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Influence of W on the reduction behaviour and Brønsted acidity of Ni/TiO<sub>2</sub> catalyst in the hydrogenation of levulinic acid to valeric acid: Pyridine adsorbed DRIFTS study

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Graphical abstract



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Highlights

- Strong interaction between W and Ni leads to increased Ni<sup>2+</sup>/Ni<sup>0</sup> ratio on surface
- ➤ At ambient H<sub>2</sub> pressure levulinic acid was converted to valeric acid over W-Ni/TiO<sub>2</sub>
- > Lewis acid site in combination with Ni<sup>0</sup> active for  $\gamma$ -valerolactone
- Brønsted acid sites close to nickel sites are responsible for valeric acid formation

#### Abstract

Effect of W on 20wt%Ni/TiO<sub>2</sub> catalyst is examined in the hydrogenation of levulinic acid (LA) to valeric acid at ambient H<sub>2</sub> pressure. The interaction between W and Ni had a significant influence on the hydrogenation activity and product selectivity. The H<sub>2</sub>-TPR (temperature programmed reduction) results emphasized a shift in  $T_{max}$  to very high temperatures due to W species which are in close proximity to Ni particles. The N<sub>2</sub>O decomposition measurements showed a decrease in N<sub>2</sub>O uptake with the increase in 'W' loadings due to a high ratio of Ni<sup>2+</sup>/Ni<sup>0</sup> species at higher tungsten content. X-ray photoelectron spectra (XPS) demonstrated a shift in binding energy to higher owing to a strong interaction between W and Ni particles by the presence of ionic Ni at the near surface region. The ionic Ni species seems to be involved in the conversion of  $\gamma$ -valerolactone (GVL) to valeric acid (VA). Pyridine adsorbed infrared (IR) spectra revealed an enormous increase in surface Brønsted acidity originated from tungsten interacted Ni/TiO<sub>2</sub> are the sites responsible for ring opening of GVL to form VA.

Key words: Levulinic acid, Valeric acid,  $\gamma$ -Valerolactone, DRIFTS, W-Ni/TiO<sub>2</sub>, Brønsted-Lewis acidity.

#### **1. Introduction**

Development of catalysts for the production of fine chemicals and fuels additives from biomass-derived compounds has become a topic of interest [1-3]. Inedible biomass feedstock, namely lignocellulose is an attractive raw material for the synthesis of secondgeneration biofuels and fuel additives [4]. A variety of multi-step processes to convert inedible biomass into fuels include; hydrolysis, gasification and pyrolysis of biomass [5-6]. Of the many, production of levulinic acid (LA) has received significant interest due to the potential conversion of LA into a range of fine chemicals and fuel additives [7-8]. Numerous studies have been reported on LA hydrogenation to  $\gamma$ -valerolactone (GVL) over both homogeneous and heterogeneous catalytic systems using noble and non-noble metal catalysts in liquid phase as well as in the vapour phase [9-12]. Studies pertaining to GVL conversion to other useful compounds such as valeric acid (VA), 1,4-pentanediol and 2methyltetrahydrofuran (MTHF) were also reported [13-18]. Among various compounds, the high energy density liquid; valeric acid (VA) has been found to be a potential candidate in the bio-fuel production as the valerate esters are being used as blending agents for both gasoline and diesel [19]. Conversion of LA over non-noble metal based catalysts is a promising approach when compared to the use of expensive noble metal catalysts [20]. From R&D perspectives, catalytic processes with zero waste and reduction of multitude processes into a single step are mandatory [21]. Exploration of base metal catalysts for the conversion of levulinic acid to valeric acid is economically attractive. Thus, surface modification of Nibased catalysts for the single-step conversion of LA to VA is gaining momentum [22].

Lange et al. reported the synthesis of valerate esters in a multi-step process using Pt/TiO<sub>2</sub> catalyst for LA to GVL conversion followed by subsequent GVL conversion to VA and esterification of VA to valerate ester over Pt/H-ZSM-5 catalyst [23]. In a systematic

study, Weckhuysen et al. examined the zeolite supported Ru catalyst for LA to VA with 45.8% yield using dioxane as solvent at 200 °C and 40 bar H<sub>2</sub> pressure [24]. Fu et al. tested the LA hydrogenation over Ru/SBA-SO<sub>3</sub>H catalyst in ethanol resulted in the co-production of VA and ethyl valerate with a total yield of 94% at 240 °C and 40 bar H<sub>2</sub> pressure [25]. Kenichi et al. developed direct and selective catalytic route for VA from LA over Pt/HMFI catalyst at 200 °C and 8 bar H<sub>2</sub> pressure [26]. Shell laboratory obtained a patent on the conversion of LA to GVL and subsequent GVL conversion to VA with 70% yield over the Pt/H-ZSM-5/SiO<sub>2</sub> catalyst [27]. An excellent paper reported from Dumesic group on the hydrogenation of LA to VA and 5-nonanone through GVL over a combination of Ru/C (LA to GVL) and Pd/Nb<sub>2</sub>O<sub>5</sub> (GVL to VA and 5-nonanone) catalysts [28]. Most of these reports were on supported noble metal catalysts at slightly elevated H<sub>2</sub> pressures.

To the best of our knowledge, very few reports are published on single-step conversion of LA to VA in the vapour phase at ambient H<sub>2</sub> pressure and the reaction temperature maintained in this study otherwise is also very close to the reported studies on the conversion of LA in liquid and vapour phase. Earlier we have reported the hydrogenation of LA to GVL over supported Ni and Ru catalysts [29-31]. The 20wt%Ni/TiO<sub>2</sub> has been modified using several promoters such as Fe, Co, Cu, Bi, W and Sn, which showed promising activity towards valeric acid in the vapour phase hydrogenation of aqueous LA (Table S1). Among them, the W modified 2wt%W-20wt%Ni/TiO<sub>2</sub> has demonstrated interesting results. Hence, a detailed study on W modified Ni/TiO<sub>2</sub> catalysts are investigated. The addition of W to Ni/TiO<sub>2</sub> drastically modified the reduction behaviour of Ni species and surface acidity which in turn influenced the hydrogenation activity to produce GVL along with valeric acid. The reduction behaviour of W modified Ni/TiO<sub>2</sub> catalysts are investigated by H<sub>2</sub>-TPR analysis. Nature of acid sites on W modified Ni/TiO<sub>2</sub> catalyst is rationalised using pyridine adsorbed DRIFTS and the Ni dispersion is estimated by N<sub>2</sub>O titration. Long term stability

tests and post characterization studies were also conducted on the optimized catalyst composition.

#### 2. Experimental

#### **2.1 Catalyst Preparation**

The Ni supported on TiO<sub>2</sub> (P25 Degussa BET surface area 56 m<sup>2</sup>/g) catalyst was prepared by an incipient wet impregnation (IW1) method. In a typical procedure, required amount of aqueous Ni(NO<sub>3</sub>)<sub>3</sub>· 6H<sub>2</sub>O solution mixed with TiO<sub>2</sub> (to give 20wt%Ni) under constant stirring at 100 °C until the water evaporated, dried at 120 °C for 12 h subsequently calcined in static air at 500 °C for 4 h. The W modified 20wt%Ni/TiO<sub>2</sub> catalysts with different loadings (1.0 - 2.5wt%W) were impregnated on calcined 20wt%Ni/TiO<sub>2</sub> by using (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41.x</sub>H<sub>2</sub>O precursor. Then the samples were dried at 120 °C followed by calcination in static air at 500 °C for 4 h. For comparison, two different samples were prepared namely (i) a 1.5wt%W/TiO<sub>2</sub> and 98.5wt% of 20wt%Ni/TiO<sub>2</sub> (calcined) followed by calcination in static air at 500 °C for 4 h. The elemental analysis (ICP-MS) of these samples is reported in Table S2. The metal contents in all the catalysts were denoted by their weight percentage.

#### 2.2 Characterization of catalysts

Powder XRD patterns of the catalysts were recorded with Bruker D4 Endeavor wide angle X-ray diffractometer (M/s. Bruker Corporation, Germany) using Ni-filtered Cu K $\alpha$ radiation ( $\lambda = 0.15418$  nm) with a scan rate of 2° min<sup>-1</sup> in the 2 $\theta$  range of 10-90° at 40 kV and 20 mA. The crystallite size (*D*) was measured by applying Debye-Scherrer equation w.r.t. Ni (111) plane. The acid site distribution on 20wt%Ni/TiO<sub>2</sub> (fresh) and 20wt%Ni-1.5wt%W/TiO<sub>2</sub> (fresh and used) catalysts were recorded on Micromeritics (Auto Chem 2910) by temperature programmed desorption (TPD) of NH<sub>3</sub>. In a typical method, about 0.15-0.2 g

of the sample was reduced at 500 °C for 1 h in 4.97% H<sub>2</sub>/Ar (v/v) at a flow rate of 30 mL min<sup>-1</sup>. After reductive pretreatment, the sample was cooled to 100 °C followed by saturation with NH<sub>3</sub> gas and subsequently flushed in helium flow at 100 °C for 1 h to remove the physisorbed NH<sub>3</sub>. The desorption of NH<sub>3</sub> was then carried out by heating the sample up to 600 °C at a ramping rate of 5 °C min<sup>-1</sup>. The inductively coupled plasma-mass spectroscopy (ICP-MS) analysis was done using Thermo Jarrell Ash model IRIS Intrepid II XDL, USA instrument to determine the elemental composition of the catalysts. In the current study, prior to the analysis, ~0.05 g of the catalyst sample was added to the mixture of aqua regia and excess distilled water. Again 10 mL of the above solution was further diluted with distilled water and was used for the ICP analysis. The metal surface area of W loaded Ni/TiO<sub>2</sub> catalysts was measured by N<sub>2</sub>O decomposition experiments carried out at 80 °C. In a typical method, about 0.05 g of the catalyst was reduced in H<sub>2</sub> (4.97% H<sub>2</sub>/Ar) atmosphere 500 °C for 1 h followed by cooling down the reactor to 80 °C in helium flow (30 mL min<sup>-1</sup>). The pulses (maximum of 3-4) of N<sub>2</sub>O are then injected onto the catalyst sample. The uptake of N<sub>2</sub>O is monitored using GC equipped with a TCD detector and Porapak N column. The experimental details on H<sub>2</sub>-TPR, XPS, TEM, BET-SA, and pyridine adsorbed DRIFT spectra of the catalysts used in this study are similar to what was reported in our earlier papers [29-31] and are also given in detail in the experimental section of ESI.

#### 2.3 Activity measurements

Vapour phase hydrogenation of levulinic acid was carried out in a fixed-bed quartz reactor (i.d. = 12 mm, length = 420 mm) in down flow mode. Prior to the reaction, the catalyst sample (~0.2 to 0.3 g -18/+25 BSS sieved particles) were reduced at 500 °C for 4 h in 4.97% H<sub>2</sub> (balance Ar) at a flow rate of 30 mL min<sup>-1</sup>. After reduction, the catalyst bed was brought to the desired reaction temperature and the 10wt% aqueous LA was fed using an HPLC pump along with H<sub>2</sub> at a flow rate of 30 mL min<sup>-1</sup>. The gas flow rates were monitored

using mass flow controllers (Alicat Scientific) to regulate the flow. The product mixture was collected in an ice cold trap for each 1 h and analyzed by GC-MS (QP5050A Shimadzu) and gas chromatograph (Varian CP-3800 GC equipped with ZB capillary wax column and FID detector). The carbon mass balance was >98% based on inlet and outlet carbon unless otherwise stated. The gaseous products were analyzed by connecting the reactor outlet to a six-way sampling valve interfaced to a GC with TCD (Agilent 7820A).

#### 3. Results

#### **3.1 Powder X-ray diffraction (XRD)**

The powder XRD patterns of 20wt%Ni/TiO<sub>2</sub> and W modified Ni/TiO<sub>2</sub> samples are reported in Figure S1. The diffraction lines at  $2\theta = 37.2$ , 43.2, 62.8 and 75.4° due to NiO phase with face centred cubic geometry (ICDD # 78-0429) is observed. Diffraction lines at  $2\theta = 19.2$ , 31.0 and 65.8° are due to NiWO<sub>4</sub> that has monoclinic geometry (ICDD # 72-0480) corresponding to (100), (111) and (202) planes respectively. The diffraction peaks at  $2\theta =$ 14.2, 28.8 and 32.6° are attributed to the presence of different mono and polymeric W<sub>x</sub>O<sub>y</sub> species (such as WO<sub>3</sub> and W<sub>18</sub>O<sub>49</sub>). The remaining diffraction lines are due to the TiO<sub>2</sub> support both anatase and rutile; ICDD # 78-2486 and ICDD # 87-0710 respectively.

In the reduced samples, metallic Ni emerged as the main phase (ICDD # 04-0850) at  $2\theta = 44.5$ , 52.0 and 76.5° (Figure 1). The diffraction lines due to NiWO<sub>4</sub> are also found at 2 $\theta$  = 19.2, 31.0 and 65.8° (ICDD # 72-0480). Reduction of W-Ni/TiO<sub>2</sub> samples led to strong diffraction lines due to NiWO<sub>4</sub> and WO<sub>2</sub> (ICDD # 02-0414) species. From the XRD spectra (inset of Figure 1), it is also observed that after the reduction at 500 °C, the W loaded Ni/TiO<sub>2</sub> samples showed the presence of ionic Ni (NiO; ICDD # 78-0429) along with metallic Ni, whereas Ni/TiO<sub>2</sub> catalyst showed only metallic Ni.

The W<sub>x</sub>O<sub>y</sub> species are reduced to various W<sub>x</sub>O<sub>y</sub> species (W<sub>18</sub>O<sub>49</sub>, W<sub>20</sub>O<sub>56</sub> and W<sub>20</sub>O<sub>58</sub>) along with WO<sub>2</sub>, whereas the 1.5wt% W/TiO<sub>2</sub> sample has shown (Figure S2) WO<sub>3</sub> along with TiO<sub>2</sub> phase. These results indicate that WO<sub>x</sub> species are not reduced and its existence is different when impregnated on 20wt%Ni/TiO<sub>2</sub>. Reduction of W<sub>x</sub>O<sub>y</sub> species seems to occur while W<sub>x</sub>O<sub>y</sub> species are in close contact with nickel particles by the hydrogen activation on Ni surface. At lower W loadings (1.0 and 1.5wt.%), the diffraction lines of W<sub>x</sub>O<sub>y</sub> species are absent. Interestingly, the 1.5wt%W loaded 20wt%Ni/TiO<sub>2</sub> sample showed more prominent and sharp diffraction line due to NiWO<sub>4</sub> phase and above this loading; the intensity of diffraction lines due to WO<sub>2</sub> species are strong. The XRD spectra also revealed the presence of WO<sub>2</sub> species at higher loading (W = 2.5wt%) after reduction of 2.5wt%W-20wt%Ni/TiO<sub>2</sub> sample at 500 °C for 4 h (Figure S3).

#### **3.2 Physico chemical characteristics**

The Physico chemical characteristics of the TiO<sub>2</sub> supported Ni catalysts are compiled in Table 1. The N<sub>2</sub>-sorption analysis showed a small decrease in the surface area of the Ni/TiO<sub>2</sub> catalyst after W addition and the similar trend is observed as W loading is increased from 1 to 2.5wt.%. TPD of NH<sub>3</sub> results showed a significant increase in the total acidity after W modification to the Ni/TiO<sub>2</sub> catalyst. Similarly, a higher number of acid site distribution is observed for the 2.5wt.% W loaded Ni/TiO<sub>2</sub> catalyst. The results of NH<sub>3</sub>-TPD analysis results are also in good agreement with the results obtained from the pyridine adsorbed DRIFTS analysis; where significantly higher BAS/LAS ratio is observed for the W modified Ni/TiO<sub>2</sub> catalyst compared to that of un-promoted one. The crystallite size of Ni is also calculated (Table 1) for all the W loaded Ni/TiO<sub>2</sub> catalysts and the results showed a small increase in the Ni crystallite size after W modification to the Ni/TiO<sub>2</sub> catalysts (increase in average particle size of Ni after W addition to the Ni/TiO<sub>2</sub> catalyst).

#### **3.3** H<sub>2</sub>-Temperature programmed reduction (TPR)

The TPR patterns of 1.5wt%W/TiO<sub>2</sub> (IWI) sample did not show any reduction signals indicating the inert behaviour of tungsten oxide species even up to 1000 °C (Figure 2a). It should be noted that WO<sub>3</sub> species require high temperatures for reduction when deposited on TiO<sub>2</sub> alone i.e. in the absence of Ni [32]. In contrast, the 20wt%Ni/TiO<sub>2</sub> with W loadings of 0.0, 1.0, 1.5, 2.0 and 2.5wt.% showed two reduction peaks. The low-temperature reduction peak around 452 °C (Figure 2b) is due to Ni<sup>2+</sup> to Ni<sup>0</sup> (dispersed NiO) and the hightemperature signal at 648 °C is ascribed mostly to the reduction of large clusters of NiO particles and also due to the reduction of NiO particles interacted with tungsten to some extent [33]. Both of these reduction peaks are shifted to high temperatures upon increasing the W loading on 20wt%Ni/TiO<sub>2</sub> (Figure 2c-2f). The reduction peak shift towards high temperatures with the increase in W loading is probably due to an interaction between nickel and tungsten oxide particles. The H<sub>2</sub> uptakes are marginally increased upon doping of W to 20wt%Ni/TiO<sub>2</sub> catalyst (Table S2). This increase is probably due to hydrogen activation on Ni site which is catalysing the reduction of tungsten oxide species to some extent as the 1.5wt%W/TiO<sub>2</sub> alone did not show any reduction signal. From these results it can be inferred that a reduction temperature of 500 °C is insufficient to convert the total  $Ni^{2+}$  to metallic Ni and a minimum of temperature >750 °C is required to obtain the metallic Ni for the W loaded samples (Figure 2b-2f). Therefore, the W modified 20wt%Ni/TiO<sub>2</sub> samples reduced at 500 °C demonstrated the existence of both metallic and ionic Ni particles (inset Figure 1). The shift in reduction signal to very high temperatures is originated from the strongly interacted NiO with W oxide particles which is also further supported by the UV-DR spectra (Figure S4) of the 20wt%Ni/TiO<sub>2</sub> and 1.5wt%-20wt%Ni/TiO<sub>2</sub> catalysts.

#### 3.4 X-ray photo electron spectroscopy (XPS)

The X-ray photoelectron spectra of reduced  $20wt\%Ni/TiO_2$  and  $1.5wt\%W-20wt\%Ni/TiO_2$  samples are reported in Figure 3. The Ni 2p signals of  $20wt\%Ni/TiO_2$  showed nickel in both Ni<sup>0</sup> and Ni<sup>2+</sup> species in the near surface region with binding energy (BE) of 852.1 eV (Ni<sup>0</sup>) and Ni<sup>2+</sup> signal at 855.4 eV respectively [33]. No significant shift (in BE) is observed for metallic Ni over  $20wt\%Ni/TiO_2$  however, after W modification the BE of ionic Ni is shifted to higher BE in the  $1.5wt\%W-20wt\%Ni/TiO_2$  compared to  $20wt\%Ni/TiO_2$  sample, thus emphasizing the interaction of ionic Ni with tungsten particles on the catalyst surface. A high ratio of ionic Ni is observed from the TPR analysis wherein a drifting of reduction signals towards high temperatures suggesting the interaction between Ni and W. These results are in good agreement with earlier reports on a strong interaction between W and Ni particles [34].

#### **3.5 Pyridine adsorbed DRIFTS analysis**

The nature of acid sites is investigated by pyridine adsorbed DRIFT spectroscopy (Figure 4). The vibrational bands due to pyridine-surface acid site interactions are distinguished by a peak fitting using the Gaussian function. These spectra show the formation of both protonated pyridine (1540 and 1636 cm<sup>-1</sup>) and co-ordinated pyridine (at 1620 and 1450 cm<sup>-1</sup>) in the presence and the absence of W in 20wt%Ni/TiO<sub>2</sub> catalyst. The other bands present in the DRIFT spectra correspond to both protonated and coordinated pyridine at 1489 cm<sup>-1</sup> and 1513 cm<sup>-1</sup>. The bands present in 1580-1600 cm<sup>-1</sup> region is due to a weak interaction of pyridine with the acid sites present on the catalyst surface [35-36]. The characteristic pyridine adsorbed IR bands attributed to Lewis acid (1448 cm<sup>-1</sup>) and Brønsted acid sites at 1539 cm<sup>-1</sup> (quantified DRIFT spectra is obtained using Kubelka-Munk correction) are used to measure the relative distribution of the acid sites on 20wt%Ni/TiO<sub>2</sub> and 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts. The spectra clearly demonstrated a high proportion of Brønsted to Lewis acid sites over 1.5wt%W-20wt%Ni/TiO<sub>2</sub> compared to 20wt%Ni/TiO<sub>2</sub> catalyst.

#### **3.6 Measurements of the catalytic performance**

The vapour phase hydrogenation of LA carried out over various W loaded (0.0 to 2.5 wt%) 20wt%Ni/TiO<sub>2</sub> catalysts and the data is reported in Table 2. Conversion of LA decreased from 92.3 to ~73.0% upon doping of W to 20wt%Ni/TiO<sub>2</sub> and a marginal difference even at higher tungsten loadings is found. Interestingly, the rate of angelica lactone is increased with increase in tungsten loading. However, the rate of VA increased up to a loading of 1.5wt%W and beyond this, it is slightly decreased. It is also found that the rate of VA formation is at the cost of GVL. The enhanced rate of angelica lactone in the W loaded 20wt%Ni/TiO<sub>2</sub> catalysts may be due to a higher number of acid sites contributed from W-TiO<sub>2</sub> interacted species. Formation of other products such as MTHF, C<sub>4</sub>, and/or C<sub>5</sub>-alcohols are absent in the absence of tungsten. On the contrary, yields of these products are increased with increase in W loading. The addition of tungsten to 20wt%Ni/TiO<sub>2</sub> seems to enhance the Brønsted acid sites which are identified as active sites for the ring opening of GVL to form valeric acid [26].

The 1.5wt%W/TiO<sub>2</sub> catalyst showed about 5% LA conversion with 92% angelica lactone selectivity (Table 3). Products such as VA and GVL are absent on the 1.5wt%W/TiO<sub>2</sub> catalyst. These results thus explain that 1.5wt%W/TiO<sub>2</sub> sample seems to dehydrate the LA and the active sites present on 1.5wt%W/TiO<sub>2</sub> are inactive for the hydrogenation of angelica lactone into either GVL or other products. Modification of surface Ni by W drastically changed the product distribution (Table 2 and Table 3). The rate of GVL is reduced consequently the VA rate is improved in the presence of tungsten with an optimum tungsten loading of 1.5wt% demonstrated 48.5% selectivity of VA.

In the absence of Ni, the 1.5wt%W/TiO<sub>2</sub> demonstrated angelica lactone as the major product. These results thus indicate the involvement of Ni sites that are crucial for the hydrogenation particularly, the reduction of AL to GVL on metal sites and the ring opening

of GVL over Brønsted acid sites. To further understand the role of the W and the NiO-WO<sub>x</sub> interacted species on LA conversion and on the product selectivity; the reaction is carried out using mixed oxides composed of  $20wt\%Ni/TiO_2 + 1.5wt\%W/TiO_2$  prepared by mechanical mixing. The mechanically mixed catalyst showed selective GVL formation and very poor VA yields (Table 3). Therefore, it can be concluded that Ni interacted with W are prone to ring opening of GVL to form VA on Brønsted acid sites.

To gain an insight into the reaction mechanism, catalytic activities were evaluated using aqueous GVL (Table 4). The rate of VA over 20wt%Ni/TiO<sub>2</sub> catalyst is an order of magnitude lower than on 1.5wt%W-20wt%Ni/TiO<sub>2</sub>. The selectivity of VA was considerably good (>58%) over 20wt%Ni-1.5wt%W/TiO<sub>2</sub> with a 60% conversion of GVL. However, the conversion of GVL over both the catalysts was lower compared to LA conversion under identical experimental conditions (Table 4). Using angelica lactone as a substrate, the 20wt%Ni/TiO<sub>2</sub> exhibited better conversion (~68.8%) compared to 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst (~44.6%). The rate of GVL is almost twice over 20wt%Ni/TiO<sub>2</sub> than on 1.5wt%W-20wt%Ni/TiO<sub>2</sub> (Table 4). Whereas GVL as a substrate, the hydrogenation rate of -keto group (in GVL) to MTHF is slightly higher in the absence of tungsten. The hydrogenolysis rate (i.e. ring opening via C-O cleavage) of GVL to diols is low over 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst emphasizing that metallic Ni sites influencing GVL ring to a large extent.

#### **3.7** Time on stream activity results

Catalyst longevity test was conducted (60 h) to investigate the stability of the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> for VA formation (Table 5). The results of this analysis showed no significant loss in activity even after 60 h of the reaction.

The CHNS analysis of the used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst showed a small amount of coke deposition (Table 6). A comparison between XRD analysis of reduced (at 500 °C for 4 h) and used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst (recovered after 60 h of

continuous operation) showed no significant changes in the intensity of diffraction lines due to metallic Ni and/or TiO<sub>2</sub> except the formation of polymeric  $W_xO_y$  species only in the used sample (Figure 5). The Ni crystallite size measured by using Debye-Scherrer equation for both the reduced and used forms of 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst is found to be *ca*. 22.7 nm which is very close to the Ni particle size (*ca*. ~25.0 nm) measured by TEM analysis of the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> (reduced and used) catalyst (Table 6).

Figure 6 shows the Ni 2p spectra of both the reduced (at 500 °C for 4 h) and used (recovered after 60 h of continuous operation) forms of the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> sample. It shows that Ni is present in both metallic  $(2p_{3/2})$  at a BE of 851.8 eV (satellite peak at 862.8 eV) and oxidic form  $(2p_{3/2})$  with the binding energy of 856.7 eV in both the reduced and used samples. No significant changes were observed in peak positions due to binding energies of metallic and ionic Ni present 1.5wt%W-20wt%Ni/TiO<sub>2</sub> sample exemplifying the stability of the catalyst. The XPS of W4f spectra showed the presence of W in +6 oxidation state with corresponding BE at 37.5 eV and 35.6 eV ascribed to W4f<sub>5/2</sub> and W4f<sub>7/2</sub> respectively (Figure 7) [34]. The emergence of satellite peak is an indication  $W_xO_y$  species, observed only in the case of used catalyst. The surface characteristics are in good agreement with the bulk properties of the used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts revealed by XRD analysis that showed polymeric W<sub>x</sub>O<sub>y</sub> species (Figure 5).

The TPD of  $NH_3$  studies revealed a marginal decrease in acidity of the used  $1.5wt\%W-20wt\%Ni/TiO_2$  compared to its reduced form. The decrease in acidity was most likely due to the irreversible chemisorption of a fouling agent such as angelica lactone (one of the intermediates in the reaction sequence) leads to deposition of carbon on the catalyst surface during the course of the reaction (Table 6). The ICP-MS analysis of fresh and used samples revealed that there is no leaching of either Ni or W species even after 60 h of

continuous operation thus suggesting the stability of the catalyst under the reaction conditions maintained in this study.

#### **4 Discussion**

According to the results compiled in Table 2, the drastic fall in the rate of GVL can be explained by a decrease in surface Ni metal sites by the interaction with tungsten which is confirmed from N<sub>2</sub>O decomposition measurements (Table 2). This phenomenon is further supported by the H<sub>2</sub>-TPR analysis of the tungsten loaded 20wt%Ni/TiO<sub>2</sub> catalysts (Figure 2). Though the rate of VA is increased up to 1.5wt%W; the GVL rate is further decreased at higher W loadings. This indicates that at higher loadings of tungsten; conversion of GVL either to MTHF or other products occurs. In the comparative analysis, the 20wt%Ni/TiO<sub>2</sub> catalyst (Table 2).

Further increase in W loading led to a marginal decrease in VA selectivity with the formation of other products such as MTHF and 1, 4-diol. At higher W loaded (2.0 and 2.5wt.%) Ni/TiO<sub>2</sub> catalysts, an increase in the Brønsted acidity is expected (Figure 4 and Table 1), at the same time formation of WO<sub>2</sub> species are higher compared to lower W loading samples (confirmed by X-ray line broadening studies and XPS analysis of the 2.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst; Figure S3 and Figure S5). It is also found that the addition of W to Ni/TiO<sub>2</sub> led to a decrease in GVL selectivity which confirms the ring opening of GVL occurring on the Brønsted acid sites to form VA. Therefore, from the aforementioned results, it is clear that the influence of W loading is effective at W = 1.5wt% for the optimized VA yield under the reaction conditions maintained in this investigation.

Reduction of the tungsten modified  $20wt\%Ni/TiO_2$  samples at 500 °C results in the formation of both metallic and ionic Ni species. The TPR analysis showed the increased interaction between nickel and tungsten particles caused the difficulty in the reduction of

nickel oxide species as indicated a dramatic shift in  $T_{max}$  to very high temperatures (Figure 2). We believe that metallic Ni seems to be more reactive than the ionic Ni and the Ni sites that have closely interacted with W-TiO<sub>2</sub> particles may be involved in the further conversion of GVL to VA. This effect is clearly seen as all the samples were reductively pre-treated at 500 °C prior to the reaction and the TPR patterns demonstrated that upon increasing W loading; the peak intensity of high-temperature reduction signal attributed to ionic Ni is increased. On the other hand, Ni particles interacted with TiO<sub>2</sub> are selective for the formation of GVL through the hydrogenation of angelica lactone.

The overall VA rate is higher by an order of magnitude in presence of W. The  $Ni/TiO_2$  is selective for the conversion of LA to GVL and GVL as a substrate the ring opening of GVL occurred to form diols rather than VA (Table 2 and Table 4). Quiet contrast to this, the rate of VA is higher by an order of magnitude over 1.5wt%W-20wt%Ni/TiO<sub>2</sub> with GVL as a substrate compared to 20wt%Ni/TiO<sub>2</sub>. Therefore formation of VA has occurred in presence of W adjacent to Ni site on the catalyst surface.

Based on the results obtained and from earlier reports [29, 31], the hydrogenation of AL to GVL is rapid relative to ring opening of GVL to form other products such as VA and MTHF (Scheme 2). The LA stream that contained large amount of H<sub>2</sub>O (90wt.%) tends to influence the surface ionic Ni species rather than metallic Ni during the course of the reaction. One would expect two possibilities wherein (i) first case the metallic Ni reacts with H<sub>2</sub>O to form NiO and H<sub>2</sub> and the second case (ii) is the reaction between WO<sub>x</sub>-NiO and H<sub>2</sub>O leads to the formation of enhanced Brønsted acid sites such as  $W_x(OH)_y$ -Ni(OH)<sub>2</sub>. It is unlikely that the metallic Ni reacts with H<sub>2</sub>O to form H<sub>2</sub> and NiO (reversal of H<sub>2</sub>-TPR; first case). It has been observed that the reduced 1.5wt%W-20wt%Ni/TiO<sub>2</sub> sample showed the presence of Ni<sup>2+</sup> species due to a strong interaction between Ni and W particles (Figure 1 in set). These species seems to be stabilising the ionic Ni. Hence, the first case may be ruled out

where in the reduced 20wt%Ni/TiO<sub>2</sub> exhibited diffraction lines attributed to metallic Ni. The second case can be considered as the Ni particles in close contact with W particles are highly populated with ionic Ni than the Ni<sup>0</sup> which is higher on 20wt%Ni/TiO<sub>2</sub> (Table S3). We believe that either  $W_xO_y$  or a combination of  $W_xO_y$ -NiO interacted species behave as Brønsted acid sites rather than basic sites that are contributing to the enhanced VA selectivity.

The catalyst stability test showed no significant loss in the activity (towards VA) over the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst even after 60 h of reaction time. The used catalyst (after 60 h of the reaction time) is also characterized by XRD, CHNS, XPS, ICP-MS, TEM, and TPD of NH<sub>3</sub> analyses and compared with that of reduced 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst (Table 6). The results of this analysis showed no significant differences between the fresh (reduced at 500 C) and used (after 60 h) 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst except a small loss in acidity of the catalyst. This shows the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst is stable under the experimental conditions used to produce the VA from aqueous LA.

#### **5** Conclusions

The W modified Ni/TiO<sub>2</sub> catalyst prepared by simple impregnation method has been identified as a promising catalyst for single step synthesis of valeric acid (an important intermediate in the production of valeric biofuels) from biomass derived levulinic acid at ambient H<sub>2</sub> pressure and moderate reaction temperatures. The bulk and surface properties of the 20wt%Ni/TiO<sub>2</sub> catalyst is significantly altered by the addition of W which is corroborated by H<sub>2</sub>-TPR, XPS and N<sub>2</sub>O titration. H<sub>2</sub>-TPR results showed the interaction between W and Ni particles and the interaction became stronger with the increase in W loadings. It was found that the synergism between Ni and W is virtuous at W loading of 1.5wt% on 20wt%Ni/TiO<sub>2</sub>. The N<sub>2</sub>O decomposition measurements revealed that higher the Ni metal surface area; higher

the selectivity of  $\gamma$ -valerolactone. On the contrary, a drastic decrease in surface metallic Ni due to interaction with W resulted in the formation active sites for increased valeric acid selectivity in parenthesis a decrease in the selectivity of GVL is observed. The pyridine adsorbed DRIFT spectroscopic studies demonstrated a dramatic increase in the Brønsted acidity of 20wt%Ni/TiO<sub>2</sub> by the addition of tungsten. 20wt%Ni/TiO<sub>2</sub> alone was selective for the hydrogenation of levulinic acid to  $\gamma$ -valerolactone whereas the Ni interacted with W are the active species for formation of valeric acid. The enhanced Brønsted acid sites on W modified 20wt%Ni/TiO<sub>2</sub> catalyst was responsible for the formation of valeric acid through the ring opening of  $\gamma$ -valerolactone. The 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst was also found to be stable up to 60 h of continuous operation. Finally, it can be concluded that a combination of metallic Ni and the Ni interacted with W species are active and selective for the single-step conversion of levulinic acid to valeric acid.

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#### References

- [1] D. M. Alonso, J. Q. Bond, J. A. Dumesic, Green Chem. 12 (2010) 1493-1513.
- [2] A. V. Bridgwater, Catal. Today 29 (1996) 285-295.
- [3] G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044-4098.
- [4] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, Green Chem. 15 (2013) 584-595.
- [5] N. A. S. Ramli, N. A. S. Amin, Appl. Catal. B: Environ. 163 (2015) 487-498.
- [6] M. Stocker, Angew. Chem. Int. Ed. 47 (2008) 9200-9211.
- [7] Y. Guo, K. Li, X. Yu, J. H. Clark, Appl. Catal. B: Environ. 81 (2008) 182-191.
- [8] J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenscwander, S. W. Fitzpatrick, R. J. Bilski, J. L. Jarnefeld, Resour. Conserv. Recy. 28 (2000) 227-239.
- [9] M. Chalid, A. A. Broekhuis, H. J. Heeres, J. Mol. Catal. A: Chem. 341 (2011) 14-21.
- [10] M. Chia, J. A. Dumesic, Chem. Commun. 47 (2011) 12233-12235.
- [11] M. Sudhakar, M. L. Kantam, V. S. Jaya, R. Kishore, K. V. R. Chary, A. Venugopal, Catal. Commun. 50 (2014) 101-104.
- [12] S. G. Wettstein, J. Q. Bond, D. M. Alonso, H. N. Pham, A. K. Datye, J. A. Dumesic,Appl. Catal. B: Environ. 117-118 (2012) 321-329.
- [13] J. Xin, D. Yan, O. Ayodele, Z. Zhang, X. Lu, S. Zhang, Green Chem. 17 (2015) 1065-1070.

[14] X. L. Du, Q. Y. Bi, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, Green Chem. 14 (2012)935-939.

[15] J. Q. Bond, D. Martin Alonso, R. M. West, J. A. Dumesic, Langmuir 26 (2010)16291-16298.

[16] C. E. Chan-Thaw, M. Marelli, R. Psaro, N. Ravasio, F. Zaccheria, RSC Adv. 3 (2013)1302-1306.

[17] W. Luo, P. C. A. Bruijnincx, B. M. Weckhuysen, J. Catal. 320 (2014) 33-41.

[18] M. Li, G. Li, N. Li, A. Wang, W. Dong, X. Wang, Y. Cong, Chem. Commun. 50(2014) 1414-1416.

[19] L. Xin, Z. Zhang, J. Qi, D. J. Chadderdon, Y. Qiu, K. M. Warsko, W. Li, ChemSusChem 6 (2013) 674-686.

[20] P. P. Upare, J. Lee, Y. K. Hwang, D. W. Hwang, J. Lee, S. B. Halligudi, J. Hwang, J. Chang, ChemSusChem 2011, 4, 1749-1752.

[21] Y. Qiu, L. Xin, D. J. Chadderdon, J. Qi, C. Liang, W. Li, Green Chem. 16 (2014)1305-1315.

[22] P. Sun, G. Gao, Z. Zhao, C. Xia, F. Li, Appl. Catal. B: Environ. 189 (2016) 19-25.

[23] J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Angew. Chem. Int. Ed. 49 (2010) 4479-4483.

[24] W. Luo, U. Deka, A. M. Beale, E. R. H. van Eck, P. C. A. Bruijnincx, B. M.Weckhuysen, J. Catal. 301 (2013) 175-186.

- [25] T. Pan, J. Deng, Q. Xu, Y. Xu, Q. X. Guo, Y. Fu, Green Chem. 15 (2013) 2967-2974.
- [26] K. Kon, W. Onodera, K. i. Shimizu, Catal. Sci. Technol. 4 (2014) 3227-3234.
- [27] J. P. Lange, US Patent 2011/0112326, Shell Int. B.V. 2011.
- [28] J. C. Serrano-Ruiz, D. Wang, J. A. Dumesic, Green Chem. 12 (2010) 574-577.
- [29] V. V. Kumar, G. Naresh, M. Sudhakar, J. Tardio, S. K. Bhargava, A. Venugopal,Appl. Catal. A: Gen. 505 (2015) 217-223.
- [30] M. Sudhakar, V. V. Kumar, G. Naresh, M. L. Kantam, S. K. Bhargava, A. Venugopal,Appl. Catal. B: Environ. 180 (2016) 113-120.
- [31] V. V. Kumar, G. Naresh, M. Sudhakar, S. K. Bhargava, J. Tardio, V. Karnakar, A. H Padmasri, A. Venugopal, RSC Adv. 6 (2016) 9872-9879.

[32] M. I. Zaki, N. E. Fouad, S. A. A. Mansour, A. I. Muftah, Thermochemica Acta 523(2011) 90-96.

[33] W. Lin, H. Cheng, L. He, Y. Yu, F. Zhao, J. Catal. 303 (2013) 110-116.

[34] S. V. Green, A. Kuzmin, J. Purans, C. G. Granqvist, G. A. Niklasson, Thin Solid Films 519 (2011) 2062-2066.

[35] N. Scotti, M. Dangate, A. Gervasini, C. Evangelisti, N. Ravasio, F. Zaccheria, ACS Catal. 4 (2014) 2818-2826.

[36] H. Knozinger, P. Ratnasamy, Catal. Rev. 17 (1978) 31-70.

#### **Figure captions:**

Table 1: Physico chemical characteristics of the TiO<sub>2</sub> supported Ni catalysts

Table 2: Hydrogenation of LA over W modified  $20wt\%Ni/TiO_2$  catalysts prepared by coimpregnation of 20wt%Ni and varied W loadings on TiO<sub>2</sub>. Reaction temperature = 270 °C; catalyst wt ~0.25 g; 10wt% aqueous LA; GHSV = 4.56 mL g<sup>-1</sup> s<sup>-1</sup>

Table 3: Effect of method of preparation of W-Ni/TiO<sub>2</sub> catalysts in the hydrogenation of LA Reaction temperature =  $270 \text{ }^{\circ}\text{C}$ ; 10 wt% aqueous LA; catalyst wt: ~ 0.25 g

Table 4: Hydrogenation of different feeds over 20wt%Ni/TiO<sub>2</sub> and 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts, reaction temperature: 270 °C; 10wt% aqueous (LA and/or GVL) feed and 4wt% aqueous AL, H<sub>2</sub> flow rate 30 mL min<sup>-1</sup> (GHSV = 4.56 mL g<sup>-1</sup> s<sup>-1</sup>); Catalyst: ~ 0.25 g

Table 5: Time on stream study of LA hydrogenation over the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst Reaction conditions: 270 °C, 10% aqueous LA, GHSV=4.56 mL g<sup>-1</sup> s<sup>-1</sup>

Table 6: Physicochemical properties of the reduced and used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst

Scheme 1: Catalytic hydrogenation of levulinic acid to valeric acid

Scheme 2: Reaction pathways during LA hydrogenation over W-Ni/TiO2 catalysts

Figure 1: Powder XRD patterns of the reduced 20wt%Ni-W/TiO2 with W loadings of (a) 0.0

(b) 1.0 (c) 1.5 (d) 2.0 and (e) 2.5wt% catalysts

Figure 2:  $H_2$ -TPR profiles of the (a) 1.5wt%W/TiO<sub>2</sub> and 20%Ni/TiO<sub>2</sub> loaded with W (b) 0.0

(c) 1.0 (d) 1.5 (e) 2.0 (f) 2.5wt% catalysts

Figure 3: Ni 2p XPS spectra of fresh a)  $20wt\%Ni/TiO_2$  and b)  $1.5wt\%W-20wt\%Ni/TiO_2$  catalysts

Figure 4: Pyridine adsorbed DRIFT spectra of a) 20wt%Ni/TiO<sub>2</sub> and b) 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts

Figure 5: Powder XRD patterns of a) reduced and b) used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts Figure 6: Ni 2p XPS of reduced and used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts Figure 7: XPS spectra of W 4f of the reduced and used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst

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#### Tables

1 able 1. I hysic	5 chemical chai	deteristies of the	1102 supported	i i catalysts	
W-Ni/TiO <sub>2</sub>	BET-SA	NH <sub>3</sub> uptake	BAS/LAS	Crystallite/A	verage particle size (nm)
(20wt% Ni)	$(m^2/g)^a$	$(\mu mol g^{-1})^b$	ratio <sup>c</sup>	$XRD^{d}$	TEM <sup>e</sup>
0.0wt%W	42.1	41.2	0.2	21.5	22.4±1.6
1.0wt%W	41.8	-	-	22.1	-
1.5wt%W	40.5	64.8	1.8	22.7	24.8±1.1
2.0wt%W	39.6	-	-	22.5	-
2.5wt%W	36.1	76.8	-	22.8	-

Table 1: Physico chemical characteristics of the TiO<sub>2</sub> supported Ni catalysts

<sup>a</sup> Obtained from N<sub>2</sub> sorption analysis; <sup>b</sup> Obtained from TPD of NH<sub>3</sub>; <sup>c</sup> Calculated using quantified pyridine adsorbed DRIFTS curves; <sup>d</sup> Crystallite size of Ni calculated form XRD patterns using Scherrer equation; <sup>e</sup> Average particle size calculated from TEM images.

Table 2: Hydrogenation of LA over W modified 20wt%Ni/TiO <sub>2</sub> catalysts prepared by co-impregnation of	
20wt%Ni and varied W loadings on TiO <sub>2</sub> . Reaction temperature = 270 °C; Catalyst wt ~0.25 g; 10wt% aqueous	
LA; GHSV = $4.56 \text{ mL g}^{-1} \text{ s}^{-1}$	

LA; GHSV = 4.56  m	nL g ' s '								
W loading in	N <sub>2</sub> O uptake	$X_{\rm LA}$	Select	ivity (%)			<sup>a</sup> (TOF	5 s <sup>-1</sup> )x 10	3
W-20wt%Ni/TiO2	$(\mu mol g_{cat}^{-1})$	(%)	VA	GVL	AL	Others <sup>b</sup>	VA	GVL	AL
0.0	237.0	92.3	0.6	98.5	0.9	-	0.04	7.3	0.06
1.0	162.0	74.2	29.3	52.0	13.0	5.7	2.56	4.5	1.13
1.5	116.8	73.5	48.5	36.0	11.3	4.2	5.83	4.3	1.36
2.0	130.5	74.3	39.0	37.5	13.5	10.0	4.24	4.0	1.47
2.5	124.2	68.0	35.0	32.5	18.0	14.5	3.66	3.4	1.88

<sup>a</sup> TOF = Rate / N<sub>2</sub>O uptake; <sup>b</sup> Others include MTHF and C<sub>5</sub>-alcohols .

Reaction temperature = 270 °C; 10 wt% aqueous LA; Catalyst: ~ 0.25 g								
Catalyst	$X_{\rm LA}$				Rate (mol s <sup>-1</sup> g <sup>-1</sup> ) x 1			<sup>1</sup> ) × 10 <sup>-8</sup>
	(%)	VA	GVL	AL	Others <sup>a</sup>	VA	GVL	AL
(20%Ni/TiO <sub>2</sub> +1.5wt%W/TiO <sub>2</sub> )-MM <sup>b</sup>	32.7	2.4	90.0	1.0	6.6	1.5	56.3	0.62
1.5wt%W/TiO <sub>2</sub>	5.0	0.0	0.0	92.1	7.9	0.0	0.0	8.81

Table 3: Effect of method of preparation of W-Ni/TiO<sub>2</sub> catalysts in the hydrogenation of LA Reaction temperature =  $270 \text{ }^{\circ}\text{C}$ : 10 wt% aqueous LA: Catalyst: ~ 0.25 g

<sup>a</sup> Others include MTHF and C<sub>5</sub>-alcohols; <sup>b</sup> Catalysts prepared by mechanical mixing of Ni/TiO<sub>2</sub> and W/TiO<sub>2</sub>.

Table 4: Hydrogenation of different feeds over 20wt%Ni/TiO<sub>2</sub> and 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalysts, reaction temperature: 270 °C; 10wt% aqueous (LA and/or GVL) feed and 4wt% aqueous AL, H<sub>2</sub> flow rate 30 mL min<sup>-1</sup> (GHSV = 4.56 mL g<sup>-1</sup> s<sup>-1</sup>); Catalyst: ~ 0.25 g.

Feed	Catalyst	Conversion		Selectivity (%) Rate					Rate (1	Late (mol $s^{-1} g^{-1}$ ) x 10 <sup>-8</sup>		
		(%)	VA	GVL	AL	MTHF	1,4-Diol	2-pentanol	VA	GVL	AL	
GVL	20wt%Ni/TiO <sub>2</sub>	35.3	10.0	-	0.0	19.7	41.5	28.8	6.75	-	0.0	
GVL	20wt%Ni-1.5%W/TiO <sub>2</sub>	60.8	58.6	-	0.0	13.3	19.2	8.9	68.1	-	0.0	
AL	20wt%Ni/TiO2	68.8	10.0	88.8	-	1.2	0.0	0.0	13.0	114.5	-	
AL	20wt%Ni-1.5%W/TiO <sub>2</sub>	44.6	24.2	75.8	-	0.0	0.0	0.0	20.6	64.6	-	

Reaction	LA	Selectivity	y (%)		
Time (h)	Conversion (%)	VA	GVL	Others <sup>a</sup>	
6	73.5	48.5	36.0	15.5	
12	72.9	48.7	36.2	15.1	
24	73.8	48.3	35.8	15.9	
48	73.4	48.5	36.1	15.4	
60	72.3	47.5	36.3	16.2	

Table 5 Time on stream study of LA hydrogenation over the 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst Reaction conditions: 270 °C, 10% aqueous LA, GHSV=4.56 mL g<sup>-1</sup> s<sup>-1</sup>

 $a^{-a}$  Others include diol, MTHF and C<sub>5</sub>-alcohols.

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Tuble 0. Thysicoenen	neur properties or	the reduced u	ind used 1.5 wt/0 W 2	0 10 10 10 2	Juluiyst	
20wt%Ni-	NH <sub>3</sub> uptake	Average pa	article size (nm)	ICP-MS (w	Carbon	
1.5wt%W/TiO <sub>2</sub>	$(\mu mol g^{-1})^a$	$XRD^{b}$	TEM <sup>c</sup>	Ni	W	(% wt) <sup>e</sup>
Reduced	64.8	22.7	24.8±2.1	19.93	1.48	-
Used	56.1	22.8	25.2±2.3	19.80	1.44	0.26

Table 6: Physicochemical properties of the reduced and used 1.5wt%W-20wt%Ni/TiO<sub>2</sub> catalyst

<sup>a</sup>Obtained from TPD of NH<sub>3</sub>; <sup>b</sup>Calculated from XRD patterns using Debye-Scherrer equation; <sup>c</sup>Calculated from TEM images; <sup>d</sup>Obtained from ICP-MS analysis; <sup>e</sup>Obtained from CHNS analysis of the catalyst recovered after 60 h of continuous operation.

















