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TITLE:

Tuning the Acidity of Pt/ CNTs Catalysts for Hydrodeoxygenation of Diphenyl Ether

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KEYWORDS:

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SUMMARY:

A protocol for the synthesis of HNbWO₆, HNbMoO₆, HTaWO₆ solid acid nanosheet modified Pt/CNTs is presented.

ABSTRACT:

We herein present a method for the synthesis of HNbWO₆, HNbMoO₆, HTaWO₆ solid acid nanosheet modified Pt/CNTs. By varying the weight of various solid acid nanosheets, a series of Pt/xHMNO₆/CNTs with different solid acid compositions (x = 5, 20 wt%; M = Nb, Ta; N = Mo, W) have been prepared by carbon nanotube pretreatment, protonic exchange, solid acid exfoliation, aggregation and finally Pt particles impregnation. The Pt/xHMNO₆/CNTs are characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and NH₃-temperature programmed desorption. The study revealed that HNbWO₆ nanosheets were attached on CNTs, with some edges of the nanosheets being bent in shape. The acid strength of

the supported Pt catalysts increases in the following order: Pt/CNTs < Pt/5HfNbWO₆/CNTs < Pt/20HfNbMoO₆/CNTs < Pt/20HfNbWO₆/CNTs < Pt/20HTaWO₆/CNTs. In addition, the catalytic hydroconversion of lignin-derived model compound: diphenyl ether using the synthesized Pt/20HfNbWO₆ catalyst has been investigated.

INTRODUCTION:

Many industrial processes for the manufacture of chemicals involve the use of aqueous inorganic acid. One typical example is the conventional H₂SO₄ process for the hydration of cyclohexane to produce cyclohexanol. The process involves a biphasic system, with the cyclohexane being in the organic phase and the cyclohexanol product being in the acidic aqueous phase, thus making the separation process by simple distillation difficult. Apart from difficulty in separation and recovery, inorganic acid is also highly toxic and corrosive to equipment. Sometimes, the use of inorganic acid generates byproducts that will lower the product yield and must be avoided. For example, the dehydration of 2-cyclohexene-1-ol to produce 1,3-cyclohexadiene using H₂SO₄ will lead to polymerization byproducts¹. Thus, many industrial processes shift towards using solid acid catalysts. Various water tolerant solid acids are used to solve the above problem and to maximize the product yields, such as the use of HZSM-5 and Amberlyst-15. The use of high-silica HZSM-5 zeolite has been shown to replace H₂SO₄ in the production of cyclohexanol from benzene². Since the zeolite is present in the neutral aqueous phase, the product will go to the organic phase exclusively, thus simplifying the separation process. However, due to Lewis acid-base adduct formation of water molecules to the Lewis acid sites, zeolitic materials still demonstrated lower selectivity due to the presence of inactive sites³. Among all these solid acids, Nb₂O₅ is one of the best candidates that contain both Lewis and Brønsted acid sites. The acidity of Nb₂O₅·nH₂O is equivalent to a 70% H₂SO₄ solution, due to the presence of the labile protons. The Brønsted acidity, which is comparable to protonic zeolite materials, are very high. This acidity will turn to Lewis acidity following water elimination. In the presence of water, Nb₂O₅ forms the tetrahedral NbO₄·H₂O adducts, which may decrease in Lewis acidity. However, the Lewis acid sites are still effective since the NbO₄ tetrahedral still have effective positive charges⁴. Such phenomenon has been demonstrated successfully in the conversion of glucose into 5-(hydroxymethyl)furfural (HMF) and the allylation of benzaldehyde with tetraallyl tin in water⁵. Water-tolerant catalysts are thus crucial in biomass conversion in renewable energy applications, especially when the conversions are performed in environmental benign solvents such as water.

Among the many environmental benign solid acid catalysts, functionalized carbon nanomaterials using graphene, carbon nanotubes, carbon nanofibers, mesoporous carbon materials have been playing an important role in the valorization of biomass due to the tunable porosity, extremely high specific surface area, and excellent hydrophobicity^{6,7}. The sulfonated derivatives are particularly stable and highly active protonic catalytic materials. They can either be prepared by incomplete carbonization of sulfonated aromatic compounds⁸ or by sulfonation of incompletely carbonized sugars⁹. They have proven to be very efficient catalysts (e.g., for the esterification of higher fatty acids) with activity comparable to the use of liquid H₂SO₄. Graphenes and CNTs are carbon materials with a large surface area, excellent mechanical properties, good acid resistance, uniform pore size distributions, as well as resistance to coke deposition. Sulfonated graphene has been found to efficiently catalyze the hydrolysis of ethyl acetate¹⁰ and bifunctional graphene

catalysts has been found to facilitate the one-pot conversion of levulinic acid to γ -valerolactone¹¹. Bifunctional metals supported on CNTs are also very efficient catalysts for application in biomass conversion^{12,13} such as the highly selective aerobic oxidation of HMF to 2,5-diformylfuran over the VO₂-PANI/CNT catalyst¹⁴.

Taking advantage of the unique properties of Nb₂O₅ solid acid, functionalized CNTs and bifunctional metal supported on CNTs, we report the protocol for the synthesis of a series of Nb(Ta)-based solid acid nanosheet modified Pt/CNTs with a high surface area by a nanosheet aggregation method. Furthermore, we demonstrated that Pt/20HNBWO₆/CNTs, as a result of the synergistic effect of well-dispersed Pt particles and strong acid sites derived from HNBWO₆ nanosheets, exhibit the best activity and selectivity in converting lignin-derived model compounds into fuels by hydrodeoxygenation.

PROTOCOL:

CAUTION: For the proper handling methods, properties and toxicities of the chemicals described in this paper, refer to the relevant material safety data sheets (MSDS). Some of the chemicals used are toxic and carcinogenic and special care must be taken. Nanomaterials may potentially pose safety hazards and health effects. Inhalation and skin contact should be avoided. Safety precautions must be exercised, such as performing the catalyst synthesis in the fume hood and catalyst performance evaluation with autoclave reactors. Personal protective equipment must be worn.

1. Pretreatment of CNTs¹³

1.1. Immerse 1.0 g of CNTs into 50 mL of nitric acid in a 100 mL conical flask.

1.2. Sonicate the solution at 25 °C for 1.5 h to remove surface impurities and to enhance the anchoring effect of the catalyst.

1.3. Transfer the solution into a 100 mL round bottom flask.

1.4. Reflux the solution in a mixture of nitric acid (65%) and sulfuric acid (98%) at 60 °C for overnight. Set the volume ratio at 3:1. This will create surface defects on the CNTs.

1.5. Filter the solution to obtain the multiwall carbon nanotube solid. Wash the solid with deionized water and then wash with ethanol 3x, respectively.

1.6. Dry the solid at 80 °C for 14 h.

2. Preparation of HNBWO₆ solid acid nanosheets¹⁵ by protonic exchange followed by exfoliation

2.1. Mix stoichiometric amounts of Li₂CO₃ (0.9236 g) and metal oxides Nb₂O₅ (3.3223 g) and

WO₃ (5.7963 g) at a molar ratio of 1:1:2.

2.2. Calcine the solid mixture at 800 °C for 24 h with one intermediate grinding.

2.3. Place 10.0 g of LiNbWO₆ powder in 200 mL of 2 M HNO₃ aqueous solution at 50 °C and stir the solution mixture for 5 days (120 h) with one replacement of the acid at 60 h.

2.4. Exchange the acid liquid every day and repeat step 2.3.

2.5. Filter the solid and wash the solid with deionized water 3x.

2.6. Dry the solid at 80 °C overnight.

2.7. Add an amount of 25 wt.% TBAOH (tetra (n-butylammonium) hydroxide) solution to 150 mL of deionized water solution with 2.0 g of protonated compound obtained in step 2.6 until the pH reaches 9.5 – 10.0.

2.8. Stir the above solution for 7 days.

2.9. Centrifuge the above solution and collect the supernatant solution that contains the dispersed nanosheets.

3. Preparation of HNbMoO₆ solid acid nanosheets

NOTE: The procedure is similar to that of step 2 except for the first and third steps.

3.1. Mix stoichiometric amounts of Li₂CO₃ and metal oxides Nb₂O₅ and MoO₃ in a molar ratio of 1:1:2.

3.2. Calcine the above solid mixtures at 800 °C in air for 24 h with one intermediate grinding.

3.3. Place 10.0 g of LiNbMoO₆ powder in 200 mL of 2 M HNO₃ aqueous solution at 50 °C and stir the solution mixture for 5 days (120 h) with one replacement of the acid at 60 h.

4. Preparation of HTaWO₆ solid acid nanosheets

NOTE: The procedure is similar to that of step 2 except for the first and third steps.

4.1. Mix stoichiometric amounts of Li₂CO₃ and metal oxides Ta₂O₅ and WO₃ in a molar ratio of 1:1:2.

4.2. Calcine the above solid mixtures at 900 °C in air for 24 h with one intermediate grinding.

4.3. Place 10.0 g of LiTaWO₆ powder in 200 mL of 2 M HNO₃ aqueous solution at 50 °C and stir

the solution mixture for 5 days (120 h) with one replacement of the acid at 60 h.

5. Preparation of HNbWO₆/MWCNTs by the nanosheet aggregation method

5.1. Add 2.0 g of multiwall CNTs obtained in step 1 to a 100 mL solution of HNbWO₆ nanosheets in a 250 mL round bottom flask.

5.2. Add 100 mL of 1.0 M HNO₃ aqueous solution into the round bottom flask dropwise. This will aggregate the nanosheets samples.

5.3. Continue to stir the solution at 50 °C for 6 h.

5.4. Filter the solid and wash the solid with deionized water 3x.

5.5. Dry the solid at 80 °C overnight.

5.6. Weigh the dried solid and record the % loading of the solid acid on the MWCNT.

6. Preparation of Pt/20HNbWO₆/CNTs by the impregnation method

6.1. Dissolve the H₂PtCl₆·H₂O into water (1.0 g/100 mL).

6.2. Impregnate the as-prepared nanosheets modified CNTs materials with 1.34 mL of the above Pt aqueous solution.

6.3. Dry the nanosheets CNTs materials at 80 °C, and calcinate the materials at 400 °C for 3 h.

6.4. Obtain the Nb(Ta)-based solid acid nanosheets modified Pt/CNTs catalysts.

7. Hydrodeoxygenation of lignin-derived aromatic ether

NOTE: The chosen lignin-derived aromatic ether is diphenyl ether in this experiment. The chosen lignin-derived aromatic ether is diphenyl ether in this experiment. The activity of Pt/20HTaWO₆/CNTs (88.8% conversion, not shown in this paper) is lower than Pt/20HNbWO₆/CNTs (99.6%), thus the yield of cyclohexane decreases. Hence, although, higher selectivity of cyclohexane was obtained over Pt/20HTaWO₆/CNTs, lower conversion of diphenyl ether limits its utilization. Using appropriate protective equipment and fume hood to perform the reaction using carcinogenic reagents.

7.1. Dilute 0.05 g of catalyst in 5 mL of liquid quartz and load it in the middle of the reactor between two pillows of quartz wool.

7.2. Reduce the catalyst in H₂ (40 mL/min) at 300 °C for 2 h.

7.3. Pump the diphenyl ether feedstocks (including 5.0 wt.% reactant in *n*-decane and 2.0 wt.% *n*-dodecane as an internal standard for gas chromatography analysis) into the fixed bed reactor at different flow rates (0.05-0.06 mL/min)

7.4. Collect the products at different space times defined as the ratio between the mass of catalyst *W* (g) and the flow rate of the substrate *F* (g/min).

$$\text{Space Time} = \frac{W}{F} (\text{min}) = \frac{\text{Mass of Catalyst (g)}}{\text{Substrate Flow Rate } \left(\frac{\text{g}}{\text{min}}\right)}$$

7.5. Identify the liquid products by an GC (HP-5, 30 m x 0.32 mm x 0.25 μm) with 5977A MSD and analyze off-line by gas chromatography (GC 450, FID, FFAP capillary column 30 m x 0.32 mm x 0.25 μm).

7.6. Determine the conversion of reactants (*conv.*%), selectivity towards product *i* (*S_i*%), and yield of product *i* (*Y_i*%) using the following equations:

$$\text{Conv. \%} = \frac{n(\text{reactant})_{\text{initial}} - n(\text{reactant})_{\text{end}}}{n(\text{reactant})_{\text{initial}}} \times 100\% \quad (1)$$

$$S_i \% = \frac{n_i}{n(\text{reactant})_{\text{initial}} - n(\text{reactant})_{\text{end}}} \times 100\% \quad (2)$$

$$Y_i \% = \frac{n_i}{n(\text{reactant})_{\text{initial}}} \times 100\% \quad (3)$$

REPRESENTATIVE RESULTS:

X-ray diffraction patterns (XRD) have been studied for the precursor LiNbWO₆ and the corresponding proton-exchanged catalyst sample HNbWO₆ to determine the phase (**Figure 1** and **Figure 2**). NH₃-temperature programmed desorption (NH₃-TPD) was used to probe the surface acidity of the catalyst samples (**Figure 3**). Scanning electron microscopy (SEM) with X-ray microanalysis and transmission electron microscopy (TEM) were recorded to study the morphology (**Figure 4** and **Figure 5**). Specific surface area measurements were also recorded for the as-prepared catalysts (**Table 1**).

The XRD pattern of the precursor LiNbWO₆ and the corresponding proton-exchanged catalyst samples HNbWO₆ are shown in **Figure 1**. There are three distinctive diffraction peaks at 2θ = 9.5°, 26.9° and 34.7°. This represents a well-ordered layered structure and is in good agreement with the tetragonal orthorhombic phase with that observed for LiNbWO₆ (JCPDS 84-1764). After the proton exchange reaction using aqueous nitric solution, the diffraction peak at 2θ = 6.8° was observed, which agreed with the patterns observed in HNbWO₆ (JCPDS 41-0110). The presence of this peak indicates the existence of a layered structure. After the layer was exfoliated with tetrabutyl ammonium hydroxide (TBAOH) and mixed with CNTs by nitric acid aggregation, the XRD pattern was obviously changed. The characteristic XRD peak at 2θ = 25.6° was attributed to

C(002), while the peaks at $2\theta = 26.4^\circ$ and 37.9° were attributed to the (110) and (200) lattice plane of the HNbWO_6 nanosheets, respectively. As seen in **Figure 2**, the intensity of the diffraction peak strengthened with increasing content of HNbWO_6 nanosheets. After exfoliation, the diffraction peak at $2\theta = 6.8^\circ$ almost entirely disappeared. This indicated that layered compounds were completely transformed into a nanosheet structure¹⁶. The diffraction peak at $2\theta = 39.8^\circ$ was assigned to the Pt(111) lattice plane.

TEM can be used to observe the Pt particles size distribution of the as-prepared catalysts. Pt particles were evenly distributed on the CNTs. By counting 20-40 Pt particles on each sample, the mean size is determined to be about 3-5 nm. Monolayers of HNbWO_6 nanosheets were attached on CNTs, with some edges of the nanosheets being bent in shape.

SEM of the Pt/20HNbWO₆/CNTs (**Figure 4a**) and the corresponding elemental mapping analysis of the different elements of the catalysts were shown in **Figure 4b-4f**. The analysis directly illustrated the distribution of the Pt particles. This further demonstrated that Pt particles, as well as Nb and W elements, are all uniformly dispersed on the surface of the catalysts.

Using NH_3 -TPD technique, the acidity of different catalysts can be compared. The desorption profiles of the Pt/CNTs, Pt/5HNbWO₆/CNTs, Pt/20HNbWO₆/CNTs, Pt/20HNbMoO₆/CNTs, and Pt/20HTaWO₆/CNTs catalysts are all depicted in **Figure 5** for comparison of the acid strength. It has been known that the concentration of the acid sites on the catalysts are directly related to the area under the peaks while the strength of the acid sites is related to the temperature during NH_3 desorption¹⁷. Generally, the order of acidity is as follows: weak acid sites ($<300^\circ\text{C}$), medium acid sites (between 300°C and 500°C), and strong acid sites ($>500^\circ\text{C}$)¹⁸. All the nanosheet modified catalysts have the weak acid characteristic sites that are depicted by the peak centered at 210°C . The broad desorption peaks indicated that the acid sites are generated on the surface of the CNTs after acid treatment^{19,20}. In addition, two peaks indicating medium acid strength are centered at 360°C (Pt/20HNbWO₆/CNTs) and 450°C (Pt/20TaWO₆/CNTs), respectively. Thus, the order of acid strength of the catalysts can be concluded as follows: Pt/CNTs < Pt/5HNbWO₆/MWNTs < Pt/20HNbMoO₆/CNTs < Pt/20HNbWO₆/CNTs < Pt/20HTaWO₆/CNTs. The acid strength is actually related to the number of Brønsted acid sites which is due to the presence of bridged OH groups (M(OH)N, where M and N represent an element, respectively) formed only on nanosheets^{16,21}. Due to the poor light transmittance of CNTs, pyridine-infrared cannot be used to prove the existence and extent of Brønsted acid sites.

The catalytic performance of the as-prepared Pt/20HNbWO₆/CNTs has been selected for the investigation of conversion of biomass lignin-derived model compound and the mixed model compounds to deoxygenated fuel components. The reaction was performed in a fixed bed reactor at 200°C under 3.0 MPa H_2 and the substrates were pumped into the reactor by a liquid feeding pump. With 0.05 g of Pt/20HNbWO₆/CNTs catalyst, H_2/oil ratio = 300 and at $W/F = 27.3$ min, the conversion of diphenyl ether was completed almost quantitatively at 99.7% with cyclohexane selectivity of 96.4%. When half of the diphenyl ether was replaced with anisole, due to the different interaction between the substrates and the catalyst, the conversion of the mixture was lowered to 82% with cyclohexane selectivity of 70.1%. Current efforts have focused

on the conversion of other lignin-derived model compound mixtures with higher complexity and the elucidation of the mechanism of the competitive interaction between different substrates and the catalyst.

FIGURE AND TABLE LEGENDS:

Figure 1. XRD patterns of the LiNbWO₆ and the corresponding proton-exchanged sample.

X-ray diffraction patterns (XRD) have been studied for the precursors LiNbWO₆ and the corresponding proton-exchanged catalyst samples HNbWO₆ to determine the phase. There are three distinctive diffraction peaks at $2\theta = 9.5^\circ$, 26.9° and 34.7° ¹⁶. This represents a well-ordered layered structure and is in good agreement with the tetragonal orthorhombic phase with that observed for LiNbWO₆ (JCPDS 84-1764). After the proton exchange reaction, a diffraction peak at $2\theta = 6.8^\circ$ was observed which agrees with the patterns observed in HNbWO₆ (JCPDS 41-0110). The presence of this peak indicates the existence of layered structure²².

Figure 2. XRD patterns of supported Pt catalysts with different amount of the solid acid nanosheets.

After the layer was exfoliated with tetrabutyl ammonium hydroxide (TBAOH) and mixed with CNTs by nitric acid aggregation, the XRD pattern was obviously changed. The characteristic XRD peak at $2\theta = 25.6^\circ$ was attributed to C(002), while the peaks at $2\theta = 26.4^\circ$ and 37.9° were attributed to the (110) and (200) lattice plane of the HNbWO₆ nanosheets, respectively. The intensity of the diffraction peak strengthened with increasing content of HNbWO₆ nanosheets. After exfoliation, the diffraction peak at $2\theta = 6.8^\circ$ almost entirely disappeared. This indicated that layered compounds were completely transformed into a nanosheet structure¹⁶. The diffraction peak at $2\theta = 39.8^\circ$ was assigned to the Pt(111) lattice plane.

Figure 3. TEM images and Pt particle size distribution of different catalysts: (A) Pt/CNTs (B) Pt/5HNbWO₆/CNTs (C) Pt/20HNbWO₆/CNTs.

Pt particles were evenly distributed on the CNTs. By counting 20-40 Pt particles on each sample, the mean size is determined to be about 3-5 nm. It can be seen that the monolayer of HNbWO₆ nanosheets were attached on CNTs, with some edges of the nanosheets being bent in shape.

Figure 4. SEM image (a) and elements mapping of Pt (b), O (c), Nb (d), W (e) and C (f) over Pt/20HNbWO₆/CNTs.

SEM of the Pt/20HNbWO₆/CNTs (Figure 4a) and the corresponding elemental mapping analysis of the different elements of the catalysts was shown in Figure 4b-4f. The analysis directly shows the distribution of the Pt particles. This further demonstrated that Pt particles, as well as Nb and W elements, are all uniformly dispersed on the surface of the catalysts.

Figure 5. NH₃-TPD profiles of different catalysts.

NH₃-TPD was used to determine the acid strength of each nanosheets. All the nanosheet modified catalysts have the weak acid characteristic sites that are depicted by the peak centered at 210 °C. The broad desorption peaks indicated that the acid sites are generated on the surface of the CNTs after acid treatment. Also, two peaks indicating medium acid strength are centered

at 360 °C (Pt/20HNbWO₆/CNTs) and 450 °C (Pt/20TaWO₆/CNTs) respectively. Thus, order of acid strength of the catalysts can be concluded as follows: Pt/CNTs < Pt/5HNbWO₆/MWNCTs < Pt/20HNbMoO₆/CNTs < Pt/20HNbWO₆/CNTs < Pt/20HTaWO₆/CNTs.

Table 1. Textural properties of supported Pt catalysts.

The specific surface area of Pt/CNTs was 134 m²/g. After incorporation of various solid acid nanosheets, the specific surface area and the pore volume both decrease, suggesting that partial surface pores of CNTs were blocked by nanosheets.

Table 2. Conversion yields and selectivities of various substrates catalyzed by Pt/HNbWO₆/CNTs

With 0.05 g of Pt/20HNbWO₆/CNTs catalyst, H₂/oil ratio = 300 and at W/F = 27.3 min, the conversion of diphenyl ether was completed almost quantitatively at 99.7% with cyclohexane selectivity of 96.4%. When half of the diphenyl ether was replaced with anisole, due to the different interaction between the substrates and the catalyst, the conversion of the mixture was lowered to 82% with cyclohexane selectivity of 70.1%.

DISCUSSION:

Pretreatment of CNTs with nitric acid does increase the specific surface area (S_{BET}) significantly. Raw CNTs have a specific surface area of 103 m²/g while after treatment, the surface area was increased to 134 m²/g. Therefore, such pretreatment to create defects on the CNT surface will have a positive effect on the specific surface area on the catalysts after solid acid modification and platinum particle impregnation. Since the surface area will decrease after incorporation of nanosheets, this step is very crucial to maximize the surface area of the final catalysts. This is because after nanosheet incorporation and metal impregnation, part of the surface pores will be blocked by nanosheets and metal nanoparticles, leading to a decrease in the overall surface area, as well as the total pore volumes. Such a phenomenon has already been reported by Ma et al.¹². When the amount of HNbWO₆ nanosheets increased from 5 wt% to 20 wt%, S_{BET} of the resulting Pt/HNbWO₆/CNTs has dropped from 117 m²/g to 107 m²/g. While the S_{BET} of Pt/20HTaWO₆/CNTs has dropped to 70 m²/g, the S_{BET} of Pt/20HNbMoO₆/CNTs has reached 118 m²/g. The average pore diameters of all the catalysts, including the un-modified Pt/CNTs, generally remained unchanged (i.e., 3.4 nm). Generally, the strength of the acidic sites impacts the degree of C-O bond cleavage while the S_{BET} impacts the degree of hydrogenation reactions. As a result, Pt/20HNbMoO₆/CNTs have excellent performance in the conversion of diphenyl ether to cyclohexane, while Pt/20HTaWO₆/CNTs have limited deoxygenation properties but excellent hydrogenation properties. Therefore, a catalyst can be fine-tuned to produce different products depending on different product requirements. **Table 1** summarizes the above descriptions.

During the solid-state reaction to prepare LiNbWO₆ powder, it is noteworthy that the samples must be ground during the middle stage of the calcination. This ensures that the samples are mixed as even as possible to ensure homogeneity. During the protonic exchange treatment, care must be taken to ensure that the nitric acid is of high enough acid strength. Therefore, in the half way of the protonic exchange, it is advised that fresh 2 M HNO₃ aqueous solution is used to replace the old one. Normally, 5 days of treatment can ensure complete protonic exchange.

Liquid exfoliation was used to prepare 2D nanosheets from 3D layered bulk materials in this study. Apart from liquid exfoliation, there are other methods to prepare 2D nanosheets, such as mechanical exfoliation, chemical vapor deposition, sonication. Exfoliation can generally be applied to prepare 2D materials such as graphene²³, boron nitride nanosheets²⁴, transition metal dichalcogenides such as MoS₂²⁵, layered metal oxide such as MnO₂, Cs₄W₁₁O₃₆ and LaNbO₇^{26,27}, etc. Exfoliation enables a material to increase surface area significantly. Among these methods, mechanical liquid exfoliation has the advantage of producing high quality samples. However, the yield is still low for this method and it is still currently technically infeasible for scale-up to be realized due to the difficulty in producing uniform samples. Chemical vapor deposition is another common method to prepare 2D nanosheets samples, particularly for transition metal dichalcogenides. For many substrates, large-scale production is feasible, such as the wafer-scale MoS₂²⁸. However, care must be taken to ensure an accurate control of the experimental conditions. Thus, for scale-up production, the process could be rather complicated and costly. Sonication could have the same problem. The use of liquid exfoliation can have a very high product yield with relatively lower cost. Thus, liquid exfoliation (ion exchange method) was used in this study as a part of the process to prepare Pt/HNbWO₆/CNTs.

Catalysts are substrate-specific and it is interesting to know whether other substrates, apart from diphenyl ether, will lead to different results. We have chosen to mix diphenyl ether (2.5 wt%) with 2.5 wt% of anisole as the liquid feedstock. The overall conversion of the mixture is 82.0% and the selectivity for cyclohexane is 96.4%, which is less than conversion of both substrates if feeding alone, diphenyl ether (conversion = 99.7%, S_i = 96.4) and anisole (conversion = 96.2%, S_i = 34.4). This can be explained by the difference of bond dissociation energy between C_(sp2)-OMe (91.5 kcal/mol) and C-O bond in diphenyl ether (78.9 kcal/mol)²⁹. Moreover, due to less steric hindrance, anisole may be more preferably bound to the catalyst in competition with diphenyl ether, leading to a lower conversion of diphenyl ether.

In summary, we demonstrate a series of processes to prepare a Pt/20HNbMoO₆/CNTs supported catalyst, namely, protonic-exchange, nanosheet exfoliation followed by nanosheet aggregation and finally Pt particle impregnation. It has been found to successfully prepare the nanomaterials with high surface areas and in high yield. Above all, the as-prepared nanomaterials showed excellent catalytic conversion activity for the hydrodeoxygenation of diphenyl ether to cyclohexane, though the catalytic reaction is very substrate-specific.

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DISCLOSURES:

We have nothing to disclose.

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515

Figure 1

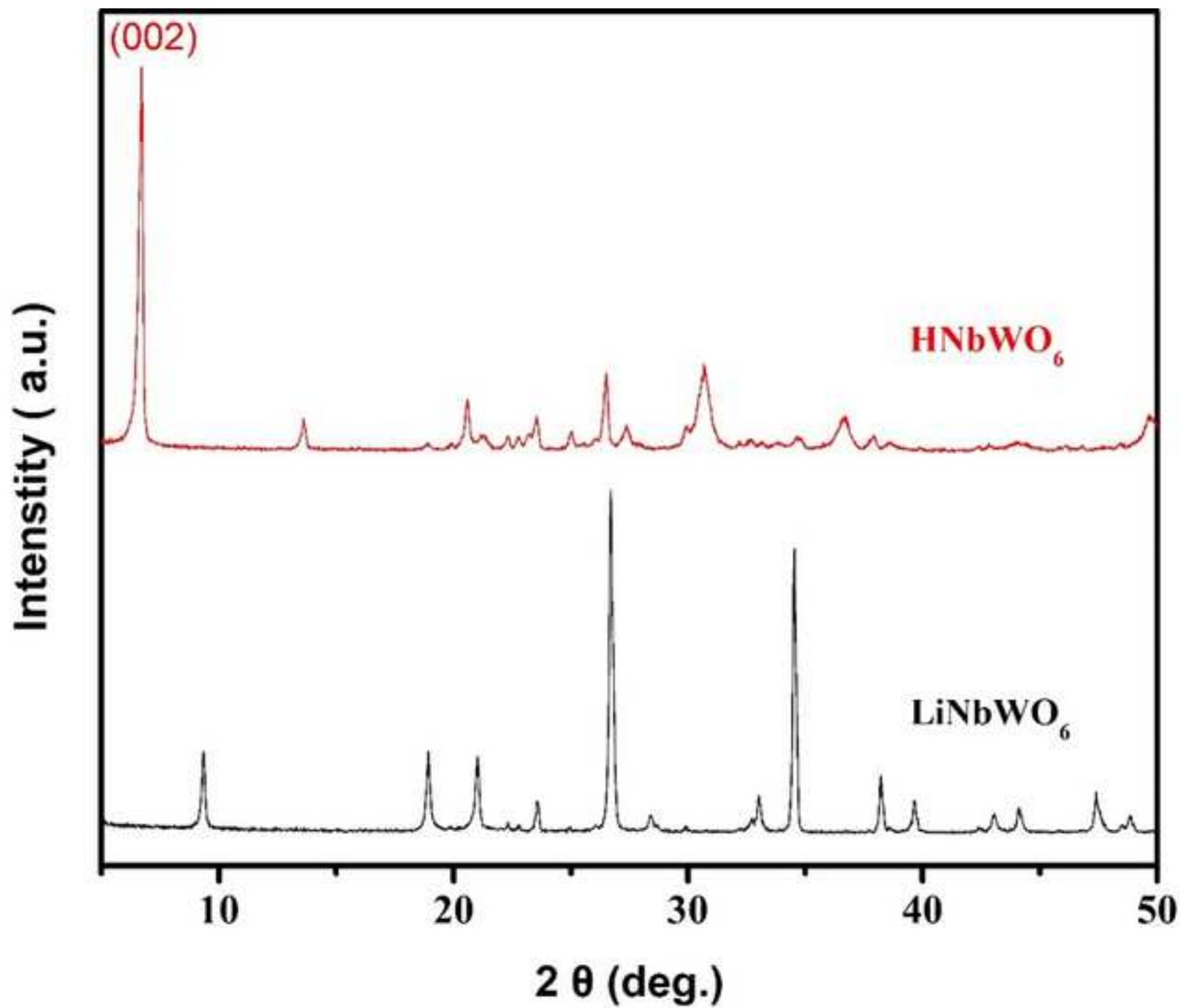


Figure 2

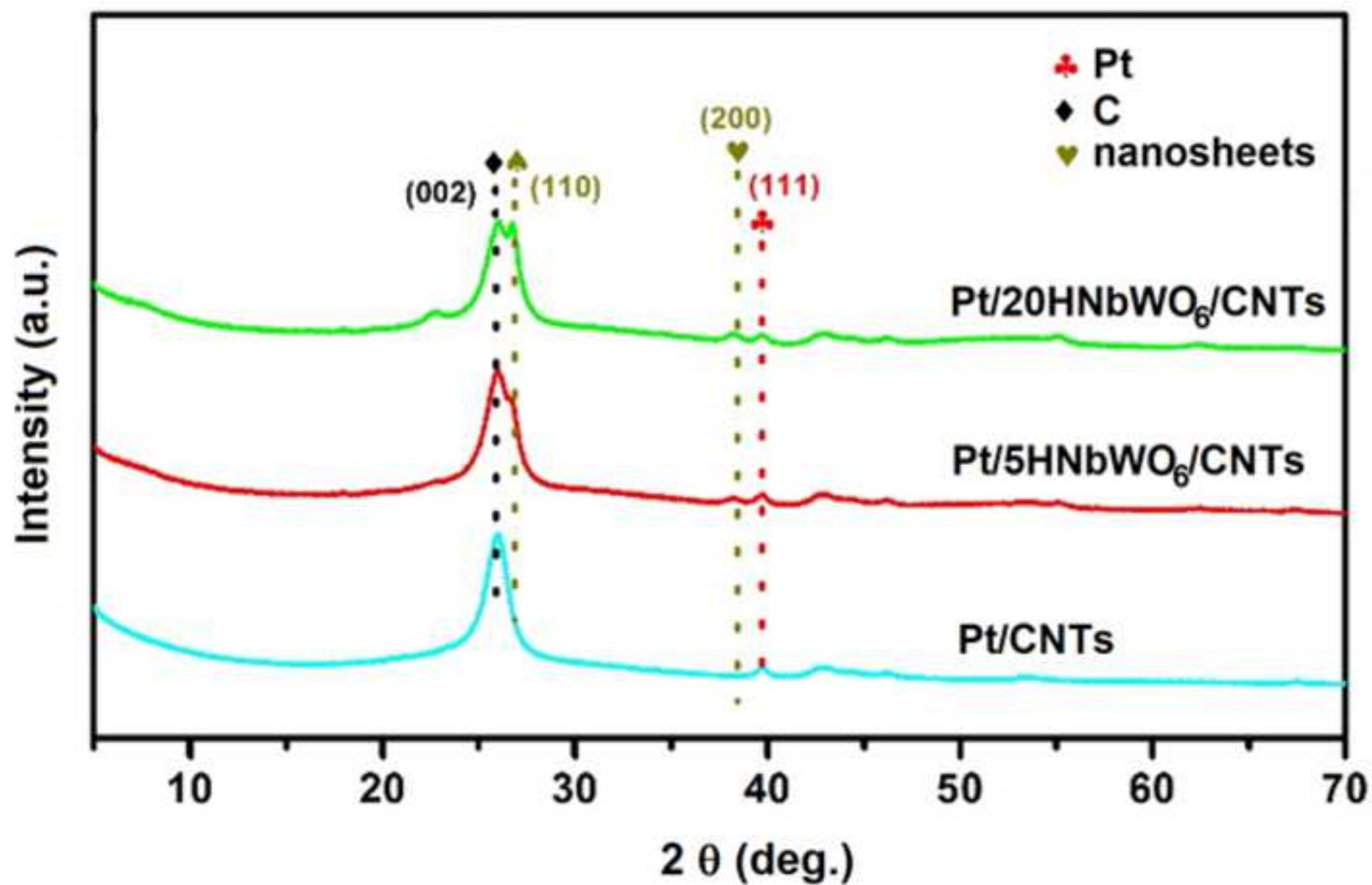
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Figure 3

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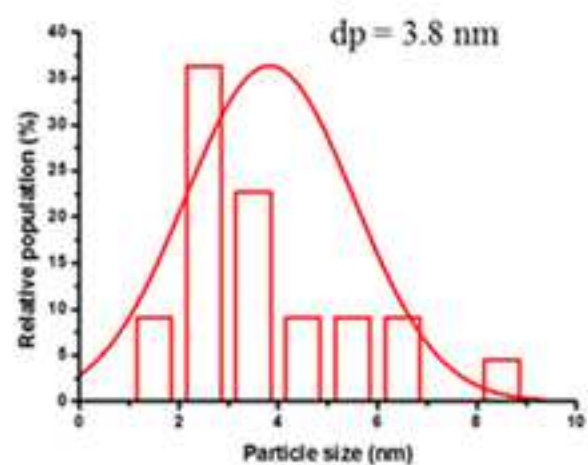
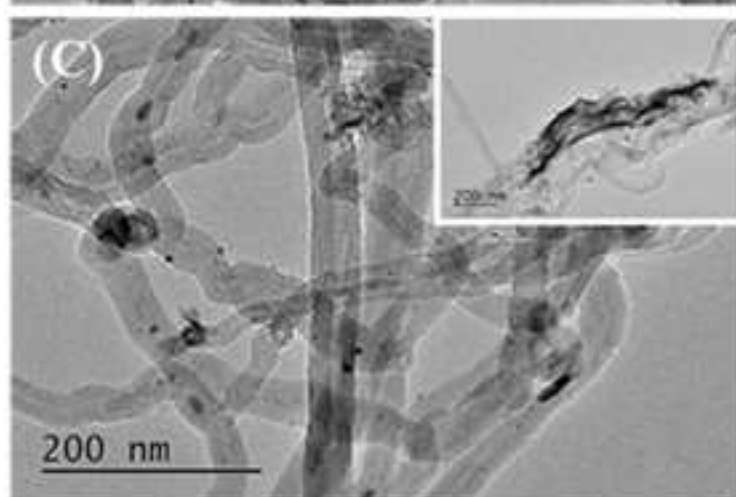
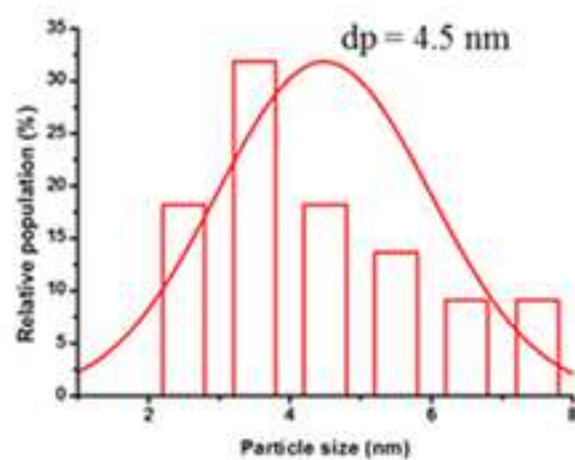
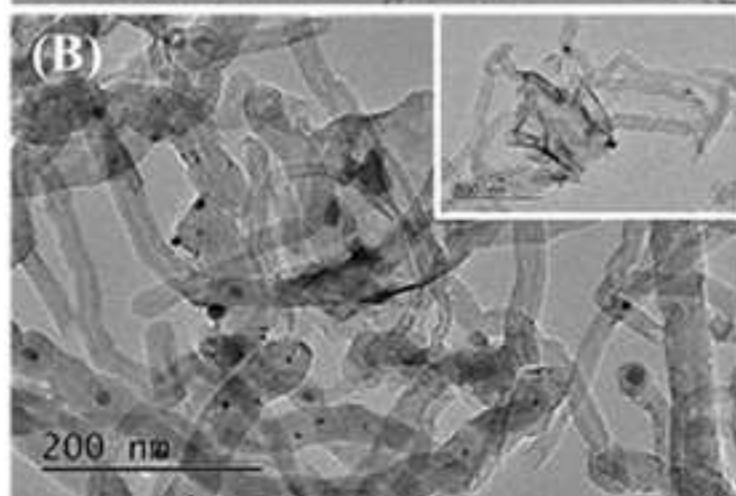
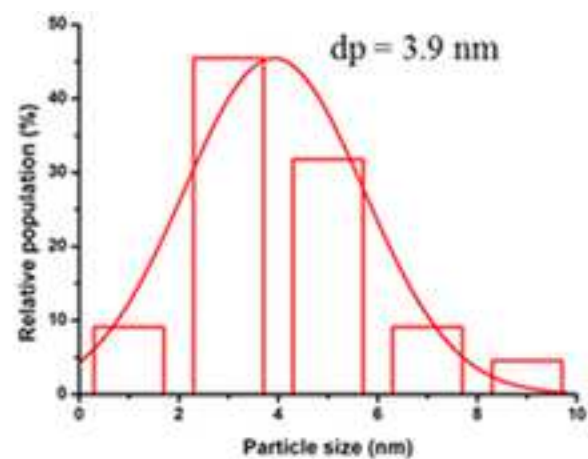
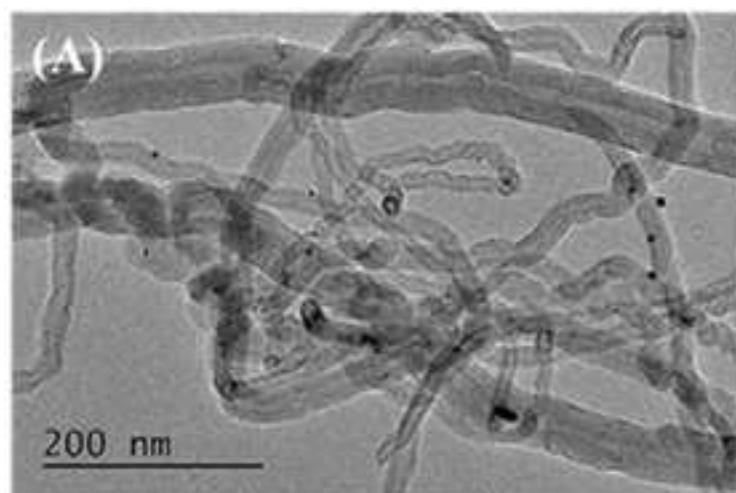


Figure 4

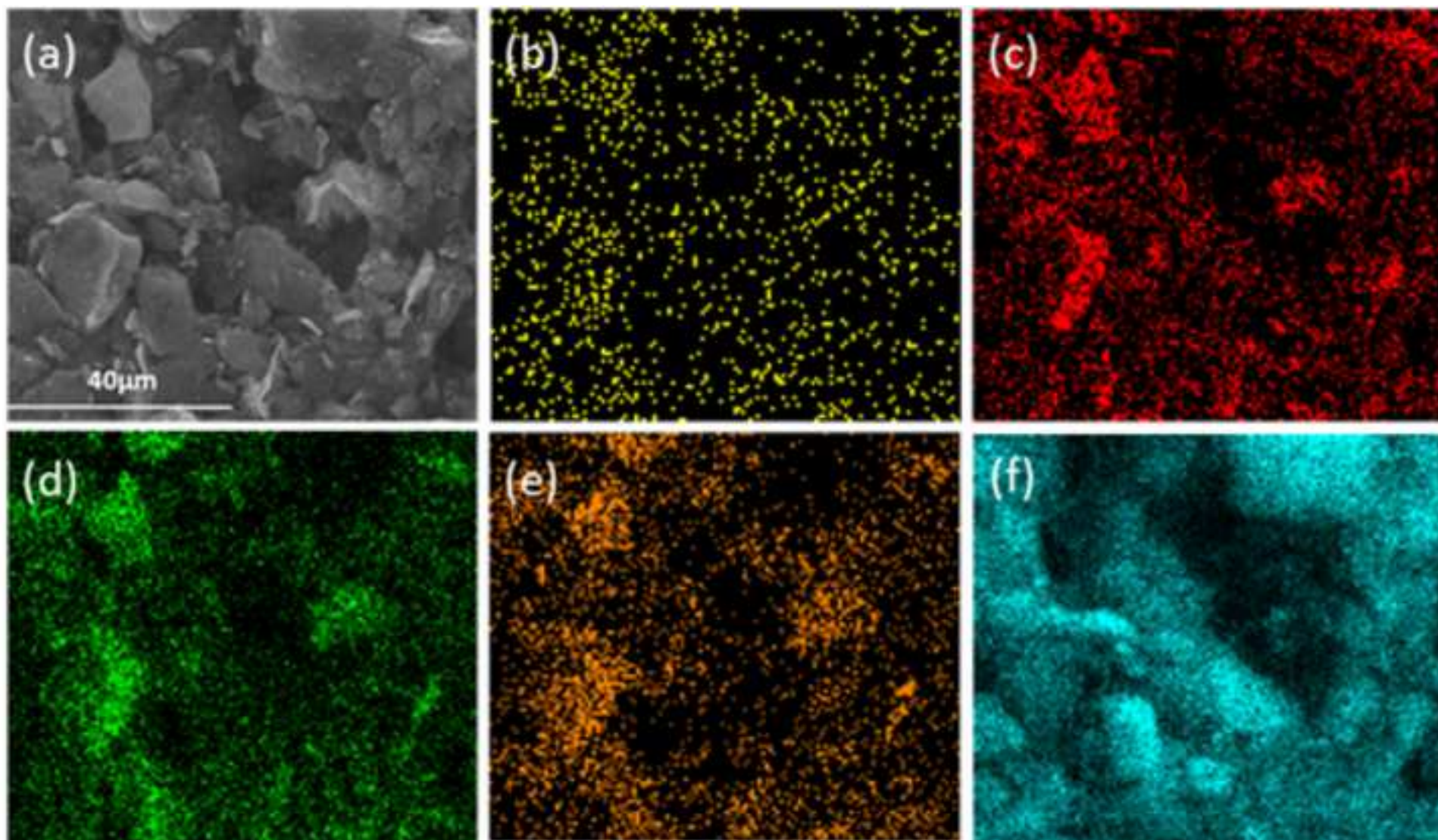
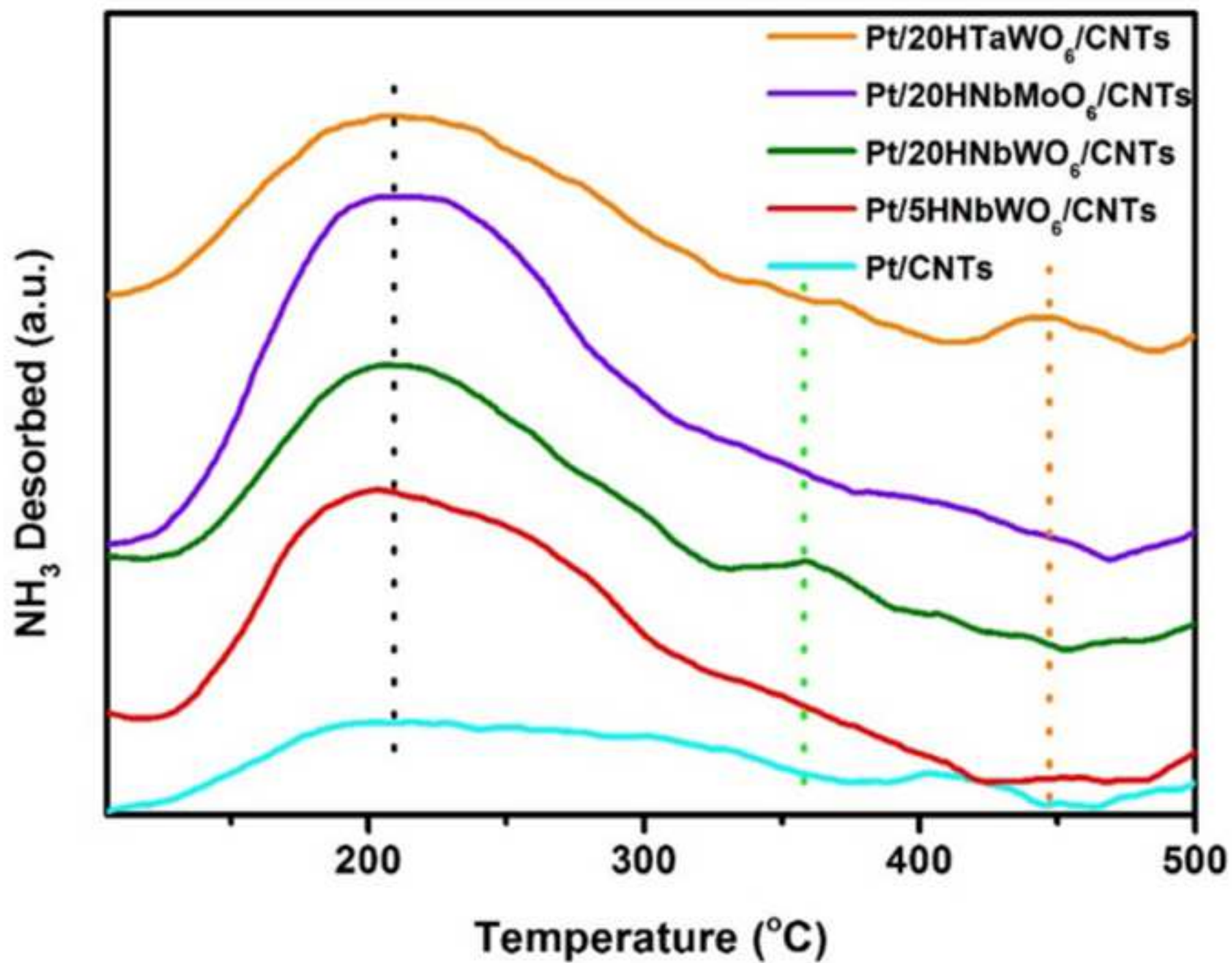


Figure 5



Catalysts	Pt (wt %)	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Pt/CNTs	0.43	134	1.07	3.4
Pt/5HNbWO ₆ /CNTs	0.37	117	0.85	3.1
Pt/20HNbWO ₆ /CNTs	0.42	107	0.78	3.4
Pt/20HNbMoO ₆ /CNTs	0.45	118	0.74	3.4
Pt/20HTaWO ₆ /CNTs	0.46	70	0.62	3.4

Substrates	Temperatures (°C)	Conversion (%)		
			Cyclohexane	ethylcyclohexane
Diphenyl ether	200	99.7	96.4	0
Anisole	200	96.2	34.4	0
anisole + diphenyl ether (1:1)	200	82	70.1	0

Selectivity (%)				
cyclohexanol	cyclohexan-1,2-diol	cyclohexyl methyl ether	dicyclohexyl ether	
1.1	0	0	0	0
0	0	65.6	0	0
3.1	0	20.1	3.1	3.1

cyclohexyl phenyl ether

2.1

0

3.6

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Carbon nanotubes (multi-walled)	Sigma Aldrich	724769	
Nitric acid (65%)	Sigma Aldrich	V000191	
sulphuric acid (98%)	MERCK	100748	
Lithium carbonate (>99%)	Aladdin	L196236	
Niobium pentaoxide (99.95%)	Aladdin	N108413	
Tungsten trioxide (99.8%)	Aladdin	T103857	
Molybdenum trioxide (99.5%)	Aladdin	M104355	
Tantalum oxide (99.5%)	Aladdin	T104746	
Chloroplatinic acid hexahydrate, ≥ 37.50% Pt basis	Sigma Aldrich	206083	
tetra (n-butylammonium) hydroxide 30-hydrate	Aladdin	D117227	
Diphenyl ether, 98%	Aladdin	D110644	
2-Bromoacetophenone,98%	Aladdin	B103328	
Diethyl ether,99.5%	Sinopharm	10009318	
n-Decane,98%	Aladdin	D105231	
n-Dodecane,99%	Aladdin	D119697	
Autoclave Reactor			CJF-0.05—0.1L (Dalian Tongda Equipment Technology Development Co., Ltd)
Tube furnace			SK2-1-10/12 (Luoyang Huaxulie Electric Stove Co., Ltd)



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Dr. Bing Wu

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Dear Dr. Wu,

We sincerely thank you for your rapid handling on our manuscript (JoVE59870). Enclosed please find an electronic version of the revised version of manuscript entitled “Tuning the acidity of Pt/CNTs catalysts for hydrodeoxygenation of diphenyl ether” for your consideration of publication as an *Article* in *Journal of Visualized Experiments*. We have revised our manuscript carefully with **red** marked according to your suggestions and the reviewer’s comments. Meanwhile, we have answered all questions from the reviewers. A point-by-point response to the reviewers’ concerns and a detailed description of the changes are attached in the letter.

In response to your kind comments, we have made the following revision:

Editorial comments:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Reply: Thanks for your reminding, we have checked our spelling and grammar carefully.

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Reply: Thanks. We have obtained the letter of permission and should have already uploaded during the last submission and we will upload it again this time. The Figure Legend will be added, as can be seen from the following answer points.

3. For in-text referencing, please put the reference number before a comma or period.

Reply: Thanks for your reminding, we have revised it. For example:

Before modification:

“For example, the dehydration of 2-cyclohexene-1-ol to produce 1,3-cyclohexadiene using H₂SO₄ will leads to polymerization byproducts.¹”

After modification:

“For example, the dehydration of 2-cyclohexene-1-ol to produce 1,3-cyclohexadiene using H₂SO₄ will leads to polymerization byproducts¹.”

4. Please use a single space between numerical values and their units.

Reply: We are really for our careless, we have revised it.

Before modification:

“Sonicate the solution at 300K for 1.5 hour to remove surface impurities and to enhance anchoring effect of the catalyst.”

After modification:

“Sonicate the solution at 300 K for 1.5 h to remove surface impurities and to enhance anchoring effect of the catalyst.”

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Reply: We have revised it based on your suggestion, for example:

Before modification:

“7.5 Identify the liquid products by an Agilent 7890B GC (HP-5, 30 m×0.32 mm×0.25 μm) with 5977A MSD and analyzed off-line by gas chromatograph (Bruker GC 450, FID, FFAP capillary column 30 m×0.32 mm×0.25 μm).”

After modification:

“7.5 Identify the liquid products by an GC (HP-5, 30 m×0.32 mm×0.25 μm) with 5977A MSD and analyzed off-line by gas chromatograph (GC 450, FID, FFAP capillary column 30 m×0.32 mm×0.25 μm).”

6. Step 1.1: What’s the concentration of nitric acid?

Reply: The concentration of nitric acid used in this work is 14.4 mol/L (65.0 wt.% by weight).

7. Each figure must be accompanied by a title and a description after the Representative Results of the manuscript text.

Reply: We are really sorry for our careless mistakes, we have revised it as follows:

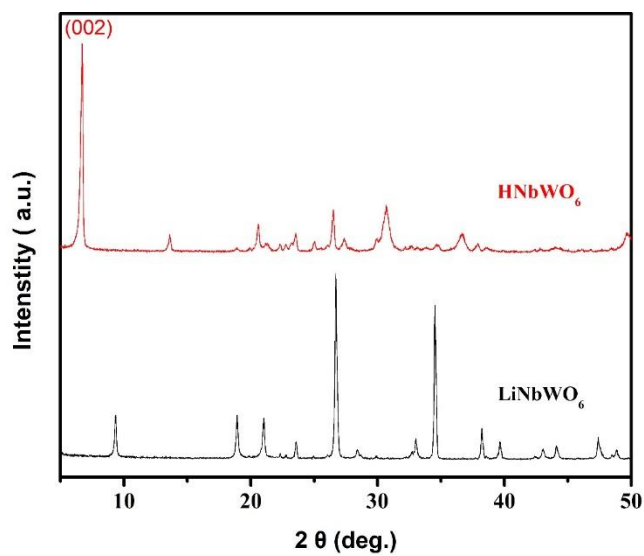


Figure 1. XRD patterns of the LiNbWO_6 and the corresponding proton-exchanged sample.

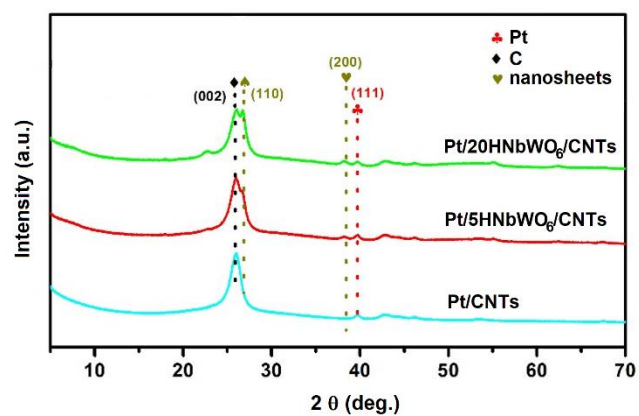


Figure 2. XRD patterns of supported Pt catalysts with different amount of the solid acid nanosheets.

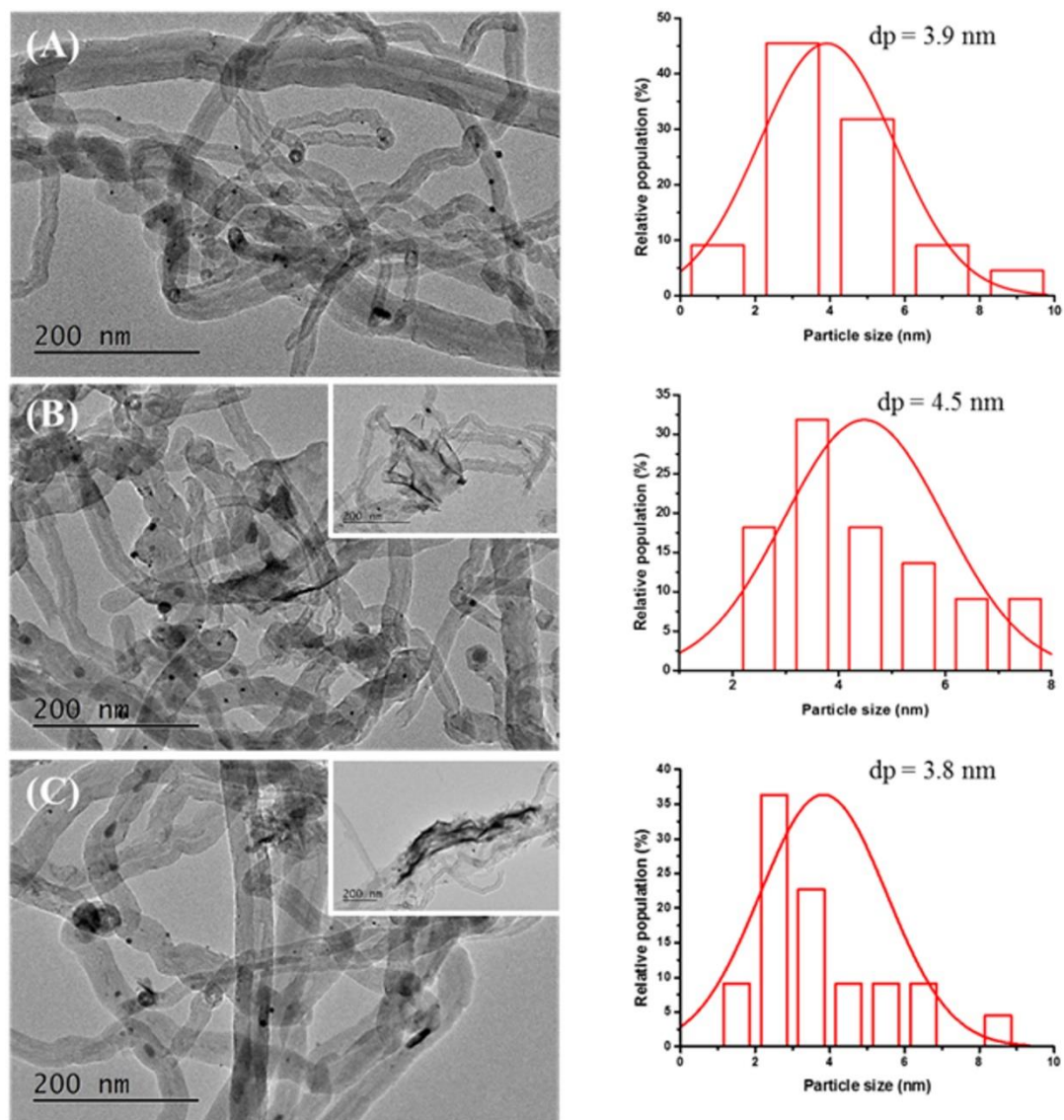


Figure 3. TEM images and Pt particle size distribution of different catalysts: (A) Pt/CNTs, (B) Pt/5HNbWO₆/CNTs, (C) Pt/20HNbWO₆/CNTs.

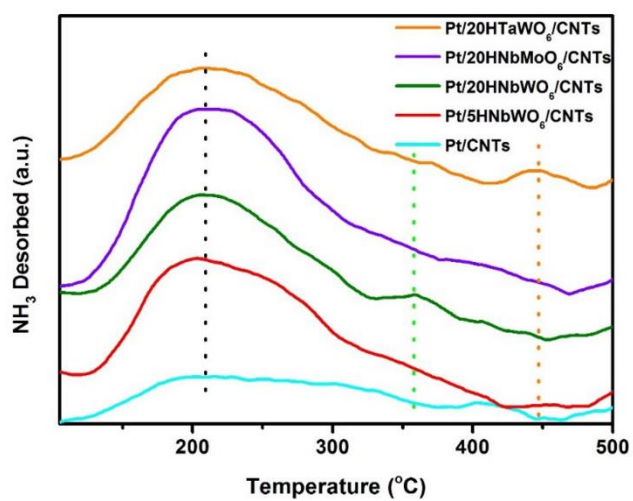


Figure 5. NH₃-TPD profiles of different catalysts.

8. Please remove the embedded figure(s) from the manuscript. All figures should be uploaded separately to your Editorial Manager account.

Reply: We have removed figures from manuscript and placed it in a separately file.

9. Please remove the embedded Table from the manuscript. All tables should be uploaded separately to your Editorial Manager account in the form of an .xls or .xlsx file.

Reply: We have removed Table from manuscript and placed it in a separately file in the form of an .xls file.

Reviewers' comments

Reviewer #1:

this manuscript described detailed process and it can be accepted as it is.

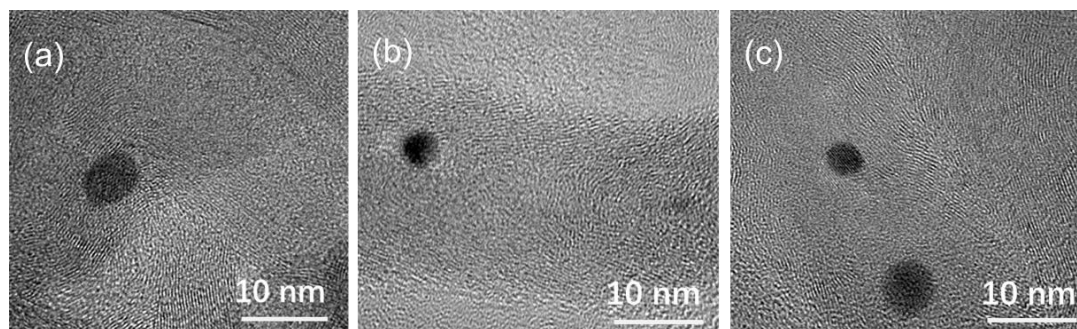
Reply: We really thank for your appreciation.

Reviewer #2:

This paper reports on the preparation of Nb and Ta-based solid acids nanosheets modified Pt/carbon nanotubes. The authors also investigated the catalytic hydroconversion of lignin-derived compounds using such Pt/20HNbMoO₆ as catalyst. I would like to recommend its acceptance for publication after the following revisions:

1. HRTEM images for the composites should be provided.

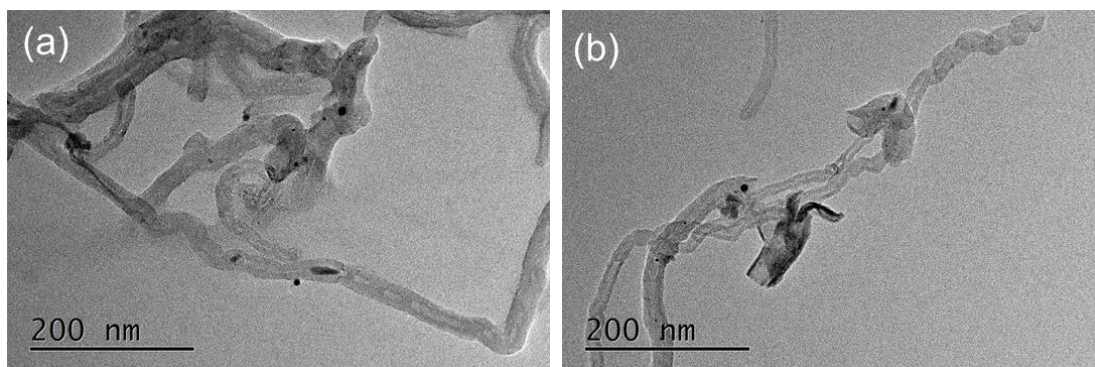
Reply: The HRTEM images of Pt/CNTs, Pt/5HNbWO₆/CNTs, and Pt/20HNbWO₆/CNTs are presented as follows:



The HRTEM images of (a) Pt/CNTs, (b) Pt/5HNbWO₆/CNTs, and (c) Pt/20HNbWO₆/CNTs.

2. After catalysis, can the catalyst maintain its morphology and structure?

Reply: The TEM images of Pt/20HNbWO₆ catalyst after reaction are shown below. Obviously, the catalyst maintains the morphology and structure quite well.



Reviewer #3:

Guan et al. reported an interesting work on improving the acidity of carbon nanotubes supported Pt catalyst for highly selective biomass conversion. The reported results are convincing and hence, I recommend this article for the publication after the adequate revision.

1. The title can be modified. Try to use a concise and attractive title, for instance "Tuning the acidity of Pt/carbon nanotubes based catalysts for selective biomass conversion"

Reply: Thanks for your suggestion, we have modified based on your comment.

Before modification:

"Solid Acid Modification of Carbon Nanotubes Supported Pt Catalyst for Highly Selective Biomass Conversion"

After modification:

"Tuning the acidity of Pt/ carbon nanotubes catalysts for hydrodeoxygenation of diphenyl ether"

2. Abstract: it was reported that "We herein present a method for the synthesis of Nb and Ta-based solid acids nanosheets modified Pt/carbon nanotubes". However, Mo and W species also exhibit acid properties and sometimes much better than the Nb and Ta oxides. So, the above sentence must be modified.

Reply: Thanks for your comment, we have modified the sentence.

Before modification:

"We herein present a method for the synthesis of Nb and Ta-based solid acids nanosheets modified Pt/carbon nanotubes"

After modification:

"We herein present a method for the synthesis of HNbWO₆, HNbMoO₆, HTaWO₆ solid acid nanosheets modified Pt/carbon nanotubes"

3. Abstract: Pt/CNTs < Pt/5HNbWO₆/MWNCTs < Pt/20HNbMoO₆/CNTs < Pt/20HNbWO₆/CNTs < Pt/20HTaWO₆/CNTs. here, only in the second catalyst nomenclature, MWCNTs is mentioned?

Reply: We are sorry for our mistakes. MWCNTs which is multi-walled carbon nanotubes.

Before modification:

"Pt/CNTs < Pt/5HNbWO₆/MWNCTs < Pt/20HNbMoO₆/CNTs < Pt/20HNbWO₆/CNTs < Pt/20HTaWO₆/CNTs"

After modification:

“Pt/CNTs < Pt/5HNbWO₆/CNTs < Pt/20HNbMoO₆/CNTs < Pt/20HNbWO₆/CNTs < Pt/20HTaWO₆/CNTs”

4. There is a nice review article (Chem. Soc. Rev., 2018, 47, 8349-8402) on catalytic biomass conversion; including carbon nanotubes based catalysts for lignin conversion. It would be useful to improve the introduction part.

Reply: Thanks for your suggestion. We have added some more examples within line 81 – 95.

5. Line 209, why the only Pt/20HNbWO₆/CNTs catalyst is selected for the reaction? Pt/20HTaWO₆/CNTs catalyst exhibits higher acidity. I think it will exhibit higher activity than the Pt/20HNbWO₆/CNTs catalyst as the hydrodeoxygenation also depends on the acidic properties including redox properties.

Reply: The activity of Pt/20HTaWO₆/CNTs (88.8% conversion, not shown in this paper) is lower than Pt/20HNbWO₆/CNTs (99.6%), thus the yield of cyclohexane decreases. Hence, although, higher selectivity of cyclohexane was obtained over Pt/20HTaWO₆/CNTs, lower conversion of diphenyl ether limits its utilization. We have corrected our description.

6. Fig. 1, LiNbWO₆? There is no XRD of Pt/20HTaWO₆/CNTs.

Reply: We have LiNbWO₆ as shown in Fig. 1 and Pt/20HNbWO₆/CNTs as shown in Fig. 2. We have the XRD results of Pt/20HTaWO₆/CNTs published elsewhere “Molecular Catalysis 467 (2019) 61-69”. However, only LiNbWO₆ series are presented here in this paper as an example, as we believe that the scope of Jove focuses on the protocol, and not the characterization data.

7. Provide another table or figure with the activity results

Reply: The activity results are presented in Table 1, as an excel file.

8. Take care of English and type errors.

Pt supported catalysts to supported Pt catalysts, line 48

have been to has been, line 51

Bronsted, line 72

Units of temperatures, K in line 115, 127 but oC in line 135, 144, etc.

Temperate units, line 202.

Reply: We have corrected it in revised manuscript.

We believe that all the points raised have now been sufficiently addressed and the paper should now be in its proper form acceptable for publication. We thank you for your time and consideration. I hope that the referees and you are satisfied with our responses to the referees' comments and with the changes to our manuscript. Thank you for your kind attention.

Yours sincerely,

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