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Total hydrogenation of bio-derived furans over supported Ru subnanoclusters prepared via amino acid-assisted deposition

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Development of a highly efficient and robust catalyst with reduced usage of noble metals is extremely desirable for selective hydrogenations of furan-containing bio-based feedstocks, which represents an attractive and sustainable alternative to petrochemical resources. Herein, we describe a new type of well-dispersed Ru subnanoclusters (ca. 0.50 wt %) supported on commercial P25 TiO₂ material obtained from a facile and effective amino acid-assisted deposition-precipitation strategy. The as-synthesized catalyst exhibits superior catalytic activity and selectivity for direct hydrogenation of industrially important furfural as well as a range of structurally diverse bio-based furanic compounds to their corresponding fully hydrogenated derivatives. An average turnover frequency (ATOF) value as high as $367 h^{-1}$ at 80 °C and 4 MPa H₂ is obtained, which is the highest reported value. This catalyst also shows stable furfural total hydrogenation in 5 reaction cycles conducted at 80 °C (52-mmol-scale, turnover number up to 12,500). In terms of the kinetic and structural characterizations, the key performances of the ultrasmall Ru clusters are proposed to mainly originate from enhanced number of unsaturated surface Ru atoms and change in local coordination environment. Our work highlights the importance of subnanometric size of Ru clusters in the advancement of efficient and affordable approaches towards biobased to mainly originate form production.

Introduction

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In the era of continued depletion of fossil resources, catalytic hydrogenation has become an increasingly important and essential part of biorefinery developments that hold promise for future bio-based economy.1-3 The overall catalytic hydroprocess requires low cost reductants and 100% atom efficiency, allowing the potential of a broad application platform to access multiple desirable chemicals from bioderived feedstocks.^{4,5} One area of particular interest is the feasible adapting of existing technologies to enable the fossilto-bio-based transition in a shorter time frame.⁶ Despite tremendous efforts, due to the inherent oxygen-rich nature of the bio-feedstocks, the successful implementation of such approach is currently limited by the lack of suitable catalysts allowing highly efficient and chemospecific hydrogenation under mild conditions.^{7,8} Various types of nanoparticulatebased catalysts, including $noble^{9,10}$ and $non-noble^{11,12}$ metals, have been developed for such a purpose. However, they are respectively expensive or require harsh conditions, impeding their widespread implementation.

Recently, subnanometer-sized metal clusters, having dimensions between metal atoms and nanoparticles (NPs), have elicited significant interest in heterogeneous catalysis due to their high catalytic activity, selectivity and efficient utilization of critical metals.¹³ However, owing to the high mobility and agglomerative character of the small metal clusters, their synthesis and utilization remains a major challenge.¹⁴ One strategy to achieve improved stability is to disperse and anchor active metal species on solid supports.¹⁵ In this respect, titanium oxide (TiO₂), with wide availability, high thermal stability and promise of strong metal-support interactions (SMSI) is an attractive support for the preparation of supported small metal clusters.¹⁶ In this rapidly evolving research area, subnanometer metal catalysts have been demonstrated to be excellent catalysts for a wide variety of reactions. including CO oxidation¹⁷, carbon dioxide methanation¹⁸, methanol synthesis¹⁹, electrochemical²⁰ and photoelectrochemical reactions²¹. Nonetheless, upgrading biobased feedstocks through subnanometer metal catalysis has scarcely been investigated.

As a result of an ever-increasing demand for more affordable and viable technologies suitable for bio-upgrading, the development of new and cost-effective heterogeneous catalysts that can capitalize on the use of more abundant metals is a highly desired goal.²² Due to the limited successes in finding suitable non-noble metal catalysts sufficiently efficient for biomass upgrading, special attention has been directed to the use of less noble metals such as Ru as an integral part of the catalyst design and process optimization.²³

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Indeed, a number of recent studies have established Ru-based materials as potent heterogeneous catalysts transformation of biomass-derived feedstocks to a variety of products.²⁴ value-added However, these documented Scheme 1 Illustration of the preparation of Ru/TiO2-Iys-DP and Ru/TiO2-DP

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specification of the potential benefits of hydrogenation catalysis of Ru in the subnanometer regime is not yet available,

observations were mostly made with catalysts, in which Ru was dispersed as particles no smaller than 18a1.039/hmG6P2With dispersion no higher than 60-70%.²⁵ A clear

the potential to provide catalysts containing ultradispersed platinum group metals (PGMs) it still remains largely



probably because of the difficulty to prepare such highly dispersed metal catalysts on conventional supporting oxides.

Small Ru clusters with diameters in the size range of 1-2 nm dispersed on mesoporous silica or TiO₂ have been previously reported, however the success of such a strategy is highly dependent on using high-cost ruthenium carbonyl cluster complexes as a catalyst precursor.^{26,27} Herein, we describe the development of a new methodology for deposition of subnano Ru clusters onto the surface of commercial P25 TiO₂ for the first time. Lysine (lys), an essential amino acid, is used as the mediate reagent as illustrated in Scheme 1 (see Experimental section). UV-vis absorption spectra (Fig. S1) show the color change, provoked by delicate interactions between Ru complexes with lys, occurs upon blending the metallic/lys precursor solutions. The subsequent deposition-precipitation (DP) processing and reduction in H₂/Ar atmosphere gives rise to highly effective and robust catalysts (Ru/TiO₂-lys-DP) for the total hydrogenation of biomass-derived furans and furan/acetone aldol adducts, which is a key catalytic process for green biorefinery concepts based on platform chemicals.²⁸ Our facile synthetic approach for attaching subnano catalysts onto commercially available solid supports not only promotes the furan hydro-upgrading as a prospective renewable resource harvesting technology but also provides useful insights into the design of future high performance catalysts.

Results and discussion

DP has been extensively used as an effective means of supported Au-based catalyst preparation, displaying superior metal dispersion.²⁹ However, although DP-based strategy has

unexplored. Therefore, we began our investigations by assessing the viability of Ru subnanocatalysts preparation via DP method. Preliminary experiments focused on the utilization of P25 TiO₂ as the underlying support, with the resultant catalyst denoted as Ru/TiO2-lys-DP. Transmission electron microscopy (TEM) images (Fig. 1a, 1b) show that Ru species are well dispersed on P25 TiO₂ surface. High-angle annular dark-field scanning transmission electron microscopy (HADDF-STEM) (Fig. 1c) shows the subnano-size of Ru clusters (0.9 nm, Fig. 1d), which is favorable for high catalytic performance. In contrast, the control catalyst (Ru/TiO₂-DP), bereft of lys, shows the presence of much larger aggregated particles (Fig. S2), confirming the important role of lys in mediating the formation of ultrasmall Ru clusters.

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Fig. 1 TEM images (a, b), HAADF-STEM image (c) and size distribution (d) of Ru/TiO -lys-DP DOI: 10.1039/C9GC02943E



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0.4 0.6 0.8 1 Particle size (nm)

Fig. 2 Structural characterizations of Ru catalysts. (a) C 1s and Ru 3d XPS spectra. (b) Ti 2p and Ru 3p3/2 XPS spectra. (c) O 1s XPS spectra (O1 refers to stoichiometric O in TiO₂, O2 to O in reduced TiOx and O3 to organic and hydroxylic O). (d) DRIFT spectra in the carbonyl region of Ru/TiO2-lys-DP and Ru/TiO2-DP. (e) XANES spectra at the Ru K-edge of Ru/TiO₂-Iys-DP, Ru/TiO₂-DP, RuO₂ and Ru foil. (f) Fourier transform (FT) at the Ru K-edge of Ru/TiO₂-Iys-DP and Ru/TiO₂-DP. Note: The quantified fitting results are shown in Table

1.4 1.6

1.2



To gain greater insight into the nature of the supported Ru species, we characterized the catalysts using several methods. The X-ray diffraction (XRD) scans (data not shown) confirm that Ru metal is well dispersed in both cases, with no

observable features from Ru phases being detected. H₂temperature programmed reduction (H2-TPR) profiles of unreduced Ru-containing samples show a single peak at temperatures lower than 120 °C (Fig. S3).30 Although Ru

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species in unreduced Ru/TiO₂-lys-DP may appear more easily reduced compared to Ru/TiO₂-DP, analysis of the degree of reduction (Table S1) reveals the presence of unreducible Ru species in Ru/TiO₂-lys-DP. As shown in Fig. 2a, Ru 3d X-ray photoelectron spectroscopy (XPS) further suggests the coexistence of both metallic and oxidized Ru species (Ru⁰ and Ru^{δ+}) in Ru/TiO₂-lys-DP.³¹ In contrast, only Ru⁰ is present in Ru/TiO₂-DP. Therefore, since Ru/TiO₂-lys-DP has considerably more Ti³⁺ defective sites (Fig. 2b, 2c) it confirms strong interactions between subnano Ru clusters and the underlying support.³²

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of CO adsorption provides more information regarding the chemical state and structure of Ru (Fig. 2d). DRIFTS spectrum of Ru/TiO₂-lys-DP shows a higher population of multicarbonyl bands (2130 and 2060 cm⁻¹)³³ attributed to Ruⁿ⁺(CO)_x species, indicating the presence of excessive partially oxidized Ru sites, as well as CO species linearly and bridged bonded (2000 and 1950 cm⁻¹, respectively)³⁴ on reduced Ru crystallites. Comparison of the relative intensity of the CO-Ru⁰ species shows that Ru/TiO₂-lys-DP exhibits a higher fraction of the linear CO species than Ru/TiO₂-DP, confirming a smaller domain size of the Ru crystallites in Ru/TiO₂-lys-DP. It is noted

that signals arising from multicarbonyl species adsorbed on partially oxidized Ru sites are also identified 1949 Ru/19029DF, despite the fact that both XPS and H₂-TPR analyses indicate the sole presence of metallic Ru species in this material. This could be a consequence of the high oxygen affinity of Ru, which would lead to the re-oxidation of small Ru crystallites on TiO₂ surface upon CO exposure during DRIFTS measurements.³⁵

Ru K-edge of X-ray absorption near-edge structure (XANES) in Ru/TiO₂-DP (Fig. 2e) exhibits a very similar near-edge structure to Ru foil, which confirms that the same valence (Ru⁰) is in agreement with the above XPS analysis. In comparison, the Ru K-edge of Ru/TiO₂-lys-DP is shifted to higher energy, displaying greater resemblance to RuO₂ reference. The Ru local environment was further probed by extended X-ray fine structure (EXAFS). The low intensity oscillations directly following the near-edge region indicates the short-range and low coordinate environment of Ru on TiO₂ in Ru/TiO₂-lys-DP.³⁶ In addition, the distances of Ru-O coordination in Ru/TiO₂-DP (1.91 Å) are slightly shorter than Ru/TiO₂-lys-DP (1.96 Å) or standard RuO₂ (1.98 Å) (Table S2).³⁷ The accumulated data,

Table 1 Hydrogenation of FFR over various Ru catalysts

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		FFR	THFA	FA					
Entrad	Catalust	+ (b)	Tamp (0C)		Conv (9/) -	Selectivity (%) ^b			
Entry	Caldiysi	t (n)	Temp. (°C)	P _{H2} (IVIPa)	CONV. (%)	THFA	FA		
1	TiO ₂	1.5	80	4	<1	-	-		
2	Ru/TiO ₂ -lys-DP	1.5	80	4	>99	>99	0		
3c	Ru/TiO ₂ -lys-DP	1.5	80	4	>99	97	3		
4	Ru/TiO ₂ -DP	1.5	80	4	>99	49	51		
5	Ru/TiO ₂ -DP	4	80	4	>99	>99	0		
6	Ru/TiO ₂ -trp-DP	1.5	80	4	>99	89	11		
7	Ru/TiO ₂ -tyr-DP	1.5	80	4	>99	85	15		
8	Ru/TiO ₂ -imp	1.5	80	4	98	18	82		
9	Ru/TiO ₂ -lys-imp	1.5	80	4	92	6	94		
10 ^d	Ru/TiO ₂ -lys-DP	1.5	80	4	<1	-	-		
11	Ru/TiO ₂ -lys-DP	1	80	6	>99	>99	0		
12	Ru/TiO ₂ -lys-DP	8	25	4	>99	>99	0		
13	Ru/TiO ₂ -lys-DP	25	2	4	>99	>99	0		
14 ^e	Ru/TiO ₂ -lys-DP	12	80	4	>99	97	3		
15 ^{e f}	Ru/TiO ₂ -lys-DP	12	80	4	>99	94	6		

^a Reaction conditions: FFR (5.2 mmol), EtOH (10 mL), catalyst (metal 0.18 mol%). ^b Determined by GC methods using naphthalene as internal standard. ^c The 10th reuse of catalyst recovered from entry 2. ^d Operated under N₂ ^e FFR (52 mmol), EtOH (45 mL), catalyst (metal 0.04 mol%). ^t The 4th reuse of catalyst recovered from entry 14.

together with the much weaker amplitude of FT peaks assigned to Ru-Ru shells of Ru/TiO₂-lys-DP (Fig. 2f), further support that both $Ru^{\delta +}$ and Ru^0 are found in this catalyst. 38

We evaluated the catalytic ability of the prepared catalysts to produce tetrahydrofurfuryl alcohol (THFA) via direct hydrogenation of furfural (FFR), a key commercially manufactured furan-based building block originating from large-scale hemicelluloses.^{39,40} This transformation has gained recent interest due to THFA being a valuable green solvent, or a potential precursor in the production of renewable diols.^{41,42} Amenable catalysts are highly desirable, which promote concurrent hydrogenation of the aldehyde and furan-ring moiety while avoid unwanted decarbonylation, hydrogenolysis and ring opening. Current industrial strategies for THFA

production from FFR rely on sophisticated two-step catalytic conversion via a furfuryl alcohol (FA) intermediacy.³⁹ A singlestep hydrogenation approach recently became possible with the development of various nanoparticulate based catalysts including noble metals such as Pd/Al₂O₃⁴³ or Ru@C/TiO₂,²⁵ non-noble metals such as Ni/C⁴⁴ or Ni/NAC⁴⁵ and alloys such as Pd- Ir⁴⁶ or Pd-Ni,⁴⁷ although the majority requires very high catalyst loadings to attain reasonable THFA yields.

Table 1 shows the conversion of 5.2 mmol FFR in 10 mL ethanol using various supported Ru catalysts. Preliminary assays conditions consisted of 80 °C, 4 MPa H₂, and 0.18 mol% catalyst loading (the amount of the active metal species relative to the substrate). The time-course plot for the conversion of FFR in the presence of Ru/TiO₂-lys-DP (0.18 mol%), as outlined in Fig. S4, showed that the reaction was essentially completed within 1.5 h. It is important to note the extremely low catalyst loading employed in these assays. The reaction did not proceed using Ru-free TiO₂ (Table 1, entry 1); thus, the presence of ultrasmall Ru is essential for the high activity observed in the targeted conversion of FFR to THFA. Ru/TiO₂-lys-DP proved very effective, displaying an average turnover frequency (ATOF) of 367 h⁻¹ towards THFA (Table 1, entry 2), which clearly outperforms all the other catalysts reported for single-step liquid phase hydrogenation of FFR to

give THFA (Table S3). Furthermore, FFR can be quantitatively converted to THFA over Ru/TiO2-lys-ወም፡ ነውቶቶችጠር ግር \$0ቶን,435 remarkable feat. Moreover, the catalyst can be recovered and reused at least ten times with minimal decrease in the yield (97%; Table 1, entry 3; Fig. S5).

With the absence of lys during catalyst preparation, Ru/TiO₂-DP exhibits a significant decrease in catalytic activity toward hydrogenative conversion of FFR (Table 1, entry 4), although high THFA yield is attainable by extending the reaction time (Table 1, entry 5). Therefore, lys-mediated precursor complexation during the DP process is extremely important for kinetic enhancement. Interestingly, we found that a somewhat similar catalytic enhancement over Ru/TiO₂-DP (Table 1, entry 6, 7) can also be achieved by replacing lys with identical amounts of tryptophan (trp) and tyrosine (tyr) during the above mentioned DP process (Fig. S6). To further assess the effectiveness of lys in promoting the desired catalysis, we have prepared Ru/TiO₂-lys-DP with various amounts of 0.02 M lys solution added in 0.1 mmol RuCl₃ precursor solution (Fig. S7) and discovered that the Ru/TiO₂-lys-DP prepared with 0.1 mmol lys exhibited the best catalytic performance in FFR-to-THFA



Fig. 3 Kinetic results of Ru catalysts. Reaction profile of Ru/TiO₂-lys-DP (a) and Ru/TiO₂-DP (b) in FFR hydrogenation. Reaction conditions: FFR (5.2 mmol), EtOH (10 mL), catalyst (metal 0.18 mol%), H2 (4 MPa), 40 °C. Fitted profiles of TFFR (c) and FA (d) hydrogenation over Ru catalysts. Reaction conditions: TFFR (c) or FA (d) (5.2 mmol), EtOH (10 mL), catalyst (metal 0.18 mol%), H2 (4 MPa), 40 °C.

conversion (Fig. S8). This suggests that a small amount of lys during Ru deposition is sufficient to improve the catalytic activity of Ru/TiO₂-DP.

It is worth mentioning in this context that a similar lysmediated promotion was not accomplished in a separate experiment focusing on the use of conventional impregnation **Green Chemistry Accepted Manusc**

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method to prepare Ru/TiO₂ (Table 1, entry 8, 9), thus emphasizing the benefits of using DP in the preparation of ultrafine Ru catalysts. At this point, it is pertinent to point out that, in line with the above-mentioned DP case, the addition of small amount of lys in impregnation solution can also promote a notable decrease in the average size of supported Ru NPs, as verified by TEM analysis (Fig. S9). We postulated that this seemingly unexpected finding is due to the adverse effects of trace surface-bound contamination. In fact, additional spectroscopic observations show the presence of residual lys molecules adsorbed on the prepared catalyst (Fig. S10). This finding, in conjunction with the absence of CO adsorption feature in the DRIFT spectrum of the as-prepared Ru/TiO₂-lysimp sample (Fig. S11), supports the view that, apart from the particle size, the creation of clean accessible Ru surface is also an essential factor in optimum THFA formation during hydrogenative FFR conversion.

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As a unique titania with biphasic nature, P25 TiO₂ is superior to other kinds of nanocrystalline TiO2 as a support for catalysts. For comparison, Ru clusters deposited on singlephase anatase- and rutile-TiO₂ nanocrystallites were synthesized in the presence of lys. Surprisingly, despite their similar particle size, distribution and chemical state (Fig. S12, S13), both catalysts are inferior to those prepared P25 TiO_2 for FFR conversion (Fig. S14), highlighting the strong interaction between the active clusters and P25 TiO2. To further determine the effect of the choice of the underlying support on the catalytic performance, we also evaluated Ru deposited on a selection of common supporting materials, including CeO₂, Al₂O₃ and SiO₂ (Fig. S15). In this case all catalysts showed significantly lower activity under the same condition (Fig. S14). Therefore, this suggests that the nature of P25 TiO₂ as a support is capable of providing a specific interaction with Ru species, which may be the key factor in facilitating the production of THFA via single step selective FFR hydrogenation.

An additional set of experiments was conducted to examine the influence of the solvent on the catalytic performance of Ru/TiO₂-lys-DP for hydrogenative FFR conversion. Methanol, 2propanol, THFA, THF, DMF, toluene, *n*-heptane and H₂O were examined, with ethanol displaying far superior selectivity toward THFA formation (Table S4, entries 1-9). This shows that specific nature of the solvent can markedly influence both the product distribution and reaction rate. According to the results, nonpolar (toluene and *n*-heptane) and polar aprotic solvents (THF and DMF) are detrimental for FFR conversion. Despite the relatively high rate of organic solvent-free FFR hydrogenation observed with H₂O (Table S4, entry 9), the selectivity towards THFA decreased by 98% compared to the reaction in ethanol. This decrease in THFA selectivity is associated with a 98% increase in the selectivity towards FA, which indicates that hydrogenation of C=O bond is more favorable than that of the unsaturated bonds within the furan ring.

When conducting the reaction under N_2 over $Ru/TiO_2\mbox{-lys-DP},$ no FFR conversion was observed (Table 1, entry 10). Hence, possibility that the catalytic transfer hydrogenation occurs

within the present catalytic system is excluded. This is further confirmed by the absence of aldehyde \oplus 100 \oplus 2005 \oplus 2005

To further examine the reaction performed with Ru/TiO₂-lys-DP, the kinetic profile for FFR conversion at 40 °C followed by GC analysis was conducted (Fig. 3a). The reaction process did not show the products derived from decarbonylation of the carbonyl moiety in furfural or other unwanted by-products (such as furan and 2-methylfurfural), indicative of preferential activation of C=O and C=C bonds on Ru/TiO₂-lys-DP surfaces. Upon investigating the effect of pressure, we found that the reaction time is shortened from 1.5 to 1.0 h when H₂ is increased from 4 to 6 MPa (Table 1, entry 2, 11). In the case of the effect of the reaction temperature, THFA is quantitatively obtained at 25 °C (Table 1, entry 12). Notably, even at a subambient temperature of 2 °C, quantitative formation of THFA can be attained within 25 h (Table 1, entry 13). Of yet further interest is that, in this particular case the specific activity based on FFR conversion is 22 h⁻¹, which compares favorably with the state-of-the-art catalyst Pd-Ir/SiO₂ (Table S3).46

The catalytic amount of Ru can be lowered to 0.04 mol% without depleting its inherent catalytic activity for THFA formation (Table 1, entry 14). Thus, in a gram-scale reaction of FFR (52 mmol scale up) for 12 h, 97% yield of THFA was obtained (Fig. S16). After the reaction, Ru/TiO₂-lys-DP was easily separated from the reaction mixture by filtration. Analysis by inductively coupled plasma (ICP) confirmed that no Ru was present in the filtrate (limit of detection: <24 ppb), thus indicating a strong binding of the subnano Ru clusters to the TiO₂ surface under these reaction conditions. Moreover, the recovered Ru/TiO₂-lys-DP can also be reused at least four times without any major loss in activity, with a total turnover number (TON) of approx. 12,500 (Fig. S17). This value is far greater than those in reported catalytic systems.23,25,43-47 Additionally, STEM and XPS confirmed almost no change in the metal dispersion or chemical state of Ru before and after reuse (Fig. S18, 19).

To further elucidate the influence of Ru dimensions on the total hydrogenation pathway, we evaluated the kinetics of FFR hydrogenation over Ru/TiO₂-DP under conditions identical to those for Ru/TiO₂-lys-DP. Operation under negligible mass

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Fig. 4 Catalytic activities of Ru/TiO₂-lys-DP and Ru/TiO₂-DP reduced at different temperatures. Reaction conditions: FFR (5.2 mmol), EtOH (10 mL), catalyst (metal 0.18 mol%), H₂ (4 MPa), 80 °C, 1.5 h.

transfer resistance was established using the Madon and Boudart approach.⁴⁸ As shown in Fig. 3, the enhanced performance of Ru/TiO₂-lys-DP relative to Ru/TiO₂-DP originates from the dramatically accelerated hydrogenation of the furan ring rather than from the reduction of C=O moiety, presumably owing to the strongly favored interaction of FA enabled by the surface anchored subnano Ru sites. Notably, Table 2 Comparison of activities of various furans over Ru/TiO₂- the selectivity before 2 h reaction time favors the intermediate formation of FA over both catalysts, Dolgeoting that 2010 hydrogenation is preferential over C=C hydrogenation within the furan ring at the initial stage of the reaction. Additionally, the two separate control experiments utilizing tetrahydrofurfural (TFFR) and FA as the starting substrates, respectively, showed that TFFR hydrogenation proceeds much faster than FA over both catalysts (Fig. 3c, 3d).

In contrast to the situation identified for TFFR hydrogenation, FA hydrogenation proceeds at a higher rate over Ru/TiO₂-lys-DP than Ru/TiO₂-DP (Fig. 3d). To examine the role of Ru particle size, the rate dependence on the H₂ pressure and FA concentration was studied. The reaction orders with respect to FA concentration were calculated as 0.02 and 0.35 for Ru/TiO₂-lys-DP and Ru/TiO₂-DP, respectively (Fig. S20, S21), indicating that FA is more strongly adsorbed on Ru/TiO₂-lys-DP surface. The reaction orders with respect to H₂ pressure over Ru/TiO₂-lys-DP and Ru/TiO₂-DP were estimated as 0.36 and 0.33, respectively (Fig. S22, S23), suggesting that Ru dimensions does not induce changes associated with H₂ activation. In combination with the infrared (IR) spectroscopic analysis, we found a greater red shift of furan ring stretching for furan adsorption on Ru/TiO2-lys-DP relative to Ru/TiO2-DP (Fig. S24), further supporting the decisive role of subnano Ru sites in facilitating the essential furan ring hydrogenation step.49

Table 2 Comparison of activities of various furans over Ru/TiO ₂ -lys-DP and Ru/TiC	₂ -DP
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Entry	Substrate	Product	Ru/TiO ₂ -lys-DP			Ru/TiO ₂ -DP		
			t (h)	Yield (%)	ATOF (h-1)	t (h)	Yield (%)	ATOF (h ⁻¹)
1ª	но	HO O OH	2	>99	275	10	95	52
2	o l	OH OH	4	95	131	18	88	27
3	on in	C OH	6	92	84	24	68	16
4	Ori	O OH	7	90	71	36	78	12
5	он	он	6	89	82	48	64	7
6	он	он	8	82	56	60	59	5
7	он	он	12	78	36	72	48	4
Reactior	n conditions: substrate (1 mn	nol), EtOH (10 mL), cataly	rst (meta	l 0.18 mc	ol%), H ₂ (4	MPa),	80 °C. ª	HMF (5 mmol

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It is worth mentioning that, as opposed to the kinetic pattern seen with Ru/TiO_2 -DP, the reaction rates are practically independent of the FA concentration but distinctly sensitive to the hydrogen pressure for the Ru/TiO₂-lys-DP sample. These contrastive kinetic parameters imply that Ru/TiO₂-lys-DP breaks through the limitation of FA activation, and hydrogen activation is the rate-controlling step. Therefore, it can be concluded that the total hydrogenation of FA over Ru/TiO₂-lys-DP is largely limited by the rate of H₂ dissociation due to the high activation barrier to dissociate H₂.⁵⁰ It is interesting to note at this point that the degree of rate acceleration with increasing H₂ pressure from 4 to 6 MPa as indicated by the catalytic data shown in Table 1 seems to infer a first order dependence on H₂ pressure. However, it must be emphasized that the above-discussed kinetic analysis is based on the dependence of initial reaction rate on the initial composition of reaction mixture rather than on the data obtained at high conversion levels.

To gain greater insight into the influence of the chemical states of Ru clusters and the underlying support on the performance of Ru/TiO₂-lys-DP, a series of control samples bearing different levels of Ru and TiO₂ reduction were prepared. A systematic approach was used to modulate the electronic states of the catalysts with minimal change in Ru dimensions (Fig. S25, S26). This was achieved by subjecting asdeposited Ru/TiO₂-lys-DP and Ru/TiO₂-DP samples to H₂/Ar at different temperatures (100 °C, 300 °C and 500 °C). In this approach, high temperature H_2 could reduce Ru species strongly interacting with the support and promote further reduction of TiO₂ via hydrogen spillover. As corroborated by XPS analysis (Fig. S27, S28; Table S5, S6), it is possible to gradually decrease the unreducible Ru species and create more Ti³⁺ defective sites by H₂ reduction at elevated temperatures. The performances of the prepared catalysts (Fig. 4) were studied, confirming that the state of Ru clusters, rather than TiO₂, contributes to the overall reactivity. Importantly, a moderate amount of $Ru^{\delta+}$ species (ca. 20%) is essential to achieve a reasonable yield of THFA (Ru/TiO2-DP with 20% Ru^{$\delta+$}, THFA yield 65%). Therefore, a suitable $Ru^{\delta+}/(Ru^{0}+Ru^{\delta+})$ ratio is one of the key factors in contributing to the observed high efficiency.

Lastly, the scope and utility of this new total hydrogenation methodology was examined, showing that Ru/TiO_2 -lys-DP efficiently hydrogenated a range of other furan-based compounds. As illustrated in Table 2, the reaction proceeds successfully with a number of sugar-derived furans. For example, 5-hydroxymethylfural (HMF), one of the most important C6 platform chemicals derived from cellulosic biomass, is quantitatively hydrogenated (Table 2, entry 1) to

2,5-dihydroxymethyltetrahydrofuran (DHMTHF), a promising renewable source for the production of industrially relevant monomer 1,6-hexanediol.⁵¹ In addition, the catalytic system readily adapts to various furan/acetone aldol adducts to afford the corresponding products in high yields (Table 2, entries 2-7). High yields of the corresponding saturated derivatives are generally obtained with ATOFs at least threefold as high for Ru/TiO₂-lys-DP than for Ru/TiO₂-DP. Hence, Ru/TiO₂-lys-DP is the most active catalyst for the total hydrogenation of the biobased furan derivatives reported to-date.

Conclusions

In conclusion, we have presented a facile and effective procedure for surface-decorating commercial P25 TiO₂ material with ultrasmall Ru clusters, whose size is controlled to obtain particles smaller than 1 nm. Subnanometric structure of RuOx are verified and demonstrated for efficient and robust single-step total hydrogenation of FFR for the first time. The optimal average TOF of FFR-to-THFA conversion is 367 h⁻¹, which far surpasses those of the current state-of-the-art catalysts that usually require considerably rarer and expensive Ir or Pd as essential components. With its robust total hydrogenation for a range of structurally diverse bio-based furanic compounds, the as-obtained Ru/TiO₂-lys-DP holds promise for the development of a practical biorefinery technology based on catalytic hydroprocessing.

Experimental section

Materials (source and purity)

The reagents used were 5-Hydroxymethylfurfural (99%, Aladdin), furfuryl alcohol (97%, Aladdin), tetrahydro furfuryl alcohol (99%, Aladdin), furan (>99.5%, Aladdin), lysine (99%, Aladdin), tryptophan (99%, Aladdin), tyrosine (98%, Aladdin), ruthenium chloride hydrate (RuCl₃·xH₂O, 35%-42%Ru, Aladdin), CeO₂ (99.9%, Degussa), Al₂O₃(99.9%, Degussa), SiO₂ (99.9%, Degussa), P25 TiO₂ (99.99%, Degussa), acetone (>99%, J&K), 2-pentanone (>99%, J&K), 4-methyl-2-pentanone (>99%, J&K) and tetrahydrofurfural (97%, fluorochem).Furfural (98%, Aladdin) were distilled under reduced pressure before use.

Catalyst preparation

Preparation of anatase-TiO₂: Single-phase anatase-TiO₂ was isolated from commercial P25 TiO₂ by chemical treatment.⁵² Briefly, 6.0 g P25 TiO₂ was added to an aqueous mixture of H_2O_2 (200 mL, 30 wt%) and NH₃ (6 mL, 25 wt%) and stirred at room temperature for 15 h. To obtain anatase-TiO₂ particles,

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the resultant solid was washed thoroughly with deionized

water, dried in vacuum and calcined at 200 °C for 3 h. **Preparation of rutile-TiO₂:** Single-phase rutile-TiO₂ was isolated from commercial P25 TiO₂ by chemical treatment.⁵³ Briefly, 1.0 g P25 TiO₂ was added to 50 mL HF solution (10 wt%) and stirred at room temperature for 24 h. To obtain rutile-TiO₂ particles, the resultant solid was washed thoroughly with deionized water, dried in vacuum and calcined at 200 °C for 3 h.

Preparation of Ru/TiO₂-lys-DP: Ru/TiO₂-lys-DP was prepared by a facile modified deposition-precipitation (DP) method. In a typical synthesis, 0.1 mmol RuCl₃ and 0.1 mmol lysine was stirred in 100 mL deionized water for 15 mins before the pH was adjusted to 8.0 by diluted NaOH solution. After 1.0 g P25 TiO₂ was dispersed, the pH of the slurry was readjusted to 8.0 by NaOH, followed by a subsequent 18-hour stirring at room temperature. During deposition, the pH was carefully monitored and intermittent addition of NaOH was needed. The resulting solid was washed extensively with deionized water, dried at 100 °C overnight, and reduced under 5 vol% H₂/Ar (80 mL·min⁻¹) at 300 °C for 2 h to obtain the product Ru/TiO₂-lys-DP (0.49 wt% Ru by elemental analysis). Ru/TiO₂-DP (0.56 wt% Ru) was prepared by the same method except for the absence for lysine.

Preparation of Ru/TiO₂-lys-imp: Ru/TiO₂-lys-imp was prepared by incipient-wetness impregnation of 1.0 g P25 TiO₂ with aqueous mixture of 0.1 mmol RuCl₃ and 0.1 mmol lysine. After a perfect mixing of the slurry, the resulting mixture was vigorously stirred at 80 °C for 4 h. Then samples were dried at 100 °C overnight and then reduced in 5 vol% H₂/Ar (80 mL·min⁻¹) at 300 °C for 2 h. Ru/TiO₂-imp was prepared by the same method except for the absence for lysine. The Ru content of both catalysts were measured to be 0.92 wt% and 0.90 wt%, respectively.

Characterizations

Elemental analysis of catalysts was conducted with a PerkinElmer inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 8300 DV. Transmission electron microscopy (TEM) images were taken by a JEOL JEM 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoparticles was determined by measuring about 100 random particles in the images. Highangle annular dark-field scanning transmission electron microscopy (HAADF- STEM) images were obtained on a Tecnai G2 F20 S-Twin electron microscope, operating at 200 kV. X-ray diffraction (XRD) was operated on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Ka radiation source at 40 kV and 40 mA. Temperature programmed reduction (H₂-TPR) was conducted using a BEL-CAT (BEL Japan, Inc.) instrument by heating a 100 mg Ru catalyst at 10 °C ·min⁻¹ from room temperature to 750 °C under a 10 vol% H_2/Ar flow. X-ray photoelectron spectroscopy (XPS) measurements were

performed with an Escalab 250Xi spectrometer (Thermo Fisher Scientific) using 200 W mono-chromated $^{10}AP^{3}Rdc^{9}$ fadiation (1486.6 eV). The catalyst, formed into a small disk (4.0 mm diameter), was mounted on the sample stage, reduced in the pretreatment chamber at 300 °C for 2 h under 40 mL·min⁻¹ flow of 5 vol% H₂/N₂, and then transferred to the analyzing chamber, where the background pressure was lower than 2 x10⁻⁹ Torr. The spectra were collected with an analyzer pass energy of 23.5 eV and an electron takeoff angle of 45°. The binding energy scale was calibrated by the adventitious C 1s peak at 284.6 eV as a reference.

Fourier transform infrared spectroscopy (FT-IR) was carried out with a Nicolet iS10 FT-IR spectrometer equipped with a DTGS detector, in the range 400–4000 cm⁻¹, by applying an optical resolution of 0.4 cm⁻¹. The samples were investigated by using the KBr pellet technique. Diffuse reflectance infrared fourier transform (DRIFT) spectra of chemisorbed CO were recorded in an in-situ diffuse reflectance cell (Harick Scientific) equipped with a CaF window on a Nicolet 6700 spectrometer (Thermo Fisher Scientific), using an Hg-Cd-Te (MCT-A) detector. The sample was pre-reduced in the cell with flowing 5 vol% H₂/Ar (80 mL·min⁻¹) at 300 °C for 30 mins. The temperature was then lowered to 15 °C for CO chemisorption. After collecting a background spectrum of the sample under the Ar flow, the cell was switched to flowing 1 vol% CO/Ar (20 mL·min⁻¹) for CO adsorption for 45 mins, followed by purging with Ar. The collected spectra were subtracted from the sample background spectra in Ar to obtain the spectra for chemisorbed CO. For furan-FTIR spectra, a vacuum pump was used to pull the furan vapor through the chamber for in situ FTIR measurements. X-ray absorption fine structure (XAFS) measurements at Ru K³-edge in fluorescence mode were performed at the BL14W15 in Shanghai Synchrotron Radiation Facility (SSRF). The electron beam energy was 3.5 GeV and the stored current was 230 mA (top-up). A 38-pole wiggler with the maximum magnetic field of 1.2 T inserted in the straight section of the storage ring was used. Given that the elemental states and structure of the catalyst might be changed when exposed to air, we carried out these analyses in the absence of air using a special holder with a gas cell to transfer the sample from an inert gas environment to the inside of the instrument. XAFS data were collected using a fixed-exit double-crystal Si (311) monochromator. The energy was calibrated using Ru foil. Data processing was performed by ATHENA.54

Catalytic activity measurements

Procedure for the hydrogenation of furanic compounds and reusability test: A mixture of FFR or HMF (5.2 mmol), supported metal catalysts (metal loading: 0.18 mol%), ethanol (10 mL) were charged into a 100 mL Hastelloy-C high pressure Parr reactor. The reactant mixtures were then stirred at a rate of 800 rpm under given H₂ pressure for certain reaction time at a given temperature. After reaction, the H₂ atmosphere was removed and 2 mmol naphthalene was added as internal standard. The samples were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-

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INNOWAX column (30 m \times 0.32 mm \times 0.25 μm) and FID detector. For adol adducts, 1 mmol of substrate was subjected to catalytic test. Each experiment was repeated three times and average activities were given in the figures and tables. The carbon balance of each run exceeded 98%, if not especially stated. For the reusability test, the following procedure was employed to minimize possible experiment errors arising from the possible loss of catalyst. 200 mg Ru/TiO₂-lys-DP was added into each of 13 identical reactors for hydrogenation of FFR. After the reaction run for 1.5 h, the spent catalyst was collected after filtration and washed thoroughly with ethanol, dried at 100 °C overnight and reduced under 5 vol% H₂/Ar (80 mL·min⁻¹) at 300 °C for 2 h. After that, the same procedure as the ones described above was performed in 12 reactors, with each containing same amount of the recovered Ru/TiO₂-lys-DP, and so on.

Procedure for the gram-scale transformation of FFR and reusability test: A mixture of FFR (52 mmol), Ru/TiO₂-lys-DP (metal loading: 0.04 mol%), ethanol (45 mL) were charged into an autoclave (250 mL capacity) and heated to 80 °C in less than 15 minutes. The reactant mixtures were then stirred at a rate of 800 rpm under 4 MPa H₂. After 12 h of reaction, 55 mL of ethanol was added to dilute the mixture. 5 mL of this diluted sample was transferred into the vial and 1 mmol naphthalene was added for further analysis. For the reusability test, the procedure was identical to that applied on small scale except that 6 separate reactors operating under otherwise identical conditions were conducted on the first run.

Conflicts of interest

There are no conflicts to declare.

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