Effect of Niobium Oxide Phase on the Furfuryl Alcohol Dehydration

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Abstract

Different structural phases (e.g., TT, T, and H) of niobium oxide were synthesized, characterized by XRD and Raman, and utilized for the furfuryl alcohol dehydration and condensation under mild conditions (100°C and ambient pressure). Furfuryl alcohol conversion was dependent on reaction time and niobium oxide phase. Niobic acid and T/H phase transitional niobium oxide showed higher catalytic activity in comparison to a single crystalline phase niobium oxide. While T/H phase transitional niobium oxide showed higher conversion than that of niobic acid and TT phase niobium oxide, higher C₉-C₁₅ products' selectivity (> 60%) was obtained with the latter catalysts.

KEYWORDS: Furfuryl Alcohol, Niobic acid, Niobium Oxide Phase, XRD, Raman.

1. Introduction

Lignocellulosic biomass has been considered as an attractive feedstock for fuels and chemicals [1]. One of the attractive chemical products during the lignocellulose conversion reaction is furfuryl alcohol (FA), which is the product obtained by a selective hydrogenation process from furfural [2]. FA has been considered as an important building block for the production of levulinic acid and ethyl levulinate which are platform molecules for the production of liquid hydrocarbon fuels [3]. FA dehydration and condensation reaction into oligomer and polymer have been also extensively investigated because of a wide range of applications, such as nanocomposite carbon, carbon nanotubes, and fuel blending components [4,5]. FA oligomers have the capacity to be converted to alkanes using hydrodeoxygenation (HDO) reactions [6]. Recently, Kim et al. investigated furfuryl alcohol dehydration into oligomers using mineral acid (i.e., sulfuric acid) [7]. Nevertheless, the method of using sulfuric acid is not industrially favorable as it is highly corrosive and presents considerable difficulties in separation and recycling after the reaction. Instead, solid acids catalysts have attracted significant attention due to their easiness of separation from product and versatility of surface modification [8]. Metal oxides such as TiO₂, Al₂O₃, and ZrO₂ have been widely studied as catalysts for dehydration of carbohydrates and simple alcohols [9-11]. In addition to these metal oxides, Nb₂O₅ has long been known as its acidic properties and potential to be applied as a solid acid catalyst and a catalyst support [12]. Nb₂O₅ compounds generally possess a series of distorted NbO₆ octahedral structure where its Lewis and Brønsted acidity are associated with the Nb=O and Nb-OH bonds, respectively [13]. It also reported that H₂O coordinated NbO₆ (niobic acid, Nb₂O₅·nH₂O), containing highly polarized Nb-OH, shows Brønsted acid character and can be applied to dehydration and hydrolysis reaction [14,15]. It has been investigated the phase transformation of Nb₂O₅ happens during the thermal treatments process [16]. F. Wang et al. synthesized TT-phase Nb₂O₅ with different surface areas (5.7 m²/g ~ 194.1 m²/g) by calcining niobic acid at temperature ranged from 400°C to 700°C [17]. C. Guo and Z. Qian reported that calcined niobic acid at 300°C shows higher activity for the 2-propanol

dehydration than untreated niobic acid [18]. Thus, we hypothesize that calcination temperature can be used as a simple yet reliable parameter to modify the properties of the niobium oxides to favor the corresponding catalytic reaction.

In this paper, we describe a number of observations regarding the Nb₂O₅ phase effect on FA dehydration activity and products selectivity. The physicochemical properties of these samples are carefully investigated by Raman, XRD, and BET. FA conversion and product selectivity were analyzed by gas chromatography (GC) and GC-mass spectrometry (MS). For comparison, commercial Nb₂O₅ also has been investigated.

2. Experimental sections

Niobic acid was obtained from CBMM (AD5015HY340). Niobium oxide (99.99%) and FA (98%) were obtained from Sigma-Aldrich. Nb₂O₅ solid acid catalysts with different surface area were prepared by calcination of niobic acid at various temperature (500-1000°C) in flowing air (Airgas, extra dry) for 2 h with a ramping rate of 4°C/min. Specific surface area and pore size distribution of the catalysts were measured with a Micromeritics ASAP 2010 apparatus at liquid N₂ temperature (-196°C). To determine Nb₂O₅ phase identity, powder X-ray diffraction (XRD) data were collected using a Rigaku Ultima-IV diffractometer at ambient conditions using Cu K α ($\lambda = 1.5418 \text{ \AA}$), at a range of $5^\circ \leq 2\theta \leq 60^\circ$, with a scanning rate of 0.2°/min. A quantitative Rietveld analysis was used to determine the phase percentages in the 800°C-1000°C calcined and commercial Nb₂O₅ (details in the Supporting Information. S.1). The change of Nb₂O₅ molecular structure was also determined by Raman spectroscopy (details in the Supporting information. S.2). The batch FA oligomerization experiments were carried out in 7mL clean glass vials in an aluminum block covered by heating tape (HTS/Amptek). 3.00g FA and 0.03g catalysts were added in vials, and heated to 100°C for 2 h, 4 h and 6 h under constant stirring conditions. After finishing FA dehydration reaction, the glass vials were immediately quenched in an ice water to stop further reaction. After centrifuging, the glass vials were stored properly in the fridge before GC analysis. Compositions and concentrations of products were identified by GC/MS and GC/FID (details in the Supporting information. S.3).

3. Results and discussion

It was reported that calcination temperature critically affects the surface area of niobic acid [19]. The BET surface areas of the niobium based catalysts are summarized in Table 1. The BET surface areas decreased continuously from 130 m²/g (niobic acid) to 5 m²/g (700°C calcined sample) with increasing calcination temperature, due to the formation of Nb₂O₅ crystalline structure. For the samples calcined at $\geq 800^\circ\text{C}$, the surface area was measured to be less than 1 m²/g. Pore volume of catalysts followed the same pattern to that of the surface area. Micro-porosity was not observed on any of the investigated catalysts in the present work. Similar surface areas pattern was shown in a previous study [17]. For

comparison, surface area and pore volume of commercial Nb_2O_5 are also shown in Table 1. The commercial Nb_2O_5 may possess similar structural properties as 800°C -1000°C calcined Nb_2O_5 samples, since all of them have similar surface area and pore volume.

The XRD patterns of the niobic acid, Nb_2O_5 samples obtained at different calcination temperatures, and commercial Nb_2O_5 catalysts are shown in Figure. 1. No diffraction pattern was observed for the niobic acid catalyst indicating that it contains amorphous structure. For Nb_2O_5 (500°C), TT phase peaks were observed at 22.6°, 28.6°, 36.8°, 46.3°, 50.7°, and 55.2° [20]. Nb_2O_5 (600°C) show similar XRD pattern that of 500°C, while weak shoulder peak was shown at 28.9°. The XRD pattern of the 700°C calcined Nb_2O_5 sample shows splitted peaks at 28.9° and 37.1° which indicates that TT phase Nb_2O_5 was transformed into T phase. Previously, R. Fiz et al. observed similar phase transformation (TT to T phase) at 500°C and pointed out the main difference lies in the broadening of the peaks in the TT- Nb_2O_5 , as well as a clear split of the peaks in the more crystalline and lower symmetry of T- Nb_2O_5 [21]. Thus, the 600°C calcined Nb_2O_5 could be a transition state between TT and T phase. With the calcination temperature continuously increased, the intensity of the peaks assigned to T phase become resolved. Further increasing temperature up to 800°C lead to the complete formation of T phase Nb_2O_5 [22]. Another transition state between T- Nb_2O_5 and H- Nb_2O_5 phase was observed in the Nb_2O_5 (900°C) XRD pattern, while the 1000°C calcined sample contains H phase only. It was also observed that the commercial Nb_2O_5 contains both T and H phase Nb_2O_5 although H phase dominates. Further Rietveld refinement showed 900°C Nb_2O_5 has 91.3% H phase and 8.7% T phase while commercial Nb_2O_5 is composed of 24.5% H and 75.5%T (Table S1). The obtained XRD spectra proved that Nb_2O_5 crystalline phase can be controlled by calcination temperatures. (Table 1)

In addition to the XRD spectroscopy, Raman spectroscopy also provides molecular structural insights into the hydrated (amorphous), dehydrated (crystalline), and different crystalline phases of Nb_2O_5 as shown in Figure 2. Niobic acid Raman spectrum shows broad bands at ~262 cm^{-1} , ~660 cm^{-1} , and ~850 cm^{-1} , which are assigned to Nb-O-Nb bending mode, symmetric stretching mode of the niobia polyhedral, and antisymmetric stretching mode of the Nb=O (niobyl) terminal bond in the hydrated state (Nb=O---H), respectively [23,24]. J.M. Jehng et al., reported that niobyl band shifted to ~900 cm^{-1} under dehydration condition at 120°C. It was also reported that the observed broad Raman bands reflects the distorted NbO_x (x=6,7, and 8) structures in niobic acid [23-26]. At 500°C-900°C, the broad Raman band at ~850 cm^{-1} shifted to ~930 cm^{-1} and intensity was decreased due to the decreasing of Nb=O bond distance and concentrations correspondingly [25]. Symmetric stretching mode of the niobia polyhedral band was shifted from ~685 cm^{-1} to ~693 cm^{-1} due to the increased bond order. In addition to the peak shift, full-width half-maximum (FWHM) value was also sharply decreased from 158 cm^{-1} (Nb_2O_5 500°C) to 111 cm^{-1} (Nb_2O_5 900°C) due to the more ordered crystalline structure. XRD results explained that calcination Nb_2O_5 at $\geq 600^\circ\text{C}$ leads to a well crystalized T/TT phase which is

reflected by the sharpening of the strong Raman band at $\sim 693\text{cm}^{-1}$. The $\geq 600^\circ\text{C}$ calcined sample's Raman spectrum also clearly show two Nb-O-Nb bending mode peaks at $\sim 251\text{ cm}^{-1}$ and $\sim 315\text{ cm}^{-1}$. XRD and Raman spectra provide that $600\text{-}900^\circ\text{C}$ calcined Nb_2O_5 samples possess both TT and T phase which are very similar structure, while Nb_2O_5 (900°C) XRD also shows small H- Nb_2O_5 peaks. For the Nb_2O_5 calcined at 1000°C , multiple new Raman bands were observed, indicating a phase transformation of structure from T- Nb_2O_5 to H- Nb_2O_5 . Raman bands at $\sim 901\text{ cm}^{-1}$ and $\sim 993\text{ cm}^{-1}$ are assigned to antisymmetric and symmetric stretching modes of the Nb=O terminal double bond [24,25,27]. The new Raman bands below 900cm^{-1} are assigned to stretching modes of the slightly and highly distorted octahedral NbO_6 ($\sim 627\text{ cm}^{-1}$ and $\sim 671\text{ cm}^{-1}$) and related to a linear Nb-O-Nb bond ($\sim 842\text{ cm}^{-1}$) in the H- Nb_2O_5 . Raman bands at $\sim 264\text{ cm}^{-1}$ and $\sim 306\text{ cm}^{-1}$ are characteristic of the Nb-O-Nb bending modes in the orthorhombic Nb_2O_5 phase. It is also observed that commercial Nb_2O_5 Raman spectrum shows similar band position with Nb_2O_5 (1000°C) one, even though previous XRD results showed that commercial Nb_2O_5 is a mixture of both T and H phase structures.

Figure 3 shows the catalytic performance of various Nb_2O_5 samples. As shown in Figure 3(a), niobic acid, TT phase (500°C) and T/H mixed phase Nb_2O_5 (900°C and commercial) showed higher catalytic activity compared to other single phase crystalline Nb_2O_5 (T or H). Due to its strong Lewis and Brønsted acidity [14,28], niobic acid (amorphous) presents a higher FA conversion than well crystallized T or H phase Nb_2O_5 . Previously, Shiju et al also found that amorphous Nb_2O_5 has better catalytic activity than T phase Nb_2O_5 during the acetalization of glycerol [19]. By using DRIFT spectroscopy with pyridine absorption, they attributed the above activity difference to the decreased Brønsted acid sites in T phase Nb_2O_5 . Similarly, S. Chai et al also found the increase in the calcination temperature (up to 700°C) reduced the Nb_2O_5 acidity [29]. Since the $>700^\circ\text{C}$ calcined Nb_2O_5 samples have quite small surface area, it is hard to determine their surface Brønsted and Lewis acidity by a temperature-programmed-desorption process, such as NH_3 -TPD or pyridine absorption. Previously J.M. Jehng et al., reported that Brønsted acid sites correspond to the slightly distorted NbO_6 , NbO_7 , NbO_8 Raman bands between 500 and 700 cm^{-1} , while the Lewis acid sites are associated with the highly distorted NbO_6 Raman bands in the $850\text{-}1000\text{cm}^{-1}$ region [23]. Figure 2 shows that the intensity of Raman bands in the $850\text{-}1000\text{cm}^{-1}$ region decreased with elevated calcination temperature up to 900°C , indicating a decreased Lewis acid sites in T phase Nb_2O_5 . Thus, based on Raman spectra, the relative low conversion obtained by T phase Nb_2O_5 could be explained by the decreased Lewis acid sites although it still plays an important role for FA dehydration. However, even though both T and H phase Nb_2O_5 are not very active during FA dehydration, T/H phase transitional Nb_2O_5 showed a high conversion rate, comparable with niobic acid. This result provides that FA dehydration was affected by not only acidity, but structure of phase transition. It is also worth noting that the surface area of Nb_2O_5 gradually decreased during the amorphous to crystalline transformation. Thus the catalytic performance, for instance conversion/ nm^2 , of 900°C calcined Nb_2O_5 could be even better than niobic acid consider the former one has a far

less surface area. In order to further investigate the double phase effect on the catalytic activity of 900°C calcined Nb₂O₅, a control experiment was done using Nb₂O₅ prepared by physically mixing 800°C Nb₂O₅ (pure T) and 1000°C Nb₂O₅ (pure H) in a ratio of 75.5/24.5. As shown in Figure S2(a) left, the control group showed a relative lower conversion rate indicating the transitional structure in the 900°C calcined Nb₂O₅ plays an important role in boosting its activity. Meanwhile we also observed a similar high activity on Sigma Nb₂O₅, which is also a double phase Nb₂O₅. Thus a similar control experiment was also done using physically mixed Nb₂O₅ composed of 8.7% 800°C Nb₂O₅ (pure T) and 91.3% 1000°C Nb₂O₅ (pure H). The low conversion rate provided on Figure S2(a) right proves that the commercial Nb₂O₅ should also possess the T-H transitional structure. In conclusion, the FA conversion rate can be boosted by a T-H transitional structure and it's independent of the phase composition. The FA conversion for all catalysts gradually increases when reaction time increases from 2 h to 6 h, with the maximum FA conversion rate obtained by 900°C calcined Nb₂O₅ at 6 h.

FA oligomerization produces multiple dimers and trimers in the range of C₉-C₁₅. Here, we chose the top four high conversion samples and showed their selectivity to C₉-C₁₅ oligomers in Figure 3(b). Among the several dimers and trimers, ether bridge and terminal-OH dimers are dominant products [7]. The proposed reaction mechanisms for these dimer formation are shown in Figure S3 (details in the Supporting information. S4). The highest selectivity rate (61.4%) was obtained by niobic acid at 2 h. For niobic acid and Nb₂O₅ (500°C), the selectivity decreased as a function of reaction time, while Nb₂O₅ (900°C) and commercial Nb₂O₅ showed that the selectivity rate increased with increasing reaction time. Even though all the four catalysts show the similar high conversion rate, T/H phase transitional Nb₂O₅ sample was observed to show a relative low selectivity value compared with niobic acid and TT phase Nb₂O₅. Meanwhile as shown in Figure S2(b), the selectivity value of the two physically mixed Nb₂O₅ are all higher than their corresponding T/H phase transitional Nb₂O₅. Thus we believe although the T-H transitional structure could boost the convers rate, it can possibly limit the selectivity value. It can be deduced that continually increase the reaction time could further increase the selectivity over T/H phase mixed Nb₂O₅ since their selectivity value continuously increases within the first 6 h. Thus in order to acquire a high yield to C₉-C₁₅ oligomers (1) shorter reaction times for niobic acid and TT phase Nb₂O₅ and (2) longer reaction times for T&H phase mixed Nb₂O₅ are required.

It has been reported that the Nb₂O₅ contains several polymorphic phases [30]. Figure 4 illustrates the different phases of Nb₂O₅. In the case of niobic acid and Nb₂O₅ (500°C) sample, the Brønsted acid site and distorted octahedral geometry can be related to the higher FA conversion. Large area hexagonal shape limited the number of active sites on TT-phase Nb₂O₅ (500°C). Large coordination number also limited the affinity to hydroxyl groups, which gives possible explanation to the low activity of TT-phase Nb₂O₅. In the case of Nb₂O₅ (700°C -1000°C) and commercial catalysts, the relationship between Nb₂O₅ phase and FA activity is more complicated and still not

clear, because both T (700°C and 800°C) and H phase (1000°C) Nb₂O₅ show lower catalytic activity compare to T-H phase transitional Nb₂O₅ (900°C and commercial). This synergetic phase effect on FA dehydration, **especially brought by the T/H transitional structure**, is under investigation. We can hypothesize that intrinsic defect sites or the order of polymorphic phase distortion in T/H phase transitional structure can possibly improve the FA-Nb₂O₅ interaction.

4. Conclusions

In this paper, we investigated the FA oligomerization over different Nb₂O₅ phase catalysts prepared by calcination of niobic acid from 500°C to 1000°C. During the calcination, Nb₂O₅ showed phase transformations (e.g., amorphous → TT → T → H) accompanied by a serious decreasing of surface area and pore volume. It was found that the FA dehydration and condensation reaction was significantly affected by the Nb₂O₅ phases and phase transitional structure. The T/H phase transitional Nb₂O₅ catalyst exhibited higher conversion than single phase catalysts, while its selectivity to C₉-C₁₅ oligomers value was lower than that of niobic acid. The commercial bulk Nb₂O₅ was believed to have a similar T/H transitional phase due to its similar conversion rate and phase character compared with synthesized T/H phase transitional Nb₂O₅. Both acid sites and distorted structures during the phase transition were believed to play a vital role during FA oligomerization reaction.

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Table 1. Physical properties of the studied Nb₂O₅ catalysts.

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Figure 1. X-ray diffraction (XRD) patterns of niobic acid, 500°C -1000°C calcined Nb₂O₅ and bulk Nb₂O₅ obtained from Sigma-Aldrich. (■) TT phase; (▼) T phase; (●) H phase.

Figure 2. Raman spectra of niobic acid, 500°C -1000°C calcined Nb₂O₅ and bulk Nb₂O₅ obtained from Sigma-Aldrich.

Figure 3. Conversion of FA (a) and selectivity to dimers and trimers (b) using niobic acid, 500°C -1000°C calcined Nb₂O₅ and bulk Nb₂O₅ obtained from Sigma-Aldrich. Reaction condition: FA=3.00g, Catalysts=0.03g, Temp = 100°C, Pressure = atmosphere, Time = 2hrs(orange), 4hrs(green), 6hrs(blue).

Figure 4. Illustration of Nb₂O₅ phases.

Table 1. Physical properties of the studied Nb₂O₅ catalysts.

Catalysts ^a	Surface area (m ² /g) ^b	Pore Volume (cm ³ /g) ^c	Nb ₂ O ₅ crystalline Phase ^d
Niobic acid	130	0.11	amorphous
Nb ₂ O ₅ (500°C)	65	0.10	TT
Nb ₂ O ₅ (600°C)	12	0.08	TT&T
Nb ₂ O ₅ (700°C)	5	0.05	T
Nb ₂ O ₅ (800°C)	< 1	< 0.01	T
Nb ₂ O ₅ (900°C)	< 1	< 0.01	T&H
Nb ₂ O ₅ (1000°C)	< 1	< 0.01	H
Sigma-Aldrich	< 1	< 0.01	T&H

a (): Calcination temperatures.

b Surface area determined by BET method. Pretreatment: 250 °C for 6hrs, under vacuum conditions.

c Pore Volume determined by BJH method. Pore volume with pore diameter less than 70 nm is reported.

d Crystalline phase determined by XRD.

Figure 1. X-ray diffraction (XRD) patterns of niobic acid, 500°C -1000°C calcined Nb₂O₅ and bulk Nb₂O₅ obtained from Sigma-Aldrich. (■) TT phase; (▼) T phase; (●) H phase.

Figure 2. Raman spectra of Niobic acid, 500°C -1000°C calcined Nb_2O_5 and bulk Nb_2O_5 obtained from Sigma-Aldrich.

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Figure 4. Illustration of Nb_2O_5 phases.

Graphical abstract