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Green-synthesized MIL-100(Fe) modified with palladium as a selective catalyst in the hydrogenation of citronellal to citronellol

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Abstract

The influence of palladium embedded into green-synthesized MIL-100(Fe) and its role as a selective catalyst in the hydrogenation of citronellal into citronellol were investigated. MIL-100(Fe) was synthesized in water at 95 °C without addition of hydrofluoric acid (HF). The loading of Pd was carried out using wet impregnation method with Pd loadings of 1 and 3 wt%. The obtained materials were then tested as catalyst in hydrogenation of citronellal in a batch reactor. XRD analysis confirmed the high crystallinity of the synthesized MIL-100(Fe). FTIR analysis indicated the deprotonation of carboxylic ligand and its coordination with Fe3+ metal ions. The materials had thermal stability up to 287 °C according to TG/DTA analysis. The modification with palladium changed the morphology and decreased the crystallinity, surface area, and porosity as shown by XRD, SEM, TEM and nitrogen sorption isotherm analysis. The presence of Pd successfully increased the catalytic performance and selectivity to convert the citronellal into citronellol through a hydrogenation reaction, and an optimum 63.7% conversion and 22.2% selectivity to citronellol was attained over 3% Pd/MIL-100(Fe).

1. Introduction

Indonesia exports 90% of the world’s raw materials for perfume. However, in 2016, the value of Indonesia’s essential oil exports was only USD 318.4 million while its imports reached USD 554.7 million [1]. Hence, the processing of essential oils is important to increase its value as an export commodity. One of the essential oil derivatives that is used for making perfumes is citronellol. Citronellol can be obtained from lemongrass (Cymbopogon nardus), whose main components are citronellal (32%–45%), citronellol (12%–15%), and geraniol (12%–18%) [2]. Considering the limited citronellol content, it is necessary to optimize citronellol products through the selective hydrogenation of citronellal to citronellol.

Citronellal can be converted to citronellol through hydrogenation reactions using additional reducing agents, such as the metal hydrides sodium borohydride (NaBH4) and lithium aluminum hydride (LiAlH4). LiAlH4 has a greater reduction power than NaBH4, but both reducing agents are not environmentally friendly [3]. The use of heterogeneous catalysts is an attractive choice according to the principle of green chemistry, given the easier separation factor, higher thermal stability, and potential reuse and corrosion prevention of such catalysts [4]. Several heterogeneous catalysts based on porous materials that have been studied for citronellal conversion into citronellol are Ru/SiO2 [5], RuSiO2 and RuTiO2 [6], Ni/Zr-BEA [7], and Pt-multiwalled carbon nanotubes [8]. However, the low conversion value and selectivity of existing catalysts encourage a search for...
more promising catalyst innovations. One class of materials that has the potential to be a heterogeneous catalyst in the citronellal hydrogenation reaction is a hybrid material called metal–organic frameworks (MOFs).

MOFs are hybrid porous materials composed of metal ions or metal oxide clusters as nodes and bidentate or polydentate ligands as linkers, which can form three-dimensional networks and act as host materials for various types of guest molecules with good porosity and thermal stability [9]. The existence of coordinated unsaturated metal sites in MOFs supports their interactions with substrates and metal ions, acting as central Lewis acid or redox processes [10, 11]. Several MOFs have been studied as hydrogenation catalysts, including the hydrogenation of styrene using AEPF-2/Mg(2,6-AQDS)(H2O)2 [12], hydrogenation of 1-octene using [Ru6(BTC)2Cl4] [13], hydrogenation of 1,3-butadiene using IRMOF-3-Si-Au [14], and hydrogenation of 1-octene and 2,3-dimethylbutene using MIL-101(Rh)-SO3 and ZIU-28 [15].

The innovation and development of MOFs as catalyst materials is continually improving. For example, post-synthesis modification incorporating metal or metal nanoparticles can increase the catalytic power in hydrogenation reactions and add active sites to MOFs-based catalysts [16]. MOFs based on Fe(III) are good enough to be developed as catalysts, including MIL-100(Fe) (Material of Institute Lavoisier-100(Fe)) or {Fe2O(H2O)2(OH)}C6H3(CO2)3L2nH2O. This kind of MOF is composed of Fe(III) metal ions coordinated with benzene-1,3,5-tricarboxylic acid. The Lewis acid site on Fe(III) can be produced by removing two terminals of H2O molecules from octahedral iron and by the arrival of anions on vacuum activation. Thus, MIL-100(Fe) has a large Lewis Fe acid level in the pore. This structural characteristic indicates that this material is good for absorption (e.g., the substrate diffusion process in the catalysis process) [17].

Palladium nanoparticles supported on MOF has been studied in several catalytic reactions, including hydrogenation reaction [18]. Palladium is a noble transition metal that has a high affinity for hydrogen, so it is expected to be highly beneficial in the catalytic reaction of citronellal hydrogenation. The development of Pd metal in MOFs has been widely carried out, among others, in Pd/ZIF-8 [19], Pd/DUT-67 [20], Pd-in-USY-67 [21], Pd@MIL-125(Ti) [22] and Pd@MIL-101 [23]. Cirujano et al reported the hydrogenation of citronellol to isopulegol using the catalyst Pd@MIL-100(Cr) showed conversion with a selectivity of 86% for 18 h [24]. More recently, Pd@MIL-100(Fe)-series were developed and used for some catalytic reactions. For instances, Wang et al demonstrated the utilization of Pd@MIL-100(Fe) and PdAu@MIL-100(Fe) to enhance the photocatalysis efficiency in N-alkylation reaction of amines with alcohols under visible light irradiation [25, 26].

In case of catalytic hydrogenation, Pd@MIL-100(Fe) was tested for reduction of 2/3/4-nitrophenol which exhibiting high catalytic activity and the synergistic effect between Pd nanoparticles and MIL-100(Fe) as reported by Xu et al [27]. Moreover, Li et al studied hydrogenative ring-rearrangement of 5-hydroxyethyl furfural over Pd/MIL-100(Fe) with a conversion rate of 99.9% was achieved at 150 °C and after 24 h [28]. So far, research on the hydrogenation of citronellol to citronellol using Pd-modified MIL-100(Fe) catalyst has never been reported. The encapsulation of palladium in MIL-100(Fe) is expected to increase the number of catalytic active sites and thereby increase the binding capacity with hydrogen and maximize the interaction of MIL-100(Fe) with citronellol substrates to achieve high catalyst activity and selectivity.

2. Experimental

2.1. Reagents and materials

The reagents included Fe(NO3)3·6H2O (Merck, 98%), H2BTC (Sigma Aldrich, 95%), Pd(acac)2 (Sigma Aldrich, 99%), (±)-Citronellol (Sigma Aldrich, >95%), aquadest (Bratachem, Indonesia), chloroform (Merck, 99%), hydrogen, and nitrogen (5.0 grade. Ultra-high purity, SAMATOR Gas Indonesia). All reagents were high grade and were used as purchased without any further purification.

2.2. Synthesis of MIL-100(Fe)

MIL-100(Fe) was prepared following a modified procedure [29]. Fe(NO3)3·6H2O (4.04 g, 10 mmol) and H2BTC (1.89 g, 9 mmol) were dissolved in water (6 ml) into a three-neck round-bottom flask equipped with a magnetic stirrer and reflux condenser. The solutions was heated at 95 °C and stirred at 400 rpm for 12 h. The solution was then cooled, and the reddish brown precipitate was purified three times with water (35 ml) and ethanol (35 ml) at 70 °C for 24 h and filtered, dried, and activated at 120 °C for 2 h.

2.3. Preparation of Pd/MIL-100(Fe)

Pd/MIL-100(Fe) was prepared following a modified procedure [30]. A series of Pd/MIL-100(Fe) catalysts with varying Pd loadings (1 and 3 wt%) were prepared by the impregnation of a MIL-100(Fe). The solution of Pd(acac)2 (0.028 g, 0.093 mmol) and (0.085 g, 0.281 mmol) were dissolved in chloroform (5 ml) and slowly drop-wise added to MIL-100(Fe) (2 g, 1.996 mmol) under continuous stirring for 2 h forming an orange paste,
respectively. The solvent was then evaporated under vacuum. The resulting powder was reduced under hydrogen flow for 2 h at 140 °C.

2.4. Materials Characterization
XRD patterns were recorded on a Philips X’Pert MPD diffractometer with CuKα1 (λ = 0.15405 nm) radiation (40 kV), 30 mA and 2θ between 5–50°. The relative crystallinities of the samples were calculated according to equation (1). FTIR spectroscopy patterns were obtained from a Shimadzu IR prestige-21 using KBr pellet (2 cm⁻² area, 1:200 sample:KBr) in the range of 4000–400 cm⁻¹. Nitrogen physisorption isotherms were measured at 77.3 K using a Quantachrome Autosorb-iQ. Specific surface areas were calculated using the single point BET plot at p/p° ~0.99, and the pore size distribution was calculated from the desorption branch using the BJH model. TG and DTA curves were measured using a STA Linseis PT-1600 over the temperature range 25 °C up to 800 °C (under nitrogen atmosphere, with heating rate 10 °C/min). The SEM–EDX observations were obtained using a Field Electron and Ion (FEI)-type Inspect S50. Palladium particle size distributions were obtained by a TEM with JEM-1400 model (voltage 120 kV).

\[
\text{% Relative crystallinity} = \left( \frac{\text{Total area of three strongest crystalline peaks}}{\text{Total area of all peaks}} \right) \times 100\% \tag{1}
\]

2.5. Hydrogenation reaction of citronellal
The reactor was first purged with nitrogen for 15 min. The citronellal oil (0.5 ml) was added to 100 ml batch-stirred autoclave reactor as a feed and dissolved in 50 ml of cyclohexane. A small amount of 0.05 g for each MIL-100(Fe) and Pd/MIL-100(Fe) (in various loading Pd of 1 and 3 wt%) was used as a catalyst. The catalytic reaction was performed at 80 °C, with a 550 rpm stirring rate and 10 bar of H₂ pressure for 2 h. The catalytic tests were monitored using a Shimadzu GCMS-QP2010S.

2.6. Evaluation of hydrogenation products
Catalyst performance in hydrogenation reaction was estimated as the conversion of citronellal. The conversion and selectivity were defined using equations (2) and (3), according to Liu et al [31]:

\[
C = 100\% - C(\text{Citronellal}) \tag{2}
\]

\[
S = \frac{Y}{C} \times 100\% \tag{3}
\]

where Y is the yield of citronellol (%), as determined by GC analysis, and C is the conversion of citronellal (%) calculated by equation (2).
Materials characterization

This was probably due to the low Pd content of Fe. The highest characteristic peak of the standard MIL-100 stretching absorption band at 3300 cm$^{-1}$ occurred at 0.6% vibration band of the carboxylic group before and after deprotonation and then coordinating with Fe ions. The band from C–O stretching also sharpened from 1320–1210 cm$^{-1}$ to 1381 cm$^{-1}$. Then, the O–H stretching absorption band at 3300–2500 cm$^{-1}$ shifted to 3600–2800 cm$^{-1}$. This was reflected by the occurrence of Fe(III) ion binding with water molecules and the interactions occurring in the form of hydrogen bondings [4].

The inclusion of Pd metal in MIL-100(Fe) structure was hardly analyzed using XRD since there is no peaks characteristic to Pd metal at 2θ = 40.2° (111) and 46.5° (200) [32]. Moreover, the decreasing peak intensity at 2θ = 10.31° indicates a decrease in the crystallinity of the material (see figure 2). However, in the diffractogram of the 1% Pd/MIL-100(Fe) and 3% Pd/MIL-100(Fe) materials, the characteristic peaks of Pd were not detected. This was probably due to the low Pd content (loading 1% and 3%) and the small particle sizes [30]. This also occurred at 0.6%–2% Pd loading at UiO-67 [21] and Pd loading up to 2.9% on ZIF-8 [19]. Another reason could be that the palladium were homogeneously distributed into MIL-100(Fe). Similar results were obtained by Ren et al [33] who prepared a MIL-101 supported Pd nanoparticles (Pd@MIL-101) via a sol-gel method for the 0.5 wt% Pd@MIL-101 sample, which no obvious characteristic signal for Pd NPs. The crystallinity of MIL-100(Fe) decreased as the percentage of Pd loading increased. This can be seen from the characteristic peaks of MIL-100(Fe) decreasing in intensity, which is possible because the presence of Pd causes changes in the crystal parameters so that crystallinity decreases (table 1).

The results of XRD analysis were strengthened by a functional group analysis using FTIR spectroscopy (ESI, figure S1). Some significant changes were recorded include the C=O bond from the H$_3$BTC ligand (absorption peak at 1722 cm$^{-1}$), which shifted significantly to 1626 cm$^{-1}$ in MIL-100(Fe), corresponding to a stretching vibration band of the carboxyl group before and after deprotonation and then coordinating with Fe(III) metal ions. The band from C–O stretching also sharpened from 1320–1210 cm$^{-1}$ to 1381 cm$^{-1}$. Then, the O–H stretching absorption band at 3300–2500 cm$^{-1}$ shifted to 3600–2800 cm$^{-1}$. This was reflected by the occurrence of Fe(III) ion binding with water molecules and the interactions occurring in the form of hydrogen bondings [4].

The formation of an Fe–O bond was also detected at the absorption peak at 484 cm$^{-1}$ [34] in MIL-100(Fe) spectra, which indicated that Fe coordinated with the ligand. Meanwhile, the absorption band from C–H stretching from 3000 to 3100 cm$^{-1}$ remained at 3100 cm$^{-1}$ in the MIL-100(Fe) spectra. Absorption peak from 937–1111 cm$^{-1}$ in MIL-100(Fe) corresponded to benzene ring vibration [34].

Table 1. Relative crystallinities of the MIL-100(Fe) and Pd/MIL-100(Fe).

| Sample            | Rel. Intensity | Value % |
|-------------------|----------------|---------|
| MIL-100(Fe)       | 2157           | 100     |
| 1% Pd/MIL-100(Fe) | 1835           | 85      |
| 3% Pd/MIL-100(Fe) | 1704           | 78      |

3. Results and discussion

3.1. Materials characterization

Based on the XRD analysis (figure 1), the main peak on the diffractogram of synthesized MIL-100(Fe) had the highest characteristic peak of the standard MIL-100(Fe) (CCDC No. 640536), which were at 2θ = 6.33° (5 1 1); 10.31° (8 2 2); and 11.11° (8 4 2) [4]. This shows that MIL-100(Fe) was successfully synthesized. However, the synthesis in water using the reflux method tended to produce a material with lower crystallinity compared to the hydrothermal method.

Figure 2. Diffractograms of MIL-100(Fe) and Pd/MIL-100(Fe).

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After modification with Pd, the FTIR spectra of MIL-100(Fe) remained unchanged, as shown in ESI figure S2 (available online at stacks.iop.org/MRX/8/045504/mmedia). This shows that the presence of Pd metal does not change the chemical structure of the MIL-100(Fe). Hence, it can be concluded that Pd metal is not chemically bonded with the MIL-100(Fe). Possible interaction which might be occurred are Van der Waals, π–π force, and ion-dipol interactions [35].

Based on table 2, the synthesized MIL-100(Fe) had a BET surface area of 907.437 (m²/g) and a pore volume of 0.5024 (c.c./g). After modification with Pd, a significant decrease in surface area to 1/3 of the initial surface area occurred. This is related to the presence of metal Pd, which might be fill the pore volume or surface of MIL-100(Fe). Empirically, the metal size of Pd (1.4 Å) [36] is much smaller than the pore size of MIL-100(Fe) in this study (around 11 Å). Hence, Pd particles can enter the pores of MIL-100(Fe). The surface area of Pd/MIL-100(Fe) decreases with the percentage of Pd loading. The more Pd metal is produced, the more particles fill the MIL-100(Fe) pore, resulting in a decrease in surface area as shown in table 2. The presence of Pd metal also has an impact not only on decreasing MIL-100(Fe) pore volume as well as the crystallinity of the MIL-100(Fe) material according to XRD analysis.

Nitrogen sorption isotherm of MIL-100(Fe) and Pd/MIL-100(Fe) (figure 3) shows that the adsorption-desorption of MIL-100(Fe) is much higher than that of Pd/MIL-100(Fe). This is related to the character of the surface area and the pore size listed in table 2. The adsorption–desorption curves of MIL-100(Fe) and Pd/MIL-100(Fe) indicate that the adsorption mechanism is type I adsorption isotherm, which is a micropore classification [37]. It appears that the pore volume filled tended toward a relative pressure ($p/p^0$) < 0.1, which according to Ren et al [38] indicates a high microporosity. The microporosity properties of MIL-100(Fe) and Pd/MIL-100(Fe) are further reinforced by the pore size distribution, as shown in figure 4. The data show that the pore size mostly ranged between 17 and 20 Å, indicating the existence of micropore structures.

TG/DTA analysis (ESI figure S3) showed that the MIL-100(Fe) material has thermal stability up to 287°C. There was a mass decrease in the MIL-100(Fe) thermogram curve, with the first decrease of 35.29% in the temperature range of 30.2°C–168.3°C, indicating a loss of water molecules that occupy the MIL-100(Fe) pores [4] and that there were about 20 H₂O molecules that evaporated from the pores. The second mass decrease was relatively small (5%), in line with the research conducted by Horcajada et al [4]. The decrease was due to water

![Figure 3. Nitrogen Sorption Isotherm of MIL-100(Fe) and Pd/MIL-100(Fe).](image-url)
molecules that coordinated with the Fe trimeric unit. The third decrease of 46.66% at 256.7°C–398.5°C shows the decomposition of H3BTC ligands and the MIL-100(Fe) frameworks as a whole [4]. Based on the DTA curve (ESI, figure S3), there was one endothermic peak and one exothermic peak. In the phase of water molecule removal, the reaction occurs endothermally, while the decomposition of the framework of the structure occurs exothermally.

Applying Pd metal to MIL-100(Fe) did not affect its thermal stability (figure S4, see ESI). The development of metal Pd slightly reduced the range of mass loss during the first stage of decline, reaching 17%–20%. This is because part of the mass of the solvent was lost first due to the metal impregnation process of Pd, involving calcination and reduction using heating up to 140°C. In MIL-100(Fe), the remaining residues are 13% of iron oxides species such as Fe3O4, Fe2O3, and FeO, which change successively as temperature increases [39]. Meanwhile, the development of metal Pd also had an effect on the increase in residual mass: the greater the loading Pd, the higher the residual mass remaining. The residual Pd/MIL-100(Fe) was 27% and 28%, respectively, with the addition of Pd 1% and 3% (figure ESI, S4). The remaining residue consisted of iron oxide belonging to MIL-100(Fe) as well as Pd–O.

Figure 4. Pore Size Distribution of MIL-100(Fe) and Pd/MIL-100(Fe).

Figure 5. SEM image of: (a) MIL-100(Fe), (b) 1% Pd/MIL-100(Fe) and (c) 3% Pd/MIL-100(Fe) at 5000x magnification.
SEM-EDX analysis (figure 5 and ESI figure S5) showed that the MIL-100(Fe) material has an irregular morphology and a non-uniform particle size. The encapsulation of palladium tends to result in an irregular morphology due to the clumping of Pd particles dispersed on the surface of the MIL-100(Fe) material and due to mechanically stirring factors, which reduce the crystallinity of the material. Even so, the dispersion of Pd is more evenly distributed with the addition of Pd loading. Figures 5(b) and (c) show the Pd metal, which increasingly covers the surface of MIL-100(Fe). MIL-100(Fe) gives a particle size distribution of 10.66 μm, whereas Pd/MIL-100(Fe) particle sizes are 4.74 and 5.71 μm, respectively, at 1% Pd/MIL-100(Fe) and 3% Pd/MIL-100(Fe) (figure 5).

Further measurements with EDX analysis (ESI, figure S5, and table S1) showed that the percentage of Pd metal contained in each Pd/MIL-100(Fe) was in accordance with theoretical calculations. The results of the SEM-EDX analysis complement the previous XRD data. Although the XRD did not show the peak of Pd(0) upon modification of 1 and 3% wt, the analysis of the element composition revealed the presence of Pd content. In TEM micrographics (figure 6), the Pd nanoparticles (represented by black points) were well distributed in the MIL-100(Fe) material. In samples with minimum metal loading, Pd tended to produce small particle size distributions. The average size of the Pd particles was 8.56 ± 3.23 nm and 9.34 ± 2.42 nm, respectively, for Pd loadings of 1 and 3 wt%. Pd-nano particle size distribution is shown in ESI figure S6.

3.2. Catalytic test
Quantitative analysis was carried out by GC-MS to determine the product conversion. The catalytic performances of the citronellal hydrogenation reaction with MIL-100(Fe) and Pd/MIL-100(Fe) as catalysts are shown in figure 7. MIL-100(Fe) succeeded in converting citronellal with 42.6% of conversion. The incorporation of Pd metal increased the catalytic performance of MIL-100(Fe). The successively increasing hydrogenation reaction activities by catalysts 1% and 3% Pd/MIL-100(Fe) were 58.1% and 63.7%, respectively.

The hydrogenation of citronellal as unsaturated aldehydes results in several possible types of reaction products, four dominant selected products of which are unsaturated alcoholic products, saturated alcohols, saturated aldehydes, and alkanes (figure 8). Unsaturated alcohol products are formed by hydrogenation, which only occurs in C=O group. This product yields the maximum percentage of conversion compared to the other types of products (reaching 36.3%) and tends to increase as the Pd content increase in MIL-100(Fe). Furthermore, saturated alcohol products are formed by the hydrogenation of the C=O group, but this is followed by hydrogenation of the C-C double bond found in the aldehyde. However, this product is not dominant in conversion, which is below 7%. The other possible product type is
saturated aldehyde. This product occurs due to hydrogenation, which does not attack the C=O group but only the C=C double bond in the aldehyde. The percentage of conversion is also very small, ranging below 5%. The last possible product type is alkane resulting from the deoxygenation process of C=O groups and hydrogenation of C=C double bonds. This product produces very small conversions below 3%. Hence, the possible reaction products with the dominant product are unsaturated alcohols.

The catalyst selectivity of MIL-100(Fe) and Pd/MIL-100(Fe) against citronellol formation is shown in figure 9. Catalyst MIL-100(Fe) did not produce citronellol products (0% selectivity) against citronellol. The encapsulation of Pd metal made the MIL-100(Fe) catalyst more selective for the formation of citronellol products. Indeed, the selectivity increased with increasing Pd loading in MIL-100(Fe). The selectivity of the catalysts with 1 and 3 wt% Pd/MIL-100(Fe) were 20.3% and 22.2%. This result provides better data than the previous studies (table 3), which only demonstrated 6% selectivity with a 5% Ni/Zr-beta catalyst [7]. Comparison with other catalysts such as 5% Ir/H-Beta [40], 3% Ir/CBV 20A [41], 5% Ir/Beta [41], Pt/WO3/TUD-15** and Pt/WO3/TUD-20** [42] showed that with shorter reaction time catalyst 3% Pd/MIL-100(Fe) gave the highest selectivity.

The Lewis acid site Fe(III) in the MIL-100(Fe) framework continuously polarize the C=O bond on citronellal and reduces the electron cloud density in the C=O bond. Therefore, the distance of the C=O bond is getting far apart, and the C=O bond on the citronellal is easily absorbed by the active site, so hydrogenation

![Figure 8. Selected product distribution (yield) of hydrogenation reaction of citronellal.](image)

![Figure 9. Selectivity of citronellol product using MIL-100(Fe) and Pd/MIL-100(Fe) as catalyst.](image)
tends to lead to unsaturated alcohol [8]. While Pd metal is able to produce the effect of hydrogen spillover, it can bind hydrogen molecules and then break them down into hydrogen atoms [43]. Then, these hydrogen atoms hydrogenate the aldehyde group in citronellal. The higher the Pd content, the more hydrogen is available for hydrogenation reactions. Hydrogen molecules are transferred to electron-rich Pd particles to form Pd hydrogen moieties [18]. Hence, MIL-100(Fe) catalyst activity increases with the addition of metal-content Pd. The expected reaction mechanism can be seen in figure 10.

However, getting unsaturated alcohol is quite difficult thermodynamically because the C=O bond has a lower bond energy than the C=C bond [44], so the C=C bond is more easily hydrogenated. As a result, it tends to produce saturated alcohol products and is accompanied by other reactions beyond the formation of citronellol. This makes the citronellal hydrogenation reaction by MIL-100(Fe) catalyst not selective for citronellol products.

The presence of Pd as a Lewis acid metal not only affects the supply of hydrogen atoms but also plays a role in polarizing the C=O bond in citronellals, thereby weakening the C=O bond. The Pd–O bond has a bonding energy of 234 kJ mol⁻¹ [45], whereas initially Fe–O has a bonding energy of 407 kJ mol⁻¹ [46]. Thus, the ability of Fe to weaken the C=O bond is further enhanced by Pd. As a result, the hydrogenation reaction leads only hydrogen to attack the C=O bond. This causes the MIL-100(Fe) catalyst to become more selective for citronellol products after Pd metal is encapsulated, and the selectivity increases as the amount of metal Pd is increased.

In addition, the increase in Pd particle size also affects the selectivity of unsaturated alcohol. This is in line with research conducted by Jiang et al [48] regarding the effect of Pd particle size on the selective hydrogenation of unsaturated aldehydes. In this study, Pd particle size affected the adsorption of cinnamaldehyde. Adsorption by small Pd particles tends to reduce the C=C bonds rather than the C=O bonds, whereas larger Pd particles tend to adsorb C=O rather than C=C bonds. A high surface area also affects the activity of the catalyst. This is not only related to the increasing availability of active sites; the high surface area also increases the adsorption of the substrate [49]. The combination of bifunctional catalyst effects on the Pd/MIL-100(Fe) derived from the

![Figure 10. Proposed mechanism of catalytic reaction using Pd/MIL-100(Fe) in hydrogenation reaction of citronellal.](image)

### Table 3. The selectivity of citronellol in this study compared to other catalysts.

| Catalyst                  | Conv. (%) | Sel. (%) | t (h) | T (°C) | P (bar) | References. |
|---------------------------|-----------|----------|-------|--------|---------|-------------|
| 5% Ni/Zr-beta            | 96        | 6        | 22    | 80     | 20      | [7]         |
| 5% Ni/Zr-beta            | 96        | 8        | 10    | 80     | 20      | [7]         |
| 5% Ir/H-Beta             | 100       | 7        | 16    | 80     | 5       | [40]        |
| 5% Ir/H-Beta             | 95        | 16       | 16    | 60     | 15      | [40]        |
| 3% Ir/CBV 20A            | 91        | 9        | 24    | 80     | 8       | [41]        |
| 5% Ir/Beta               | 94.8      | 16.2     | 10    | 60     | 15      | [41]        |
| Pt/VOₓ/TUD-15            | 100       | 10.4     | 21    | 80     | 20      | [42]        |
| Pt/VOₓ/TUD-20            | 99.9      | 11.4     | 21    | 80     | 20      | [42]        |
| 3% Pd/MIL-100(Fe)        | 63.7      | 22.2     | 2     | 80     | 10      | Present study |

*a CBV: Mordenite with ratio molar Si:Al = 20.

*b TUD: Mesoporous material (Technische Universität Delft).
effect of hydrogen spillover, the synergy between the two active metal sites (Fe and Pd), and the porosity and surface area characteristics succeeded in increasing the activity of citronellal hydrogenation and increasing the selectivity of citronellal into unsaturated alcohol products.

4. Conclusions

Modification MIL-100(Fe) with Pd metal nanoparticles affect the morphology and decreases the crystallinity, surface area, and porosity of the host material. The present of Pd also increase the selectivity of the MIL-100(Fe) catalyst, leading to unsaturated alcohol products as well as increasing the performance of the MIL-100(Fe) catalyst in the citronellol hydrogenation reaction (up to 63.7% conversion) and increasing the selectivity of citronellol products up to 22.2%.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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