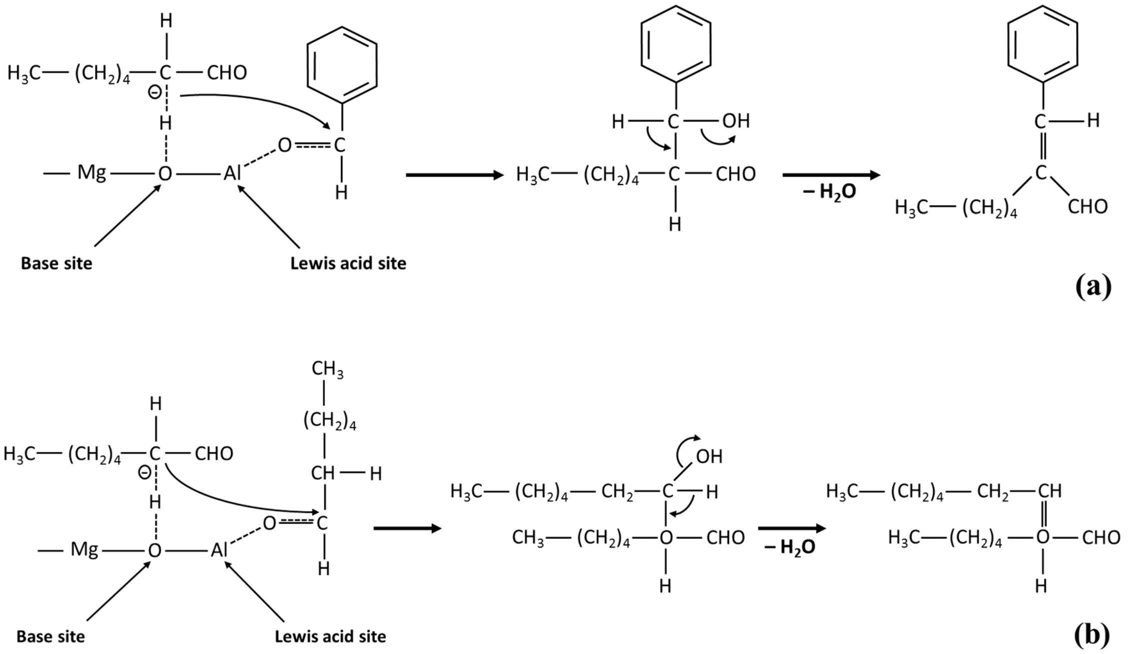
Figure 5. Aldol condensation of heptanal and benzaldehyde in a fixed-bed flow reactor over Mg-Al catalyst at (**a**) 100 °C, and (**b**) 140 °C. Reaction condition: P = 1 MPa, molar ratio benzaldehyde to heptanal = 2. HA: heptanal, JA: jasminaldehyde, 2P2N: 2-n-pentyl-2-n-nonenal.

By increasing the reaction temperature from 100 °C to 140 °C (Figure 5b), after 10 h of reaction, conversion of heptanal significantly increased to about 80%, which is about 2.5 times higher than the conversion at 100 °C, at same reaction time. However, after 14 h of reaction, the heptanal conversion decreased gradually and reached 36% after 76 h of reaction, which is still 2.2 times higher than the conversion at 100 °C. The selectivity to jasminaldehyde also slightly increased from 30% to 34% by increasing the reaction temperature (after 10 h) and gradually increased to 43% after 76 h of reaction. At 140 °C, the selectivity to 2-n-pentyl-2-n-nonenal was almost the same as jasminaldehyde during the reaction. Selectivity to 2-n-pentyl-2-n-nonenal was lower at 140 °C than its selectivity at 100 °C. The formation of other by-products (long-chain aldehydes) was lower at the higher temperature, especially in the first 32 h of reaction. By increasing the formation of jasminaldehyde and 2-n-pentyl-2-n-nonenal after 32 h of reaction, the formation of other products slightly decreased.

Improvement of heptanal conversion and jasminaldehyde selectivity by increasing the reaction temperature was also reported by other researchers [4,5,10,30], which is in line with the results obtained in the current study. Aldol condensation of benzaldehyde with heptanal using the zinc-modified Mg/Al oxides was studied by Tišler et al. [5], and they reported that the reaction rate increased by raising the temperature and the selectivity to jasminaldehyde also increased from 57% to 71% by increasing the reaction temperature from 80 °C to 140 °C. According to their findings, this increase in selectivity could be due to the higher heptanal reflux at the higher temperature, and consequently, lower concentration of heptanal in the reaction mixture, which decreased the possibility of self-condensation of heptanal, and increased the selectivity to jasminaldehyde. The same results were reported by Vrbková et al. [4,30], where the aldol condensation of benzaldehyde with heptanal was investigated using Mg-Al mixed oxides, Cs-MCM, and 1.5-K-Al_2O_3 catalysts. Adwani et al. [10] also reported that with an increase in the temperature from 80 °C to 160 °C the conversion of heptanal and selectivity to jasminaldehyde both increased, when chitosan-hydrotalcite nano-bio composite was used as the catalyst for this reaction. In another study by Fan [3], the aldol condensation reaction was studied using an acid-base bi-functional magnesium oxide catalyst, and they also reported that increasing the temperature from 100 °C to 140 °C, increased the heptanal conversion around 35% to around 94% after 5 h of reaction. The selectivity of jasminaldehyde remained almost unchanged by increasing the reaction temperature. All these aforementioned reported results for aldol condensation of benzaldehyde with heptanal were obtained in the batch mode reactors, and generally, a round-bottomed flask equipped with a condenser was used as the reactor. The aldol condensation in fixed-bed flow reactors has not been investigated in the reported literature.

A possible reaction mechanism for the production of jasminaldehyde via aldol condensation of benzaldehyde with heptanal is shown in Scheme 2a. The main basic sites in the un-calcined hydrotalcites are the Brønsted base sites (OH^- groups), while after calcination, Brønsted and Lewis base sites (O^{2-} anions) exist on the surface of the Mg-Al catalyst. Deprotonation of α–C atoms through the accessible base sites on the catalyst surface resulted in an initially activation of heptanal, and generates carbanion and leads to the formation of enolate anions. Simultaneously, benzaldehyde, by its O atom, is attached to the weak Lewis acid site (Al). The C=O groups of benzaldehyde are interacting with Lewis acid sites to polarize the C=O group and increase the positive charge on that α–C atom. Increasing the positive charge of α–C of benzaldehyde increases the possibility of it being attacked by enolate anions of heptanal. After attacking the α–C atom of benzaldehyde with enolate anion, an intermediate alkoxide is formed, which quickly deprotonates a water molecule and produces hydroxide and aldol product or a β-hydroxyaldehyde. Both acidic and basic sites cooperate for the production of jasminaldehyde [9,13]. Self-condensation of heptanal also resulted in the formation of 2-n-pentyl-2-n-nonenal during the reaction. The possible mechanism for this reaction is depicted in Scheme 2b. First, heptanal molecules are adsorbed on two acid and base sites of the catalyst, and an intermediate formed, which is then transformed into 2-n-pentyl-2-n-nonenal by releasing a water molecule.

In addition to jasminaldehyde and 2-n-pentyl-2-n-nonenal, the formation of another by-product was also observed. After 10 h of reaction at 100 °C, 26% of the other by-product was formed and increased to 40% after 32 h of reaction, then sharply decreased to around 10%. Formation of another by-product at 140 °C also slightly increased after 14 h, and then gradually decreased till the end of the reaction. It has been reported that in the oxidizing atmosphere and the presence of oxygen, oxidation of heptanal and benzaldehyde may result in the formation of heptanoic acid and benzoic acid [3,31]. However, in this study, due to the absence of air or oxygen in the reactor, there is not any possibility for oxidizing of the reactants, and these two acids were not detected in the gas chromatography analysis of product mixture. Heptanal, as an aliphatic aldehyde, is more reactive than benzaldehyde and competes for the acidic site along with benzaldehyde. The activated heptanal can continuously react with other heptanal or 2-n-pentyl-2-n-nonenal molecules. In the current study, it is hypothesized that owing to the presence of active sites on the surface hydrotalcites, heptanal and 2-n-pentyl-2-n-nonenal molecules are adsorbed on two base and acid sites, and the heptanal carbanion attacks the positively charged molecule, and longer chain aldehydes are formed. The formation of by-products could be decreased by increasing the molar ratio of benzaldehyde to heptanal, which can increase the chance of attacking the activated heptanal to positively charged benzaldehyde molecules, which are adsorbed on the Lewis acid sites on the surface of the catalysts.



Scheme 2. The possible reaction mechanism for the production of (**a**) jasminaldehyde via aldol condensation of benzaldehyde with heptanal, (**b**) 2-n-pentyl-2-n-nonenal via self-condensation of heptanal.

3. Materials and Methods

3.1. Catalyst Preparation

The Mg-Al catalyst derived from hydrotalcite-like precursors with the Mg/Al molar ratio of 3 was synthesized by coprecipitation of metal precursors at 60 °C and a constant pH of 9.5. Typically, the catalysts were prepared as follows: aqueous solutions of metal precursors, containing 1 mol/dm^3 of aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ (Lachner, p.a. purity) and magnesium nitrate $Mg(NO_3)_2{\cdot}6H_2O$ (Lachner, p.a. purity), was precipitated with a mixture of basic solution containing 2 mol/dm^3 potassium hydroxide KOH (Lachner, p.a. purity) and 0.2 mol/dm^3 potassium carbonate K_2CO_3 (Penta, p.a. purity). The filtered cake was washed with demineralized water until neutral pH of the filtrate, then dried in an oven overnight at 65 °C. Prior to the aldol condensation reaction, the dried sample was calcined in situ at 450 °C for 3 h under nitrogen atmosphere (5 °C/min).

3.2. Evaluation of Catalyst

The aldol condensation reaction was performed in a stainless steel fixed-bed reactor, with 700 mm length and an inner diameter of 17 mm. Three thermocouples were located at three different points of the reactor, at the beginning, center, and end of the catalyst bed. The reactor was loaded with a mixture of 5 g catalyst, with particle size of 224–560 µm, and silicon carbide SiC (0.1 mm) with the catalyst to SiC ratio of 1:1. A layer of SiC (1–2 mm) was also placed above and below the catalyst. Quartz wool plugs separated all individual layers. Before the reaction, the catalyst was calcined in situ at 450 °C for 3 h under nitrogen atmosphere, then the temperature was reduced to 100 °C, and the pressure was fixed at 1 MPa under a flow of N_2 (5 L/h).

After activation of the catalyst, the feedstock containing benzaldehyde and heptanal (both Sigma-Aldrich, St. Louis, MO, USA, 97%), with the benzaldehyde to heptanal molar ratio of 2, was pumped into the reactor with the flow rate of 10 g/h. The products of the reaction were analyzed by a gas chromatograph (Agilent 7890A, Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a flame ionization detector (FID), using a GC capillary column HP-5 (length: 30 m, inner diameter: 0.32 mm, film thickness: 0.25 μm).

3.3. Characterization of Catalyst

Inductively coupled plasma-optical emission spectrometry (ICP-OES; Agilent 725/Agilent Technologies Inc., Santa Clara, CA, USA) was used for the determination of the bulk metal contents in the prepared catalyst. For the analysis of the catalyst composition, around 500 mg of Mg-Al catalyst was dissolved in 10 mL aqueous solution of sulfuric acid H_2SO_4 and the solution heated. Then, the temperature of this solution was decreased and it was diluted with demineralized water, and heated to 100 °C for two minutes. Finally, the obtained solution was used for the analysis.

The TGA Discovery series (TA Instruments, Lukens Drive, NW, USA) was used for the thermogravimetric analysis (TGA). About 20 mg of the Mg-Al catalyst was located in an open aluminum crucible and the temperature increased from 50 °C to 900 °C (10 °C/min) under a flow of nitrogen (20 mL/min). An OmniStar GSD320 quadrupole mass detector (Pfeiffer Vacuum Austria GmbH, Vienna, Austria) was used to detect the fragments.

The morphology of the synthesized Mg-Al hydrotalcite was studied by a scanning electron microscope (SEM) (LYRA3 TESCAN; TESCAN ORSAY HOLDING, as, Brno, Czech Republic).

The crystallographic structure of the prepared catalyst was measured using a D8 Advance ECO (Bruker AXC GmbH, Karlsruhe, Germany) with CuKα radiation (λ = 1.5406 Å). The step time and step size were 0.5 s, and 0.02°, respectively. The Diffrac.Eva software with the Powder Diffraction File database (PDF 4 + 2018, International Centre for Diffraction Data) was used for the analysis of diffractograms.

The Autosorb iQ (Quantachrome Instruments Boynton Beach, FL, USA) was used for N_2-adsorption/desorption at −196 °C for the determination of surface textural properties (specific surface area, pore size distribution, and pore volume). Before the analysis, the sample was pretreated at 110 °C for 16 h, under vacuum.

The Autochem 2950 HP (Micromeritics Instrument Corporation, Norcross, GA, USA) was used for the CO_2 temperature-programmed desorption (CO_2-TPD) and ammonia temperature-programmed desorption (NH_3-TPD) analysis to determine the acid-base properties of the catalysts. Prior to the TPD analysis, about 100 mg of Mg-Al catalyst was pretreated at 450 °C with the heating rate of 10 °C/min for 1 h under flow of helium (25 mL/min), and then cooled down to °C. After pretreatment, the sample was subjected to the 10 vol.% CO_2/He (for CO_2-TPD) and 10 vol.% NH_3/He (for NH_3-TPD) with the flow rate of 25 mL/min for 30 min at 50 °C. Then, the gas was changed to helium (25mL/min) for 1 h at 50 °C to remove the weak physically adsorbed CO_2 or NH_3 molecules. Finally, the CO_2-TPD and NH_3-TPD were carried out by increasing the temperature from 50 °C to 400 °C with the heating rate of 10 °C/min, under helium (25 mL/min). The desorbed CO_2 and NH_3 in the outlet gas were detected by a thermal conductivity detector (TCD).

4. Conclusions

Solvent-free synthesis of jasminaldehyde via aldol condensation of benzaldehyde with heptanal was investigated in a fixed-bed flow reactor, using the Mg-Al catalyst derived from hydrotalcite-like precursors with the Mg/Al molar ratio of 3. Results showed that the catalytic performance is attributed to the presence of both Brønsted and Lewis (O^{2-} anions) base sites, and Lewis acid sites on the surface of the Mg-Al catalyst. First, heptanal is adsorbed on the available basic sites on the surface of the catalyst, and an enolate anion is formed by deprotonation of α–C atoms. At the same time, a benzaldehyde molecule is adsorbed on the weak acid site via its O atom; the C=O groups of benzaldehyde interact with Lewis acid sites, and the positive charge on that α–C atom increased by the polarization of the C=O group, which make it more likely to a nucleophilic attack by the heptanal carbanion. Both heptanal conversion and selectivity to jasminaldehyde are increased by increasing the reaction temperature from 100 °C to 140 °C. Simultaneous self-condensation of heptanal also resulted in the formation of 2-n-pentyl-2-n-nonenal. Heptanal as an aliphatic aldehyde is more reactive and competes for the acidic site along with benzaldehyde molecules; consequently, the possibility of the interaction between two heptanal molecules increases, especially at a low molar ratio of benzaldehyde to heptanal. In addition to jasminaldehyde and 2-n-pentyl-2-n-nonenal, other by-products are formed during the reaction. It is assumed that due to the presence of the active sites on the surface of the catalyst, the reactive heptanal molecule and 2-n-pentyl-2-n-nonenal also can be adsorbed on basic and acidic sites; the positively charged molecule is attacked by the heptanal carbanion and longer chain aldehyde, and produces the longer chain aldehyde. Formation of jasminaldehyde could be enhanced by increasing the molar ratio of benzaldehyde to heptanal to reduce the formation of by-products that are forming due to the self-condensation of heptanal molecules, or the interaction of heptanal and 2-n-pentyl-2-n-nonenal molecule that exists in the product mixture.

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