

Article

Spillover Hydrogen on Electron-Rich Ni/m-TiO₂ for Hydrogenation of Furfural to Tetrahydrofurfuryl Alcohol

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Abstract: Conversion of biomass-derived furfural (FFA) platform molecule to value-added tetrahydrofurfuryl alcohol (THFA) molecule is a sustainable route using an efficient non-noble metallic catalyst in water solvent. In this work, Ni in various loadings on mesoporous titanium dioxide (m-TiO₂) was synthesized in one pot by Evaporation-Induced Self-Assembly (EISA). The synthesised catalysts were evaluated for the hydrogenation of furfural to tetrahydrofurfuryl alcohol. The catalysts were characterised using a combination of spectroscopic techniques such as XRD, H₂-TPR, H₂-TPD, XPS, SEM-EDX, TEM, and HR-TEM. The characterization results show that the Ni/m-TiO₂ materials exhibit enhanced electron-rich active sites, facilitated hydrogen spillover, uniform dispersion of small Ni particles (~5 nm), and strong metal support interaction between Ni and TiO₂. Among the various Ni dopings, 7.5 wt.% Ni/m-TiO₂ catalyst exhibited the best performance and achieved 99.9% FFA conversion and 93.2% THFA selectivity in water solvent at 100 °C and under 2 MPa H₂. Additionally, detailed kinetic studies, process parameters, the stability and reusability of the catalyst were also studied. The results demonstrated that the 7.5 wt.% Ni/m-TiO₂ catalyst is highly active and stable.

Keywords: biomass; furfural hydrogenation; electron-rich Ni; SMSI; spillover



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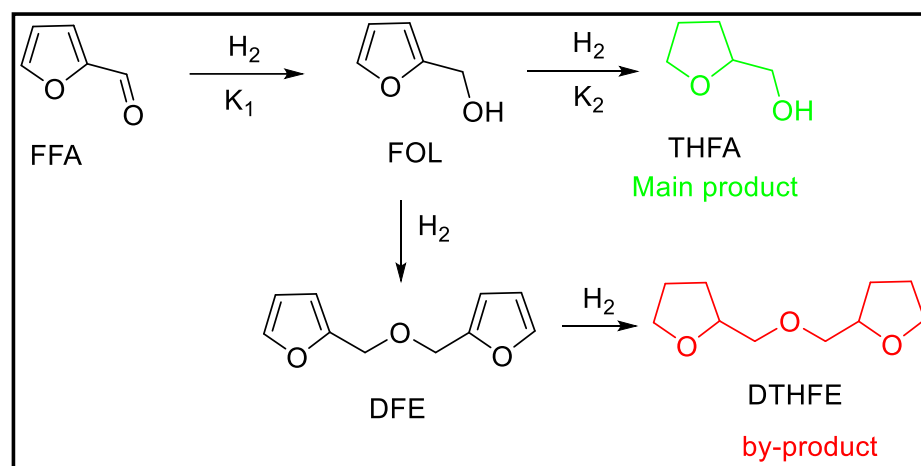
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1. Introduction

The increasing global demand for fuels and renewable materials makes sustainable biomass a potential alternate feedstock to fossil resources in chemical industries [1]. Lignocellulosic biomass derived platform molecules such as furfural (FFA), 5-hydroxymethylfurfural (HMF), and levulinic acid hold great potential for the production of biofuels [2]. FFA is produced from dehydration of C-5 xylose, which is derived from hemicellulose [3–5]. Also, industrial use of FFA has significantly grown as it has been successfully transformed into other value-added chemicals [6–8].

FFA can be converted into various value-added chemicals like furan, tetrahydrofuran (THF), furoic acid, furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFA), etc. Among them, THFA has generally considered a green solvent in industrial applications because of its low toxicity and biodegradability. It has been used as a solvent in agriculture and epoxy coatings, as well as one of the intermediates in many industrial applications [7]. THFA is synthesized by complete hydrogenation of FFA in the industry (Scheme 1). Typically, the hydrogenation of FFA first to furfuryl alcohol (FOL) is carried out over CuCr₂O₄ catalyst and is followed by further hydrogenation into THFA using a noble metal catalyst. The drawbacks of the above process are the long reaction time and high energy consumption, as well as the toxicity of Cr-based catalyst. Therefore, a variety of Cr-free catalysts have been

studied for the hydrogenation of FFA to THFA. Different catalytic systems were investigated for hydrogenation of FOL to THFA by varying reaction parameters such as hydrogen pressure and temperature [9]. Very recently, Lan et al. reported the hydrogenation of FOL to THFA on a Pd-Si-ZSM catalyst, with 99.9% selectivity to THFA at 99.9% conversion of FOL in 2-propanol at 150 °C, 3 MPa hydrogen pressure in 24 h [10]. FOL hydrogenation to THFA is a difficult step since it requires a high hydrogen pressure and reaction temperature with respect to selective product formation of THFA [11,12]. To improve the economic viability, it is most desirable to use FFA as the substrate and perform the hydrogenation reactions in a one-step process. Bhogeswararao et al. [13] reported the hydrogenation of FFA to THFA over 5 wt.% Pd/Al₂O₃ catalyst that showed 79.5% conversion of FFA with 99.9% selectivity of THFA in 2-propanol solvent at 25 °C and 6 MPa of initial H₂ pressure. Recently, Matsagar et al. [14] investigated the hydrogenation of FFA to THFA; 95% selectivity of THFA was achieved over 5 wt.% Rh/C catalyst in N, N-dimethylacetamide (DMA) solvent at 30 °C and 1 MPa H₂ pressure after 32 h of reaction time.



Scheme 1. General pathway of furfural hydrogenation to tetrahydrofurfuryl alcohol.

In view of the cost for commercial applications, it remains desirable to develop a non-noble catalyst for FFA hydrogenation. Ni and Cu-based catalysts are mostly considered economically favorable non-noble metals for the hydrogenation of FFA. Ni-based catalyst has been reported in the hydrogenation of FFA to THFA in a liquid phase [15]. Over a Ni catalyst, furfural is mainly adsorbed in $\eta^1(\text{O})$ -aldehyde and $\eta^2(\text{C}, \text{O})$ -aldehyde modes, which are favorable for the hydrogenation of FFA to THFA [16]. Liu et al. [17] demonstrated that nickel supported on carbon nanotubes catalyst resulted in 90% selectivity to THFA in ethanol solvent at 130 °C and 4 MPa of H₂ pressure after 10 h of reaction. A 99% selectivity of THFA from total hydrogenation of FFA was reported by Wei et al. using Ni/MMO-CO₃ (synthesized by using Na₂CO₃ solution in an ion exchange method) catalyst in 2-propanol solvent in 6 h reaction at 110 °C, 3 MPa hydrogen pressure [18]. The THFA yield was 98% over a bimetallic catalyst with a Cu-Ni in 2-butanol solvent at 140 °C and 3 MPa of H₂ for 4 h [19]. In the past few years, the hydrogenation of FFA to THFA has also been reported in various organic solvents, such as 2-propanol, N, N-dimethylacetamide, ethanol, etc., which produced a representative by-product, 2-furaldehyde diethyl acetal (FDA) [17]. However, the hydrogenation of FFA in an environmentally friendly water solvent remains challenging for mild reaction conditions, recyclability and no formation of humins. Some promising works have been reported on the hydrogenation of FFA to THFA using water as a solvent, although process development needs to address additional challenges. For example, Yang et al. [20] reported results of the hydrogenation of FFA in water at 140 °C and 4 MPa H₂ pressure using alkaline earth metals modified Ni/Al₂O₃ catalysts. Although Ni-Ba/Al₂O₃ showed 96% selectivity to THFA with more than 99% conversion of FFA, the leaching of Ba in a water solvent was an issue for recycled catalyst use. Another report

by Gong et al. for FFA hydrogenation to THFA over Ni/NCNT catalyst in water solvent showed 99% selectivity to THFA at 99% conversion of FFA, but it required 4 MPa hydrogen pressure and 7 h reaction time to optimize the product yield [21]. Therefore, the preparation of non-noble metals, such as Ni and Cu catalysts for FFA to THFA in the aqueous phase hydrogenation with good stability is still quite challenging.

Catalyst support plays a significant role in hydrogenation reactions, the hydrogenation reaction influenced by surface acidic/basic sites [16,22]. TiO_2 has been reported as a water-tolerant material [23,24]. TiO_2 in an anatase structure specifically is known to exhibit a strong metal–support interaction (SMSI) [25–28]. The classical SMSI effect mainly includes electron transfer from support to metal nanoparticles or encapsulation of metal nanoparticles by the support, which are typically considered to significantly change the electronic and geometric structure of supported metal catalysts. However, the activity of Ni-doped TiO_2 catalysts depends on the method of preparation. For example, Xu et al. [29] compared the hydrodechlorination of chlorobenzene performances of the Ni/ TiO_2 catalysts prepared using two different methods, one by in situ method, i.e., one-step synthesis using a mixture of a specific amount of NiCl_2 and $\text{Ti}(\text{O}i\text{Bu})_4$, and another by ex situ method, i.e., impregnation by a two-step process supporting a specific amount of NiCl_2 on pre-synthesised TiO_2 . The in situ prepared catalyst was reported to be more stable and active than the ex situ catalyst due to the appropriate electron density of Ni active sites; partially embedded Ni into TiO_2 exhibited high stability and strong SMSI. However, the catalysts prepared by using ex situ method are easily sintered or leached during the reaction due to weak interaction between metal and support, especially those supported on metal oxides derived from conventional impregnation or precipitation methods [12,18,30]. Further, Shi et al. [31] reported that the in situ prepared Ni/ TiO_2 catalyst for CO methanation was more stable and active than the ex situ due to the formation of uniformly dispersed smaller Ni nanoparticles on the TiO_2 surface as well as strong SMSI effect. Tian et al. [32] also reported that in situ prepared ordered mesoporous Ni/ Al_2O_3 for CO methanation provides a high active surface area. This catalyst was also stable with less aggregation of metal particles during the time on stream than the conventional impregnation or precipitation method. Gao et al. [33] reported that in situ prepared Ni/ TiO_2 -C composite catalyst having a mesoporous structure with a large active surface area showed a synergetic effect in catalytic activity between Ni and TiO_2 towards the reduction of 4-nitrophenol to 4-aminophenol with NaBH_4 . Overall, in situ prepared catalysts showed high active surface area and stability. In situ prepared Ni/ TiO_2 catalyst showed the SMSI, which may be beneficially leveraged to prevent Ni agglomeration and Ni leaching in an aqueous phase for the hydrogenation of FFA to THFA.

In this work, the Evaporation-Induced Self-Assembly (EISA) method is developed for in situ preparation of Ni-doped mesoporous titanium dioxide (m- TiO_2) catalysts, which are evaluated for hydrogenation of FFA to THFA in aqueous phase. The catalysts are characterized by XRD, H_2 -TPR, H_2 -TPD, TGA, FT-IR, TEM, HR-TEM, XPS, BET, and SEM-EDX. The effects of reaction time, temperature, and nickel loading on the hydrogenation of FFA are thoroughly examined. The catalytic stability from recyclability studies and kinetics are studied to verify the best performing catalyst in the hydrogenation of FFA to THFA.

2. Results & Discussion

2.1. Characterization Results

The X-ray diffractograms show the crystalline nature of the synthesized catalysts. As shown in Figure 1a, the diffraction peaks of pure m- TiO_2 and xNi/m- TiO_2 (x-2.5, 5, 7.5, and 10 wt.%) catalysts at $2\theta = 25.3^\circ$, 37.8° , 48.1° , 53.9° , and 55.0° were attributed to the TiO_2 anatase phase (JCPDS No. 21-1272) [18]. The m- TiO_2 phase was unchanged with the incorporation of doped Ni in the TiO_2 lattice. There are no significant peaks related to the rutile phase. The peak of Ni-doped m- TiO_2 samples has shown a slight shift in the peak position at 25.3° and 37.8° (Figure 1b). The change of 2θ angles indicates the Ni ions are incorporated into the TiO_2 crystal lattice [34]. The diffraction peaks of NiO crystalline phases are not found up to 7.5 wt.% Ni loading, indicating that the Ni ions are

well dispersed in TiO_2 [35]. In the XRD patterns of 10Ni/m- TiO_2 catalyst, a small diffraction peak appeared at 43.34° , which corresponds to (200) planes of NiO phase (JCPDS No-04-0835). From the XRD profiles, the intensity of Ni-doped TiO_2 samples was decreased as compared to the pure m- TiO_2 ; it may be that Ni^{2+} ions occupy the interstitial sites to some extent and distort the crystal lattice, which results in a slight amorphous nature [34].

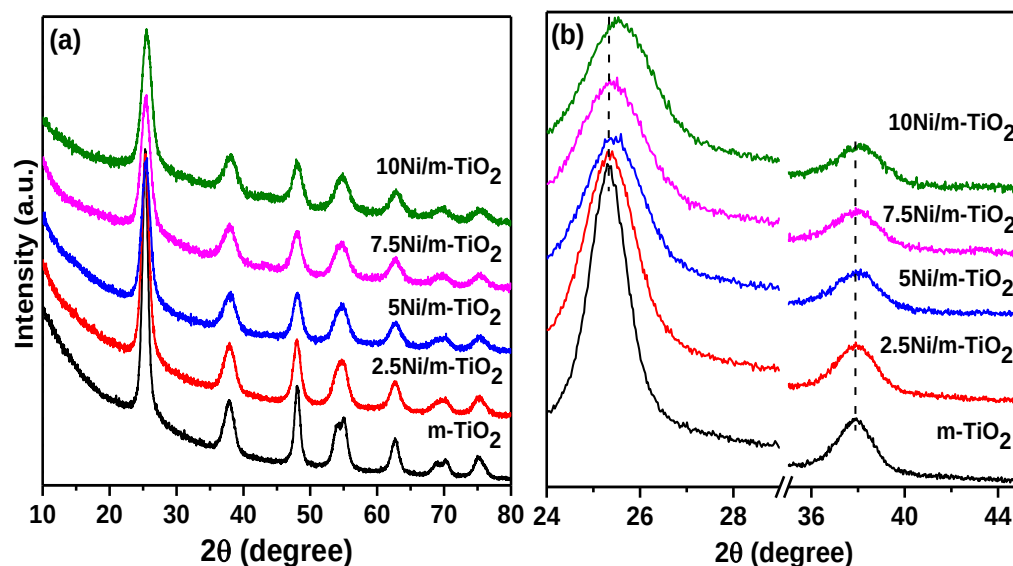


Figure 1. (a) XRD patterns of different wt.% of Ni/m- TiO_2 catalysts. (b) expanded view of XRD patterns in 2θ from 24° to 44° for different wt.% of Ni/m- TiO_2 catalysts.

FT-IR spectroscopy was used to investigate the surface functional groups of the pure and Ni incorporated m- TiO_2 after the annealing process. In Figure 2a, all the samples showed weak absorption peaks at 3327 cm^{-1} and 3444 cm^{-1} due to hydroxyl stretching frequency from adsorbed water [36]. The second adsorption peak at 1637 cm^{-1} corresponds to OH bending frequency [37]. The peak at 650 cm^{-1} may be attributed to the stretching and bending vibration mode of Ti-O [38]. From the spectra of pure m- TiO_2 and Ni-doped m- TiO_2 , it is noticed that the Ti-O bond peak was slightly shifted to a lower wavenumber and changed in the intensity of peak (Figure 2b), likely due to the presence of the Ni^{2+} ions in the interstitial sites of the crystal lattice [39], which was also consistent with the XRD results (see Figure 1). No other additional peaks are observed related to an organic moiety after calcining samples. It indicates that the addition of P123 and nitrate does not leave noticeable residual impurities on the TiO_2 surface after calcination. The temperature at which the complete decomposition of organic moieties can be determined by TG/DTG (Figure S1). In Figure S1, there are two types of weight losses observed, the first weight loss corresponds to desorbed water, and the second one is attributed to the decomposition of nitrate groups and triblock polymer [40,41]. Titanium isopropoxide is an organometallic precursor, and the side product of hydrolysis is isopropanol which can be easily removed by calcination. In the case of inorganic precursors such as titanium chloride, nitrate etc., it is difficult to remove residual impurities in the catalyst even after calcination. According to the TG/DTG results the synthesized catalyst required 450°C to decompose all organic moieties.

The surface morphology of synthesized pure m- TiO_2 and 7.5Ni/m- TiO_2 catalysts was examined by SEM image (Figure S2). The SEM image of pure m- TiO_2 shows a distorted spherically shaped structure with agglomeration. In the case of 7.5Ni-doped TiO_2 , the particles are visible by reducing the agglomeration [34]. In Figure 3a, it is seen that most of the particles are spherical in shape with a uniform size distribution. It may be due to the aggregation of nanocrystalline TiO_2 particles. The existence of Ni, Ti, and O elements in 7.5Ni/m- TiO_2 is confirmed through EDX analysis. The EDX analysis shows that the Ni content of the 7.5Ni/m- TiO_2 sample is 7.9 wt.%, which matches well with the value

determined by ICP and may imply the homogeneous distribution of Ni on the m-TiO₂. The TEM graphs further confirmed the actual size of the particles and their distribution. For 7.5Ni/m-TiO₂, Ni nanoparticles are well dispersed on m-TiO₂, and the average particle size of the 200 Ni nanoparticles from various TEM images is $\sim 5 \text{ nm} \pm 1.6$. The results of TEM and EDX indicate that Ni nanoparticles are successfully doped in the TiO₂ crystal lattice. HR-TEM images (Figure 4b,e) show the anatase phase of TiO₂ (particle size: 10–30 nm) decorating the surface of Ni nanoparticle: the nickel lattice fringe 0.20 nm shows a cubic phase of the (111) plane, while TiO₂ anatase d space at 0.34 nm is indexed to the (101) plane. It is well matched with a base peak of titania in the XRD pattern.

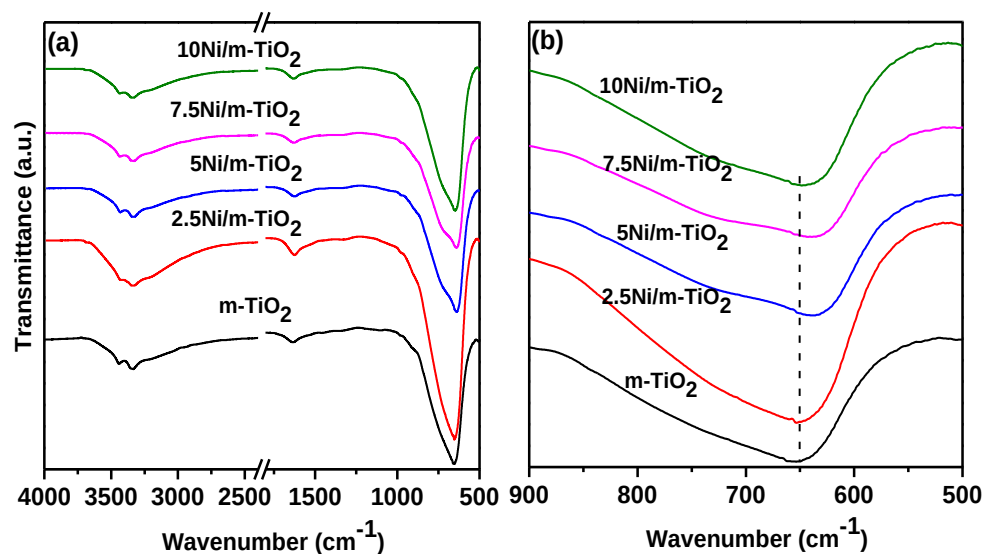


Figure 2. FT-IR spectra of synthesized xNi/m-TiO₂ catalysts (x=2.5, 5, 7.5, and 10 wt.%) (a) 4000–500 cm^{−1} range and (b) 900 to 500 range cm^{−1}.

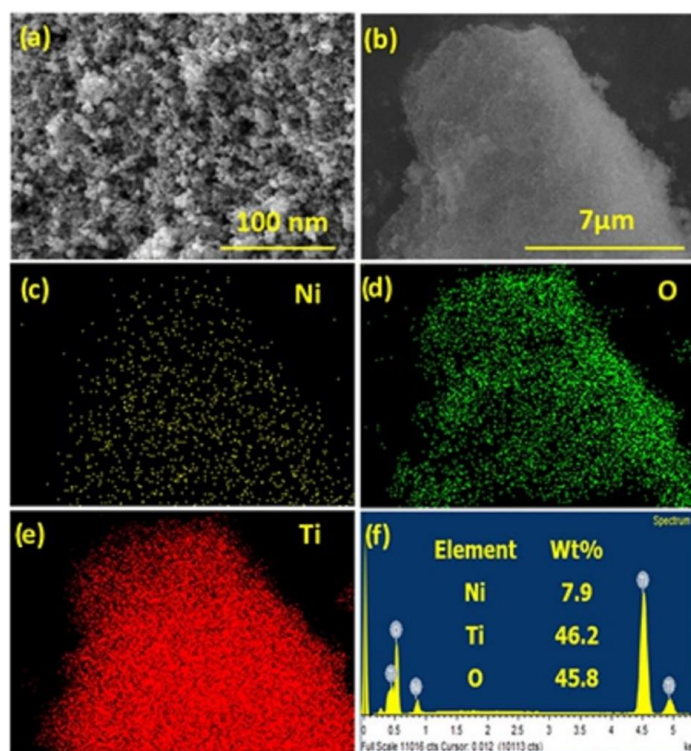


Figure 3. (a,b) SEM images, EDX mapping of (c) Ni, (d) O, (e) Ti, and (f) EDX spectrum of 7.5Ni/m-TiO₂.

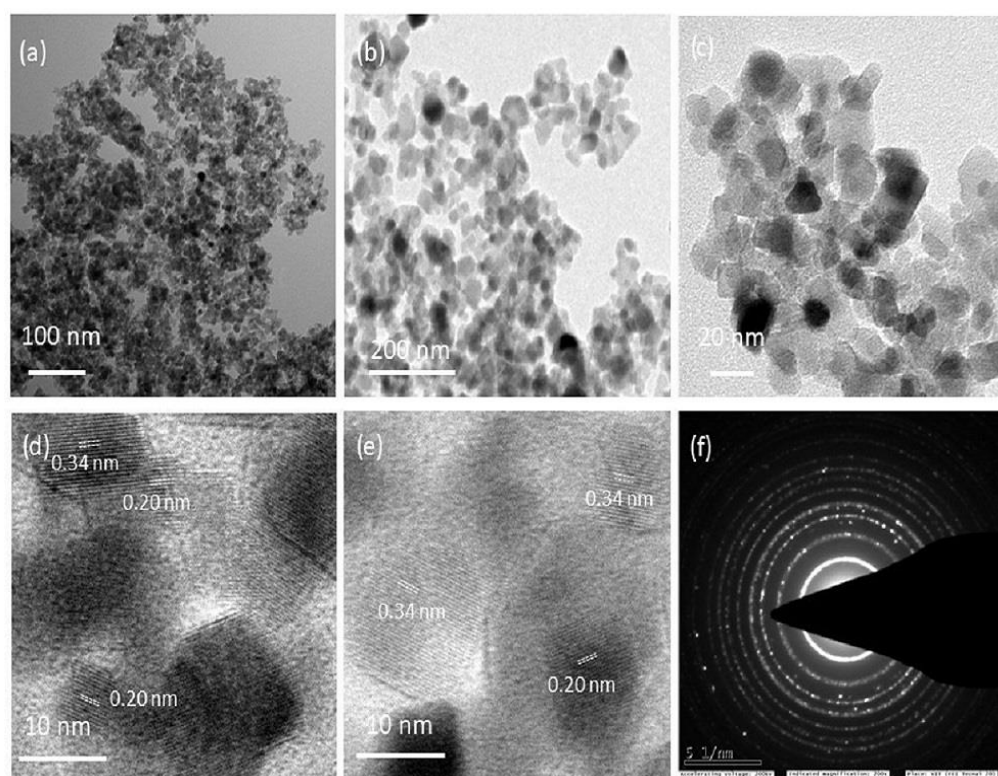


Figure 4. 7.5Ni/m-TiO₂ catalyst (a) TEM image, (b–e) HRTEM images, (f) SAED pattern.

The reducibility of the m-TiO₂ and Ni-doped m-TiO₂ was investigated through H₂-TPR measurements using 10% H₂/Ar (Figure 5a). The pure m-TiO₂ showed a broad and low intensity TPR peak obtained in the temperature range of 430–670 °C [38]. A distinct peak at 353 °C was observed for the 2.5Ni/m-TiO₂ sample. Another peak appeared at a lower temperature of 300 °C, as the Ni loading was increased from 5 to 10 wt.%, on m-TiO₂. The peak at the lower temperature is assigned to the reduction of bulk NiO, which interacts weakly with TiO₂, whereas the higher temperature ~360 °C peak is attributed to the reduction of highly-dispersed NiO species with strong bonding to the TiO₂ support [42]. The H₂ consumption results are summarized in Table 1. Based on the H₂-TPR results, with increasing Ni loading, the reduction peak (430–670 °C) of TiO₂ shifted towards a lower temperature (insert Figure 5a), possibly due to the strong interaction between Ni and TiO₂. Furthermore, some TiO₂ is partially reduced to TiO_{2-x} at high temperatures, which promotes the formation of oxygen vacancies and changes the electronic structure of active metal Ni since the unstable TiO_{2-x} donates its electron to Ni [43]. Further, this metal/metal oxide interaction is supported by H₂-TPD (Figure 5b).

Table 1. Ni loading and properties of xNi/m-TiO₂ catalysts.

S.No	Catalyst	Ni Loading (%)		H ₂ Consumption * mmol/g	N(H ₂)/N(Ni) *
		ICP	SEM-EDS		
1	m-TiO ₂	—	—	—	—
2	2.5Ni/m-TiO ₂	2.85	2.82	0.611	1.26
3	5Ni/m-TiO ₂	5.46	4.78	1.070	1.15
4	7.5Ni/m-TiO ₂	7.97	7.90	1.624	1.20
5	10Ni/m-TiO ₂	10.97	10.17	1.931	1.03

*—H₂-TPR analysis.

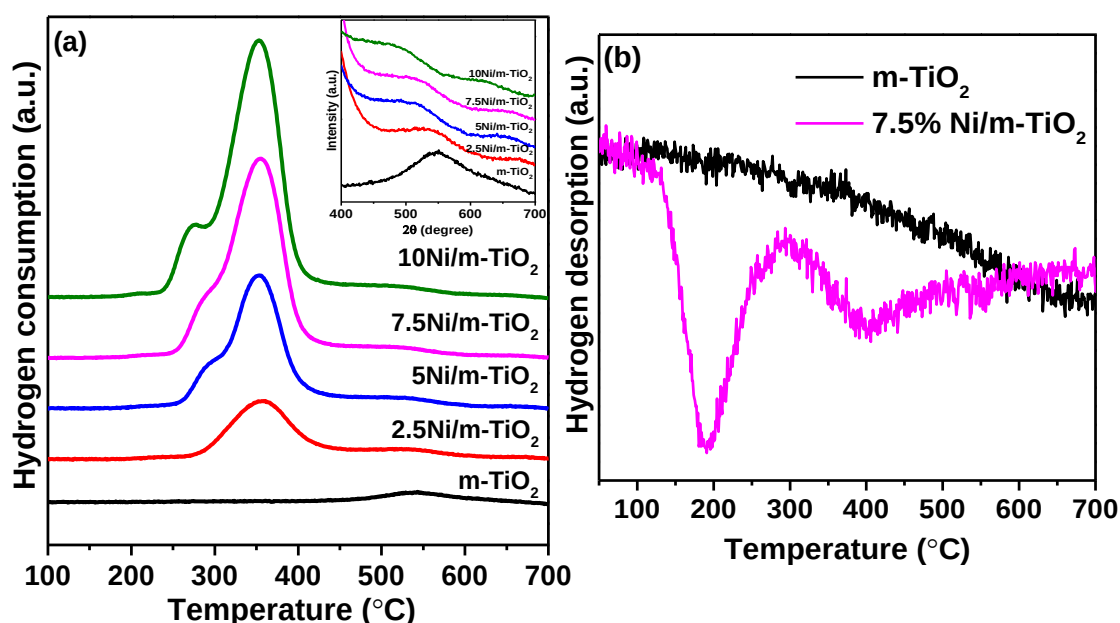


Figure 5. (a) H_2 -TPR profile of $x\text{Ni}/\text{m-TiO}_2$ catalysts, (b) H_2 -TPD profile of m-TiO_2 and $7.5\text{Ni}/\text{m-TiO}_2$ catalysts.

H_2 -TPD profile of $7.5\text{Ni}/\text{m-TiO}_2$ exhibits two strong peaks at 190°C and 400°C (Figure 5b). The low-temperature H_2 -TPD peak at 190°C with high intensity may be associated with the chemisorbed hydrogen on the highly dispersed Ni NPs surface with the increased density of surface defects. It explains that surface defects serve as an arresting net for diffused hydrogen on the surface, leading to a decrease in the hydrogen dissociation activation energy [42]. In contrast, a high temperature peak at 400°C may be due to strong interaction between Ni and TiO_2 because the desorption of hydrogen species at high temperature has been proposed to be spillover hydrogen [29,44]. Hydrogen spillover from metal to oxide support usually occurs at the interface between the adsorbing and accepting surfaces, where H_2 dissociates on the metal into atomic H and then spills onto the support [45]. Generally, the adsorbed atomic H species move across the surface to the interface between the activating and the accepting surface. Hydrogen spillover can break the bonds with the metal surface and form new bonds with the support surface. This process is endothermic and requires large activation energy, which can be lowered by increasing the strength of metal-support interaction. It is to be noticed that the higher nickel dispersion enhanced dissociated surface hydrogen property seen in the $7.5\text{Ni}/\text{m-TiO}_2$ sample through the lower desorption temperature with stronger intensity.

X-ray photoelectron spectroscopy (XPS) was performed to study the elemental electronic state of Ni-TiO_2 nanocomposites as well as an interaction between Ni and TiO_2 in the catalyst (Figure 6). The $\text{Ni } 2p_{3/2}$ core level XPS of the $7.5\text{Ni}/\text{m-TiO}_2$ catalyst is shown in Figure 6a. The Ni species exists in both elemental state ($\text{Ni}^{\delta-}$) at 851.9 eV [46] and an oxidized state (Ni^{2+}) at 855.1 eV , [47] along with a satellite peak located at 860.8 eV . These indicate the strong interaction between metallic Ni and TiO_2 support [48] and also the electron transfer from the unstable partial reduced species, TiO_{2-x} to Ni [46,49]. The Ni in +2 state can be assigned to NiO from air exposure during the sample transfer. From XPS data, it reveals that Ni composition in $7.5\text{Ni}/\text{m-TiO}_2$ is 6.3%, which is well matched by the ICP and SEM-EDX analysis.

In Figure 6b, the doublets $\text{Ti } 2p_{3/2}$ at 458.5 eV and $\text{Ti } 2p_{1/2}$ at 464.2 eV arise from the spin orbit-splitting [50]. These peaks are consistent with Ti^{4+} in TiO_2 lattice. After doping with Ni, the binding energies newly located at 458.6 and 464.3 eV are corresponding to $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$, respectively [51]. The shift in these peaks indicates the electron deficient on $\text{Ti}^{(4+\delta)+}$ species due to the coexistence of $\text{Ni}^{\delta-}$ and $\text{Ti}^{(4+\delta)+}$ [46]. From Figure 6c, the

peaks at 529.8 and 529.7 eV are attributed to the O 1s state. An infinitesimal shift is observed between these peaks. The difference in the area of the peaks indicates the oxygen vacancy created, which is created when Ni ions replace the Ti ions [52].

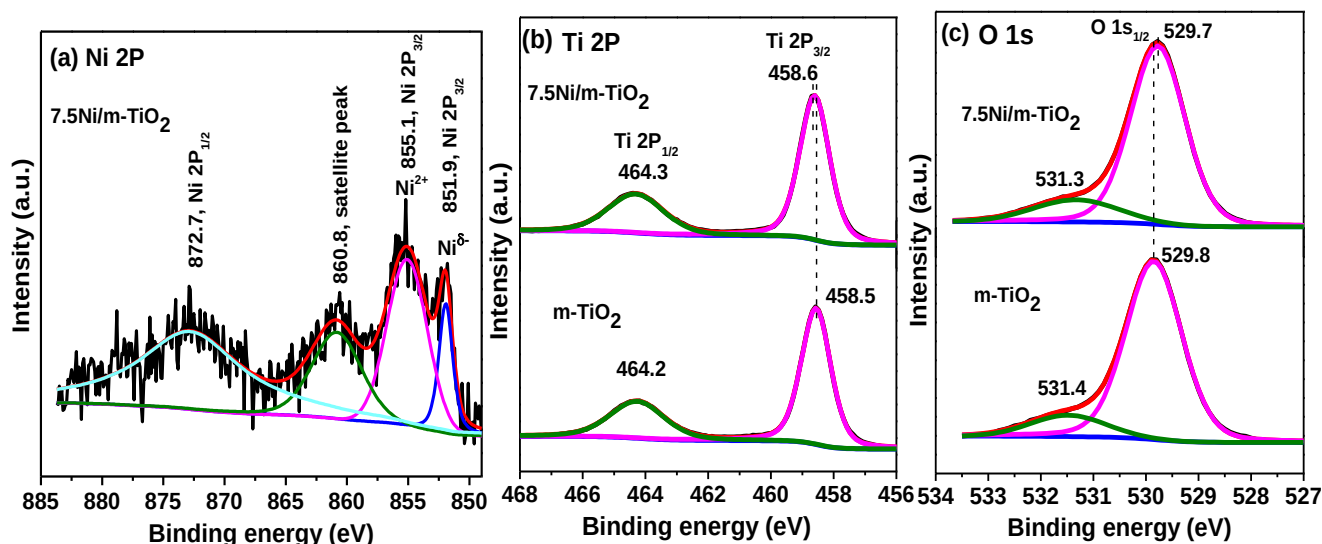


Figure 6. XPS analysis of 7.5Ni/m-TiO₂ and m-TiO₂ catalyst (a) Ni 2p_{3/2}, (b) Ti 2p_{3/2}, and (c) O 1s.

The nitrogen adsorption-desorption isotherms and pore size distributions for m-TiO₂ and 7.5Ni/m-TiO₂ catalysts are shown in Figure S3. Both catalysts show the type-IV isotherm and have H2 hysteresis loops. The obtained BET surface area, pore size and pore volume of both catalysts are summarized in Table S1.

2.2. Catalytic Activity

Generally, a metal site on the catalysts is necessary to reduce the aldehyde functional group, especially in the conversion of furfural to furfuryl alcohol, which is the reaction intermediate, and it is easy to facilitate. The more challenging task is the hydrogenation of C=C bonds in the FFA ring. Metal sites and their metal oxide support are necessary to produce appropriate products. Excess acid sites lead to secondary side products such as methyl furan, tetrahydromethylfuran, difurfuryl ether (DFE), cyclopentanone (CPO), cyclopentanol (CPL), and resinification products [53]. To find out the catalytic activity of the prepared catalyst, the furfural hydrogenation reaction was performed in a 10 mL stainless steel reactor with various temperatures between 80–120 °C and H₂ pressures at 2 MPa in a water solvent; the obtained results are shown in Figure 7. The pure m-TiO₂ catalyst showed no catalytic activity in the furfural hydrogenation reaction. In the case of 2.5Ni-doped m-TiO₂, it showed 76.7% conversion of FFA with 83.5% of FOL selectivity and 14.1% of THFA. An interesting observation was that the conversion of FFA was increased with an increasing amount of Ni loading on the m-TiO₂, and FOL selectivity was reduced with the increased selectivity of THFA. The activity of 10Ni/m-TiO₂ is shown to be almost the same as that of 7.5Ni/m-TiO₂, which may be due to the saturation of Ni nanoparticles on support. Among these catalysts, the 7.5Ni/m-TiO₂ catalyst showed the highest selectivity of THFA, which is around 93.2%.

At low temperatures, FOL was predominantly produced via nickel-based catalysts by C=O hydrogenation to yield THFA [54]. The presence of furfural suppresses the adsorption of furfuryl alcohol because furfural is more strongly adsorbed onto the catalyst surface than furfuryl alcohol [16]. Hydrogenation of FOL to THFA by saturating the adsorbed C=C bond on the Ni catalyst surface following the full conversion of FFA becomes the main reaction. As a result, a catalyst with a greater number of Ni sites increases THFA production via hydrogenation of C=C in the furan ring, resulting in increased THFA selectivity. Similarly in our work with increasing Ni loading the selectivity to THFA increased from FFA and

FOL hydrogenation. The full conversion reached in 5% Ni loading, although FOL was not yet fully hydrogenated to THFA in the set reaction time. Within the same reaction time, increasing Ni loading, the hydrogenation of FOL to THFA is accelerated due to increased Ni surface area.

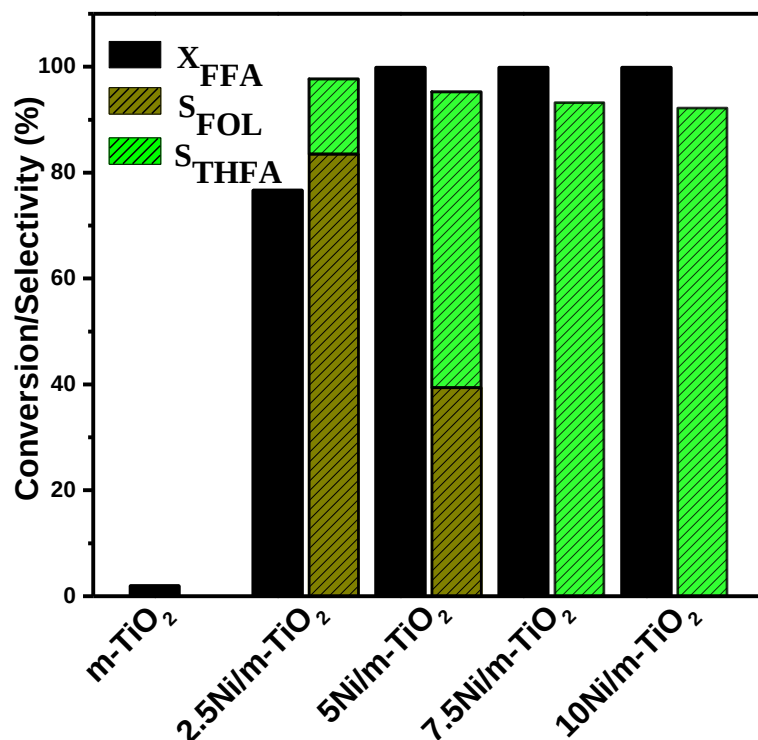


Figure 7. Furfural hydrogenation over xNi/m-TiO₂ catalysts. Reaction conditions: 0.030 g catalyst, 1 mmol furfural, 2 mL water, 2 MPa H₂, 100 °C, and 4 h.

The enhancement in catalytic activities of the 7.5Ni/m-TiO₂ catalyst may be ascribed to the hydrogen spillover, strong interaction between Ni and m-TiO₂ support, which provides electron rich Ni active sites as evidenced by XPS, H₂-TPR, H₂-TPD, and HR-TEM studies. Zhang et al. [43] reported aqueous phase hydrogenation of furfural over Ni/TiO₂ towards more selective to FOL, it was attributed to the particle size of the Ni around 27 nm. Nakagawa et al. [16] reported that the smaller Ni particles (~6 nm) supported on SiO₂ tend to show more selectivity towards THFA. Therefore, the selectivity of the product depends mainly on the particle size of active metal sites on the catalyst. In this study, the smaller size Ni particles (~5 nm) and uniform dispersion of active metal sites on the 7.5Ni/m-TiO₂ catalyst provide higher selectivity towards THFA in optimum conditions. All catalytic systems showed additional product such as total hydrogenated difurfuryl ether (DTHFE such as ditetrahydrofurfuryl ether), and the selectivity of DTHFE is ~6%. The formation of DTHFE is caused by intermolecular dehydration of formed FOL, followed by total hydrogenation of DFE. The additional product may be formed by over acidic sites (0.80 mmol/g) on the catalyst from NH₃-TPD (Figure S4) [53]. In large-scale production, FFA hydrogenation products can be easily isolated using the distillation process from the reaction mixture because DTHFE has a lower boiling point (74 °C) than THFA (178 °C).

The furfural hydrogenation reaction is carried out in water solvent because of environmental concerns and low cost; the polar solvents promote the furfural hydrogenation [14]. It may be a polarizing effect of water solvent, which helps to adsorb the carbonyl group of furfural on the surface of the catalyst. The hydrogen adsorbed on the active metal sites is more likely to launch a nucleophilic attack on the carbonyl group of furfural, resulting in speed up the rate of reaction and decreasing the activation energy (E_a) [55].

Further, the rate of reaction and activation energy (E_a) are calculated for the furfural hydrogenation using 7.5Ni/m-TiO₂ catalyst. The reaction rate is expressed as $r = kC^n$, where r is the reaction rate, k is the rate constant, C is the concentration of reactant furfural, and n is the reaction order. The hydrogenation of furfural to furfuryl alcohol and furfuryl alcohol to THFA over 7.5Ni/m-TiO₂ catalysts, respectively. Both reactions are followed the first-order kinetic model according to a linear correlation of $\ln(1-C)$ versus time t (Figure S5a,b) [18]. The rate of FFA hydrogenation reaction is 1.97 h^{-1} which is higher than reported catalysts [18,56]. Based on these results, the Arrhenius plot is depicted in Figure S5b with the temperature range between 27 and 60 °C. The apparent activation energy is calculated based on the Arrhenius Equation: $\ln k = \ln A - E_a/RT$, where A is the pre-exponential factor. The apparent activation energy of FFA hydrogenation (E_{a1}) and FOL hydrogenation (E_{a2}) are 49.23 kJ/mol and 39.8 KJ/mol in the aqueous-phase, respectively. The activation energies are recorded corresponding to the FFA and FOL conversion and similar trend observed in reported literature [54,57]. The value of the calculated E_{a1} is comparable with that obtained from other reported non-noble based catalysts [56].

Temperature-dependent hydrogenation of furfural using H₂O as a solvent was meticulously temperatures ranging from 80 to 120 °C, and the measured results were presented in Figure 8a. A result shows nearly complete conversion in 4 h at the temperatures of 80, 100, and 120 °C. FOL and THFA were obtained as the main products. When the reaction temperature is raised to 100 °C, 99.9% conversion of FFA and 93.2% selectivity of THFA are obtained. Further, the reaction temperature was raised to 120 °C, the selectivity of THFA was decreased to 88.7%, and a trace amount CPO was detected in GC-MS [43]. Other time dependent hydrogenation reactions were carried out using D₂O as a solvent at 100 °C, and the results are shown in Figure 8b. The reaction process was carefully monitored using ¹H NMR spectroscopy, and the ¹H NMR results are shown in Figure S6. It provides direct evidence of the reaction product formation. The maximum yield of product THFA is obtained at 93.4% in the first 4 h. The THFA selectivity was almost the same when the reaction time was prolonged. These results indicate that the maximum selectivity of THFA is obtained at 100 °C with 2 MPa of H₂ pressure and 4 h of reaction time.

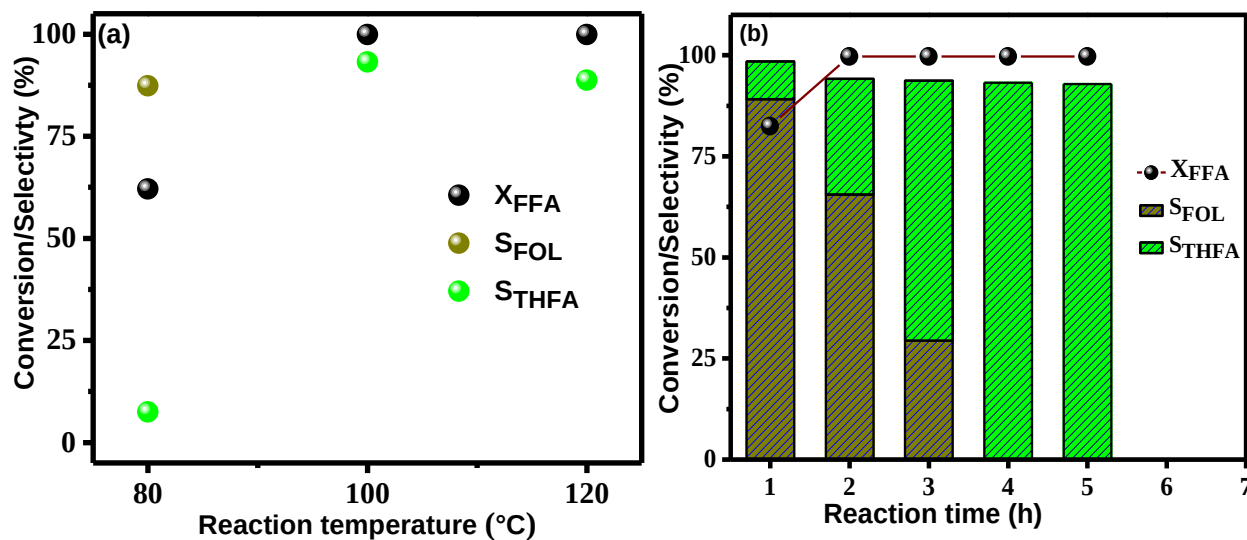


Figure 8. Conversion and selectivity (a) at different temperatures for 4 h, and (b) with reaction time at 100 °C. Reaction conditions: 0.030 g of 7.5Ni/m-TiO₂, 1 mmol of furfural, 2 mL of water, and 2 MPa of H₂ pressure.

To determine the stability of the synthesized 7.5Ni/m-TiO₂ catalyst, a reusability test was carried out towards the hydrogenation of FFA to THFA, and the obtained results are presented in Figure 9. The catalyst was carefully separated after each successful reaction test using a centrifugation technique. Separated catalysts were washed five times with

2 mL mixture of water/ethanol (1:1 ratio) and finally, washed with 2 mL of pure ethanol. After each cycle, the recovered catalyst was calcined at 450 °C, followed by reduction, and further applied for the next cycle. Interestingly, the synthesized catalysts showed no loss in catalytic activity even after five successive cycles. It indicates that the catalysts are stable for a minimum of five cycles. Figure S7 shows the results of leaching test of FFA hydrogenation using the 7.5Ni/m-TiO₂ catalyst. The FFA conversion was increased with extended reaction time, and finally, the conversion reached 99.99% at 2 h. We noticed that after the catalyst was removed by centrifugation at 1.5 h of the fifth recycled test, the furfural conversion remained unchanged as the reaction time proceeded (Figure S7, red data points), indicating the FFA hydrogenation was stopped after removing the catalyst. The results further indicate that there is no leaching of the active species from the solid catalyst.

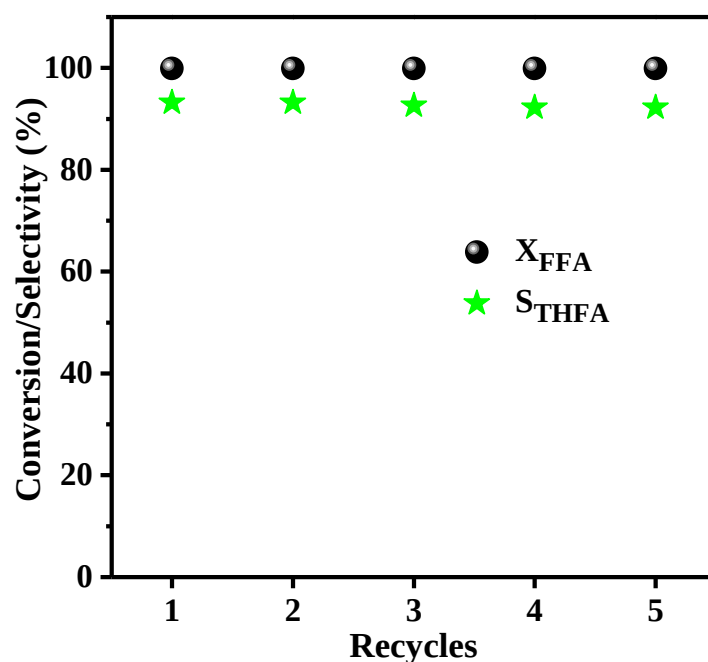


Figure 9. The catalyst reusability test in the hydrogenation of FFA. Reaction conditions: 0.030 g of 7.5Ni/m-TiO₂, 1 mmol of furfural, 2 mL of H₂O, 2 MPa of H₂, 100 °C, and 4 h.

Further, the used catalysts were examined with several spectroscopic techniques, such as XRD (Figure S8) and ICP (7.1% of Ni determined) techniques. Results indicate that there is no leaching of Ni NPs from the catalyst even after five successive cycles.

A comparison of this synthesized 7.5Ni/m-TiO₂ catalyst with existing literature data is summarized in Table 2. The selectivity of the product THFA can be tuned based on the chemical state, active phase, particle size, and distribution of the catalysts. However, the structural properties and composition of the catalysts are also crucial in attaining high hydrogenation activity.

Furthermore, the formation of by-products and the reaction condition have a significant impact on the overall performance of the catalyst. The synthesized 7.5Ni/m-TiO₂ catalyst showed the simplicity of preparation, enhanced stability, good reusability, uniform Ni nanoparticle distribution, and better conversion and selectivity with relatively low metal loading.

Table 2. Comparison of Ni-based catalysts reported in the literature on FFA hydrogenation to THFA.

S.No	Catalyst	Gram of Metal (10 ⁻²)	FFA (mmol)	T # (°C)	H ₂ (MPa)	Rate (mol/g/h) *	Solvent	X _{FFA} (%)	S _{THFA} (%)	Ref.
1	NiCo/SiO ₂ -MOF	3.10	41 €	80	3	0.59	EtOH	99.8	99.1	[11]
2	15Ni/Al ₂ O ₃	15.0	76 €	130	4	0.49	EtOH	99.7	97.6	[12]
3	8.9Cu-9.8Ni/CNT	1.87	6.0	130	4	0.25	EtOH	99.9	90.0	[17]
4	Ni@C@CNT	35.6	84.1	120	4	0.12	EtOH	99.1	96.7	[58]
5	12.7%Ni/C	0.63	5.0	120	3	0.59	2-PrOH	99.9	90.0	[30]
6	Ni/MMO-CO ₂	2.80	6.0	110	3	0.14	2-PrOH	99.9	99.9	[18]
7	51.1Ni/C	15.3	0.31	120	1	0.02	2-PrOH	99.9	99.9	[59]
8	Cu ₁ Ni ₃ /MgAlO	1.75	5	110	3	0.26	2-PrOH	99.9	94.4	[60]
9	NiLaO ₃	0.78	1.0	120	1	0.03	H ₂ O	98.8	87.2	[56]
10	Ni(40)/MgO-M	24.0	15.3	140	4	0.05	H ₂ O	99.9	99.9	[61]
11	Ni@NCNTs	1.20	1.0	100	4	0.07	H ₂ O	99.9	99.0	[21]
12	Ni@NiAlO-LDH	53.3	60.5	150	3	0.05	H ₂ O	99.9	33.0	[62]
13	10Ni-Ba-Al ₂ O ₃	2.00	5.2	140	4	0.20	H ₂ O	99.0	99.0	[20]
14	7.5Ni/m-TiO ₂	0.24	1.0	100	2	0.36	H ₂ O	99.9	93.2	PW

#: reaction temperature (°C), €—Furfuryl Alcohol is a starting material, * rate of reaction is calculated from equation 3. PW-present work.

3. Material and Methods

Pluronic P123 (~5800 g/mol from Sigma Aldrich company, Louis, MO, USA), titanium isopropoxide (Sigma Aldrich company), nickel nitrate anhydrous (Aladdin Co., Ltd., Shanghai, China), ethanol, deionized water, and furfural (Sinopharm chemical reagent Co., Ltd., Shanghai, China, used after distillation at 120 °C under vacuum) were used in this work.

3.1. Catalyst Preparation

In a typical synthesis via Evaporation-Induced Self-Assembly method [63]. Solution A contains 2.1 g of Pluronic P123 in 20 mL ethanol at room temperature. Solution B was prepared from 4.08 g titanium isopropoxide in 20 mL ethanol by adding 3.2 mL 67% nitric acid. Both solutions were mixed under vigorous stirring. Next, a stoichiometric amount of nickel nitrate, in 2.5, 5, 7.5, and 10 wt.% of Ni with respect to TiO₂, dissolved in ethanol (0.2 mmol/L) was added to the above mixture. The solution was covered with a polyethylene film, stirred at room temperature for 72 h, and then dried at 60 °C until the removal of solvent. The final gel was calcined at 450 °C for 4 h at a temperature ramp rate of 1 °C/min. These catalysts were labelled as xNi/m-TiO₂ (x in 2.5, 5, 7.5, and 10, corresponding to the wt.% Ni loading). The m-TiO₂ was prepared by the same method without nickel nitrate addition.

3.2. Catalyst Characterization

The Ni containing samples were analyzed using a PerkinElmer Optima 8000 inductively coupled plasma-optical emission spectrometer (ICP-OES) from PerkinElmer, Waltham, MA, USA. The samples were dissolved in mixed nitric acid and hydrofluoric acid. After dissolving the catalysts, 10 ppm concentration using 2% HNO₃ was used for the elemental percentage by ICP analysis using Ni standard solution (1000 µg/mL, in 5% HNO₃, 100 mL).

The X-ray diffraction (XRD) patterns of the samples were measured on an X-ray diffractometer (X'Pert powder, PANalytical) from Almelo, Netherlands with a graphite monochromator and Cu-Kα radiation source. The measurements were conducted using a PIXcel 1D detector and operated at 40 kV. The materials were identified by comparing the diffraction data with reference patterns in the database (PDF2-2004).

Temperature-programmed reduction in hydrogen (H₂-TPR) was performed on a micromeritics AutoChem II 2920 chemisorption analyzer (Norcross, GA, USA). For the H₂-TPR experiment, approximately 0.08 g of sample was placed in a tubular quartz reactor. The sample was reduced in a 10% H₂/Ar stream by heating from ambient temperature to 700 °C at a heating rate of 10 °C/min. The consumed hydrogen was detected using

a thermal conductivity detector (TCD) and quantified using a calibration plot based on quantitative measurement of Ag₂O TPR profiles using a similar protocol.

The hydrogen temperature-programmed desorption (H₂-TPD) was performed on a Micromeritics AutoChem II 2920 chemisorption analyzer. A 0.3 g catalyst sample was first reduced in 5% H₂/Ar mixture at 400 °C for 1 h and cooled to −40 °C under the same atmosphere. The sample was then purged with Ar at a flow rate of 50 mL/min for 1 h to remove physically adsorbed hydrogen. H₂-TPD was performed by heating the sample from 0 to 800 °C with a heating rate of 10 °C/min under Ar atmosphere. The desorbed hydrogen was detected with a thermal conductivity detector (TCD).

A field emission scanning electron microscope (FESEM, JEOL, JSM-7800F, 15 kV, JEOL Ltd., Tokyo, Japan) equipped with an Oxford X-Max silicon drift detector was used to perform EDX analysis.

The catalyst surface area was measured using a commercial BET analyzer (ASAP2020 Micromeritics volumetric adsorption, Micromeritics, Norcross, GA, USA) using N₂ adsorption at −196 °C. Before the N₂ adsorption, a 0.100 g catalyst sample was degassed under vacuum at 250 °C for 5 h. The textural properties were measured from the nitrogen isotherms using the BET and BJH methods (N₂ adsorption/desorption).

The transmission electron microscopy (TEM) images were taken on a Hitachi HT7700 microscope (M.k, Tokyo, Japan) operated at 100 kV. The sample grid was prepared by ultrasonically dispersed the sample in ethanol, deposited droplets of the suspension onto a carbon-enhanced copper grid, and dried under the lamp. The high-resolution transmission electron microscopy (HR-TEM) images of the samples were obtained on an FEI-TECNAI G²-20 TWIN microscope operated at 200 kV.

The elemental composition of the samples was measured by X-ray photoelectron spectroscopy (Thermo Fisher Model, Madison, WI, USA) with K α radiation as the exciting source. For calibration, the binding energies were referenced to the C 1s peak at 284.8 eV.

3.3. Catalytic Evaluation

Hydrogenation of FFA was conducted in a sealed 10 mL stainless steel parr batch reactor. In a typical process, 1 mmol of furfural, 2 mL of water, and a 0.030 g of catalyst pre-reduced at 400 °C for 1 h was loaded into the reactor at ambient temperature. The reactor was purged 3 times with 0.5 MPa N₂ to remove air and then filled with H₂ up to 2 MPa. The reactor was heated to operating reaction temperatures and kept for a specified reaction time. The reaction mixture was stirred at a rate of 700 rpm. After completion of the reaction, the reactor was cooled to room temperature. The solid catalyst was separated by centrifugation (4000 rpm, 5 min). The reaction mixture was diluted with 0.250 g ethanol at room temperature and sonicated for 5 min. The products were identified by Gas chromatography-mass spectrometry (GC-MS) (Agilent 7890A-5975C HP-5MS, California, CA, USA) and also quantified by gas chromatography (Agilent 7890A) equipped with a flame ionization detector (FID) and a HP-5 column (30 m $\times$ 0.32 mm $\times$ 0.25 μ m).

The conversion of furfural and the selectivity of the products were calculated using Equations (1) and (2), respectively.

$$\text{FFA conversion (\%)} = \left[1 - \frac{(\text{moles of FFA reactant})_{\text{out}}}{(\text{moles of FFA reactant})_{\text{in}}} \right] \times 100 \quad (1)$$

$$\text{THFA selectivity (\%)} = \frac{\text{moles of THFA}}{(\text{moles of FFA reactant})_{\text{in}} - (\text{moles of FFA reactant})_{\text{out}}} \times 100 \quad (2)$$

$$\text{Rate of reaction (mol/g/h)} = \frac{\text{moles of FFA converted}}{\text{gram of metal loading} \times \text{time}} \quad (3)$$

The rate of reaction was calculated based on furfural conversion for the first 1 h time reaction.

4. Conclusions

The catalytic hydrogenation process in water has a lower environmental impact, cost, and toxicity than in organic solvents. However, the major problem in the aqueous phase is that most metal-based catalysts suffer from low activity, low selectivity, and deactivation due to leaching. Here, this study reported a highly active and stable Ni/m-TiO₂ supported catalyst for the hydrogenation of FFA to THFA in water solvent. The electron-rich Ni and uniform dispersion of ~5 nm Ni nanoparticles over m-TiO₂ nanocrystals provide a greater number of active sites as a result of strong metal-support interaction at the catalyst surface in the 7.5Ni/m-TiO₂ catalyst. The 7.5Ni/m-TiO₂ showed 99.9% conversion of FFA with 93.2% selectivity of THFA and 6% selectivity of ditetrahydrofurfuryl ether (DTHFE) after 4 h under 2 MPa of H₂ pressure at 100 °C. THFA has a high boiling point and is easily separated by the distillation process from the reaction mixture in large-scale production. The FFA hydrogenation reaction follows first order and activation energy (E_{a1}) is 49.23 KJ/mol. The obtained rate of reaction for the hydrogenation of FFA to THFA is nearly two times higher than the reported in the literature. The catalyst was stable without detected leaching of Ni as verified by five recycled tests of the catalyst. The strong metal support interaction between Ni and the TiO₂ surface prevents the leaching of active species during the catalytic reaction. The process for the one-pot synthesis of Ni metal-doped mesoporous TiO₂ proposed in this work is extendable to many applications in catalysis, adsorption, and energy storage.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12101286/s1>, Figure S1: TGA analysis of uncalcined m-TiO₂ catalyst, Figure S2: SEM image of (a) pure m-TiO₂, (b) 7.5Ni/m-TiO₂, Figure S3: BET of pure m-TiO₂ and 7.5Ni/m-TiO₂, Figure S4: NH₃-TPD of 7.5Ni/m-TiO₂, Figure S5: First order kinetics fit for (a) hydrogenation of FFA to FOL, (b) hydrogenation of FOL to THFA at various time and T = 100 °C, (c) Arrhenius plot of the activation energy (E_{a1} FFA hydrogenation, E_{a2} for FOL hydrogenation) at T = 30–60 °C, substrate = 1 mmol, water = 2 mL, catalyst = 0.03 g, p = 2 MPa H₂, time = 1 h, Figure S6: ¹H NMR of conversion of FFA to THFA in isotopic D₂O. The red arrows show the consumption of FFA and FOL, and the green one leads the formation of THFA, Figure S7: XRD of spent 7.5Ni/mTiO₂ catalyst, Figure S8. XRD of spent 7.5Ni/mTiO₂ catalyst, Table S1: Physicochemical properties of various catalysts.

Author Contributions: R.B.: design of the work, data curation, formal analysis, investigation; K.R.: visualization; X.Z.: Characterization of H₂-TPR and H₂-TPD; P.Y.: Characterization of XRD, TG, ICP; M.R.M.: investigation; V.P.: interpretation of data, writing draft; Z.C.Z.: project administration, supervisor, writing-review and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained in the Article and Supplementary Material. Any additional data are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflict of interest related to this work.

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