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Solvothermal hydrodeoxygenation of hydroxymethylfurfural derived from biomass towards added value chemicals on Ni/TiO₂ catalysts

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Abstract

Lignocellulosic biomass is one of the most abundant renewable source of commodity chemicals like hydroxymethylfurfural. Solvothermal hydrodeoxygenation of hydroxymethylfurfural towards value added chemicals was performed with a series of nickel based catalysts supported on different titania materials, ie. hydrothermally-prepared high aspect ratio and commercial TiO₂ with different morphologies and crystallographic structures. The kind of titania strongly influenced the properties of the supported nickel nanoparticles, which allowed to tune the reaction selectivity towards specific products. Rutile-containing titania forced stronger Ni-Ti interaction, enhanced hydrogen adsorption, and formed larger Ni particles which resulted in high activity. Hydrothermally-prepared materials allowed to obtain selectively 2,5-bishydroxymethyltetrahydrofuran (biopolymer precursor) due a relatively small surface acidity and large Ni particles. By contrast, large surface area anatase with small nickel particles and small surface acidity allowed to selectively obtain 2,5-dimethylfuran (biofuel additive).

Keywords: hydrothermally prepared titania, Ni/TiO₂, hydrodeoxygenation, HMF, DMF

1. Introduction

Lignocellulosic biomass is one of the most abundant renewable source of commodity chemicals [1,2] 5-(hydroxymethyl)furfural (HMF) that can be obtained via cellulose hydrolysis has been identified as valuable fuel, polymer, or chemical precursor.[3-5] Depending on the catalysts and reaction conditions HMF can be transformed towards a large variety of chemicals including 2,5-dimethylfuran (DMF), 5-methylfurfural (5-MF) or 2,5-bishydroxymethyl-tetrahydrofuran (BHMTHF) through hydrodeoxygenation (HDO) reaction (scheme 1).[6]

Scheme 1. Reaction pathway of HMF hydrodeoxygenation

Scheme 1 illustrates the HMF hydrodeoxygenation reaction pathway, with as first step the competitive HMF hydrodeoxygenation (path A) and hydrogenation (path B), that leads to the formation of 5-MF or of 2,5-bishydroxymethylfuran (BHMTHF). In the next step, BHMTHF undergoes a hydrodehydration reaction into 5-methylfurfuryl alcohol (5-MFA), while 5-MFA may also be obtained by hydrogenation of 5-MF. Next, 5-MFA undergoes either hydrogenation into 5-methyltetrahydrofurfuryl alcohol (MTHFA), or hydrodehydration with the formation of DMF which can be further hydrogenated to 2,5- dimethyltetrahydrofuran (DMTHF). DMTHF

may also be obtained via the hydrodeoxygenation of BHMTHF, through the formation of the MTHFA intermediate. [7]

Among the HMF hydrodeoxygenation products, DMF and BHMTHF gained special attention due to their properties and functionalities. BHMTHF has been used as a green solvent, an intermediate for pharmaceuticals production or can be considered as an analogue of 1,3/1,4-cyclohexanedimethanol which is used for polyester production, or can also be converted to 1,6-hexanediol which is an important monomer for special applications. [8-12]. DMF is known as a biofuel additive, competitive to known alternatives and fully compatible to the currently used engines thanks to physicochemical properties similar to those of gasoline.[13]

The crucial issue is related with the selective transformation of HMF towards desired components in an economically feasible way. This can be achieved by the application of a selective and active catalyst or through the modification of the reaction conditions. Most of the works which concentrate on DMF and BHMTHF production via HMF hydrodeoxygenation describe catalysts based on noble metals such as Pd, Pt, Rh and Ru dispersed on oxide and carbon supports [14-20] giving less attention to their non-noble counterparts. [21], [22] Noble metal catalysts exhibit high activity and selectivity; however they suffer from important drawbacks, such as the need to operate under strict reaction conditions, relatively high price, limited abundance and stability issue, that alternatively could be overcome by the application of robust non-noble metal based catalysts.[5],[23]

Kong *et.al.* and Lima *et al.* studied bulk Raney®-type metals for HMF to DMF hydrogenation. While Raney Cu showed poor performance in the model reaction, Co and Ni Raney based catalysts gave promising results, with the latter being superior. Eventually, a switchable synthesis of DMF and BHMTHF over Raney® Ni was developed with 96% and 88.5% yield respectively, depending on the reaction temperature (100°C for BHMTHF and

180°C for DMF).[24] However, long reaction time (up to 30 h) and high Ni content (93%) were required to reach this activity. By contrast, Lima et al. reported that highly selective HMF hydrogenation could be obtained in a two-stage process using consecutively Raney® Cu and Ni catalysts [25].

Studies devoted to non-noble metals as active phase concerned mainly mono and bimetallic Ni-based catalysts supported on transition metal oxides such as Al₂O₃, WO₃ or TiO₂ [26-29]. One of the important factors that may affect the activity of the catalytic systems is the dispersion of the metal on the support surface. Siddiqui *et al.* showed that highly dispersed Ni/WO₃ has superior selectivity to DMF (95%).[28] Similarly, in the work of Goyal *et al.* high Ni dispersion was recognized as the key factor responsible for the good catalyst performance giving very high selectivity to DMF. In the latter case, high dispersion of Ni was reached thanks to the use of a mesoporous nitrogen-rich carbon material possessing high surface area.[30] The importance of the support was also highlighted in the work of Zhu et.al. [31] Particularly well-tuned support acidity for the selective formation of DMF was shown on the example of Ni- zirconium phosphate system. It was demonstrated that high Lewis acidity of the catalyst originating from zirconium vacant orbitals may enhance the Ni performance towards hydrodeoxygenation while a too strong acidity leads to the formation of overhydrogenated byproducts (via C=C bond reduction and C-C cleavage). Unfortunately, high reaction time (20 h) and elevated temperature 240°C were required for getting high DMF yield. In the recent work of Seemala *et al.*, [29] titania was shown as preferable support for Cu-Ni catalysts in the HMF hydrodeoxygenation. By allowing the preferential segregation of metals on the surface - namely Ni with close contact with the TiO₂ interface and Cu segregating at the Ni particle surface, high activity was reached. This segregation and preferential interaction of metals was not occurring on other non-reducible supports such as SiO₂ and Al₂O₃. [32][33]

Nevertheless, limited demonstration of a successful application of titania as a part of catalytic system in HMF hydrogenation is reported. From the other hand, it is known that the properties of titania can significantly influence the supported metal nanoparticles, and that often the titania properties are the driving force for the catalysts' activity. In the example of the levulinic acid hydrogenation, Ru supported on anatase or rutile phase exhibited fully different mean particle sizes, strength of interaction with the support and in consequence activity in the reaction. [34] A similar phenomena was noticed for Ni-based catalysts in the hydrogenation of p-nitrophenol, for which the catalytic activity of the anatase titania supported nickel catalyst was much higher than that of its rutile titania supported counterparts. The authors explained this superiority in terms of difference in the reduction behavior, and facilitation of reduction in the anatase based support.[35] In contrast, rutile-based catalysts were more active in the hydrogenation of acetophenone over Ni/TiO₂ in comparison to their anatase counterparts.[36] This was attributed to the electronic interaction between Ni and rutile which promotes the formation of electron enriched nickel species at the rutile surface which interact with the carbonyl group of acetophenone and therefore enhance activity.

So, the catalytic activity of Ni is strongly depending on both the type and the properties of the support used. Well-tuning the acidity may enable either HDO or furan ring hydrogenation, while the development of strong metal-support interaction (SMSI) may enhance the metal dispersion and affect the particle size, consequently influencing the activity. Therefore, in our work we were for the first time investigating on the use of different types of titania materials – varying in terms of polymorph nature and morphology –, as oxide supports in the catalytic hydrodeoxygenation of HMF in high pressure solvothermal reaction conditions. We compared anatase, rutile and bronze titania materials giving special attention to the one-dimensional (ie. high aspect ratio) supports prepared through the Kasuga-type hydrothermal synthesis method. This study allowed us to tune the activity of the supported catalysts to DMF or BHMTHF and

to understand which properties of the titania support are the driving force for the reaction selectivity.

2. Materials and methods

Several TiO₂ supports were used: anatase–rutile mixed phase Aeroxide© TiO₂ P25 and P90 were delivered by Evonik-Degussa (Germany). Hombikat UV100 and Cristal ACTIV PC500 consisting of pure anatase TiO₂ were delivered by Sachtleben Chemie GmbH (Germany) and Millenium-Crystal (France), respectively.

5-Hydroxymethylfurfural (98%) was purchased from Fluorochem Ltd (United Kingdom), Ni(NO₃)₂ · 6 H₂O (98 %) was purchased from Chempur (Poland). 1,4-dioxane (99 %) was purchased from Merck (Germany).

2.1. Hydrothermally prepared materials

High aspect ratio nanofibers (NF) and nanoplates (NP) were obtained through a Kasuga-type synthesis consisting in applying a hydrothermal treatment in concentrated basic conditions to a titania solid used as titanium precursor. In a typical synthesis, 1.5 g of Aeroxide© TiO₂ P25 powder were hydrothermally-treated in 90 mL of concentrated 10M NaOH solution at a temperature of 150°C or 200°C, respectively, for 24 h in a 150 mL teflon-lined stainless steel autoclave. The TiO₂ suspension was previously maintained under stirring at 360 rpm for 1 h for improving the particle dispersion. After the hydrothermal treatment, the white powder obtained was filtered, washed with 0.5M HCl solution till acidic pH and further with demineralized water till neutral pH before being overnight dried at 100°C. Then dried powder was further grinded and finally calcined at 500°C for 3 h, with a heating rate of 2°C/min.

2.2 Catalyst preparation

Catalysts with 5 wt.% and 10 wt.% of Ni content were prepared through the wet impregnation method of different types of TiO_2 as supports using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursor salt and water as solvent. After the solvent evaporation, the catalysts were dried at 120°C for 2 h with subsequent calcination in the air flow at a temperature of 500°C for 5 h. After oxidation, the catalysts were reduced in hydrogen flow at 500°C for 1 h.

2.3 Characterization methods

Temperature-programmed reduction (TPR) was performed on AMI1 system from Altamira Instruments, USA, equipped with a thermal conductivity detector and was used for examining the reducibility of catalysts. Before the measurement catalysts were calcined at 300°C (with a $10^\circ\text{C}/\text{min}$ heating rate) for 30 min in a mixture of 2 vol.% O_2 and 98 vol.% Ar at a space velocity $W/F = 1.11 \times 10^{-5} \text{ g/h cm}^3$. TPR profiles were recorded from 35°C up to 800°C , with a heating rate of $7^\circ\text{C}/\text{min}$, using a mixture of 5 vol.% H_2 and 95 vol.% Ar at a similar space velocity.

Temperature-Programmed Desorption (TPD) of NH_3 system was used to study the acidity of the catalysts. The TPD- NH_3 experiments were carried out in a quartz flow homemade micro-reactor. Before all experiments, the freshly reduced catalyst surface was purified under the flow of He at 500°C for 30 min. After the sample was cooled down to 100°C , the NH_3 was adsorbed on the catalyst surface at 100°C for 15 min. Before TPD- NH_3 experiment, physically adsorbed NH_3 has been removed from the catalyst surface by purifying the sample with the He carrier gas for 15 min and then cooled to room temperature. The temperature programmed desorption of NH_3 were carried out from room temperature to 500°C using a linear temperature ramp ($25^\circ\text{C}/\text{min}$).

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurements were performed using an ION-TOF GmbH instrument (TOF-SIMS IV) equipped with a 25 kV pulsed Bi⁺ primary ion gun in the static mode. The samples were fixed to the sample holder by double sided adhesive tape. The analyzed area of the sample surface was 500 μm x 500 μm. During analysis, a pulsed low-energy electron flood gun was used for charge neutralization.

X-ray diffraction (XRD) measurements were collected using a PANalytical X'Pert Pro MPD diffractometer. The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40 kV and 30 mA. Data were collected in the 5–90° 2θ range with 0.0167° step. Crystalline phases were identified by references to ICDD PDF-2 (version 2004) database. All calculations were performed with X'Pert High Score Plus computer program.

Scanning electron microscopy (SEM) was performed in secondary electron mode on a JEOL JSM-6700 F FEG microscope.

Transmission electron microscopy (TEM) was performed using a Philips CM200 in standard mode observation, equipped with thermo-ionic LaB₆ filament, operating at a 200 kV acceleration voltage. The samples were firstly grinded and sonicated in ethanol solution, before a drop of the solution was deposited onto a copper grid covered by holey carbon membrane for observation.

The Fourier Transform InfraRed spectroscopy (FTIR) spectra of CO adsorbed on nickel catalysts were registered on Nicolett 6700 spectrometer equipped with an MCT detector and a diffuse reflection chamber. Prior to exposure to carbon monoxide, the samples were reduced at an appropriate temperature in 5%H₂ in Ar for 1 h, then cooled to room temperature in an argon flow to remove adsorbed hydrogen and background spectra were collected. CO adsorption was carried out at 5 bar pressure of 5%CO in Ar for 30 min. Each spectrum was recorded with a resolution of 4 cm⁻¹ performing 64 scans.

2.4 Catalytic tests

The catalysts were tested in the 5-hydroxymethylfurfural (HMF) hydrogenation in high pressure solvothermal reaction conditions. The activity tests were performed in liquid phase using 1,4-dioxane as solvent within a stainless-steel autoclave (Premex, Switzerland) hydrogenation reactor operating under pressurized hydrogen, with a reaction volume of 60 ml. The reactions were carried out with 1 g of HMF, 0.15 g of catalyst and 30 mL of 1,4-dioxane. The reactor was pressurized with hydrogen to 30 bar and heated up to 220°C with a heating ramp of 6.5°Cmin⁻¹, and the reaction was further carried at 220°C for 0.25-5 h. The reactor was further cooled down and the remaining pressure was released. The obtained reaction mixture was then centrifuged to separate the catalyst from the product-containing solution. The products were subsequently analyzed on an Agilent 7820A GC instrument equipped with a CP-Wax 52 CB capillary column and flame ionization detector.

HMF conversion and product yields were calculated as follows:

$$Conversion = \frac{n_{HMF_i} - n_{HMF_r}}{n_{HMF_i}} \cdot 100\%$$

$$Yield = \frac{n_{prod}}{n_{HMF_i}} \cdot 100\%$$

n_{HMF_i} and n_{HMF_r} being the number of moles of HMF molecules before and after the reaction, respectively, and n_{prod} being the number of moles of a given product in the reaction mixture.

3. Results

3.1 Characterization of the hydrothermally synthesized titania materials

The morphology of the high aspect ratio titania materials obtained through hydrothermal syntheses was studied by SEM and TEM in Fig. 1 and 2, respectively. The morphology obtained differed strongly from the conventional morphology of commercially available titania, shown for comparison in Fig. 1. The images evidenced the total selectivity of the alkaline hydrothermal synthesis towards the high aspect ratio nanomaterials, with no nanopowder being observed in both samples whatever the hydrothermal synthesis temperature. The material synthesized at 150°C is composed of entangled nanostructures with an overall one-dimensional morphology, and highly agglomerated into micron-size fibrous clusters. The agglomeration is reported to occur already during the drying step, probably through water removal. [37] The images evidenced the nanofiber (NF) nature of the nanostructures (also labelled as nanorods), with a mean diameter of ca. 10-20 nm and short lengths of ca. 100 nm. Since the pioneering works of Kasuga et al. [38] describing the hydrothermal synthesis of one-dimensional TiO₂ or titanate nanostructures through the bending and rolling of titanate nanosheets, [39][40] the exact formation mechanism and the phase nature of such nanostructures remains still under debate.[41-44]

By contrast, the material hydrothermally synthesized at 200°C displayed a nanoplate (NP) structure (also labelled as nanoribbons), with a mean width of ca. 100-150 nm and lengths from 1 µm to several µm. The synthesis of such nanoplates or nanoribbons at 200°C was reported by Beuvier et al. [45] So, the nanostructure morphology was highly influenced by the hydrothermal synthesis temperature. This was attributed to the stability domains of the different phases in terms of temperature and of NaOH concentration as reported in Morgan *et al.* during the three-step soft chemistry Kasuga method.[46]

Figure 1 SEM images of a) NP and b) NF c) P25, d) P90, e) UV100 and f) PC500 titania materials

Figure 2 TEM images of a) NF and b) NP titania high aspect ratio materials prepared via hydrothermal synthesis.

3.2 Characterization of the TiO₂ supported Ni catalysts

3.2.1 XRD analysis of the 10 % Ni/TiO₂ catalysts

Figure 4 shows the XRD patterns of the catalysts and evidenced that the catalysts differ in terms of support phase compositions, taking into account the rutile (R) and anatase (A) or bronze (B) phase contribution. The main physico-chemical properties of the titania supports and of the 10 % Ni/TiO₂ catalysts are presented in Table 1 and 2, respectively.

Both TiO₂ P25 and P90 supported Ni catalysts contain 20 and 10 % of rutile, respectively, with the presence of the main rutile diffraction peaks at $2\theta = 27.5^\circ$, 36.0° and 41.2° (JCPDS 65-1119), in addition to the anatase as main crystalline phase, with the presence of the main anatase diffraction peaks at $2\theta = 25.3^\circ$, 38.7° , 48.0° and 55.1° (JCPDS 65-5714). Other catalysts prepared on commercially available titania only contained anatase as support phase, whereas the nanoplate titania (NP) sample consists in a bronze (B) phase, with the most intense diffraction peaks at $2\theta = 24.9^\circ$, 28.6° , 29.7° , 43.5° , 44.5° , 48.5° , 57.6° and 67.2° (JCPDS 00-0461237).[47-49]

Similarly to the difference in morphology, the nature of the high aspect ratio nanostructures was also influenced by the hydrothermal synthesis temperature, as a result of the stability domains of the different phases studied by Morgan et al.[46] and Beuvier et al. [45], the NP materials crystallizing as bronze TiO₂(B) at 500°C, while the nanofibers crystallized as anatase.

The materials differ as well in terms of specific surface area, the rutile-based supports exhibiting medium BET surface area (55-90 m²/g) which correlates with the presence of large mean size crystallites. By contrast, anatase-based titania exhibited much higher surface areas up to 336 m²/g in the case of the PC500 samples with smaller titania crystallites of 7 nm accordingly. The hydrothermally prepared high aspect ratio titania materials possess a non-microporous high specific surface area of 115 m²/g in the case of the short-length and small

diameter nanofibers exposing a high external surface area. By contrast, the hydrothermally prepared nanoplates have a lower surface area of 18 m²/g.

In all cases, diffraction reflexes assigned to metallic nickel at $2\theta = 44.5^\circ$ and 51.8° (JCPDS 04-0850) were observed. The smallest mean size of nickel crystallites were observed for the catalysts supported on UV100 and PC500 titania, at 8 nm, while the largest mean size of crystallites was obtained for rutile-containing materials (at 15 nm and 12 nm for P90 and P25, respectively) and for the NF support (13 nm).

Table 1 The main physico-chemical properties of titania materials

	TiO ₂ supports					
	P25	P90	UV100	PC 500	NF	NP.
Composition of the crystallized phase [%]	R: 21 A: 79	R: 10 A: 90	A	A	A	B
Average crystallite size [nm]^a	R: 32 A: 22	R: 23 A: 13	9	7	-	-
BET surface area [m²/g]	55	90	330	336	115	18
Pore volume [cm³/g]	0.12	0.24	0.22	0.21	-	-

a Determined from the XRD analysis by applying the Scherrer equation to the (101) and (110) peaks of anatase and rutile, at 25.7° and 27.5° , respectively, with the classical assumption of spherical crystallites.

Table 2 Main physico-chemical properties of the 10 % Ni/TiO₂ catalysts

Catalyst	Ni/P25	Ni/P90	Ni/UV100	Ni/PC500	Ni/NF	Ni/NP
Size of crystallites [nm] ^a	12	15	8	8	13	^b
Acidity [$\mu\text{mol}/\text{m}^2$] ^c	1.7	2.8	0.5	0.4	0.3	-

a Determined from the XRD analysis by applying the Scherrer equation to the mean diffraction of the metallic nickel at 44.5°, with the classical assumption of spherical crystallites.

b Not measurable due to the overlapping with one diffraction peak of the TiO₂(B) phase

c Determined through NH₃-TPD analysis

Figure 3 X-ray diffractograms of the 10 % Ni/TiO₂ catalysts. The non-assigned reflexes belong to the anatase structure

3.2.2 Temperature programmed reduction measurements

The reducibility of the Ni/TiO₂ catalysts was studied by TPR measurements (Figure 4). Although the analysis was conducted in a broad range of temperatures (30-800°C), the main reduction effect was observed in the 250-550°C range, so that only this temperature range is presented for highlighting the changes in between samples. The reduction profiles are characterized by the presence of one single reduction peak for all investigated catalysts, that however differs in terms of temperature range and maximum.

For Ni catalysts containing the rutile titania phase, both the maximum of hydrogen consumption (at 465°C and 460°C for 10 % Ni/P90 and 10 % Ni/P25, respectively) and the peak tail are located at high temperature. This can be assigned to NiO_x strongly interacting with titania [50-52] or to the presence of large crystallites.[36]

For the anatase supported catalysts (10 % Ni/UV100 and 10 % Ni/PC500), the maximum of hydrogen consumption peak was shifted towards lower temperature (at 425°C and 420°C, respectively). This may suggest the existence of weaker interactions between the NiO_x phase and the titania support, in agreement with the literature.[53]

The TPR profile of supported on titania nanofibers and nanoplates are similar to each other. The reduction profile starts for them in lowest temperature among all investigated samples (around 300°C). TPR profile is very broad and continues to high temperatures- almost like for rutile containing ones. This can be related with the presence of similar particle size and therefore similar Ni-TiO₂ interaction like for rutile -based samples. Additionally, the presence of low temperature effects can be related with the presence of amorphous NiO_x or NiO weakly interacting with the support. In the case of Ni/NP, this low temperature effect is more pronounced so that a low temperature maximum can be evidenced. This might result from the titania bronze nature of the support.

Figure 4 Temperature programmed reduction profiles of the 10 % Ni/TiO₂ catalysts

3.2.3 Acidity

The acidity of the catalysts was investigated by NH₃-TPD analysis. The highest concentration of acid sites was observed for the rutile-containing catalysts, particularly for Ni/P90. In contrast, the anatase-based materials showed significantly lower values (0.4-0.5 $\mu\text{mol}/\text{m}^2$) and the lowest one for the hydrothermally prepared material (0.3 $\mu\text{mol}/\text{m}^2$). It is well known that on the surface of titanium oxide is only composed of Lewis acid centers and that Brönsted acidity on the titania surface is the result of its interaction with water.[54] Scaranto et al. showed that the Lewis acidity of anatase and rutile is comparable, whereas acid centers on the surface of rutile are more electrophilic.[55] Taking this into account, the higher acidity of the rutile-containing catalysts compared to the anatase based samples is associated with the availability

of the surface Lewis acid centers and the polymorphic nature of TiO₂ has no major effect on the concentration of acid centers.

3.2.4 Time-of-flight secondary ion mass spectrometry analysis

Selected ions intensity identified on the surface of the catalysts by ToF-SIMS analysis are presented in Table 3. The relative nickel ions intensity on the catalyst surface, shown here as Ni⁺/Ti⁺ ratio, differ for the different analyzed samples. The highest ratio of Ni⁺/Ti⁺ ions was identified for the anatase-based materials, giving similar high values (5.7 and 4.0 for Ni/PC500 and Ni/UV100, respectively). This suggests that Ni crystallites are well-dispersed on the surface of these catalysts.[56] In contrast, the rutile-containing catalysts (Ni/P90 and Ni/P25) exhibited the lowest ratio of Ni⁺/Ti⁺ ions, probably due to the presence of large Ni crystallites, in agreement with the XRD results. The catalysts based on the hydrothermally prepared supports (Ni/NF and Ni/NP) showed similar Ni⁺/Ti⁺ ratio, at 3.0 and 3.4 respectively.

Table 3 Normalized intensity of selected ions calculated on the basis of ToF-SIMS spectra collected from the surface of the 10 % Ni/TiO₂ catalysts

Catalyst	Normalized intensity of selected ions identified on the catalysts surface		
	Ni ⁺ /Ti ⁺ (x 10 ⁻¹)	Ti ⁺ /total (x 10 ⁻¹)	NiTiO ⁺ /Ni ⁺ (x 10 ⁻³)
Ni/PC500	5.7	0.6	5.0
Ni/UV100	4.0	0.8	5.6
Ni/P90	1.9	1.2	7.2
Ni/P25	2.1	1.3	5.8
Ni/NF	3.0	1.1	6.7
Ni/NP.	3.4	1.1	-

Furthermore, the presence of NiTiO^+ ion was observed on the surface, which may suggest the existence of a strong interaction between nickel and titania or the presence of interfacial phase such as e.g. nickel titanate. The presence of this ion was detected for all samples, except in the case of Ni/NP. The highest ratio $\text{NiTiO}^+/\text{Ni}^+$ was detected for rutile-based samples particularly Ni/P90. For anatase-containing materials, the highest $\text{NiTiO}^+/\text{Ni}^+$ ions intensity was observed in the case of Ni/NF, while the lowest values were detected for the high-surface area anatase samples. This may indicate the establishment of stronger interactions of the rutile phase with NiO_x crystallites, in agreement with the literature. [53]

Figure 5 CO-adsorbed FTIR spectra of 10 % Ni/TiO₂ catalysts

3.2.5 FTIR analysis

Generally, the bands in the FTIR-CO spectra of nickel based catalysts in the 2100-2000 cm^{-1} range are attributed to the linear adsorption of CO on metallic nickel crystallites, while the bands below 2000 cm^{-1} are assigned to bridged CO adsorption on the metal crystallites. [57-60]

Therefore, the band observed at 2056 cm^{-1} in the spectra of the Ni/TiO₂ catalysts is assigned to physically adsorbed nickel carbonyl and the band at $2020 \pm 5\text{ cm}^{-1}$ appearing as a shoulder characterizes the linear CO adsorption on isolated nickel crystallites.[61-64] The highest intensity of both bands in the spectra of the pure anatase catalysts (Ni/PC500 and Ni/UV100) is due to the presence of small nickel crystallites with a high dispersion. Analogously, the lower intensity of the bands at 2056 cm^{-1} and $2020 \pm 5\text{ cm}^{-1}$ results from higher aggregation and lower dispersion of the nickel on the surface of hydrothermal titania and rutile-containing catalysts. Lower nickel dispersion explains the appearance of the band at 1980 cm^{-1} attributed to bridged CO adsorption.

Table 4 Catalytic activity of the Ni/TiO₂ catalysts in HMF hydrodeoxygenation

Catalyst	Reaction time [h]	Conversion [%]		Product yield [%]						
		HMF	5-MF	BHMF	BHMTHF	5-MFA	DMF	MTHFA	DMTHF	Others

Ni/P25	0.25	93	8	4	3	17	45	1	0	15
Ni/P25	0.5	98	5	3	4	16	57	2	1	10
Ni/P25	1	100	0	0	6	0	69	3	22	0
Ni/P25	2	100	0	0	6	1	24	6	54	9
Ni/PC500	0.25	89	23	0	0	14	44	0	0	8
Ni/PC500	0.5	98	17	0	0	4	69	1	1	6
Ni/PC500	1	98	20	0	0	3	71	1	1	2
Ni/PC500	2	100	2	0	0	1	85	0	5	7
Ni/P90	1	100	0	0	18	0	54	2	26	0
Ni/P90	2	100	0	0	8	0	54	5	29	4
Ni/UV100	1	99	29	1	1	18	49	0	0	1
Ni/UV100	2	100	6	0	0	4	79	2	6	3
Ni/NP	1	100	5	30	58	6	0	0	1	0
Ni/NF	1	100	0	0	58	1	19	6	5	11
Ni/P25 ⁽¹⁾	1	100	1	0	17	0	54	0	28	0

Reaction conditions: 220°C; time 0.25-2 h; 0.15 g of catalyst; 1 g of HMF; 30 ml of dioxane; 30 bar of hydrogen.

⁽¹⁾ the catalyst was prepared by calcination at 400°C and subsequent reduction at 350°C. Used as reference allowing to compare with the hydrothermally-prepared materials which required lower temperature treatment

3.2.6 Catalytic activity

The activity of the Ni/TiO₂ catalysts in HMF hydrodeoxygenation was presented in the Table 4. By comparing the results obtained with the catalysts supported on different TiO₂ materials, very clear tendencies can be noticed. Looking to the evolution of the reaction performance with time for the catalyst supported on P25 (ie. rutile-containing TiO₂), it is clearly possible to observe that although the DMF was the main reaction product (0.25-1 h), the reaction was proceeding further, and the reduction of the furan ring occurred with a significant DMTHF yield (54%) for a longer reaction time. This in consequence did not allow to reach high yield of DMF. Similar tendency was noticed in the case of another rutile-containing catalyst Ni/P90, where the highest yield to DMF was only 54%, as a significant amount of DMTHF was already present after 1 h. DMTHF yield did not increase significantly for longer reaction time, which could be related to the catalyst deactivation or due to the fact that this reaction step is a slow step due to a large energetic barrier.[13] In the case of the rutile-containing materials, we observed also a significant amount of BHMTHF. This suggests that path B (via BHMF) cannot be excluded as typically observed for Ni/C [13]. Lack of significant amount of BHMF can be related with the fact that the formation of BHMF is slow and is usually a rate limiting step [13] [65] in comparison to the fast formation of 5-MFA.

In contrast, a different behavior was observed in the case of the anatase TiO₂ supported catalyst Ni/PC500. Here high yield to DMF was kept already in the early reaction time (0.5 h - 69%) and was continuously increasing for reaching 85% after 2 h. The same observation can be noted for the other anatase-based material Ni/UV100 – DMF yield is continuously increasing and no further hydrogenation products are observed. In the latter case, significant yields to 5-MF and 5-MFA were observed and only traces of BHMF were detected. This might suggest

that the reaction proceeds preferentially in that case via hydrogenolysis towards 5-MF, followed by C=O hydrogenation to 5-MFA and final hydrogenolysis to DMF (path A). Such a path was also identified for Ni/zirconia based materials and explained by the presence of Lewis acid sites, which facilitated the first step of the reaction.[31]”

The presence of significant amount of BHMF was observed mainly in the case of 10 % Ni/NP catalyst. Interestingly, for both hydrothermally-prepared materials, the main reaction product was BHMTHF, that is a further ring-hydrogenation product issued from BHMF, and in both cases with a very high yield (58%) was noted. This suggests that the hydrogenation step was favored in both cases, whereas the hydrogenolysis of C-O was occurring only marginally, giving a maximum yield of only 19% towards the DMF by-product in the case of 10 % Ni/NF.

Additional results obtained for a lower Ni loading of 5% and for other reaction times are reported in Table S1 for selected catalysts.

4 Discussion

The significant support effect observed with Ni/TiO₂ catalysts in the HMF hydrodeoxygenation can be rationalized through the catalyst characterization studies. Based on the results, it is clear that the titania properties determine the size of the supported Ni particles, the character of the metal-support interaction and the catalyst acidity, with consequently a strong influence on the catalytic activity.

Large specific surface area anatase materials facilitate the formation of small Ni particles with a high dispersion. As a result, the surface exposed by the titania is reduced, so that the catalysts exhibit a moderate acidity. In contrast, the presence of the rutile phase induces the

existence of stronger Ni-support interactions. Rutile – as the more thermally stable phase – usually possesses a smaller specific surface area and in consequence larger Ni particles are formed. Additionally, for those materials, a significant acidity is observed.

Those features play a key role in hydrogen adsorption, as it is known that there is a significant electronic interaction between Ni and rutile, which can enhance the hydrogen adsorption,[36] in contrast to the Ni/anatase counterparts. From the other hand, H atoms may act as a ‘poison’ for the Ni surface due to its strong adsorption on the metal surface.[66] This effect is stronger in the case of smaller Ni crystallites which can even act as ‘hydrogen storage’ phase, whereas the adsorption/desorption of hydrogen is facilitated on larger Ni crystallites.[67] Therefore this suggests that the hydrogenation reaction might proceed *via* both 5-MF and BHMF paths in the case of the rutile-containing materials such as P90 and P25, for which large Ni crystallites are present. Further, the preferred adsorption in that case occurs most probably via $\eta^2(\text{C}=\text{O})$ which brings aromatic ring close to the surface, consequently allowing its reduction and therefore allowing only in this case the production of DMTHF in significant amount through the reduction of the furanic ring.[29]

The hydrothermally-prepared Ni/NF material stabilized relatively large Ni particles, and therefore favored the reaction path via BHMF. However, due to the low acidity of the catalyst further reactions of C-O hydrogenolysis were strongly limited and therefore BHMTHF was formed as the main reaction product due to further reduction of BHMF on Ni particles. Although the mean size of the Ni particles could not be determined on the Ni/NP material, both high aspect ratio catalysts displayed similar Ni^+/Ti^+ and Ti^+/total ratios in ToF-SIMS, so that a similar mean Ni particle size might be hypothesized in both cases, explaining that the BHMF reaction path was preferred on both catalysts.

The situation is different in the case of the large surface area anatase Ni/PC500 and Ni/UV100 catalysts. Here, the presence of acid sites and small metal particles which strongly

adsorb hydrogen and limit its desorption, favors possibly the path via hydrogenation and dehydration with the formation of 5-MF. In that case, on small Ni particles the ring-surface interaction is also limited, so that only traces of DMTHF were consequently observed.

A similar important role played by the metallic particle size was reported by the Somorjai's group in the vapor phase furfural hydrogenation. [68] The authors observed that the reaction path – and consequently the product selectivity – was highly dependent on the nanoparticle size in the case of Pt/SiO₂ catalysts, small particles being found to form predominantly furan via decarbonylation, whereas larger sized particles yielded both furan and furfuryl alcohol, the carbonyl hydrogenation product.

5 Conclusions

The activity of TiO₂ supported Ni catalysts varying in terms of morphology and crystallographic structure of the support has been investigated in the HDO of HMF. It is clear that the titania properties determine strongly the character of the supported nickel nanoparticles (in terms of both the size and the strength of the interaction with the support). By tuning the titania properties, we can force the selectivity towards the desired product.

Rutile-containing titania stabilizing larger Ni crystallites forced the existence of stronger Ni-Ti interactions and enhanced hydrogen adsorption, which resulted in high activity. Although DMF is the main reaction product, the reaction is pushed forward towards the production of DMTHF through the reduction of the furanic ring in that case.

Hydrothermally-prepared materials allowed to obtain selectively 2,5-bishydroxymethyl-tetrahydrofuran due a relatively low surface acidity and large Ni particles. By contrast, the large surface area anatase with small nickel particles allowed to achieve high selectivity to DMF (85%).

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