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Supporting Information for

High Yield of Renewable Hexanes by Direct Hydrolysis-Hydrodeoxygenation of Cellulose in Aqueous Phase Catalytic System

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Formulae:

$$Conversion\ (\%) = \frac{m_{initial} - m_{left}}{m_{initial}} \times 100\%$$

Where, $m_{initial}$ denotes the weight of feedstock (cellulose, glucose, sorbitol, isosorbide) before reaction, m_{left} denotes the weight of feedstock after reaction.

$$Yield\ (\%) = \frac{n_{product}}{n_{initial}} \times 100\%$$

,

Where, $n_{initial}$ denotes the carbon moles of feedstock before reaction, $n_{product}$ denotes the carbon moles of the product.

For cellulose,

$$n_{initial} = \frac{m_{cellulose}}{M(C_6H_{10}O_5)} \times 6$$

,

Where, $m_{cellulose}$ denotes the weight of cellulose, $M(C_6H_{10}O_5)$ denotes the molecular weight of anhydroglucose unit.

$$Carbon\ balance\ (\%) = \frac{n_{product}}{n_{conversion}} \times 100\%$$

Where, $n_{conversion}$ denotes the carbon moles of converted feedstock. A small amount of biochar was found in those tests which resulted in the low carbon balance.

$$Selectivity\ of\ hexanes\ (\%) = \frac{n_{hexanes}}{n_{total\ alkanes}} \times 100\%$$

Where, $n_{hexanes}$ denotes the carbon moles of hexanes, $n_{total\ products}$ denotes the carbon moles of all detected products in gas phase.

Experimental details

Analysis of the aqueous products and gaseous products

After the completion of these reactions, the gas samples and liquid samples were collected, and quantified by GC and HPLC, respectively. Other details were described in the supporting information.

After the reaction, the gaseous products were collected at high temperature and immediately analyzed. The liquid phase samples were collected at room temperature. Gas products were analyzed by Agilent 7890A with three detectors. FID detector with GS-GASPRO column quantified the gas component of alkanes, while TCD detector with 6ft Q +8ft 5A was used to calculate the yield of CO_x. A Waters Alliance 2695 with Waters UV/Visible detector 2489 and Waters 2414 RID was used to analyze the liquid products. RID was kept at 323 K. 10 μL liquid sample was auto-injected into HPLC through the separation of BIO-RAS Aminex HPX-87H column which was maintained at 318 K, and the mobile phase of sulfuric acid (5 mM) was at a flow rate of 0.55 mL·min^{-1}.

Equipped with a HP-INNOwax capillary column, a gas chromatography coupled with a mass spectrometer (7890A-5975C, Agilent Technologies, USA) was used to perform the gas chromatography mass spectroscopy (GC-MS) analysis of liquid products. The liquid chromatography mass spectroscopy (LC-MS) chromatogram of liquid products was performed by an Agilent 1290LC -G6540B Q-TOF. And the mobile phase of acetonitrile solution (acetonitrile water = 3 1) was at a flow rate of 1.20 mL·min^{-1}.

Catalyst preparation and characterization

Phosphoric acid and HNO_3 were supplied by Tianjin Fuyu Fine Chemical Co., Ltd. MCM-41, SBA-15, HZSM-5 (Si/Al=38), and γ-Al_2O_3 were purchased from Catalyst Plant of NanKai University, and they were used in the reactions after calcined at 723 K for 4 h in air and milled. Ru/C was purchased from Aladdin and was directly used. Microcrystalline cellulose was purchased from Alfa Aesar and was directly used. Glucose was obtained from

Tianjin Damao Chemical Reagent Factory. Sorbitol was purchased from Shanghai Yuanju Biotech Company. Isosorbide was bought from Accela. Ethylene glycol, propylene glycol, Li_2CO_3, MoO_3, WO_3 and Nb_2O_5 were purchased from Aladdin. 1,5-sorbitan and1,4-sorbitan were purchased from J&K.

$LiNbMoO_6$ was synthesized by calcination of stoichiometric mixture of Li_2CO_3, MoO_3, and Nb_2O_5 for 24 h at 853 K simply after a milling process. $HNbMoO_6$ was obtained through the proton-exchange reaction in 200 mL of 1.5 M HNO_3 solution for 8 days. After the reaction, the product was washed with distilled water and dried in air at 358 K. $LiNbWO_6$ was synthesized by calcination of stoichiometric mixture of Li_2CO_3, WO_3, and Nb_2O_5 for 72 h at 1033 K.

Morphological information of the samples was obtained by using a field-emission scanning electron microscope (SEM) Hitachi S-4800 operated at 10 kV. Quantachrome instrument (QUADRASORB SI-MP-10/PoreMaster 33) was used to analyze the structure properties and surface area of co-catalysts at 77K and N_2 was used as adsorbent. Classical BET method and BJH method were used to calculate the surface area and pore properties, respectively. An X-ray diffractometer (XPert Pro MPD, Philip) was used to measure the XRD diffractogram with Cu Kα radiation (λ=0.154 nm) at 100 mA and 40 KV.

A Nicolet iS50 FT-IR (Fourier transform infrared spectrometer) spectrophotometer (Thermo Scientific, USA) was used for characterization of layered compounds. The instrument was equipped with a MCT (mercury cadmium telluride). KBr pellet method was used.

An ASIQACIV200-2 automatic physical/chemical adsorption analyzer was used to conduct NH_3-TPD (ammonia temperature programmed desorption) tests of layered compounds.

^1H MAS NMR analysis was performed by using a Bruker AVANCE Ⅲ 300 WB spectrometer.

Tables and Figures

Table S1. Physicochemical property of the co-catalysts

Co-catalyst	BET surface area ($m^2 \cdot g^{-1}$)	Average pore diameter (nm)
MCM-41	309.82	2.49
HZSM-5	392.81	3.55
γ-Al2O3	200.66	1.44
SBA-15	583.15	7.04
$LiNbMoO_6$	5.90	6.74
$HNbMoO_6$	3.80	5.39
$LiNbWO_6$	4.76	5.86

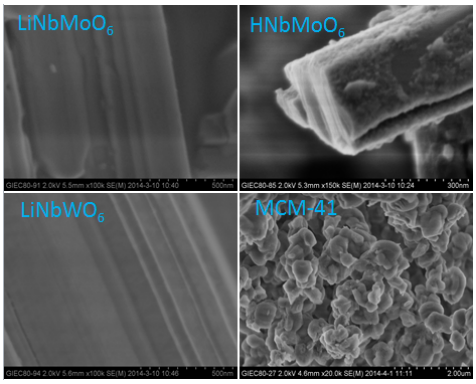

Figure S1. SEM images of MCM-41, layered $HNbMoO_6$, $LiNbMoO_6$, and $LiNbWO_6$.

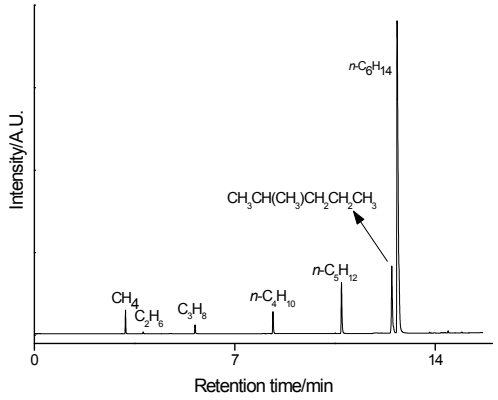

Figure S2. GC chromatogram of gas products.

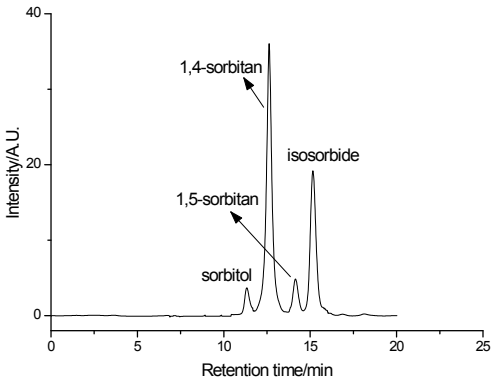

Figure S3. HPLC chromatogram of products in aqueous phase for the conversion of cellulose after 6 h by using MCM-41 as the co-catalyst. (Retention times of glucose, sorbitol, 1,4-sorbitan, 1,5-sorbitan, isosorbide, propylene glycol, and ethylene glycol were identified as 10.1, 11.3, 12.2, 14.1, 15.2, 19.1, and 18.1min, respectively. Reaction conditions: 0.8 g microcrystalline cellulose, 0.2 g Ru/C, 0.2 g MCM-41, 0.59 M H_3PO_4, 40 mL H_2O, 503 K, 6 MPa H_2.)

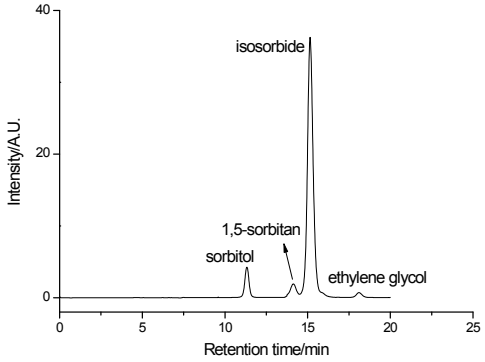

Figure S4. HPLC chromatogram of products in aqueous phase for the conversion of cellulose after 24 h by using MCM-41 as the co-catalyst. (Reaction conditions: 0.8 g microcrystalline cellulose, 0.2 g Ru/C, 0.2 g MCM-41, 0.59 M H_3PO_4, 40 mL H_2O, 503 K, 6 MPa H_2.)

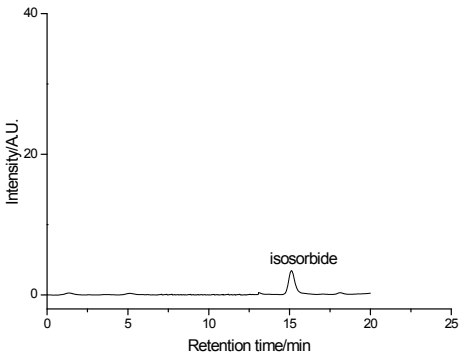

Figure S5. HPLC chromatogram of products in aqueous phase for the conversion of cellulose after 24 h by using $LiNbMoO_6$ as the co-catalyst. (Reaction conditions: 0.8 g microcrystalline cellulose, 0.2 g Ru/C, 0.2 g $LiNbMoO_6$, 0.21 M H_3PO_4, 40 mL H_2O, 503 K, 6 MPa H_2.)

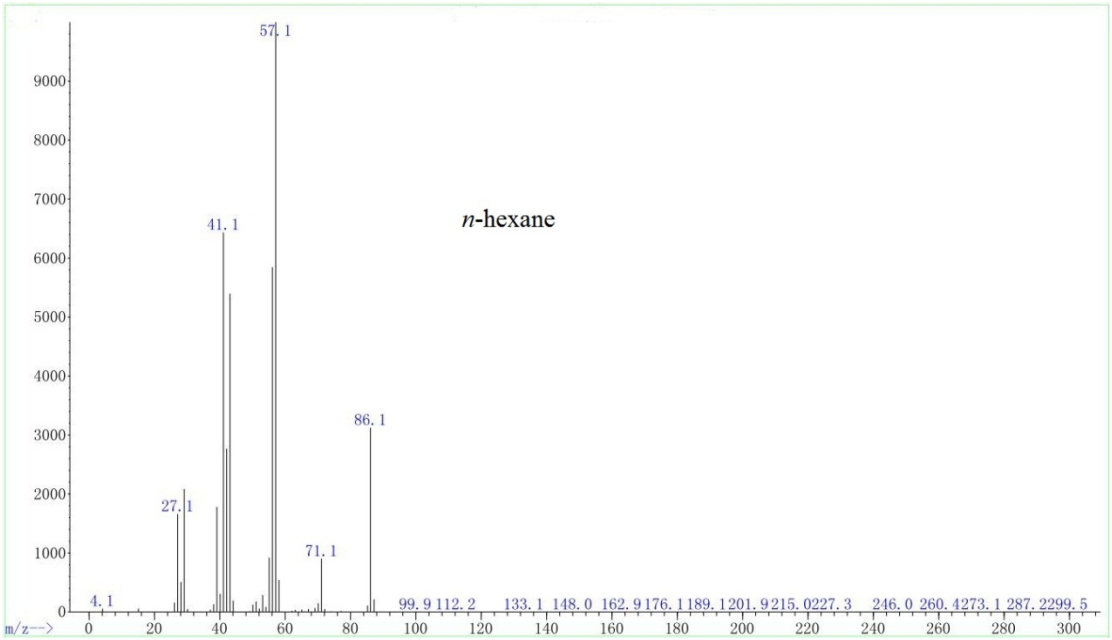

Figure S6. MS chromatogram of the product *n*-hexane obtained from cellulose conversion.

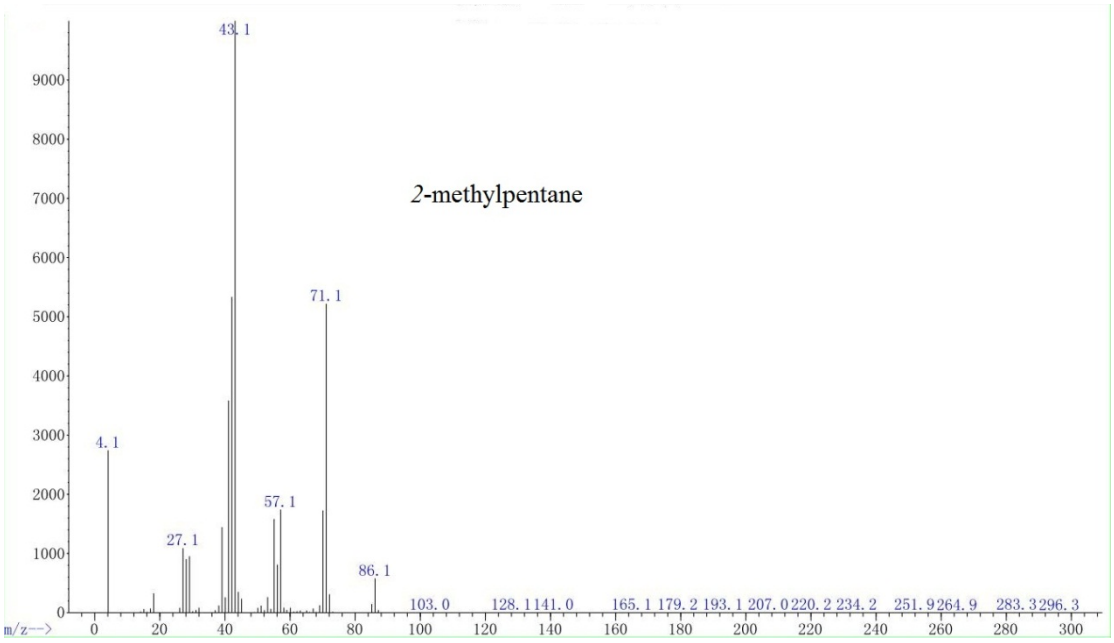

Figure S7. MS chromatogram of the product 2-methylpentane obtained from cellulose conversion.

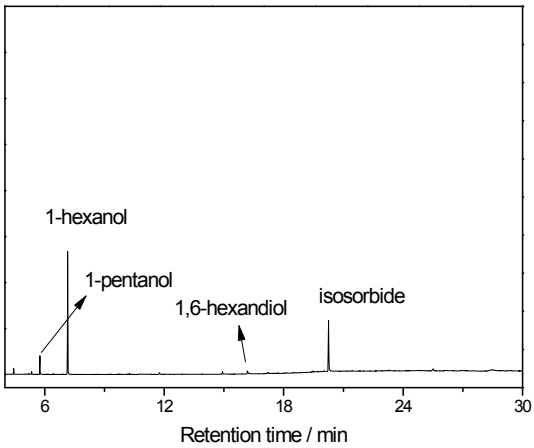

Figure S8. GC-MS chromatogram of liquid products obtained from cellulose conversion.

Figure S9. LC-MS chromatogram of liquid products obtained from cellulose conversion. A: sorbitan ($C_6H_{12}O_5$); B: sorbitol ($C_6H_{14}O_6$).

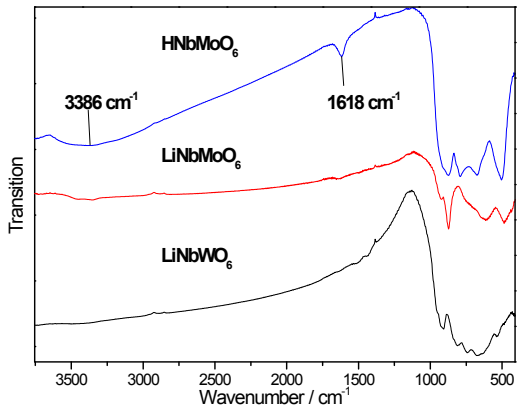

Figure S10. FT-IR spectrum of different layered compounds.

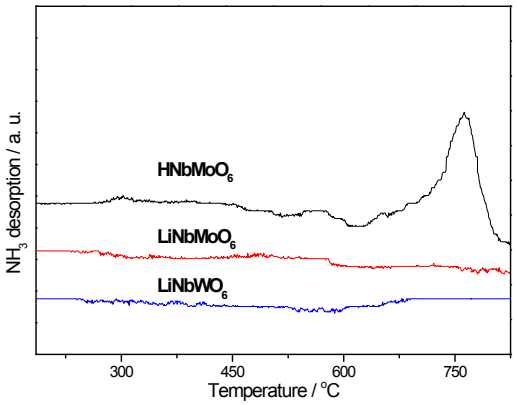

Figure S11. NH_3-TPD profiles of different layered compounds.

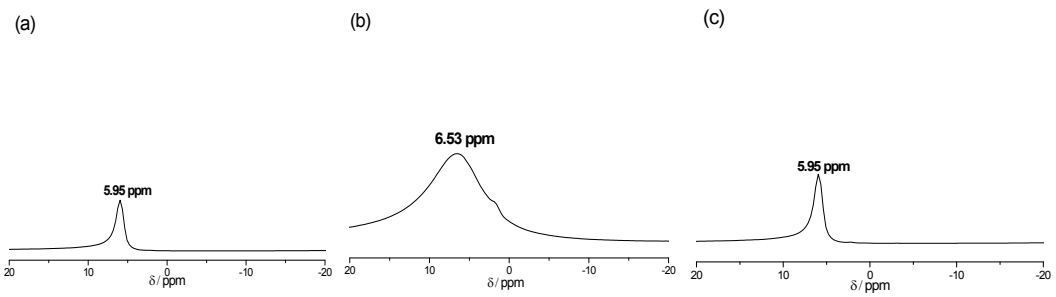

Figure S12. ^{1}H MAS NMR spectra of (a) the fresh $LiNbMoO_6$, (b) the used $LiNbMoO_6$ and (c) the recovered $LiNbMoO_6$ after calcination.