Performance of Carbon Nanofiber and Activated Carbon Supported Nickel Catalysts for Liquid-Phase Hydrogenation of Cinnamaldehyde into Hydrocinnamaldehyde

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Abstract The herringbone and platelet carbon nanofibers and the activated carbon were used as the supports of nickel catalyst for the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde (HALD). The hydrogenation of HALD and cinnamyl alcohol under the same experimental conditions was also performed to determine the susceptibility of the isolated and conjugated C=O and C=C bonds to hydrogenation. The catalytic activity and selectivity of the nickel supported on carbons of different structure were evaluated based on the determination of the rate constants of the hydrogenation reaction. The nickel particle size effect was found to be crucial for the catalyst performance.

Keywords Heterogeneous catalysis · XRD · Selective hydrogenation · Nickel catalyst · Carbon nanofibers · Cinnamaldehyde hydrogenation · Kinetics · Particle size effect

1 Introduction

Hydrogenation of α , β -unsaturated aldehydes such acrolein, crotonaldehyde, citral and cinnamaldehyde (CALD) provides the products which can be considered as precious starting materials for synthesis of fine chemicals. The final product of CALD hydrogenation is hydrocinnamyl alcohol (HALC, 3-phenyl propanol). The process can proceed via the formation of hydrocinnamaldehyde (HALD) or cinnamyl alcohol (CALC). The first route is thermodynamically more

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favored [1]. The partially hydrogenated intermediates of CALD hydrogenation are the most desirable chemicals in the market. The selective hydrogenation of the carbonyl group is preferred because the unsaturated alcohols are of high importance for the production of perfumers and pharmaceuticals. However, HALD is also valuable, for example, as an intermediate in the preparation of pharmaceuticals used in the treatment of HIV [2]. Generally, the most important task is to achieve the high selectivity of the hydrogenation reaction to partially hydrogenated CALD derivatives, CALC or HALD, for high conversion level.

Direct hydrogenation processes based on heterogeneous catalysis are being developed to produce unsaturated alcohols and hydrogenated aldehydes. Porous carbon materials such as activated carbons (ACs), carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been mainly used as support of mono- and bi-metallic Pt, Ru and Ir catalysts for the selective hydrogenation of CALD to CALC [3–7]. Some studies addressed the metal particle size effect on the hydrogenation of CALD in terms of the selectivity towards CALC. It was shown for the Pt and Rubased catalysts that the selectivity to unsaturated alcohol increases with increasing metal particle size [8–10].

The carbon support has an advantage over mineral one because organic compounds, especially aromatics, show the affinity for hydrophobic carbon surface in contrast to the mineral support. CNFs seem to be very promising carbon support due to their mesoporous nature and developed surface area, reaching up to 300 m²/g, and the open edges of graphene layers, which constitute sites that are readily available for chemical and physical interactions [11, 12]. It was reported the superiority of the Pd/CNF catalyst compared to the high surface area activated carbon supported Pd for the hydrogenation of CALD in liquidphase reactions [13]. A 90 % selectivity towards HALD

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was achieved over Pd/CNF. The higher activity of Pd/CNF compared to activated carbon supported palladium catalyst can be related to the reduced mass transfer limitation due to the absence of microporosity in the CNF support. Ruthenium supported on CNFs showed also higher selectivity towards HALD (70–90 %) than that obtained with Ru on activated carbon (30–40 %) [9]. Recently, nitrogen-doped CNTs have been revealed as promising support for Pd in the liquid-phase hydrogenation of CALD. Nitrogen incorporation in the CNT structure improved not only the catalytic activity of Pd/N-CNTs but also the selectivity towards the C=C bond hydrogenation [14, 15].

Since the nickel promotes the hydrogenation of C=C bond rather than C=O bond when both double bonds are present in the molecule of reactant, HALD is preferentially formed during hydrogenation of CALD. Chin et al. [16] obtained a high value of conversion (74 %) and HALD selectivity (80 %) during vapour phase hydrogenation of CALD at 300 °C over Ni/y-Al₂O₃ catalyst. A significant improvement of the catalytic activity and selectivity towards HALD was obtained in the liquid phase hydrogenation of CALD over Pt-Ni/CNTs catalyst reduced by KBH₄ due to the electronic synergetic effect of Pt-Ni-B [17]. In our work, the catalytic CALD hydrogenation was carried out in the presence of CNF and activated carbon supported nickel catalysts in a liquid phase medium. Until know little work has been carried out on the hydrogenation of α,β -unsaturated aldehydes over CNF supported nickel catalysts [18]. To our knowledge, the catalytic performance of the nickel supported on different types of CNF for the hydrogenation of CALD has been not reported yet. This is important in terms of searching for a highly active and selective catalyst towards HALD.

In this paper, the results of the study on the hydrogenation of the C=C bond and the C=O group in CALD over carbon nanofiber and activated carbon supported nickel catalysts have been presented. The susceptibility of the isolated and conjugated of C=C and C=O bonds to hydrogenation was evaluated based on the constant rates of hydrogenation reactions. The effects of the structure of carbon support, the nickel particle size and the catalyst method preparation on the catalytic activity and selectivity of the prepared catalysts in the hydrogenation of CALD were determined.

2 Materials and Methods

2.1 Materials

Cinnamaldehyde, HALD, HALC, CALC, nickel nitrate $Ni(NO_3)_2$ ·6H₂O, and alumina were purchased from Aldrich (Steinheim, Germany). The activated carbon Norit SX

ULTRA CAT (AC) was supplied by Norit Company. The gases used in this work, hydrogen (99.999 %), nitrogen (99.999 %), methane (99.995 %) and propane (99.95 %) were provided by Messer.

2.2 CNF Synthesis

Herringbone-type CNFs (hCNF) were synthesized by decomposition of methane at 550 °C over Ni/Al₂O₃ with a yield of 5.3 g_{CNF}/g_{cat} . Platelet-type CNFs (pCNF) were obtained by catalytic decomposition of propane at 500 °C using the same catalyst. The yield of pCNF was slightly lower, 4.9 g_{CNF}/g_{cat} . For each synthesis, 0.2 g of catalyst was spread in the bottom of a quartz boat which was placed into a horizontal type furnace. After catalyst reduction under hydrogen flow, a mixture of carbon precursor and hydrogen (1:1 v/v) was introduced into the reactor for 1 h. The as-received CNFs were purified with hydrofluoric acid at room temperature for 1 h in sonication bath to remove the nickel and alumina. Finally, the samples were thoroughly washed with hot distilled water (until the pH reached 7) and then dried overnight at 120 °C.

2.3 Catalysts Preparation

hCNF, pCNF and AC were used as the support of Ni catalyst. CNF and AC supported Ni catalysts (Ni/hCNF, Ni/ pCNF, Ni/AC) were prepared by incipient wetness method. Prior to impregnation the support was wetted with ethanol to overcome hydrophobicity of CNF and subsequently was impregnated with an appropriate amount of aqueous nickel nitrate solution to yield a Ni loading of 10 wt% in the catalyst. AC before Ni loading was demineralized with HCl and HF to remove the mineral constituents. Another ACbased Ni catalyst was prepared by spray-drying method (Ni/AC-SD) [19]. An aqueous suspension of AC and nickel nitrate was mixed for 1 h to receive a homogeneous mixture and subsequently subjected to a Büchi mini spray dryer 190 with a 0.5 mm nozzle at an inlet temperature of 230 °C. After drying, the Ni-loaded CNFs and ACs were heat treated at 400 °C for 3 h under argon atmosphere. ASA analysis showed that the Ni content in all prepared catalysts is comparable, between 9.8 and 10.1 wt%.

2.4 Catalyst Characterization

The porous structure parameters of the supports and catalysts were determined from sorption of N_2 at 77 K with a Nova 2200 gas sorption analyzer (Quantachrome). Prior to the measurements, the sample had been outgassed overnight at 300 °C. The specific surface area was calculated from the BET equation. The Gurvitch rule and Kelvin condensation theory [20] were applied to establish the

extent of microporosity and the mesopore volume distribution, respectively. The amount of nitrogen adsorbed at the relative pressure of $p p_0^{-1} = 0.96$ was applied to determine the total pore volume V_T which corresponds to the sum of the micropore V_{mic} (<2 nm) and mesopore V_{mes} (2-50 nm). The mesopore fraction is expressed as the ratio of mesopore volume to the total pore volume (V_{mes}/V_T) . The structural arrangement of graphene layers in the CNF and the dispersion of NiO nanoparticles on the carbon surface support was investigated by high resolution transmission electron microscopy (HRTEM) performed on FEI Tecnai G² 20X-TWIN microscope, operating at an acceleration voltage of 200 kV. The sample was prepared by ultrasonic dispersion in ethanol and a drop of the resultant suspension was placed on a holey carbon support grid. The X-ray diffraction (XRD) was applied to determine the size of NiO crystallites, using a Rigaku Ultima IV X-ray diffractometer and CuKa radiation.

2.5 Hydrogenation

The hydrogenation reactions were carried out in a microautoclave under hydrogen pressure of 3 MPa at 160 °C. 20 mL of substrate solution (1 % in toluene) and 50 mg of catalyst were placed into the reactor for each experiment. The reaction mixture was kept homogeneous with a magnetic stirrer at stirring frequency of 120 min^{-1} . Before starting the reaction, the catalyst was reduced at 360 °C for 1 h under a 3 MPa hydrogen pressure. Afterwards the reactor was cooled to the temperature required for the process, and the reaction substrate was injected into the reagents. Toluene was used as a solvent because cinnamyl alcohol is poorly dissolved in aliphatic hydrocarbons. It should be added that the catalytic hydrogenation of toluene was not observed in the applied process conditions. The analysis of reaction products was performed using an Agilent GC 6850 gas chromatograph equipped with a FID detector and a HP-1 column (30 m \times 0.25 mm \times 0.25 µm film thickness). The injector temperature was 250 °C, split 5, and a constant pressure of 100 kPa. The temperature of GC oven was kept constant at 100 °C. The identification of compounds in the reaction products was done by comparison of retention time of standard. Two independent chromatographic analyses were performed for each sample.

3 Results and Discussion

3.1 Carbon Supported Nickel Catalysts

The catalysts containing 10 wt% of Ni were prepared using two types of CNFs, i.e., platelet and herringbone, and the activated carbon as the supports. Both types of CNFs are constituted of graphene layers with the exposed edges but different orientation within the structure. The platelet CNFs have graphene layers orientated perpendicular to the fiber axis (Fig. 1a). In the herringbone CNFs they are stacked at an angle to the fiber axis (Fig. 1b). The different orientation of graphene layers determines the catalytic behavior of metal particles supported on the CNF. Park and Baker [21] documented well how strong influence has a change in orientation of the graphene layers within the nanofiber structure on the selectivity of the supported nickel particles for hydrogenation of alkenes and dienes. In our work, the performance of nickel supported on the traditional carbon material such activated carbon has been also studied to compare with that of supported on the CNF.

Table 1 shows the textural parameters of the supports and the prepared nickel catalysts. The CNFs are mesoporous in their nature. The mesopore ratio for the





Table 1	Characteristics of porous	texture of the supports and	the catalysts, and the s	size of NiO particles	determined by XRD
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Support/catalyst	$S_{BET} (m^2/g)$	$V_T (cm^3/g)$	V _{mes} (cm ³ /g)	V _{mic} (cm ³ /g)	Mesopore volume distribution (cm ³ /g)			Average NiO size (nm)
					2–5 nm	5–10 nm	10–50 nm	
hCNF	150	0.417	0.323	0.094	0.036	0.062	0.225	
Ni/hCNF	127	0.337	0.282	0.055	0.036	0.060	0.186	5.5
pCNF	251	0.486	0.386	0.100	0.060	0.115	0.211	
Ni/pCNF	229	0.367	0.277	0.090	0.053	0.064	0.160	4.7
AC	1020	0.809	0.437	0.372	0.117	0.076	0.244	
Ni/AC	959	0.613	0.254	0.359	0.090	0.058	0.106	5.3
Ni/AC-SD	682	0.460	0.201	0.259	0.076	0.480	0.077	4.2

synthesized CNFs is almost 0.8. Comparing the porous texture of both CNFs samples, pCNFs are characterized by better developed porosity. The BET surface area of pCNFs is high, $250 \text{ m}^2/\text{g}$, whereas $150 \text{ m}^2/\text{g}$ is obtained for hCNFs. As expected the porosity development of the catalysts is lower compared to respective support due to pore blockage by NiO particles.

However, the mesoporous character of the CNFs is preserved after Ni loading. AC shows a much lower contribution of mesopores to the total pore volume than CNFs (0.54), and its Ni loading leads to the predominance of micropores in the porous texture of the obtained catalysts. It is interesting to note that the use of spray-drying for metal loading results in a decrease of mesopore volume only, whereas incipient wetness impregnation reduces significantly both the micropores and mesopores volumes. In contrast to CNF supported Ni catalysts, AC-based catalysts are distinguished by very high surface area (Table 1).

Figure 2 shows HRTEM images of NiO particle distribution in the prepared catalysts. It can be clearly seen that the Ni/AC-SD catalyst is characterized by the largest dispersion of NiO nanoparticles on the surface.

XRD examination was applied to determine the average size of NiO crystallites in the prepared catalysts. The diffractogramms are shown in Fig. 3 and the NiO particle size determined based on XRD is given in Table 1. As can be observed the average NiO size increases in the direction: Ni/AC-SD < Ni/pCNF < Ni/AC < Ni/hCNF which confirms that the Ni/AC-SD catalyst has the smallest size of NiO particles amongst the studied catalysts. Comparing CNF-based catalysts, the size of NiO supported on pCNFs is considerable smaller than that on hCNFs (4.7 vs. 5.3 nm).

3.2 Hydrogenation of CALD Over Carbon-Supported Ni Catalysts

Cinnamaldehyde has three potential hydrogenation sites in its molecule: the carbonyl group C=O, the C=C bond conjugated with the carbonyl group, and aromatic ring. However, the aromatic ring does not undergo hydrogenation in the presence of Ni catalyst under mild process conditions. Therefore, our work is focused on the hydrogenation of C=C and C=O bonds in CALD (Fig. 4). It has been assumed that the conversion of CALD to HALC proceeds directly without desorption of intermediate product, i.e. HALD, from the catalyst surface. This implies that the hydrogenation of CALD would proceed on the active sites through three parallel transformation pathways.

Further, $k_3 = 0$ since CALC was not detected in the reaction products. k_2 corresponds to the rate constant k_{CO} for the C=O hydrogenation and the sum of $k_1 + k_2$ is attributed to the rate constant $k_{=}$ for the C=C hydrogenation.

The kinetics of hydrogenation reaction can be described by the pseudo-first order kinetics model. The rate of hydrogenolysis of the C=C bond or the C=O group is a function of one substrate only due to the hydrogen excess (3 MPa) used under the conditions examined in our work. This implies that the concentration of hydrogen is nearly constant during hydrogenation reaction. Therefore, the reaction rate can be expressed by a classical equation:

$$\ln \frac{C_0}{C} = k \times t$$

where C denotes the concentration of a given reactant, C_0 is the initial concentration and k is the rate constant. The plot of $\ln \frac{C_0}{C}$ as a function of time gives the linear relationship where the slope of the line corresponds to the reaction rate constant.

Figure 5 shows the catalytic activity of different carbon supported Ni catalysts as a function of reaction time for the CALD hydrogenation. Prior to the hydrogenation runs, we performed optimization of stirring frequency to assure that the reactions are carried out within the intrinsic kinetic region. The catalysts contain the same amount of Ni but differ in the support which determines the porous texture of the catalyst and the size of NiO particles (Table 1).

It can be seen from Fig. 5 that the CALD hydrogenation over carbon supported Ni catalyst leads mainly to HALD,

Fig. 2 TEM images of NiO distribution for different carbon supports, Ni/AC-SD (a), Ni/AC (b), Ni/hCNF (c) and Ni/pCNF (d)



Fig. 3 XRD spectra of carbonsupported nickel catalysts. Ni/ hCNF (a), Ni/pCNF (b), Ni/AC (c) and Ni/AC-SD (d). White circle, carbon; black square, NiO

indicating the preferential hydrogenation of C=C bond. The calculated values of rate constants for the catalytic hydrogenation of CALD are presented in Table 2. The

correlation coefficient (R^2) of the linear plots for the determination of $k_{=}$ and k_{CO} were in the range of 0.996–0.998 and 0.983–0.998, respectively. The high



Fig. 4 Possible reaction pathways for the hydrogenation of cinnamaldehyde

values of R^2 demonstrate that the hydrogenation of CALD under experimental conditions used in the work can be described by a pseudo first-order rate equation for two parallel reactions.

As expected the hydrogenation of double bond over Ni catalyst is much more favorite than carbonyl group. The rate for the C=C hydrogenation compared to the C=O hydrogenation is 18–44-fold higher, depending on the examined catalyst. The ratio $k_{\rm z}/k_{\rm CO}$ is considered as a measure of the catalyst selectivity toward the formation of HALD (Table 2). The $k_{\rm z}/k_{\rm CO}$ value is the largest for the Ni/AC catalyst, indicating the highest selectivity for the C=C hydrogenation, however, at the lowest reaction rate.

Generally, an increase in the catalytic activity is followed by a decrease in the selectivity to HALD. The Ni/pCNF catalyst is the most promising amongst all studied catalysts, taking into account its highest catalytic activity and a relatively high selectivity for the hydrogenation of C=C bond. Amongst platelet, ribbon and spiral-like CNFs, the best performance of the nickel dispersed on the platelet CNFs was also reported for the partial hydrogenation of 1,3butadiene to 1-butene [21]. The changes in the catalytic activity and selectivity of the nickel supported on the CNFs of different structure were explained in terms of the variations in crystallographic orientations of the metal particles associated with the structure of the support. It is believed that orientation of graphene layers determines the faces of a metal particle which are required to catalyze certain reactions [22].

Ni/AC-SD shows only slightly worse catalytic activity than Ni/pCNF, however its selectivity is poor. It seems that the high reaction rate for the hydrogenation of C=C bond

Table 2 Reaction rate constants for hydrogenation of CALD over different carbon supported Ni catalysts (160 $^{\circ}$ C, $p_{H_2} = 3$ MPa) min⁻¹

Catalyst	k_	k _{CO}	k_/k _{CO}
Ni/hCNF	0.0261	0.0008	32.6
Ni/pCNF	0.0383	0.0015	25.5
Ni/AC	0.0174	0.0004	43.5
Ni/AC-SD	0.0341	0.0019	17.9

Fig. 5 Cinnamaldehyde conversion and product distribution as a function of reaction time at 160 °C and under 3 MPa over different carbon supported nickel catalysts. *Black circle*, CALD; *white circle*, HALD; *cross*, HALC



obtained for Ni/AC-SD is attributed to the smallest NiO particles in size which makes it very active. The very fine NiO distribution in the Ni/AC-SD catalyst was obtained due to the introduction of the nickel on the carbon surface by spray drying method which does not lead to the blockage of the porosity. The Ni/AC-SD catalyst has only slightly lower BET surface area compared to the initial AC (960 vs. 1020 m^2/g). The same catalyst (Ni/AC) but prepared by classical incipient wetness impregnation shows the worst catalytic activity probably due to the larger NiO particles. This is in line with the finding reported by Giroir-Fendler et al. [8]. In case of large particles, the C=C bond remains far from the metal surface due to steric hindrance related to the phenyl group. However, there is no steric constraint for approach and adsorption of the C=C bond on the surface of smaller particles because the phenyl group lies aside the metal surface. The lower catalytic activity of Ni/hCNFs than that of Ni/pCNF can be also partially attributed to the difference in the NiO crystallite size (Table 1).

The conjugation of the C=C bond with C=O bond in the CALD molecule has an influence on their reactivity, in particular in case of contribution of the ionic reactions. Such bonds combination determines the molecular structure, affecting the configuration and rigidity of the molecule. This suggests that the hydrogenation reaction of C=C bond and C=O bond should proceed with different rate depending on the system, conjugated (CALD) or isolated (HALD and CALC).

3.3 Hydrogenation of HALD and Cinnamyl Alcohol Over Carbon Supported Ni Catalysts

HALD and CALC were subjected to the hydrogenation in the same conditions as applied for CALD, i.e., at 160 °C under a hydrogen pressure of 3 MPa for 30, 60 and 90 min, to determine the reaction rate constants for different catalysts. The hydrogenation of C=O bond in HALD and C=C group in CALC leads to the formation of HALC (Figs. 6, 7).

The reaction rate constants for the hydrogenation of HALD and CALC are given in Table 3. The R^2 of the linear plots for the determination of k_{CO}' and $k_{=}'$ were in the range of 0.951–0.990 and 0.966–0.999, respectively. The considerable higher catalytic activity of Ni/pCNF and Ni/AC-SD for the hydrogenation of both HALD and



Fig. 6 Hydrogenation pathway of hydrocinnamaldehyde



Fig. 7 Hydrogenation pathway of cinnamyl alcohol

CALC, compared to Ni/hCNF and Ni/AC, could be attributed to the size of Ni particles. Ni/pCNF and Ni/AC-SD are characterized by distincly smaller NiO particles (4.7 and 4.2 nm, respectively) in size that those of Ni/hCNF and Ni/AC (5.5 and 5.3 nm, respectively). Moreover, the small size of NiO particles ensures better dispersion of the metal, resulting in the higher concentration of the active sites on the carbon surface. The obtained results indicate that the size of nickel crystallite are crucial for the hydrogenation of C=O bond in CALD over different carbon supported catalysts in the conditions applied in this work. The lower size of metal particles the smaller steric hindrances to reach the active site by the reagent molecule.

The comparable values of the rate constants for the hydrogenation of C=O group in CALD (Table 2) to those obtained for HALD (Table 3) indicate that the hydrogenation rate of C=O group is not affected by the presence of conjugated unsaturated bond. On the contrary, the conjugation of the C=C bond with C=O group enhances the C=C hydrogenation over all catalysts to a high extent (k_{\pm} vs. k_{\pm}' , Tables 2, 3), i.e., even up to fourfold, as observed for Ni/hCNF. Presumably, the impact of the adjacent C=O group on the hydrogenation rate of the C=C bond is related to the enhancement of the polarity of CALD molecule. This leads to the higher affinity of the substrate to the support surface that increases the probability of the reaction occurrence.

The nickel supported on the hCNFs shows the lower catalytic activity compared to the Ni/pCNF and Ni/AC-SD. One of the reasons of this phenomenon could be the larger size of supported NiO particles. The lowest catalytic activity among studied catalysts for the hydrogenation of CALD, HALD and CALC was obtained for the Ni/AC catalyst prepared by incipient wetness method. While the nickel dispersed on the same support by spray drying exhibits the superior behavior. The difference between both catalysts (Ni/AC vs. Ni/AC-SD) lies in different metal

Table 3 Reaction rate constants for hydrogenation of HALD and CALC over different carbon supported Ni catalysts (160 °C, $p_{H_2} = 3 \text{ MPa}) \text{ min}^{-1}$

Catalyst	HALD k _{CO} '	CALC k='
Ni/hCNF	0.0008	0.0062
Ni/pCNF	0.0016	0.0193
Ni/AC	0.0004	0.0067
Ni/AC-SD	0.0022	0.0160

particle size (5.3 vs. 4.2 nm) and textural parameters (S_{BET} 682 vs. 959 m²/g, V_T 0.460 vs. 0.613 cm³/g). Based on the comparison of Ni/AC-SD and Ni/pCNF in terms of porosity development (Table 1) and the reaction rate constants (Table 2) it can be concluded that the nickel particle size has a crucial influence on their catalytic activity. Both catalysts differ in their porosity to a high extent, whereas the metal particle size is not so much different.

4 Conclusions

The hydrogenation of CALD and its partially hydrogenated products HALD and CALC over carbon supported nickel catalyst was found to be strongly dependent on the metal particle size. Regardless of the type of carbon support, the smaller nickel particles, the better performance of the catalyst in the liquid-phase hydrogenation of CALD to HALD at 160 °C under hydrogen pressure of 3 MPa. For a given category of carbon support, i.e. CNFs or ACs, the higher surface area enhances the dispersion of the nickel particles. It was found that Ni/pCNF and Ni/AC-SD catalysts show the highest catalytic activity in the hydrogenation reactions. The comparison of the rate constants for CALD and HALD hydrogenation under the same experimental conditions revealed that the presence of the C=O group increases strongly the hydrogen addition to the C=C bond. While the hydrogenation of the C=O group is not affected by the presence of conjugated C=C bond as was found comparing the constant rates for the hydrogenation of CALD and CALC.

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