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Production of a renewable 1,3–diene containing a functional group from furfural–acetone adduct in a fixed–bed reactor

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The synthesis of functionalized 1,3–dienes has received increasing attention due to their importance in the practical development of high–performance elastomers. In the present work, furfural and acetone, acting as renewable feedstocks, are first employed to produce a functionalized 1,3–diene containing a furan group (1–(2–furyl)–1,3–butadiene, F–Diene). After selective hydrogenation of the C=O group, the aldol adduct (4–(2–furanyl)–3–butene–2–ol, FAH) shows a nearly complete conversion, with an excellent selectivity (as high as 92%) towards F–Diene over the ceria–based catalysts in a fixed bed. BET, TEM, XRD, XPS, Raman, TPD, TPR and TGA were conducted to identify the relationship between the catalytic performance and catalyst structure. A plausible reaction pathway for the dehydration of FAH over ceria–based catalysts was proposed using a radical mechanism, which suggested the importance of the Ce⁴⁺–Ce³⁺ redox cycle for the dehydration of FAH to F–Diene. Furthermore, the ceria–based catalysts exhibited a notable carbon resistance.

1. Introduction

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Diminishing fossil resources and growing concern regarding environmental sustainability have boosted the development of research and technologies for biofuels production and valuable chemicals from biomass, which are a promising and renewable energy resource.^{1, 2} Among the platform chemicals obtained from biomass, furfural is one of most valuable and readily available compounds, which can be produced by the dehydration of hemicellulose, cellulose, xylose and glucose.³⁻⁵ Thus, it is a practical and effective strategy to produce value-added chemicals by furfural utilization. Consequently, many efforts have been devoted to exploiting the potential applications of furfural through a wide variety of catalytic processes.⁶⁻¹⁰ To manufacture liquid transportation fuels (e.g., jet and diesel fuels), furfural reacts with acetone (a by-product in phenol production) via aldol condensation, which affords furfural-acetone adducts containing 8+ carbon atoms; these adducts are then converted into liquid fuel after hydrogenation and deoxygenation reactions (Scheme 1).¹¹⁻¹⁵ During these procedures, the C8 adduct (4-(2-furanyl)-3-butene-2-one, FA) is an important intermediate, which has received a great deal of attention.16-23

Notably, FA is also a precursor of a functionalized 1,3-diene, containing a furan group. Inspired by this, we are interested in exploiting a novel application of furfural and acetone in the production of functionalized 1,3-dienes. The production of functionalized 1,3-dienes has received wide attention for decades, because of the ability to design the functional groups (polar and/or rigid groups), which can effectively solve the interfacial and compatible problems of the resulting materials.²⁴⁻²⁹ Therefore, 1,3-dienes, which bear polar and/or rigid groups such as silicon-,³⁰⁻³⁴ cyano-,^{35, 36} ester- ^{37, 38} and amino- ³⁹⁻⁴² groups, as well as other groups, have been synthesized. ⁴³⁻⁴⁵

Recently, Long et al.⁴⁶ successfully synthesized a functionalized 1,3– diene containing a furan group (1,3-2-(2-methylidenebut-3-enyl) furan) from 2-iodofuran via the Grignard reaction and coupling reactions in the presence of Pd(PPh₃)₄, vinyl magnesium bromide, suspension of magnesium in anhydrous ether, 2,3–dibromopropene and anhydrous THF. The furan displays polar and rigid properties,



Scheme 1. The production of transportation fuel from furfural and acetone.

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which are desired in a functional group. Watkins et al.⁴⁷ reported the production of 1-(2-furyl)-1,3-butadiene (F-diene) through the Wittig Reaction 3-(2-furyl)-2-propenal, using methyltriphenylphosphonium bromide in dry THF and sodium hexamethyldisilazane as starting materials, which sparked interest in this methodology.⁴⁸ Similarly, methyl phosphonium bromide and 3-(2-furyl) acrolein were utilized for the synthesis of F-diene in the presence of potassium tert-butoxide and dry THF.49 Yasukawa et al.50 synthesized F-diene using 4-(2-Furyl)-3-buten-2-one, a suspension of methyltriphenylphosphonium bromide in THF and n-BuLi. Unfortunately, the outlined methods to produce functionalized 1,3-diene (including F-diene) involve unusual feedstocks (e.g., 2-iodofuran, 3-(2-furyl)-2-propenal, 2,3dibromopropene) and hazardous reagents (e.g., Grignard reagents, organophosphorus chemicals). More importantly, all of these chemicals are non-renewable resources or could lead to environmental problems. Furthermore, these procedures require several elaborate operations under harsh conditions (e.g., inert and dry atmosphere, purified solvents). Notably, Wang et al.⁵¹ successfully employed furfural to synthesize F-diene; however, the method still requires Grignard reagent, organophosphorus compound and complicated operations. Therefore, the production of F-diene from renewable and accessible feedstocks by a facile route remains a challenge.

Herein, the present work focuses on the production of F-diene (a functionalized 1,3-diene containing a furan group) from furfural and acetone through condensation, hydrogenation and dehydration reactions. The condensation and hydrogenation first allow for an excellent yield of the target product under mild conditions. Subsequently, the furfural-acetone adduct was converted into F-diene over ceria-based catalysts in a fixed-bed reactor. The relationship between the catalytic performance and catalyst was studied, and a likely reaction pathway was proposed. To our knowledge, this is the first report of F-diene production from a furfural-acetone adduct under a readily accessible condition.

2. Experimental

2.1 Materials

Furfural and acetone were purchased from Aladdin. Ce(NO₃)₃·6H₂O, AgNO₃, NaBH₄, and (NH₄)₆Mo₇O₂₄·4H₂O were supplied by Energy Chemical. SiO₂ (100 ~ 200 mesh, 370 m²/g) was purchased from Qingdao Hailang (China), and *n*-heptane and dodecane were from TCI (Shanghai). Tetrahydrofuran, diethyl ether, methanol, H₃PO₄ and NaOH were supplied by Beijing Chemical Works (China), and phosphotungstic acid was supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2 Preparation of catalysts

All catalysts were prepared by an initial wetness method. Prior to using as a support, SiO_2 was first calcined at 550 °C for 4 h. In a typical synthesis procedure, 0.75 g of $Ce(NO_3)_3$ · GH_2O was dissolved in 8 mL of water at room temperature, and 5 g of SiO_2 was added to form a slurry. The slurry was aged over night at room temperature, dried at 70 °C for 3 h, and then at 120 °C for 5 h in an oven. Finally, the sample was calcined at 550 °C for 4 h to afford the catalyst

(15Ce/SiO₂). Similarly, 1.00 g, 1.25 g, 1.50 g, 1.75 g, $and_{A2tQO_{C}} = 0$ Ce(NO₃)₃·6H₂O were used to prepare the catalyst 20Ce/SiO₂, 25Ce/SiO₂, 30Ce/SiO₂, 35Ce/SiO₂, and 40Ce/SiO₂, respectively. In addition, Ag/SiO₂, HPW/SiO₂, P/SiO₂, MoP/SiO₂, HPW/SiO₂, P/SiO₂, and MoP/SiO₂ were prepared.

NaOH and NaBH $_4$ were employed as catalysts for the aldol condensation and reduction to allow for a high yield of the target products.

2.3 Characterization

Surface area was measured by N₂ adsorption-desorption isotherms on an Autosorb-iQ (Quantachrome), and X-ray diffraction (XRD, Bruker D8 Advance, λ =0.154 nm) was performed to examine the sample structure. The morphology of samples was studied by (highresolution) transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). Catalyst composition was revealed by inductively coupled plasma (ICP). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo) was performed to examine the fresh catalysts. Raman spectra were recorded on a LabRAM HR800 (Horiba Jobin Yvon) with a laser source of 532 nm. TGA (SDT Q600) was employed to determine the carbon deposition of spent catalysts, using a heat rate of 10 °C /min to 700 °C under air flow. The acidity of sample (NH₃-TPD) was determined on TP5080 (Tianjin Xianquan) from 100 to 700 °C with a ramp of 10 °C/min. Firstly, the sample was pretreated at 400 °C for 30 min under a flow of He (30 ml/min), followed by saturated with 5% of NH₃/He at room temperature, physical adsorbed NH₃ was removed successively at room temperature and 100 °C for 30 min under 30 mL/min of He flow, respectively. Temperature-programmed reduction (H₂-TPR) was conducted on TP5080 (Tianjin Xianquan), from 50 to 800 °C (heating rate: 10 °C/min) under 10% of H₂/Ar flow (20 mL/min). Prior to experimental, the sample was pretreated at 150 °C for 30 min under He flow (20 ml/min).

2.4 Reaction studies Production of the furfural-acetone adduct

The furfural–acetone adduct was prepared according to the reported method with some modification.¹² Furfural (10 g) and acetone (60.75 g) were charged into a 500 mL round–bottom flask, followed by the addition of a water–methanol solution (200 g, 1:1 in m/m) containing 1.0 g of NaOH. After stirring at 30 °C for 2 h, the mixture was neutralized by dilute HCl and extracted by CH₂Cl, followed by removal of the solvent to give FA. A THF–water (50mL, 9:1 in v/v) solution containing 2.0 g of NaBH₄ and 100 mg of Ba(OH)₂ was then added dropwise to a solution of THF–water (40 mL, 9:1 in v/v) containing 7.6 g of FA in an ice bath, followed by stirring at room temperature for 12 h. The reaction was stopped by the addition of dilute H₂SO₄, and THF was then removed. After extraction with ether, the resulting liquid was washed with brine. Finally, 4–(2–furanyl)–3–butene–2–ol (FAH) was obtained as yellow oil after removal of the ether (Supporting materials).

Production of functionalized 1,3-diene in a fixed-bed reactor

$\begin{array}{c} & & & \\ & & & \\ & & & \\$

1,3–Diene was produced in a conventional continuous flow fixedbed reactor (a stainless steel tube, with an inner diameter of 7 mm and length of 500 mm) under atmospheric pressure. The catalyst (400 mg) was loaded and heated to the desired temperature under N₂ (99.999%), with a flow rate of 50 mL/min. Prior to the reaction, the catalyst was heated at the desired temperature for 3 h. The reactant of FAH (2.0 wt% in THF) was fed by a syringe pump (Harvard Apparatus) with a rate of 2.6 mL/h and co–fed with 50 mL/min of N₂. The products were collected using a trap, which was charged with 20 mL of THF–dichloromethane solution in an ice bath. The products were analyzed by GC–MS (Agilent 5975 MSD with Agilent SE–54) and GC (Agilent technologies 7890B), and both *n*–heptane and dodecane were used as internal standards.

3. Result and discussion

3.1 Textural properties of the catalysts

The specific surface area, pore diameter and pore volume of the ceria-based catalysts and support are summarized in Table 1, with the N_2 adsorption isotherms and pore size distribution displayed in Fig. 1. All catalysts exhibited a similar N₂ adsorption isotherm, with a BJH pore size distribution similar to the SiO₂ support. An increase in CeO₂ loading decreased the surface area of the catalysts, and when the CeO_2 loading was relatively high (e.g., $30Ce/SiO_2$, 35Ce/SiO₂, and 40Ce/SiO₂), the surface area showed only a slight reduction (337, 336, and 334 m²/g, respectively). According to the BJH pore size distribution, the samples have pores of 5 $^{\sim}$ 20 nm, and the SiO₂ support has a pore diameter of 11.89 nm, which was significantly larger than that of the ceria-based catalysts, especially for 15Ce/SiO₂, 20Ce/SiO₂, 25Ce/SiO₂ and 30Ce/SiO₂, which had pore diameters of 8.39, 8.38, 8.39 and 8.38 nm, respectively. An apparent difference was observed when the CeO₂ loading was relatively higher, with 35Ce/SiO₂ and 40Ce/SiO₂ catalysts having pore diameters of 10.26 and 11.82 nm, respectively, which were much larger than the other catalysts but approximately the same as







Fig. 2 TEM images and particle distribution of (a) 15Ce/SiO₂, (b) 25Ce/SiO₂, (c) 35Ce/SiO₂ and (d) 40Ce/SiO₂

the SiO₂ support. Therefore, this appears to correlate with the content and morphology of CeO_2 in the catalysts (presented as fallows).

To elucidate the CeO₂ content of the catalysts, the content was first determined by ICP, which was found to be within agreement of the theoretical value (Table 1). The catalysts' morphologies were revealed by TEM, and the images were provided in Fig. 2. Fig. 2(a) shows that the CeO₂ nanoparticles (black) with a diameter of $1 \sim 3$ nm are well dispersed on the SiO₂ support for 15Ce/SiO₂.

Table 1. Catalysts characteristics								
Sample	Surface area (m ² /g)	Pore size (nm) ^a	Pore volume (cc/g)	CeO ₂ content (wt%) ^b	Acidity (µmol/g) ^c			
SiO ₂	370	11.89	0.98	-	-			
15Ce/SiO ₂	355	8.39	0.96	5.66 (5.16)	3.01			
20Ce/SiO ₂	350	8.38	0.95	7.26 (7.34)	8.63			
25Ce/SiO ₂	343	8.39	0.89	9.06 (9.01)	10.24			
30Ce/SiO ₂	337	8.38	0.90	10.97 (10.63)	10.39			
35Ce/SiO ₂	336	10.26	0.93	12.45 (12.18)	11.82			
40Ce/SiO ₂	334	11.82	0.92	14.90 (13.68)	11.29			
^{<i>a</i>} : Diameter of pore from BET								
^b : ICP results (theoretical data)								
^c : from NH ₃ –TPD								

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Additionally, 25Ce/SiO₂ exhibited CeO₂ particles with a relatively uniform size (3 ~ 6 nm) (Fig. 2(b)). Increasing of the CeO₂ loading resulted in the appearance of some large CeO₂ clusters, which were aggregated by smaller particles, such as in 35Ce/SiO₂ (Fig. 2(c)). In 40Ce/SiO₂, the CeO₂ particles presented an agglomerate form and non–uniform particle size in the range of 3 ~ 30 nm (Fig. 2(d)). Therefore, it may be inferred that the loading of CeO₂ particles resulted in a decrease in the SiO₂ support surface area, and the sufficient dispersion and smaller size of CeO₂ particles, acting as a coating on the SiO₂ surface, narrowed the pore size. Alternatively, the agglomerate form of CeO₂ clusters may embed in the pore, which has little affluence on pore diameter.

The XRD patterns of the ceria–based catalysts, as presented in Fig. 3, show the characteristic diffraction peaks of CeO_2 , which were

around 20 of 28.4°, 33.0°, 47.5°, 56.1°, 59.1°, 69.3°, 76.6°, 72.0° and 88.3°, assigned to the (111), (200), (220), (319), 1(2223) (400), (339), (420) and (422) reflections of the fluorite structure of CeO₂ respectively, according to the standard PDF cards of CeO₂ (JCPDS PDF#65-2975).⁵² Obviously, the CeO₂ (111) facet was predominant in all the samples, and the wide–range peak located within 17 ~ 23° was attributed to the presence of the amorphous SiO₂ support. Moreover, three distinct diffraction peaks of 28.4°, 33.0° and 47.5°, corresponding to the (111), (200) and (220) reflections, were consistent with the results of high resolution TEM analyses (Fig. 4). These exhibited well crystalline and defective particles with an interplanar spacing of approx. 0.319 (d₁₁₁), 0.274 (d₂₀₀) and 0.198 (d₂₂₀) nm. Furthermore, the polyhedral shape of CeO₂ particles was also confirmed.

XPS was conducted to further clarify the structure of ceriabased catalysts to afford more interface insights (Fig. 5), with the XPS spectra of CeO₂ also illustrated for comparison. The full spectra of the catalysts are displayed in Fig. S2. The O 1s spectra of CeO2 (Fig. 5(a)) was divided into three peaks and marked as O_L (529.3 eV), O_V (530.5 eV) and O_C (532.1 eV). The O_L was related to the O^{2-} species in the lattice of CeO_2 , O_V was associated with the O^{2-} species in the oxygen vacancies, and O_c originated from the contribution of the surface-chemisorbed oxygen species.⁵³ Fig. 5(c) depicts the O 1s spectra of the ceria-based catalysts, with all of the samples having one distinct peak at approx. 532.1 eV, compared to the O 1s spectra of CeO2. This may result from the absorbed oxygen, hydroxyl species and/or water species on the surface, as well as large amounts of O species from the SiO₂ support. In this respect, it is difficult to detect and evaluate the oxygen vacancies in SiO₂ supported catalysts. As displayed in Fig. 5(b), the deconvoluted peaks of Ce 3d spectra are labeled as u''' (916.6 eV), u'' (907.5 eV),

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u' (902.2 eV), u (900.5 eV), u₀ (899.3), v''' (898.3 eV), v'' (889.0 eV), v' (884.3 eV), v (882.5 eV), and v_0 (880.2 eV), where the v and u represent the spin-orbit coupling of Ce $3d_{5/2}$ and Ce $3d_{3/2}$, respectively.54, 55 Generally, the peaks labeled as v, v", v"', u, u" and u''' are attributed to Ce4+ species, and peaks labeled as $v_0,\,v',\,u_0$ and u' are assigned to Ce3+ species. Therefore, both Ce3+ and Ce4+ species were identified to coexist in CeO₂, with Fig. 5(d) implying that the two Ce species also exist in the ceria-based catalysts. The presence of Ce³⁺ species was always are associated with oxygen vacancies,⁵⁶ and which was further manifested by the Raman results as illustrated in Fig. 6.

Raman spectra of the ceria-based catalysts are shown in Fig. 6(a). A characteristic peak at approx. 465 cm⁻¹, which was derived from the symmetrical stretching vibration of Ce-O-Ce (F2g mode), was observed in 35Ce/SiO₂ and 40Ce/SiO₂. The appearance of a peak at approx. 601 cm⁻¹ confirmed the existence of the oxygen defect in both of the samples, which was ascribed to the secondorder transverse acoustic (2 TA) mode and linked to oxygen vacancies in the CeO₂ lattice.⁵⁷⁻⁵⁹ In our system, it was difficult to obtain a precise value for the ratio of peak areas at approx. 601 and 465 cm⁻¹ (A_{601}/A_{465}), which can be employed to quantitatively calculate the concentration of oxygen vacancies. Whereas, it can be inferred that 35Ce/SiO₂ may have more oxygen vacancies than 40Ce/SiO₂ due to the relatively stronger band at approx. 601 cm⁻¹







and the slight smaller band at approx. 465 cm⁻¹ observed in 35Ce/SiO₂, when compared with 40Ce/SiO₂ (Fig. 6(b)). This may result from more of the agglomerate form of CeO₂ clusters in 40Ce/SiO₂ (as TEM suggested). Unfortunately, these two bands were minimally detected in samples with a relatively lower CeO₂ loading (e.g., 15Ce/SiO₂, 20Ce/SiO₂, 25Ce/SiO₂), which can be ascribed to the presence of a large amount of SiO₂. Based on the results from XPS and Raman, it can be concluded that the Ce³⁺/Ce⁴⁺ species related to the oxygen vacancies exist in the ceria-based catalysts with various concentrations.

3.2 Production of the functionalized 1,3-diene

The functionalized 1,3-diene was produced from furfural and acetone using an aldol condensation with various acid or base catalysts. In the present work, NaOH was employed as the catalyst to obtain a complete conversion of furfural and high selectivity to the adduct product FA, FA was then converted into FAH in the presence of NaBH₄, which can have an excellent yield of the unsaturated alcohol produced from the unsaturated aldehydes/ketones under mild conditions. Finally, the FAH solution was fed through a fixed-bed reactor filled with ceria-based catalysts, and the results are shown in Table 2. Additionally, the catalytic results with some acid catalysts are summarized in Table S1.



Compared with acid catalysts (e.g., PW/SiO₂, Ag/SiO₂), all ceria-based catalysts displayed a high conversion of FAH. The effect

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Table 2. The	Table 2. The dehydration of FAH over the ceria-based catalysts							
Catalyst	Temperatur e (°C)	Conversion (%)	Selectivity (%)	Yield (%)				
15Ce/SiO ₂	300	99	50	50				
20Ce/SiO ₂	300	99	61	60				
25Ce/SiO ₂	300	99	77	76				
30Ce/SiO ₂	300	100	84	84				

4 35Ce/SiO₂ 300 100 92 92 40Ce/SiO₂ 300 100 89 89 35Ce/SiO₂ 275 99 54 53 35Ce/SiO₂ 325 100 88 88

Catalyst weight: 0.40g; N_2 flow rate: 50 mL/min; the result data are averaged within 1 h.

of reaction temperature (275, 300, and 325 °C) on the yield of Fdiene was studied. The yield of F-diene at 275 °C is much lower than that at 300 and 325 °C, which can ascribe to a lower reaction rate at a relative lower temperature. Typically, the dehydration of FA was accompanied by other endothermic processes (gasification of FAH, F-diene and THF), especially for FAH and F-diene having high boiling point (Supporting materials). However, high temperature favors the transformation of diene into carbon deposition.⁶⁰ Therefore, the reaction temperature in present work is optimized at 300 °C. It can be presumed that the pore size of the catalysts (5 ~ 20 nm) has littler influence on the catalytic procedure (e.g., diffusion) because of it pretty larger that the reactant and product molecules, in this respect, the CeO₂ loading and its nature played a crucial role in the dehydration of FAH. Thus, according to the Raman results, the catalysts can be divided into two groups: one group (G1) with a relatively high CeO₂ loading (e.g., 35Ce/SiO₂, 40Ce/SiO₂) which exhibited significant Raman bands, and the other group (G2), which included 15Ce/SiO₂, 20Ce/SiO₂, 25Ce/SiO₂ and 30Ce/SiO₂, that have no distinct Raman peaks. The yield of the desired product over G1 catalysts was significantly higher than that over G2 catalysts, with 35Ce/SiO₂ having a yield as high as 92%, which coincided with the Raman results. Notably, the yield over 40Ce/SiO₂ (89%) was slight lower than that over 35Ce/SiO₂, which can be ascribed to 35Ce/SiO2 may have more oxygen vacancies as suggested by Raman. No distinct Raman peaks were observed for G2 catalysts, which resulted from the large amounts of SiO_2 , the oxygen vacancies and Ce³⁺/Ce⁴⁺ species associated with the CeO₂ content. In addition, based on the XPS results, it may be inferred that a decrease in the oxygen vacancies and Ce³⁺/Ce⁴⁺ species occurred in G2 catalysts with reduced CeO₂ loading (ICP result), which presented the order of the desired product yield (300 °C): $30Ce/SiO_2 > 25Ce/SiO_2 > 20Ce/SiO_2 > 15Ce/SiO_2$. Therefore, the catalytic performance strongly depended on the oxygen vacancies and Ce^{3+}/Ce^{4+} species in the catalysts.

Interestingly, all ceria–based catalysts showed high activity (nearly complete conversion), with only a small amount of liquid byproducts detected (as shown in Fig. S3), while the yield of the desired product varied. To elucidate this, the spent catalysts were collected and examined by TGA (Fig. 7). The spent G1 catalysts had a much smaller carbon deposition compared to spent G2 catalysts,

in which an increase in CeO₂ loading could decrease the cashon content. This was in line with the proven result that the Ceria has a carbon–resistance property.⁶¹ Furthermore, it also implied that the main byproducts were converted into carbon deposition. Additionally, this indicated the definite relationship between the concentration of oxygen vacancies (Ce³⁺/Ce⁴⁺ species) and selectivity toward desired product, namely, more oxygen vacancies

accounting for efficiently the dehydration of FAH to F-diene.

3.3 Study of the catalytic performance

The oxygen vacancies of ceria are associated with its acid/base and redox properties. It has been suggested that the oxygen vacancies, together with the exposed Ce4+-O2- species in ceria-based catalysts, displayed Lewis acid/base properties for many reactions, 62-66 with some of these studies demonstrating that the catalytic performance relied on the concentration of the acid-base sites or oxygen in ceria-based catalysts. In this work, catalyst acidity was examined by NH₃-TPD, as presented in Fig. 8(a). A weak peak, located in the wide temperature range of 100 ~ 400 °C, was observed for all the samples, which corresponded to the desorbed NH₃ linked to the acidity of the catalysts. The intensity of these peaks displayed a slight increase with increasing CeO₂ loading, with 40Ce/SiO₂ showing a smaller peak when compared to 35Ce/SiO₂, which can be attributed to its agglomerate form of CeO₂ clusters. Raman and TEM suggested that the agglomerate of CeO₂ decreased the oxygen vacancies. The amount of acid sites of the ceria-based catalysts is summarized in Table 1, with the samples all showing a much smaller amount of acid sites.

The dehydration features with the production of water and the interaction between H_2O and Ce species have attracted great interest because of the importance of understanding the catalytic performance. Herein, the catalysts were treated in a flow of water gas at 300 °C for 30 min, followed by NH_3 -TPD analysis (Fig. 8(b)). The water-treatment catalysts showed little change in acidity when compared with the corresponding counterparts. Moreover, some of the solid acid catalysts (e.g., HPW/SiO₂, P/SiO₂, and PMo/SiO₂) displayed a low selectivity towards the desired product (Table S1).



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Therefore, in our system, the dehydration of FAH may be related to the redox property ($C^{3+} \rightleftharpoons C^{4+}$) of the ceria-based catalysts.

To estimate the redox properties of the ceria catalysts, H₂-TPR analysis was carried out (Fig. 9). Typically, the peak in the temperature range of 400 ~ 600 °C was related to the reduction of surface ceria, where probably involved the removal of surface capping oxygen (O^{2-} or O^{-} anions).^{61, 67, 68} In the present work, the H_2 consumption peak corresponding to the reduction of surface oxygen species was observed at 518 °C for 15Ce/SiO₂ (black line) and 501 °C for 35Ce/SiO₂ (red line), and a shoulder peak developed at approx. 380 °C, which were all in agreement with previous reports.^{61, 67} Specifically, compared with 25Ce/SiO₂ (blue line), 35Ce/SiO₂ exhibited an apparent and large peak in the temperature range of 450 ~ 550 °C. Thus, these findings indicated that 35Ce/SiO₂ displayed a higher activity and more active sites when compared with 25Ce/SiO₂ and 15Ce/SiO₂, which was supported by the results of Raman, XPS and catalytic performance. Therefore, the dehydration of FAH was dependently correlated with the redox properties of the ceria–based catalysts ($C^{3+} \rightleftharpoons C^{4+}$), which was similar to the dehydration of unsaturated alcohols and diols reported by Sato's group.69-73

Sato et al. suggested that three Ce cations together with an oxygen-defect site (oxygen vacancy) on the CeO₂ (111) surface are the active center for the dehydration of diols or unsaturated alcohols, which undergo a radical mechanism. Based on these findings and the dehydration of secondary alcohols to 1-alkenes over ceria,74, 75 we proposed a probable pathway for the dehydration of FAH over ceria-based catalysts, which is similar to the dehydration of an unsaturated alcohol to 1,3-diene (Scheme 3). Here, three Ce atoms formed a triangle with an oxygen vacancy on CeO₂ (111). Initially, one H atom from the terminal methyl group in FAH adsorbed on an oxygen defect site and was eliminated to produce the radical species. Next, the H radical was oxidized to the proton (H⁺) after donating one electron to reduce Ce⁴⁺ to Ce³⁺. The reduced ceria then enable the cleavage of the C-OH bond to form radicals.⁷⁶ Followed by the elimination of an OH radical, the two radicals on the intermediate combined to afford the target product. Meanwhile, the OH radical abstracted one electron from Ce3+ to yield $\mathsf{Ce}^{4\scriptscriptstyle +}$ and the OH radical itself was reduced to $\mathsf{OH}^{\scriptscriptstyle -},$ which combined with the H⁺ to produce H₂O. Therefore, the redox cycle of Ce^{4+} – Ce^{3+} on the surface plays a key role in the dehydration of FAH.

4. Conclusions

A renewable functionalized 1,3–diene containing a furan group (F– Diene) was successfully produced from furfural and acetone. After the selective hydrogenation of the C=O group, the aldol adduct (FAH) displayed a nearly complete conversion and had excellent selectivity (as high as 92%) towards the target product over the ceria–based catalysts in a fixed–bed reactor. In addition, the ceria– based catalysts exhibited an adequate carbon resistance. XPS, Raman and H₂–TPR analysis demonstrated that the oxygen vacancies on ceria were primarily associated with the redox property of the Ce³⁺/Ce⁴⁺ species, which corresponded to the catalytic performance. A plausible reaction pathway for the dehydration of FAH over ceria–based catalysts was proposed involving a radical mechanism, which suggested the importance of the redox cycle of Ce⁴⁺ \rightleftharpoons Ce³⁺ for the dehydration of FAH to F–Diene.

Conflicts of interest

There are no conflicts to declare.

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