Direct hydrodeoxygenation of raw woody biomass into liquid alkanes

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Being the only sustainable source of organic carbon, biomass is playing an ever-increasingly important role in our energy landscape. The conversion of renewable lignocellulosic biomass into liquid fuels is particularly attractive but extremely challenging due to the inertness and complexity of lignocellulose. Here we describe the direct hydrodeoxygenation of raw woods into liquid alkanes with mass yields up to 28.1 wt% over a multifunctional Pt/NbOPO₄ catalyst in cyclohexane. The superior performance of this catalyst allows simultaneous conversion of cellulose, hemicellulose and, more significantly, lignin fractions in the wood sawdust into hexane, pentane and alkylcyclohexanes, respectively. Investigation on the molecular mechanism reveals that a synergistic effect between Pt, NbOₓ species and acidic sites promotes this highly efficient hydrodeoxygenation of bulk lignocellulose. No chemical pretreatment of the raw woody biomass or separation is required for this one-pot process, which opens a general and energy-efficient route for converting raw lignocellulose into valuable alkanes.
Fossil fuel consumption is projected to increase significantly in coming decades, with potentially catastrophic consequences for the environment. Sustainable alternatives to crude oil are imperatively needed to bridge gaps in the supply of chemical fuels and feedstocks. For the production of liquid fuels in particular, the replacement of oil-based routes by renewable biomass has received increasing attention. Lignocellulose, as the main component of woody biomass, is composed of cellulose (40–50 wt%); a linear polymer of d-glucopyranose connected by β-1,4-glycosidic linkages), hemicellulose (16–33 wt%; a heteropolymer consisting of many different sugar monomers) and lignin (15–30 wt%; a heavily cross-linked, complex polymer with coumaryl, coniferyl and sinapyl alcohols as monomers). Owing to the complexity of lignocellulosic biomass and its notorious resistance to chemical transformation, energy-efficient and cost-effective production of liquid fuels from lignocellulose remains a mammoth challenge. So far, two strategies have been reported to address this challenge: (i) separation of lignocellulose into isolated sugars and lignin followed by biological or chemical (hydrolysis) processing; (ii) thermochemical treatment of lignocellulose to produce upgradeable intermediates, such as bio-oils by pyrolysis or syngas by gasification, coupled with subsequent catalytic upgrading. Thermoochemical processes offer the total conversion of lignocellulose, but are often non-selective and intractable, and the resultant bio-oils or syngas need to be upgraded for further utilisation. Although hydrolysis-based approaches offer selective production of liquid fuels, they are generally multistep and thus very energy-intensive. Moreover, the lignin by-products generated from the hydrolysis of lignocellulose are usually burned as a low-value fuel. Powerful drivers therefore exist to develop alternative efficient and selective strategies to directly convert raw lignocellulose into liquid fuels.

Direct conversion of raw lignocellulose into alcohols and phenols was realised recently in exceptional cases. For example, the conversion of lignin into alkanes and methanol has been reported through a two-step process (chemical pretreatment and sequential hydrogenolysis and hydrogenation). Recently, the one-pot conversion of cellulose feedstock into liquid alkanes in biphasic reaction systems (organic + water) were also reported over Ir-ReOx/SiO2–H–ZSM-5 or tungstosilicic acid–Ru/C catalysts. The industrial Shell/GTI hydropyrolysis and Virent Energy System’s approaches are also known to directly convert sugars or raw biomass into liquid fuel. The former is based on a catalytic thermal–chemical technique, which reacts at very high temperature (350–540 °C) (ref. 21). Virent’s approach converts water-soluble oxygenated hydrocarbons into C4+ hydrocarbons, alcohols and/or ketones in aqueous phase or vapour phase. This is achieved by aqueous phase reforming of water-soluble oxygenates, followed by condensation and deoxygenation. More recently, a three-catalyst system was reported to convert raw biomass into liquid alkanes and other mono-functional hydrocarbons over layered LiTaMgO6 combined with Ru/C in aqueous phosphoric acid medium. Gaining in-depth understanding on the reaction mechanism is of fundamental importance for the development of improved catalytic systems.

Here we report that, by using a multifunctional Pt/NbOPO4 catalyst, raw woody biomass can be directly converted into fuel alkanes in high yields in a single-phase medium (cyclohexane) with cellulose, hemicellulose and lignin fractions in solid woods being converted into hexane, pentane and alkylcyclohexanes, respectively (Fig. 1), representing direct conversion of raw lignocellulose into liquid alkanes under mild conditions over a single catalyst. Importantly, no chemical pretreatment (for example, hydrolysis and separation) to the raw wood is required for this process, and thus, tremendous energy savings can be potentially gained in comparison with the existing thermochemical- and hydrolysis-based approaches. More significantly, the pathway for this novel catalytic reaction was systematically investigated by control experiments, and the molecular mechanism for the rate-determining step in this conversion studied by in situ inelastic neutron scattering and computational studies. These complementary investigations reveal that the NbOx species promotes the crucial C–O bond cleavage over hydrodeoxygenation of tetrahydrofuran (THF) and phenol (model units of cellulose and lignin, respectively) to hydrocarbons under mild reaction conditions.

Results

Direct hydrodeoxygenation of raw woody biomass. To verify the applicability of this one-pot approach, seven different types of wood sawdusts (<75 μm), including both softwoods and hardwoods, were employed as feedstocks for direct hydrodeoxygenation over the Pt/NbOPO4 catalyst in a cyclohexane medium (Table 1). The reactions were conducted at 190 °C and 5 MPa H2 for 20 h and over 20 wt% total mass yield of liquid alkanes was achieved for all woods, among which birch wood gave the highest mass yield of 28.1 wt%. Considering that the theoretical mass yield of alkanes from raw woody biomass is limited to ~50 wt% as the removed oxygen accounts for almost half of the mass loss, the yields obtained here are excellent. In addition to C6–C8 alkanes products, surprisingly appreciable amounts of alkylcyclohexanes (for example, propylcyclohexane and ethylcyclohexane) were also detected (Supplementary Fig. 1), indicating that not only the cellulose and hemicellulose but also the lignin fraction in sawdusts were converted into alkanes. Obviously, the source/texture of lignocellulose had a significant influence on both mass and carbon yields of the alkane products. In general, higher yields of hexanes and pentanes were achieved from softwoods: the carbon yields of hexanes and pentanes on the basis of cellulose and hemicellulose fractions reached 72.8 and 69.3% on average, respectively. These yields are surprisingly high and even comparable to those using isolated cellulose as feedstock. Indeed, pure cellulose was tested as model material for carbohydrate fractions in raw woody biomass to confirm the performance of the catalyst. A total of 71.5% yield of hexanes and 8.7% yield of pentanes (by C–C cleavage) were achieved from cellulose conversion with excellent stability (Supplementary Table 1 and Supplementary Fig. 2). On the other hand, the yield of alkylcyclohexanes produced from hardwoods is much higher than that from softwoods, with an average carbon yield of 34.0% from hardwood (here only monomer alkylcyclohexanes were determined). It is worth noting that this yield is very high because there is a large proportion of C–C linkages in lignin structure (30–34% for hardwoods and 43–51% for softwoods on average), which are hardly cleaved under such mild reaction conditions, thus resulting in a maximum theoretical carbon yield of monomer alkylcyclohexanes at 44–49% from hardwoods and 42–32% from softwoods (Supplementary Note 1). This result indicates that the catalyst has excellent performance for the direct hydrogenolysis of C–O–C linkages of lignin and total hydrodeoxygenation of the resultant lignin monomers. To further confirm this, diphenyl ether and phenol, which possess aromatic ether and hydroxyl functionalities, respectively, were tested as model compounds over Pt/NbOPO4. A total of 99.9% yield of cyclohexane was achieved from both substrates, demonstrating the efficient cleavage of ether bond in lignin by this catalyst (Supplementary Table 1).
Clarification of the unique activity of Pt/NbOPO₄. A variety of catalysts with different combinations of support and metal (that is, Pt/NbOPO₄, Pt/H–ZSM-5, Pt–ReOₓ/SiO₂, Pt–ReOₓ/C and Pd, Ru, Rh loaded NbOPO₄) were tested with birch sawdust as feedstock for this reaction to clarify the unique activity of Pt/NbOPO₄ (Table 2). With Pt supported on H–ZSM-5, which possesses similar acidity to NbOPO₄ but does not contain transition metal oxide (Supplementary Fig. 3), only 8.7 wt% yields of liquid alkanes was obtained (versus 28.1 wt% for Pt/NbOPO₄). This suggests that the NbOₓ species of NbOPO₄ support has a significant promotion effect in this reaction. Such promotion effect on C–O cleavage was investigated recently in transition metal oxides of NbOₓ and ReOₓ (refs 24–26). To provide more insight, two other ReOₓ support with reduced acidity, ReOₓ/SiO₂ and ReOₓ/C, were tested for comparison, and alkane yields of 11.4 and 9.8 wt%, respectively, were obtained with a small amount of mono-functional hydrocarbons detected (for example, tetrahydropyran). This result suggests that the promotion effect should be accompanied by sufficient acidity to achieve efficient C–O cleavage in this reaction. The NbOPO₄ support fulfills these two requirements (that is, surface NbOₓ species and sufficient acidity), and thus possesses the best catalytic activity for this reaction.

Table 1 | Summary of direct hydrodeoxygenation of various woody biomass over Pt/NbOPO₄.*

| Woody biomass | Softwood | Hardwood |
|---------------|----------|----------|
| | Pine | White pine | Larch | Fir | Camphor | Birch | Poplar |
| Lignocellulose content | | | | | | | |
| Hemicellulose (wt%) | 9.3 | 10.4 | 13.1 | 10.3 | 24.8 | 25.7 | 28.2 |
| Cellulose (wt%) | 47.2 | 52.3 | 49.4 | 43.5 | 45.1 | 48.7 | 45.3 |
| Lignin (wt%) | 32.6 | 29.5 | 28.3 | 33.9 | 22.6 | 20.4 | 22.8 |
| Mass yield/carbon yield (wt%/mol%) | | | | | | | |
| Pentanes ¹ | 4.1/80.8 | 3.6/63.4 | 4.8/67.2 | 3.7/65.9 | 7.3/54.0 | 10.2/73.1 | 7.1/46.2 |
| Hexanes ² | 18.7/74.8 | 19.3/69.4 | 20.4/77.7 | 16.0/69.2 | 15.2/63.4 | 13.1/50.7 | 9.7/40.3 |
| Alkylcyclohexanes ³ | 2.1/9.6 | 2.2/11.2 | 2.6/13.7 | 2.3/10.1 | 5.1/33.7 | 4.8/35.1 | 5.1/33.3 |
| Total liquid alkanes (wt%) | 24.9 | 25.1 | 27.8 | 22.0 | 27.6 | 28.1 | 21.9 |
| Others (wt%) ⁴ | 1.7 | 1.7 | 2.0 | 1.4 | 1.9 | 2.3 | 1.6 |
| Residue (wt%) | 31.5 | 27.9 | 27.1 | 33.4 | 17.4 | 14.8 | 16.7 |

*The reactions were conducted at 190 °C and 5 Mpa H₂ for 20 h. Feedstock (0.20 g), Pt/NbOPO₄ (0.20 g) and cyclohexane (6.46 g) were put into a 50 ml stainless-steel autoclave.

¹Mass yields were calculated by the equation: mass yield of pentanes (hexanes, alkylcyclohexanes) = [mass of pentanes (hexanes, alkylcyclohexanes)]/ [mass of feedstock input]. Carbon yields were calculated by the equation: carbon yield of pentanes (hexanes, alkylcyclohexanes) = [mass of carbon in pentanes (hexanes, alkylcyclohexanes)]/ [mass of carbon in hemicellulose (cellulose, lignin)].

²Pentanes include n-pentane and iso-pentane.

³Hexanes include n-hexane and iso-hexane.

⁴Only monomer alkylcyclohexanes were determined here, including methylcyclohexane, ethylcyclohexane, isopropylcyclohexane and propylcyclohexane.

⁵Others were mainly CO₂ and C₁–C₄ alkanes.
reaction. On the metal side, Pd, Ru, and Rh were tested by loading them onto the NbOPO₄ support, and moderate yields (17.2–19.2 wt%) of liquid alkanes were achieved from the hydrodeoxygenation of birch wood. The reason that Pt gave the highest yield among the studied metals is due to its supreme activity for H₂ activation and hydrogenation (Supplementary Table 2). From these control experiments, we rationalise the superior performance of Pt/NbOPO₄ by a synergistic effect between Pt, NbO₄ and the acidic sites on the support (including both Brønsted acid sites on PO₄ and Lewis acid sites on NbO₄, Supplementary Fig. 4).

**Study of the activity and stability of the catalyst.** To investigate the applicability and recyclability of the catalyst, Pt/NbOPO₄ was tested under various reaction conditions and the results are summarised in Table 3. As the products of this conversion were only alkanes, they act as an additional solvent to drive the sequential reactions without the need of solvent separation or recycling after each run. Cyclohexane was used as a solvent to facilitate the analysis because it does not overlap with any product. Alternatively, other alkane (for example, tridecane) can be used as a solvent for this reaction to afford similar results (Table 3, entry 1). Moreover, the reaction with double solid loadings was attempted, and there was no obvious decline of the alkane yields (Table 3, entry 2), indicating that this process is capable of dealing with higher solid loadings. Mineral poisoning is widely known to reduce the catalyst activity in biomass conversion. To probe more insight, extra ashes obtained by calcination of 1 g birch sawdust at 500 °C for 3 h were added into the system to test the cellulose conversion. The result suggests that a fivefold amount of ash has no influence on the catalytic activity of this catalyst (Table 3, entries 4 and 6). Moreover, the stability of the catalyst at lower alkane yields was tested by shortening the reaction time to 8 h. Small decreases on the yields of hexanes and pentanes were observed after four successive runs (hexanes: from 41.3 to 37.5%; pentanes: from 4.6 to 4.0%; Table 3, entries 6 and 7, Supplementary Fig. 2). Characterisations of the catalyst before and after the reaction showed small reductions on the BET surface area and the Pt dispersion (Supplementary Note 2), consistent with the observed small decreases on the yields of hexanes and pentanes. On the whole, the catalyst showed good and consistent catalytic performance in repeated runs in this one-pot process. This could be due to two reasons; first, the reaction was carried out under mild conditions (190 °C), which retards the significant aggregation of Pt particles (Supplementary Fig. 5); second, the use of non-aqueous single-phase medium (cyclohexane) hinders leaching and structural change of the catalyst (Supplementary Fig. 6). Indeed, the ICP analysis of the reaction solution suggested that the concentration of Pt, P, or Nb was all below the detection limit, confirming the absence of catalyst leaching during the reaction.

**Studies of the representative reaction pathway.** In attempting to reveal the reaction pathway, model compounds were used to simplify the original reaction system for easier detection of intermediates and products. Diphenyl ether and phenol were chosen as the model compounds of the lignin fraction to investigate the cleavage of ether bond (as mentioned above), and cellulose was used to represent the carbohydrate fraction to elucidate the conversion of cellulose and hemicellulose to alkanes. To better monitor the possible intermediates, the reaction was carried out at a lower temperature of 170 °C, and water was added into the reaction mixture after reaction to extract water-soluble intermediates. After 1 h reaction, small amounts of glucose (2), sorbitol (3), sorbitan (4) and isosorbide (5) were detected by HPLC (Supplementary Fig. 7), and a mixture of 1-dehydroxylglucose (6), 1,6 anhydro glucose (7), 2-hydroxyethyltetrahydropyran (8), 5-methyl-THF-2-methanol (9) as well as many other undefined intermediates in the aqueous phase were detected by GC–mass spectrometry (MS) (Supplementary Fig. 8). As no water existed at the beginning of this reaction, this result

### Table 2 | The results of direct hydrodeoxygenation of birch wood over different catalysts.

| Entry | Catalyst | Mass yield of liquid alkanes (wt%) |
|-------|----------|-----------------------------------|
|       |          | Pentanes¹ | Hexanes¹ | Alkylcyclohexanes¹ | Total | Residue |
| 1     | Pt/NbOPO₄ | 10.2      | 13.1     | 4.8             | 28.1  | 14.8 |
| 2     | Pt/H₂-25M:Si | 4.9      | 1.3      | 2.5             | 8.7   | 35.8 |
| 3     | Pt-ReOₓ/SiO₂|| | 5.2      | 3.6      | 2.6             | 11.4  | 26.9 |
| 4     | Pt-ReOₓ/C|| | 6.4      | 1.5      | 1.9             | 9.8   | ND   |
| 5     | Pd/NbOPO₄ | 8.1      | 6.2      | 3.5             | 17.8  | 29.4 |
| 6     | Ru/NbOPO₄ | 7.3      | 8.0      | 3.9             | 19.2  | 36.3 |
| 7     | Rh/NbOPO₄ | 8.2      | 5.0      | 4.0             | 17.2  | 31.5 |

¹The reactions were conducted at 190 °C and 5 MPa H₂ for 20 h. Feedstock (0.2 g), catalyst (0.2 g), and cyclohexane (6.46 g) were put into a 50 ml stainless-steel autoclave. All metal loading was 5 wt%.

### Table 3 | Summary of direct hydrodeoxygenation of birch sawdust and cellulose under various reaction conditions over Pt/NbOPO₄.

| Entry | Feedstock | Carbon yield of liquid alkanes (%) |
|-------|-----------|-----------------------------------|
|       |           | Hexanes¹ | Pentanes¹ | Alkylcyclohexanes¹ |
| ¹      | Birch sawdust | 72.4      | 52.3      | 34.6 |
| ²      | Birch sawdust | 69.1      | 49.7      | 35.9 |
| 3      | Cellulose  | 71.5      | 8.7       | ND² |
| 4      | Cellulose  | 40.3      | 4.4       | ND³ |
| 5      | Cellulose  | 65.2      | 8.2       | ND⁴ |
| 6      | Cellulose  | 41.3      | 8.7       | ND⁵ |
| 7      | Cellulose  | 37.5      | 8.7       | ND⁶ |

¹Unless otherwise specified, the reactions were conducted at 190 °C and 5 MPa H₂ for 20 h. Feedstock (0.2 g), catalyst (0.2 g), and cyclohexane (6.46 g) were put into a 50 ml stainless-steel autoclave.

²Tridecane was employed as the reaction solvent.

³Dimensionless (0.4 g of birch sawdust, 0.4 g of catalyst, and 6.46 g of cyclohexane were put into a 50 ml stainless-steel autoclave.

⁴“ND” is the abbreviation of “not determined”.

⁵Ashes (minerals) obtained by calcination of 1 g birch sawdust at 500 °C for 3 h were added into the reaction system and reaction for 8 h.

⁶The cellulose was unmilled and used directly.

⁷The reaction time was 8 h.

⁸Data shown are for the fourth run of the stability test.
indicating that the β-1,4 linkage in cellulose was cleaved by direct hydrogenolysis rather than hydrolysis, as a result of the excellent performance of Pt/NbOPO₄ in hydrogenolysis. When further reacted for 6 h, appreciable amounts of hexane, 2,5-dimethylfuran (10), 2,5-dimethyl-THF (11), 2-methyltetrahydrofuran (12), 2-ethyl-THF (13), hexanone (14), oxepane (15) and hexanols (16–18) were observed in the organic layer (Supplementary Fig. 9). In the aqueous phase, isosorbide (5) and 2-hydroxymethyl-tetrahydropyran (8) were the main residuals (Supplementary Fig. 10), indicating that the catalyst surface (Fig. 3a). Comparison of the difference spectra from DFT calculations is straightforward (Supplementary Note 3). Here, we have successfully combined in situ INS and DFT to investigate the vibrational properties of the THF–Pt/NbO₂ system to reveal the mechanism of the challenging hydrodeoxygenation of THF. NbOPO₄ has a large amount of surface P–OH groups, the vibrational peaks of which will overlap with signals of adsorbed THF. Therefore, we here used Pt/Nb₂O₅ instead for a clearer interpretation of the experimental observation. It is worth noting that Pt/Nb₂O₅ has a similar catalytic reactivity to Pt/NbOPO₄ for this reaction under the same conditions, as evidenced by the direct comparison of the yield and selectivity data for THF conversion in Supplementary Table 3. To the best of our knowledge, this is the first example of using INS/DFT to study the mechanism of catalytic biomass conversion.

The INS spectrum of the bare catalyst gives a clean background with no prominent features (details on the discussion of background spectra are given in Supplementary Note 4 and Supplementary Figs 12 and 13). In comparison, the INS spectrum of the catalyst on THF adsorption at 130 °C shows a significant increase in total intensity, demonstrating the binding of THF to the catalyst surface (Fig. 3a). Comparison of the difference spectrum before and after THF adsorption on the catalyst (that is, signals for adsorbed THF) and that of the solid THF shows a few changes (Fig. 3d). Peaks at low energy (below 200 cm⁻¹), assigned to the translational and rotational modes of THF, shift to lower energy with a continuum profile, suggesting that the
adsorbed THF molecules are disordered over the catalyst surface, and have restricted translational motion owing to the strong binding to the catalyst. The very strong peak at 251 cm\(^{-1}\), assigned to the torsional mode of the C2–C3 bond of THF ring, is reduced significantly in intensity, indicating the loss of this motion on adsorption. The peak at 300 cm\(^{-1}\), likely due to the combination of the lattice mode at ~60 cm\(^{-1}\) and the strong mode at 251 cm\(^{-1}\), is concurrently reduced in intensity. In addition, the ring deformation mode at 587 cm\(^{-1}\) in solid THF shifts to 571 cm\(^{-1}\) when adsorbed on the catalyst. A structural...
model of solid THF and THF adsorbed on Nb₂O₅ were optimised by DFT, respectively, and calculated INS spectra were produced (Fig. 3g; Supplementary Figs 15 and 16). Comparison of the INS spectra suggests that THF is likely adsorbed intact via interaction between its O(δ−) centre to open Nb(δ+) site (O⋅⋅⋅Nb = 2.33 Å) on the surface (Fig. 4a) and that ring-opening of THF does not happen immediately on adsorption and/or in the absence of H₂. The calculation also confirms the downshift of the ring deformation mode but slightly overestimates its magnitude.

The adsorbed THF underwent a first catalytic conversion in H₂ flow for 10 min at 130 °C. The INS spectrum of the first reacted catalyst shows a large decrease in intensity (Fig. 3b,e), suggesting that the adsorbed THF underwent fast catalytic conversion to butane, which was sequentially swept out of the cell by MS. In particular, the peaks at 1,244 and 1,308 cm⁻¹ (assigned to –CH₂– twisting and internal ring deformation of THF, respectively) disappeared completely, confirming the cleavage of the THF ring. An optimised structural model of ring-opened THF on Nb₂O₅ suggests that the adsorbed THF interacts with the very strong Lewis acid sites (Nb⁵⁺), and the ring opens via binding to two adjacent Nb⁵⁺ centres simultaneously (O⋅⋅⋅Nb = 1.98 Å) (Figs 3h and 4b). Comparison of the calculated INS spectrum for ring-opened THF and experimental difference spectrum, however, does not conclusively suggest the presence of this intermediate bound on the catalyst. This could be due to two possible reasons: (i) the ring-opened intermediate is highly active and was hydrogenated instantly, and thus cannot be captured effectively; (ii) the amount of this intermediate is too low to be detected as no THF feedstock was provided during the reaction. To enrich the intermediate on the catalyst, a second catalytic reaction was conducted in THF/H₂ flow for 5 h, and the production of butane observed continuously by MS. The INS spectrum of the second reacted catalyst indeed shows an increase in intensity even compared with that of THF-adsorbed catalyst, confirming the presence of additional substrates on the catalyst surface (Fig. 3b). The corresponding difference spectra confirm the presence of adsorbed THF, and more importantly, four new peaks at 245, 744, and 805 cm⁻¹ (assigned as methyl torsion, –CH₂CH₂– rocking and –CH₃CH₂CH₃ rocking of 1-butanoxide, respectively) of the second reacted catalyst gives a clear message: three out of the four new peaks at 245, 744, and 805 cm⁻¹ (assigned as methyl torsion, –CH₂CH₂– rocking and –CH₃CH₂CH₃ rocking of 1-butanoxide, respectively) of the second reacted catalyst are consistent with the presence of 1-butanoxide bound on the surface (Fig. 3e,f). The remaining new peak at 477 cm⁻¹ is conformation-dependent and consistent with the presence of a gauche conformer of C₄ chain of bound 1-butanoxide⁸. A final INS spectrum for the reactivated catalyst shows no prominent feature (Supplementary Fig. 19), confirming the absence of formation of residual hydrocarbonaceous species and thus demonstrating the high efficiency of catalyst regeneration in cycling experiments.

The calculated and experimental INS spectra for solid THF and 1-butanol show excellent agreement; however, those for the guest-bound catalysts exhibit a number of discrepancies (Fig. 3d,i). It is worth noting that the experimental data were collected on a disordered system (poorly crystalline mesoporous metal oxide and disordered substrates), whereas the calculations assume fully periodic structures. A poorly crystalline system generates multiple sites with different binding energies, inducing the broadening of INS peaks. The presence of different conformers of the butane chain on the catalyst also induces discrepancy as the calculation was done with the gauche conformer with the lowest energy only and the low energy modes are very sensitive to the chain conformation. Indeed, the INS spectra for disordered and crystalline 1-butanol have suggested that the crystallinity of the system can induce significant changes to both peak intensity and positions (Supplementary Fig. 17). Moreover, the calculation used a model with “flat” surface, in which there is no interaction with the surface, other than through the THF/1-butanol oxygen atom. On the real, rough surface, for example, with steps (Supplementary Fig. 5), the hydrogen atoms on C1 and C4 of THF (or C1 and C2 of 1-butanol) will also be enabled to interact with the surface, further enhancing the binding and broadening of the INS bands.

In this study, we concentrate primarily on the experimental observation, which has confirmed that (i) adsorbed THF molecules on the catalyst have, in principle, an intact structure...
O and OH adsorption on NbOPO4(100) and Re2O7(010) surfaces. For clarity, only the local active sites are shown. The regions depicted in yellow indicate lengths shown. Emerald balls represent Nb atoms, dark blue for Re, white for H, grey for C and red for O. (whereas the transition states involving C–O bond cleavage of C4H9OH and C6H5OH are depicted in TS1, TS1') Black and red lines indicate NbOPO4(100) and Re2O7(010), respectively. The structures of the initial and final states on NbOPO4(100) are shown, charge accumulation and light blue for charge depletion. Emerald balls represent Nb atoms, dark blue for Re, white for H and red for O. (Figure 5 | Calculated results of computational studies. (a,b) Calculated energy profiles of C-O bond cleavage of C2H5OH and C4H9OH, respectively. Black and red lines indicate NbOPO4(100) and Re2O7(010), respectively. The structures of the initial and final states on NbOPO4(100) are shown, whereas the transition states involving C-O bond cleavage of C2H5OH and C4H9OH are depicted in TS1, TS1', TS2 and TS2', with the elongated C–O bond lengths shown. Emerald balls represent Nb atoms, dark blue for Re, white for H and red for O. (c) The isosurfaces of charge density difference for O and OH adsorption on NbOPO4(100) and Re2O7(010) surfaces. For clarity, only the local active sites are shown. The regions depicted in yellow indicate charge accumulation and light blue for charge depletion. Emerald balls represent Nb atoms, dark blue for Re, white for H and red for O. (d) The d-orbital projected density of states for the surface Nb5c and Re5c atoms, demonstrating their relative energies, in which the energy is aligned to the Fermi level (E_F). with reduced motion (esp. for the C2–C3 torsion and ring deformation modes) owing to the strong binding to the Nb5c sites; (ii) ring-opening of adsorbed THF (cleavage of C–O bond) occurs rapidly in the presence of H2 as shown by the loss of the internal THF ring deformation mode; (iii) 1-butanoxide bound to the surface Nb5c site is a relatively stable reaction intermediate, consistent with calculations (see below). Therefore, this catalytic conversion of THF follows adsorption, binding, ring-opening, partial hydrogenation and complete hydrodeoxygenation, and the surface Nb5c sites played an important role in this reaction, particularly for the binding and activation of THF substrates. It is worth noting that here the role of Pt is believed to dissociate H2 and provide [H], and such role is not exclusive in the rate-determining C–O–C bond cleavage step, considering that similar performance can be obtained by substituting Pt with Pd loaded on NbOPO4 for the hydrodeoxygenation of cellulose into alkanes (Supplementary Table 3). However, other possible roles of Pt in the whole reaction such as strengthening acidity through interface interactions29 may not be fully ruled out, which is beyond the core point of this work and will be studied further in future works.

Computational studies of the catalytic origin of NbOPO4. To probe more insight, first-principle calculations were conducted to examine the crucial C–O bond breaking process of phenol and 1-butanol, which are the model compound of lignin and important intermediate in THF conversion, respectively. Notably, the widely used ReO3 catalyst in biomass conversion was also tested for comparison. The well-ordered flat NbOPO4(100) and Re2O7(010) surfaces, which have exposed five-coordinated Nb5c and Re5c centres as the main binding sites, were chosen as the substrates (Supplementary Methods, Supplementary Figs 20,21 and Supplementary Table 4).

For 1-butanol conversion on NbOPO4, the calculation indicates that 1-butanol efficiently adsorbs on Nb5c with a corresponding adsorption energy of −1.20 eV, which is evidently stronger than that on Re5c (−0.76 eV), indicating that NbOPO4(100) possesses a stronger binding ability. Subsequently, with the aid of the surface Nb5c, the C–O bond can break with each OH and butyl occupying a Nb5c site as the product; this process is strongly exothermic by 1.72 eV and gives a barrier of only 0.79 eV (Fig. 5a), implying its feasibility in both thermodynamics and kinetics (Supplementary Note 5 and Supplementary Table 5). In contrast, on Re5c, 1-butanol dissociation is an endothermic process and has to overcome a larger barrier of 1.28 eV (Supplementary Note 5). By comparing the energy profiles (Fig. 5a), it is conclusive that NbOPO4 demonstrates an inherently better performance for 1-butanol deoxygenation than ReO3. Likewise, with respect to C–O bond cleavage of phenol, we performed the same calculation, which yields a similar conclusion that NbOPO4 catalyses phenol dissociation more efficiently with a lower barrier than ReO3 (Fig. 5b and Supplementary Note 5). Therefore, the high catalytic activity of NbOPO4 can be ascribed to better adsorption capability of surface Nb5c and a lower activation barrier in comparison to Re5c. Correlation between the C–O bond dissociation barriers and their corresponding adsorption energies (Supplementary Fig. 22) shows that stronger the bond strength of M5c–O (M = Nb, Re) leads to easier the C–O bond cleavage, which is in line with the principle of Bronsted–Evans–Polanyi relationship30–32. In other words, the outstanding binding ability of NbOPO4 is one determining factor in the efficient deoxygenation of cellulose and lignin. We also calculated and compared the adsorption energies of NbOPO4 with two other typical catalysts (ReO3, ZrO2) toward various intermediate species, such as OH, O, THF, butyl and butoxy (Supplementary Note 5).
We have presented a one-pot catalytic process for the direct conversion of raw woody biomass into liquid alkanes under mild conditions (190 °C). The exceptional activity of the Pt/NbOPO_4 catalyst enabled direct upgrading of lignocellulose into alkanes via a one-pot catalytic process, dominated by the formation of alkane products. Carbon yields were calculated by the equation: carbon yield of pentanes (hexanes, alkylcyclohexanes) = [mass of carbon in pentanes (hexanes, alkylcyclohexanes)]/[mass of feedstock input].

Reaction pathways study. The direct hydrodeoxygenation of cellulose was carried out in a similar way to that of wood sawdusts. After the reaction was quenched, the autoclave was cooled to room temperature under vigorous stirring for a few minutes to extract the hydrophilic intermediates and to dissolve cellulose for total analysis. The aqueous phase was analyzed by HPLC (Agilent 1200 series) equipped with a Shodex SUGAR SC-1011 column and a differential refractive index detector and by GC–MS to monitor the intermediates and unreacted cellulose. The organic phase was analyzed by GC–MS to observe the lipophilic intermediates.

Neutron scattering experiments. INS spectra were recorded on the TOSCA spectrometer at the ISIS Facility at the STFC Rutherford Appleton Laboratory (UK). TOSCA is an indirect geometry crystal analyser instrument that provides a wide dynamic range (16–4,000 cm⁻¹) with resolution optimised in the 50–2,000 cm⁻¹ range³⁴. In this region TOSCA has a resolution of 1.25% of the energy transfer. The Pt/NbO_4 (3.47 g) catalyst was loaded into an in situ catalysis cell with a copper vacuum seal and connected to a gas handling system. The sample was heated at 300 °C (5 °C/min ramping) under He for 3 h to remove any remaining trace water before the experiment. The sample was cooled to room temperature and a weight loss of 0.1 g was noted, assigned to loss of adsorbed water. The samples were cooled to <15 K during data collection by a closed cycle refrigerator cryostat. The procedure of the in situ catalysis experiment with the INS measurement is summarised in Supplementary Fig. 23. INS spectra for condensed THF (2.31 g) and 1-butanol (2.36 g) in the solid state were measured in a flat-plate sample container below 12 K. INS spectra for condensed THF and 1-butanol were used to (i) calculate the amount of adsorbed THF and 1-butanol onto the catalyst in each case by the integration of the peak areas; (ii) identify and compare the vibrational modes for the adsorbed and the free molecules.

Estimation of the amount of adsorbed THF on the catalyst: on the basis of the relative intensities of the INS peak at ~600 cm⁻¹ and the known mass (2.31 g) of THF in the condensed sample, there is 0.42 g of adsorbed THF present on the catalyst in the neutron beam.

Estimation of the amount of adsorbed 1-butanol on the catalyst: on the basis of the relative intensities of the INS peak at ~740 cm⁻¹ and the known mass (2.36 g) of 1-butanol in the condensed sample, there is 0.30 g of adsorbed 1-butanol present on the catalyst in the neutron beam.

Adsorption of THF was carried out by flowing THF vapour (~200 mbar) in He (1.1 bar, 0.21 min⁻¹; this flow condition was used throughout the study) over the catalyst at 130 °C for 3 h. The cell was then flushed briefly with pure He flow for 2 min to remove the free and weakly bound THF on the catalyst, sealed and cooled to below 15 K for INS data collection. The adsorbed THF underwent the first catalytic conversion in pure H₂ flow for 10 min at 130 °C, and production of butane was observed constantly by mass spectrometry. The cell was then flushed with He to remove free butane and H₂Se and cooled again for INS collection to detect the presence of possible reaction intermediates.

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Methods

Catalyst preparation. NbOPO_4 used here was synthesised by a hydrothermal method 

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M_{x}O_{1-x}(PO_{4})_{y}\text{[mass of feedstock input]} = \text{mass of pentanes (hexanes, alkylcyclohexanes)}
\]

The isosurface of charge density difference shows electron accumulation between O (or OH) and Nb in NbOPO_4 (Fig. 5c), indicating a typical covalent bond structure. The Nb-O-M bond linking the NbOPO_4 layers is thought to play a role in the reduction process. The Nb-O bond occurs at 190 K during data collection by a closed cycle refrigerator cryostat. The procedure of the IR catalysis experiment with the INS measurement is summarised in Supplementary Fig. 23. INS spectra for condensed THF (2.31 g) and 1-butanol (2.36 g) in the solid state were measured in a flat-plate sample container below 12 K. INS spectra for condensed THF and 1-butanol were used to (i) calculate the amount of adsorbed THF and 1-butanol onto the catalyst in each case by the integration of the peak areas; (ii) identify and compare the vibrational modes for the adsorbed and the free molecules.

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**Author contributions**

Q.N.X., T.S. and J.H.L. helped in preparation and characterisation of catalysts, and performing the catalytic reactions. Z.J.C., H.F.W. and X.Q.G. helped in catalytic reactions. Y.Q.W. conceived the overall direction of the project. All the authors discussed the results and co-wrote the manuscript.

**Additional information**

**Supplementary Information** accompanies this paper at http://www.nature.com/naturecommunications

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