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Role of group V elements on the hydrogenation activity of Ni/TiO₂ catalyst for the vapour phase conversion of levulinic acid to γ-valerolactone

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Graphical abstract



Highlights

- Nb modified Ni/TiO₂ showed a high ratio of surface metallic Ni and Lewis acid sites
- Presence of Ni²⁺ and Brønsted acid sites leads to formation of valeric acid, MTHF

- γ-valerolactone rate was significantly improved upon modification of Ni/TiO₂ with Nb
- Surface mechanism explained by using pyridine-DRIFTS and CO chemisorption data

Abstract

Influence of group V elements such as Ta, Nb and V on the product distribution in the vapour phase hydrogenation of levulinic acid (LA) over Ni/TiO₂ catalyst was examined at ambient pressure. The Nb promoted Ni/TiO₂ demonstrated a high selectivity towards γ -valerolactone (GVL) compared to other catalysts at 275 °C. The TPR results showed a lower H₂ uptake over Ta and V modified Ni/TiO₂ which was explained due to a strong interaction between these oxide species with nickel. Presence of a high ratio of ionic nickel (Ni²⁺) on Ta and V modified catalyst could be a possible reason for the formation of valeric acid (VA) through the ring opening of GVL. The high GVL selectivity over the Ni-Nb/TiO₂ catalyst attributed to the presence of a high proportion of Lewis acid sites in conjunction with finely dispersed Ni species on the catalyst surface. This however, is accomplished by the pyridine adsorbed diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and CO-chemisorption results.

Key words: Levulinic acid, y-Valerolactone, Ni-Nb-TiO₂, Pyridine-IR, Biomass

1. Introduction

The conversion of biomass derived levulinic acid (LA) to various fuels and fuel additives is an important process in bio-refinery [1-2]. One such conversion is its hydrogenation to γ -valerolactone (GVL; a fuel additive and green solvent) [3]. Although promising results were obtained in the liquid phase conversion of LA to GVL, the vapour phase conversion has also been considered due to additional benefits. These benefits include no

requirement for high pressure conditions, purification, space-to-time yield productivity, reduced likelihood of catalyst deactivation, efficiency, safety and waste emission [4-11]. Very few reports are available in the open domain on LA conversion to GVL in the vapour phase [12-15]. Dumesic's group reported the use of the bimetallic Ru-Sn supported on carbon catalyst for GVL synthesis from LA under continuous flow conditions with a turnover frequency of 0.051 s⁻¹ under 35 bar H₂ pressure and 180 °C reaction temperature [16]. Upare and co-workers studied the vapour phase synthesis of GVL from LA over Ni modified copper-silica catalysts using formic acid as the hydrogen source [17-21]. Although the earlier reports showed some promising results for GVL production from LA, there is still significant room for the development of better conversion strategies that use stable and active non-noble metal catalysts under mild reaction conditions. In this context, few reports have appeared on the vapour phase LA conversion to GVL which showed that supported Ni and/or Cu are suitable catalysts for GVL formation. These studies claimed that the catalysts with only surface Lewis acidity and metal sites are responsible for GVL selectivity and the presence of other surface sites such as Brønsted acid sites and basic sites will lead to the formation of products such as valeric acid (VA) and pentane diols through ring opening of GVL [11,13]. Although esters of VA has potential applications particularly in the transportation sector (diesel and gasoline blenders), special attention is required for tuning the surface acid-base properties of the catalysts for the selective one-pot conversion of LA to GVL and/or VA esters [11]. Although few reports appeared in the vapour phase conversion for LA to GVL over the supported non-noble metal catalysts, the studies carried out were not more focussed at tuning the surface properties of the catalysts [11, 13, 19]. In this attempt, our group has investigated the promoted Ni catalysts for the vapour phase LA conversion and in our recent reports it was concluded that the Ni/TiO₂ is selective towards GVL and the addition of promoter changed the product distribution, depending on the type of promoter (acid/base) [22].

Therefore, based on the previous reports on the vapour phase LA conversion to GVL, Ni/TiO₂ catalyst (catalyst with promising activity and stability towards GVL) is chosen in this study by modifying its surface using high valence metal oxides such as V, Nb and Ta to compare activity and selectivity. The group five elements (V, Nb and Ta) are known to exhibit different redox and acid properties, the Ni/TiO₂ has been modified using V, Nb and Ta and examined for the LA conversion in the vapour phase at ambient pressure [13, 23-27]. The results of these investigations revealed that the Nb promoted Ni/TiO₂ was found to be selective towards GVL, whereas, the Ta and V modified Ni/TiO₂ catalysts showed significant amount of valeric acid, at constant LA conversion. To examine the dramatic change in product distribution and the unusual behaviour of Nb modified Ni/TiO₂ relative to other catalysts, the catalysts were characterized by BET-SA, H₂-TPR, CO-pulse chemisorption, XPS and pyridine adsorbed IR spectroscopy in order to understand the surface characteristics of the catalysts.

2. Experimental Section

2.1. Chemicals and materials

Levulinic acid (LA; 98%), RuCl₃.xH₂O (99.9%), %), α -angelica lactone (AL; 98%), γ -valerolactone (GVL; 99%), acetone (>99%), methanol (>99%), anisole (99.7%) and pyridine (99.8%) obtained from Sigma-Aldrich (AR grade), NH₄VO₃ (Fluka,>99%), niobic acid (Nb₂O₅.H₂O), Ta₂O₅, oxalic acid (Merck, >99%) used without further purification. De-ionised water was used for the dilution of substrate and catalyst preparation. The TiO₂ (Degussa-P-25; BET-surface area (S_{BET}) = 56 m² g⁻¹) obtained was used as a support for the preparation of supported Ni catalysts.

2.2. Catalyst preparation

The V, Nb and Ta modified Ni supported on TiO_2 catalysts were prepared by coimpregnation method [22]. In a typical procedure, required amounts of aqueous $Ni(NO_3)_2$

.9H₂O (equivalent to 10wt% of Ni) and precursors of V, Nb and Ta (dissolved in oxalic acid) corresponding to give 2wt% was instantaneously mixed with a known amount of solid support under continuous stirring at 100 °C until the excess water was evaporated. The obtained powder samples were dried at 120 °C for overnight and calcined in static air at 450 °C for 4 h.

2.3. Catalyst characterization

The calcined samples were reduced at 450 °C in 5%H₂/Ar for 3 h and were characterized by powder XRD, BET-surface area, H₂-TPR, NH₃-TPD, CO-pulse chemisorption, CHNS, TEM, XPS and H₂O and/or pyridine adsorbed diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The hydrogenation activities were carried out in a continuous flow fixed bed quartz reactor under sub-ambient H₂ pressure. The experimental conditions and the methods adopted in the present study are identical to the experimental conditions used in our earlier studies and the complete details are given in ESI [27,28].

3. Results and discussion

3.1. Powder X-ray diffraction (XRD)

The XRD patterns of Ni loaded titania (reduced at 450 °C for 3 h) samples are shown in Fig. 1. The diffraction lines ascribed to metallic Ni are clearly observed in all Ni/TiO₂ catalysts with reflections at $2\theta = 44.3$, 52.0 and 76.5 corresponding to Ni (1 1 1), (2 0 0) and (2 2 0) planes respectively (ICDD #: 04-0850). The remaining diffraction lines are attributed to anatase and rutile TiO₂ phases (ICDD #: 84-1286 and 88-1175 respectively). Although the XRD patterns showed the diffraction signals due to TiO₂ and metallic Ni; no diffraction signal is observed due to promoters (V, Nb and Ta) indicating their fine dispersion on the surface or because of low content as compared to Ni and TiO₂. In addition, a small shift in 2 θ position of Ni is however observed in the promoted catalysts which are presumably due to an interaction

between promoter and Ni species (Fig. S1). The BET-surface area of the modified (V, Nb and Ta) Ni/TiO₂ samples are marginally decreased compared to Ni/TiO₂ sample (Table 1).

3.2. Physicochemical properties of the catalysts

The surface and bulk properties of catalysts are investigated using powder XRD, N₂sorption, H₂-TPR, CO-pulse chemisorption, and pyridine adsorbed DRIFTS analysis (Table 1). No significant changes are observed in the surface area of the catalysts after addition promoters. This result also found consistent with the H₂-TPR analysis of the catalysts where no significant changes are observed in H₂-consumption values obtained from TPR experiments. This is however attributed to the presence of same loading of Ni in all the catalysts. From CO-pulse chemisorption experiments, a higher CO uptake observed for Nb promoted Ni/TiO₂ consequently a relatively higher Ni surface area is found while compared to other catalysts (Table 2). The TPD of NH₃ results revealed that the V and Nb promoted Ni/TiO₂ catalysts exhibited slightly higher acidity compared to the un-promoted and Ta promoted Ni/TiO2 catalysts (Table 1 and Fig. S2). This increase in V and Nb promoted catalysts may be due to the different acidic properties of V and Nb species which is further supported by the pyridine adsorbed DRIFTS analysis of these catalysts which showed improved surface Brønsted and Lewis acidity respectively. Finally, it is also interesting to note that the Ni crystallite size is slightly decreased upon modification of Ni/TiO₂ with V and Nb whilst a small increase is observed in case of Ni-Ta/TiO₂.

3.3. X-ray photoelectron spectroscopy (XPS)

The Ni species at the near surface region is investigated using XPS analysis and the spectra showed the presence of both metallic (Ni⁰) and ionic Ni (Ni²⁺) species (Fig. 2). The XPS signal at a binding energy of 852.5 eV confirms the presence of metallic Ni and the second one centred at around 855.6 eV is assigned to Ni²⁺ with a satellite peak at 860.9 eV. These

results are in good correlation with the reported studies [28,29]. The ionic Ni (Ni²⁺) species observed on the surface of these catalysts is probably due to a strong interaction between nickel and the promoter or partly ascribed to the surface oxidation by air during the sample transfer for XPS analysis [30]. In addition, a small shift in binding energy of Ni 2p position is observed over Nb and Ta modified Ni/TiO₂ and no significant changes were seen in case of Ni-V/TiO₂ sample. The surface composition obtained for these catalysts showed a high proportion of ionic Ni (Ni²⁺) species on the surface of Ni-Ta/TiO₂ catalyst followed by Ni/TiO₂ and the lowest is obtained for Nb promoted one which showed relatively a high metallic Ni species on its surface (Table S1).

3.4. H₂-temperature programmed reduction (TPR)

The reduction behaviour of the catalysts is investigated by H₂-TPR analysis (Fig. 3) and the results of this analysis indicated one major signal centred around 400 °C which is explained due to the reduction of NiO species [31]. In the comparative analysis, no significant change in the T_{max} is observed after V addition to Ni/TiO₂. On the other hand a dramatic shift in T_{max} towards lower temperature is found with Nb modified Ni/TiO₂ with a shoulder peak at 235 °C. In case of Ta promoted Ni/TiO₂ catalyst, although T_{max} appeared in the same position, the reduction signal is found to be broad mostly likely due to the presence of large size clusters of nickel species which is also in well correlation with the XRD data where the crystallite size of nickel is higher (Table 1).

3.5. Pyridine adsorbed DRIFTS analysis

The nature of acid sites present on the catalyst surface is investigated by using pyridine as a basic probe molecule with FT-IR spectroscopy (Fig. 4). The spectra show a high ratio of Lewis acid sites (LAS; co-ordinated pyridine: ~1450 cm⁻¹) compared to Brønsted acid sites (BAS; protonated pyridine: ~1540 cm⁻¹) [32,33]. Although Ni/TiO₂ and Ta modified Ni/TiO₂

catalysts showed some Brønsted acidity, the vibrational band (around 1540 cm⁻¹) corresponding to the Brønsted acid sites is found more evident in case of vanadium modified Ni/TiO₂ catalyst (Fig. 4). In case of Nb promoted Ni/TiO₂ catalyst, a significant improvement in the Lewis acidity is observed with negligible Brønsted acidity on the surface of the catalyst. In the comparative analysis, the relative ratios calculated from the normalized DRIFT spectra indicated a high BAS/LAS ratio for the Ni-V/TiO₂ catalyst and the lowest ratio are observed for Nb promoted Ni/TiO₂ sample (Table 2 and Fig. S3).

The activity measurements of vapour phase LA hydrogenation to GVL is correlated with the physicochemical properties of the catalysts and the results revealed a higher GVL rate over Nb promoted Ni/TiO₂ compared to the other catalysts (Table 2). On the contrary, a lower GVL rate was observed due to the formation of VA at the cost of GVL over Ni/TiO₂. Particularly in case of V and Ta modified Ni/TiO₂ catalysts, more amount of VA is observed which is explained by the ring opening of GVL (Scheme 1). Therefore, it can be seen that the higher GVL rate over the Nb promoted catalyst can be ascribed to the presence of more surface metallic Ni species (Table S1) along with a high ratio of Lewis acid sites. Presence of surface led to the formation of VA and other products which is good correlation with the earlier reports and surface characteristics of the catalysts investigated in this study (Table 2 and Table S1)[34].

In further studies, the reaction temperature is optimised for Nb promoted Ni/TiO₂ catalysts and the results of this analysis revealed 275 °C is the optimum reaction temperature for required GVL selectivity (Fig. 5 and Fig. S4). Although slightly high conversion is obtained at high temperatures, a decrease in GVL selectivity is observed at the cost of other products formation particularly valeric acid. The formation of valeric acid at high reaction temperatures

is however attributed to the ring opening of GVL to form pentenoic acid which will be subsequently hydrogenated to VA over the metallic Ni sites.

Reaction conditions: H₂ flow: 20 cc/min; GHSV = 9.74 mL s⁻¹ g_{cat}^{-1} ; Feed: 10wt% LA in H₂O; Data collected after 6 h of continuous operation.

Based on the product distribution and surface characteristics of the catalysts, a reaction mechanism is also proposed (Scheme 1) in this study which is in good correlation with the reported studies on the LA hydrogenation to GVL [35]. It is proposed that, at 275 °C reaction temperature, first LA (enolic form) will undergo dehydration to form an intermediate called angelica lactone preferably over the mild acid sites (Lewis acid sites in this case) as it is evidenced from pyridine adsorbed DRIFTS. The formed angelica lactone is then subsequently hydrogenated to GVL over the metallic sites (Ni in this case). As mentioned, in case if there is any surface Brønsted acidity, the ring opening of GVL will take place that leads to the formation of valeric acid.

In addition to the optimization of reaction parameters, long-term stability of the best performance catalyst i.e. Nb promoted Ni/TiO₂ catalyst is also tested for 30 h of reaction time (Table S2) at 275 °C reaction temperature and atmospheric H₂ pressure. The results of this analysis showed no significant changes in the rate or TOF (both LA conversion and GVL selectivity) of GVL even after 30 h of continuous operation. This indicates the robustness of the catalyst system under the experimental conditions used.

Finally, the used catalyst is investigated using TPD of NH₃, CHNS and XRD analyses and the results are also compared with that of fresh catalyst (Table 3). The TPD of NH₃ results indicated a slight decrease in activity which is attributed to the adsorption of water molecules during the course of the reaction and the small amount of carbon deposition is due to the

irreversible chemisorption of intermediates or reactant molecules such as AL and LA respectively [11,36]. From XRD analysis of used (after 30 h) Ni-Nb/TiO₂ catalyst, no significant change in the Ni particle size is observed between the fresh and used forms.

Conclusions

Influence of promoters such as V, Ta and Nb on the modification of surface Lewis, Brønsted acid sites on Ni/TiO₂ was examined for the LA hydrogenation to GVL in vapour phase at atmospheric H₂ pressure. It is observed that Nb promoted catalyst is found to be the promising catalyst in terms of activity and stability compared to the other catalysts. The high activity of Ni-Nb/TiO₂ catalyst is attributed to the presence of highly populated Lewis acid sites in parenthesis to the Ni metal surface area of the catalyst compared to the other catalysts which were rationalized by pyridine adsorbed DRIFTS analysis in conjunction with COchemisorption experiments respectively. The detailed investigations of Ni-Nb/TiO₂ catalyst in the vapour phase LA conversion to GVL revealed that the catalyst is not only active and selective towards GVL but also stable under the optimised experimental conditions. Further studies are in progress on the exploration of HCOOH as an in-situ H₂ source for the hydrogenation of LA at low temperatures.

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Fig. 1. Powder XRD patterns of reduced (a) 10Ni/TiO₂ (b) 10Ni-2V/TiO₂ (c) 10Ni-2Nb/TiO₂ and (d) 10Ni-2Ta/TiO₂ samples.



Fig. 2. Ni 2p spectra of reduced (a) $10Ni/TiO_2$ (b) $10Ni-2V/TiO_2$ (c) $10Ni-2Nb/TiO_2$ and (d)

10Ni-2Ta/TiO2 samples.

Chillin MA







Fig. 4. Pyridine adsorbed DRIFT spectra of (a) 10Ni/TiO₂ (b) 10Ni-2V/TiO₂ (c) 10Ni-2Nb/TiO₂ and (d) 10Ni-2Ta/TiO₂ samples.



Fig. 5. Influence of reaction temperature over Nb promoted Ni/TiO₂ catalyst.



Scheme 1. Plausible surface reaction mechanism for the GVL production from LA.

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Catalyst	^a Surface area (m ² /g)	^b CO-uptake (µmol/g _{cat})	$^{c}H_{2}$ -uptake (umol/g _{cat})	^d NH ₃ - uptake	^e Crystallite size
(10wt%N1)			(† ⁰)	$(\mu mol/g_{cat})$	(nm)
Ni/TiO ₂	48	33.5	1037	40.8	29.6
Ni-2wt%V/TiO2	46	29.6	1019	55.4	22.8
Ni-2wt%Nb/TiO ₂	43	42.2	1061	53.8	23.5
Ni-2wt%Ta/TiO2	40	26.3	1011	41.2	32.1

Table 1. Physico chemical properties of the catalysts.

^a Determined from BET surface area analysis;

^bObtained from CO-pulse chemisorption experiments; ^cObtained from H₂-TPR analysis; ^dDetermined from NH₃-TPD analysis; ^eCalculated by Scherrer equation w.r.t. Ni(111) plane.

Table 2. Activity measurements of the catalysts. Reaction conditions: H₂ flow: 20 cc/min; GHSV = 9.74 mL s⁻¹ g_{cat}⁻¹; Reaction temperature: 275 °C; Feed: 10wt% LA in H₂O; Data collected after 6 h of continuous operation.

Catalyst	LA conversion	Selecti	vity (9	%)		Rate _{GVL}	^b S _{Ni}	^c BAS/LAS
	(%)	GVL	AL	VA	Others ^a	$(\mu mol g_{cat}^{-1} s^{-1})$	(m^2/g_{Ni})	ratio
10wt%Ni/TiO ₂	17.3	78.3	7.2	5.9	8.6	0.77	13.1	0.18
10wt%Ni-2wt%V/TiO2	19.2	54.3	25	16.5	4.2	0.38	11.6	0.62
10wt%Ni-2wt%Nb/TiO2	25.3	99.0	0.0	0.0	1.0	1.21	16.5	0.05
10wt%Ni-2wt%Ta/TiO2	15.5	60.9	12	11.5	15.6	0.46	10.3	0.26

^a Others include: C₄,C₅-alcohols and MTHF;

^b Calculated using CO-uptakes; ^c Calculated using pyridine adsorbed DRIFT spectra.

abic 5. Characterizatio	on of the used catalyst.			
Catalyst	NH ₃ uptake	Carbon	Particle size	-
(10% Ni-2%Nb)	$(\mu mol g_{cat}^{-1})$	(wt%)	(nm)	_
Fresh	53.8	-	23.5	-
Used	48.2	0.96	24.1	

Table 3. Characterization of the used catalyst.