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Article

Highly efficient Nb₂O₅ catalyst for aldol condensation of biomass-derived carbonyl molecules to fuel precursors

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ABSTRACT

Aldol condensation is of significant importance for the production of fuel precursors from biomass-derived chemicals and has received increasing attention. Here we report a Nb₂O₅ catalyst with excellent activity and stability in the aldol condensation of biomass-derived carbonyl molecules. It is found that in the aldol condensation of furfural with 4-heptanone, Nb₂O₅ has obviously superior activity, which is not only better than that of other common solid acid catalysts (ZrO₂ and Al₂O₃), more importantly, but also better than that of solid base catalysts (MgO, CaO, and magnesium-aluminum hydrotalcite). The detailed characterizations by N₂ sorption/desorption, NH₃-TPD, Py-FTIR and DRIFTS study of acetone adsorption reveal that Nb₂O₅ has a strong ability to activate the C=O bond in carbonyl molecules, which helps to generate a metal enolate intermediate and undergo the nucleophilic addition to form a new C–C bond. Furthermore, the applicability of Nb₂O₅ to aldol condensation is extended to other biomass-derived carbonyl molecules and high yields of target fuel precursors are obtained. Finally, a multifunctional Pd/Nb₂O₅ catalyst is prepared and successfully used in the one-pot synthesis of liquid alkanes from biomass-derived carbonyl molecules by combining the aldol condensation with the sequential hydrodeoxygenation.

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1. Introduction

As a solution to the environmental and energy problems, the catalytic upgrading of renewable biomass to value-added transportation fuels and chemicals is of key interest [1]. The production of high carbon diesel (C₁₂–C₂₂) and jet-fuel (C₈–C₁₆) range alkanes, which are widely used as transportation fuels, is drawing immense attention [2]. Biomass-derived platform compounds are light molecules with up to six carbon atoms, therefore, a chain growth process is imperative to synthesize

high carbon fuel precursors [3]. After total hydrodeoxygenation, thus-prepared oxygen-rich fuel precursors can be converted to alkanes and used as transportation fuels [4].

Following the pioneering work of Dumesic et al. [5], several types of C–C bond coupling reactions, such as aldol condensation [6,7], hydroxyalkylation/alkylation [8–11], Diels-Alder reaction [12], benzoin coupling [13], ketonization [14], Michael addition and Robinson annulation [15,16], were developed to produce fuel precursors. Among the C–C bond coupling reactions, aldol condensation is the best known C–C forming syn-

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thetic reaction, which involves the transformation of two carbonyl compounds and requires at least one carbonyl compound containing active α -hydrogen atoms [17]. Since biomass-derived carbonyl compounds are numerous, as shown in Scheme 1, employing aldol condensation reaction to increase carbon chain length has attracted considerable interest [18]. Typically, a series of fuel precursors have been obtained by the aldol condensation of furfural with biomass-derived ketones, such as acetone, methyl isobutyl ketone (MIBK), 2-pentanone, 2-heptanone, 3-pentanone, cyclopentanone, acetylacetone, angelica lactone and LA ester [5,7,16,19–25]. In addition, acetone, MIBK and cyclopentanone can be selectively converted to fuel precursors by its self-aldol condensation [26–28]. Specifically, some biomass-derived carbonyl compounds (furfural, acetone, MIBK and cyclohexanone) can be currently produced in industrial scale [18,29–32], making the promising production of fuel precursors through aldol condensation of biomass-derived carbonyl compounds possible. Besides its application to biomass transformation, the aldol reaction is also important in industry, either in polymers, or in fine chemical and pharmaceutical industry [17,33,34]. In short, aldol condensation is a cornerstone of synthetic chemistry and has received immense attention.

Generally, aldol condensation can proceed in the presence of base, acid and acid-base bifunctional catalysts. In most cases, basic catalysts are applied because they can directly abstract α -protons, forming carbanions to attack $\text{C}=\text{O}$ bond and then promote $\text{C}-\text{C}$ bond formation. Homogeneous base catalysts, such as NaOH and $\text{Ca}(\text{OH})_2$ [35–39], are generally employed to catalyze aldol condensation, but have significant disadvantages, including non-recyclability, complex separation, equipment corrosion and waste water production. To overcome these drawbacks, several heterogeneous basic catalysts were used to push aldol condensation. For example, CaO, CaAl-hydrotalcite and MgAl-hydrotalcite were considered as a promising alternative to avoid the above problems [19,27,40,41]. As we know, basic metal oxides have high sensitivity to the ambient CO_2 and face a challenge for stability in the presence of water, while aldol adducts can easily dehydrate to enone groups and produce water. Solid acid catalysts, such as TiO_2 , Hf-, Sn-, and Zr-Beta zeolites, also emerged to promote aldol condensation owing to their recyclability and water resistance [42–48]. However, the examples of using acidic materials as catalysts for

aldol condensation are still few. In addition, the hydrodeoxygenation of bio-fuel precursors is catalyzed by bifunctional metal/solid acid catalysts, so it would be promising if an excellent solid acid is found for aldol condensation, in this case, the aldol condensation and following hydrodeoxygenation can be integrated over bifunctional metal-acid catalysts and the separation can be omitted. Therefore, it is highly desirable to develop efficient solid acid catalysts to promote aldol condensation.

Nb_2O_5 is an extremely promising catalyst owing to its excellent functionality, such as water resistance, high stability, suitable acidity and $\text{C}-\text{O}$ bond cleavage ability [49–53]. Therefore, increasing attention has been paid to use Nb_2O_5 as catalyst for the catalytic upgrading of biomass to value-added transportation fuels and chemicals. These excellent properties are fully exploited in the hydrodeoxygenation of biomass and biomass-derived oxygenates. Nb-based catalysts have a unique feature, that is, NbO_x species play a key role in $\text{C}-\text{O}$ bond cleavage, especially in the cleavage of tetrahydrofuran ring, leading to the excellent performance in the hydrodeoxygenation reaction [52]. Obviously, Nb_2O_5 catalyst exhibited the superior performance in comparison with other solid acid catalysts (ZrO_2 , Al_2O_3 , TiO_2 and H-ZSM-5) [51–53].

Herein, we report that Nb_2O_5 is taken as a solid acid catalyst to catalyze aldol condensation of biomass-derived carbonyl chemicals and exhibits excellent activity and stability. Investigations on the originate of high activity reveal that Nb_2O_5 catalyst can efficiently activate $\text{C}=\text{O}$ bond of carbonyl molecules to form a metal enolate intermediate, leading to the excellent performance. We also demonstrate the scope of its application to other biomass-derived carbonyl compounds. Finally, we combine the two functions of Nb_2O_5 , namely, cleavage of $\text{C}-\text{O}$ bond which is reported before [52] and activation of $\text{C}=\text{O}$ bond, and hydrogenation function of palladium, to develop a one-pot process of the direct production of liquid alkanes from biomass-derived carbonyl molecules over a multifunctional Pd/ Nb_2O_5 catalyst.

2. Experimental

2.1. Materials

Furfural, 4-heptanone, MIBK, cyclopentanone, acetone and

Scheme 1. Aldol condensation of biomass-derived carbonyl molecules.

2,4-pentanedione were purchased from Shanghai Titan Technology Co., Ltd. $\text{Pd}(\text{NO}_3)_2$ aqueous solution was purchased from Heraeus Materials Technology Shanghai Co., Ltd. The MgO and CaO catalysts were purchased from Aladdin Industrial Inc. Before the tests, the metal oxide catalysts were pretreated in N_2 flow at 500 °C for 4 h. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Catalyst preparation

The Nb precursor (niobium oxalate) was prepared according to the literature procedure [54]. Niobium oxalate solutions with a Nb concentration of 0.4 mol L^{-1} were prepared for use. The layered Nb_2O_5 was synthesized by changing the substrates and reaction conditions following Murayama's work [55]. Typically, 19.2 g of prepared niobium oxalate and 0.711 g of ammonium oxalate were dissolved in 50 mL deionized water, and then the transparent solution was aged in a Teflon-lined autoclave for 24 h at 180 °C. After cooling down, the solid was filtered, washed with distilled water and then dried at 50 °C overnight. Finally, the Nb_2O_5 sample was obtained by calcination at 400 °C for 4 h in air with a linear heating ramp of 10 °C min^{-1} .

2% $\text{Pd}/\text{Nb}_2\text{O}_5$ catalyst was prepared by incipient wetness impregnation of $\text{L-Nb}_2\text{O}_5$ with the aqueous solution of $\text{Pd}(\text{NO}_3)_2$. After impregnation, the catalyst was dried at 100 °C for 12 h, followed by calcination in air at 400 °C for 5 h with a linear heating ramp of 2 °C min^{-1} .

Magnesium-aluminium hydrotalcite (MgAl-HT) with Mg/Al atomic ratio of 2:1 was prepared according to the literature [56]. Typically, an aqueous solution was prepared by adding 0.093 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.0465 mol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 100 g of H_2O . A second solution containing 0.219 mol NaOH and 0.0565 mol Na_2CO_3 in 100 g of H_2O was slowly added to the Mg/Al aqueous solution under constant stirring at 70 °C. Subsequently, the precipitate as obtained was aged at 70 °C for 20 h, filtered and washed with deionized water until $\text{pH} = 7$. The product was dried in an oven at 80 °C overnight and calcined in nitrogen flow at 400 °C for 8 h. The mixed oxides were rehydrated in decarbonated water at 80 °C for 3 h. Then the activated catalyst was obtained by drying under vacuum at 100 °C and denominated as MgAl-HT .

2.3. Catalytic reactions

The aldol condensation of furfural and 4-heptanone was performed in a 50 mL Teflon-lined stainless-steel autoclave. Typically, furfural (0.48 g, 5 mmol), 4-heptanone (2.28 g, 20 mmol) and catalyst (0.1 g) were transferred into the autoclave. The reactor was charged to 1 MPa N_2 pressure. The reaction was then performed at 110–140 °C under magnetic stirring for 4–7 h. The reactor was quenched in an ice-water bath to stop the reaction immediately. The liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS (Agilent 7890A-5975C) and quantitatively by GC equipped with a flame ionization detector (FID, Agilent 7890) using 2-octanone as the internal standard. Conversion of

furfural and yield of products were calculated by using the equation: furfural conversion = (moles of furfural reacted) / (moles of starting furfural) $\times 100\%$, single aldol adduct yield = (moles of single aldol adduct) / (moles of starting furfural) $\times 100\%$, double aldol adduct yield = (moles of double aldol adduct) / (moles of starting furfural / 2) $\times 100\%$. The experimental section of aldol condensation involving other molecules is the same as above process.

The one-pot conversion of furfural and 4-heptanone into branched alkanes was conducted in a 50 mL Teflon-lined stainless-steel autoclave. Furfural (0.96 g, 10 mmol), 4-heptanone (0.57 g, 5 mmol), cyclohexane (5.00 g) and 2% $\text{Pd}/\text{Nb}_2\text{O}_5$ (0.3 g) were transferred into the autoclave. The reactor was charged to 1 MPa N_2 pressure. The reaction was then performed at 130 °C under magnetic stirring for 24 h. After the aldol reaction, the reactor was purged with H_2 three times, and charged to 6 MPa H_2 pressure. The reaction was then performed at 220 °C and 6 MPa for 24 h. After the HDO reaction, the autoclave was quenched in an ice-water bath to room temperature. The liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS (Agilent 7890A-5975C) and quantitatively by GC-FID (Agilent 7890) using C_{15} chain alkane as the internal standard. Here, we employed pure straight chain alkanes (C_{12} , C_{17}) to replace targeted alkanes as standards, because pure targeted alkanes cannot be purchased or synthesized at present. The product yields were calculated by using the equation: yield = (moles of product) / (moles of starting 4-heptanone) $\times 100\%$.

2.4. Characterization

DRIFTS of acetone adsorption were collected with a NICOLET iS50 FT-IR spectrometer equipped with an MCT/A detector. Firstly, the catalysts were pretreated *in situ* in the cell in N_2 at 400 °C for 40 min and background spectra were recorded at 200, 150, 100, and 50 °C, respectively. Then acetone with N_2 was bubbled into the *in situ* cell for 40 min. Next, the cell was purged with N_2 at 35 °C for 30 min and the adsorption spectra of acetone was recorded. Finally, the temperature was increased to 70 °C and 100 °C, respectively, and the adsorption spectra of acetone were recorded with increasing the temperature.

Powder XRD patterns were recorded with a Rigaku D/max-2550VB/PC diffractometer by using $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation that was operated at 40 kV and 40 mA.

N_2 adsorption-desorption isotherms were measured at -196 °C by using a Micromeritics ASAP 2020 M sorption analyzer. The BET method was used to calculate the specific surface area.

Scanning electron microscopy (SEM) images of samples were recorded on a Nova NanoSEM 450 microscopy at 3 kV. Transmission electron microscopy (TEM) images of samples were obtained on a JEOL Model 2100F electron microscopy at 200 kV.

The actual Pd loading in the sample was detected by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer Optima 2100 DV spectrometer.

H_2 -TPR was carried out on a Micromeritics AutoChem II

2920 System in 10% H_2/He , and 0.10 g sample was loaded.

Infrared (IR) spectra of pyridine adsorption were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. The samples were pressed into self-supporting disks and placed in an IR cell attached to a closed glass-circulation system. The disk was dehydrated by heating at 400 °C for 1 h under vacuum in order to remove the physically adsorbed water. After the cell was cooled to room temperature, the IR spectrum was recorded as background. Pyridine vapor was then introduced into the cell at room temperature until equilibrium was reached, and then a second spectrum was recorded. Subsequent evacuation was performed at 100 °C for 10 min followed by spectral acquisitions. The spectra presented were obtained by subtracting the spectra recorded before and after pyridine adsorption.

NH_3 -TPD was carried out in an apparatus (PX200, Tianjin Golden Eagle Technology Co. Ltd.) equipped with a thermal conductivity detector (TCD). The samples (100 mg) were loaded into a U-shaped quartz tube. Prior to TPD measurements, the samples were pretreated in flowing N_2 (45 mL min^{-1}) for 1 h at 500 °C, and then cooled to 50 °C. NH_3 was adsorbed onto the samples by exposure to flowing 10% NH_3 in N_2 gas mixture (50 mL min^{-1}) for 45 min at 50 °C. Residual and physical adsorbed NH_3 was removed by purging the samples with flowing N_2 (45 mL min^{-1}) at 90 °C for 1 h. Desorption of NH_3 was performed by heating the samples at a rate of 10 °C min^{-1} under flowing N_2 (45 mL min^{-1}) from 90 °C to 600 °C.

Temperature-programmed desorption of carbon dioxide (CO_2 -TPD) as a probe molecule was carried out on a Micromeritics AutoChem 2920 equipped with mass spectrometry using a quadrupole spectrometer (MS OmniStar). 100 mg of the catalyst was placed in a quartz sample tube. Before TPD experiments the catalysts were outgassed at 300 °C for 90 min in a flow of helium. Subsequently, the catalysts were cooled down to 50 °C and treated under a CO_2 flow for 40 min. Weakly adsorbed CO_2 was removed by flushing with He at 50 °C for 30 min. The desorption of CO_2 was measured by heating the catalyst from 50 °C to 800 °C at a heating rate of 10 °C min^{-1} in a He flow. The desorbed products were analyzed by mass spectrometry.

3. Results and discussion

3.1. Catalyst screening

A suitable probe reaction is of significant importance for the catalyst screening of aldol condensation. Here, we employed the aldol condensation of furfural with 4-heptanone (Scheme 2) as a probe reaction to screen catalysts. 4-Heptanone is also a biomass-derived molecule and can be synthesized by the esterification-ketonization of biomass-derived *n*-butyric acid or

Scheme 2. Aldol condensation of furfural with 4-heptanone.

condensation of ABE fermentation mixture [57–59]. There are three reasons for the selection of this probe reaction. (1) The aldol condensation of furfural with biomass-derived ketones is the most common according to previous reports [3]. (2) Compared with common biomass-derived ketones, the steric hindrance of 4-heptanone is more severe, so the aldol reaction would be more challenging. In this way, the catalyst selected in this reaction can be easily used to other aldol reactions. (3) To our knowledge, there is no report on the production of branched alkanes by using 4-heptanone and furfural as precursors, so we likely provide an alternative strategy for the synthesis of branched alkanes. Generally, aldol condensation is carried out in the presence of basic catalysts. Therefore, common solid-base catalysts, such as MgO, CaO and magnesium-aluminum hydrotalcite (MgAl-HT) (the powder XRD pattern of as-synthesized MgAl-HT see Fig. S1), were tested for the aldol condensation of furfural with 4-heptanone and compared with Nb_2O_5 , a solid acid catalyst, the results are shown in Table 1. Surprisingly, Nb_2O_5 has obviously superior activity over the solid-base catalysts; the yield of aldol adducts (FH and FHF) reached 70.8% over Nb_2O_5 catalyst, it was lower than 30% over each solid-base catalyst. Given these results, we first suspected that Nb_2O_5 is an amphoteric metal oxide that may have both acidic and basic sites. It is recognized by all that Nb_2O_5 is an acid catalyst. To check whether Nb_2O_5 has basic sites or not, CO_2 -TPD was conducted and the result is presented in Fig. S2. It can be seen that there are no obvious CO_2 desorption peaks, indicating that Nb_2O_5 has no basic sites. As common Lewis acid catalysts, ZrO_2 and Al_2O_3 were also used for the aldol condensation of furfural with 4-heptanone but have relatively poor catalytic performance, and the yields of aldol adducts were only 5.5% and 29.8%, respectively. The above results show that Nb_2O_5 is an excellent catalyst for the aldol condensation of furfural with 4-heptanone. The influence of reaction conditions on the yields of the aldol products was investigated and the results (Fig. S3) show that a reaction at 130 °C for 6 h is optimal for the aldol condensation of furfural with 4-heptanone. Theoretically, the prior aldol condensation product should be a β -hydroxyketone. However, the GC result of the aldol condensation of furfural with 4-heptanone (Fig. S4) shows that the obtained products are mainly α,β -unsaturated carbonyl compounds (FH and FHF), rather than β -hydroxyketones. Driven by the conjugated structure of furan ring and C=C bond, the β -hydroxyketone can be easily converted into the stable α,β -unsaturated carbonyl compound. Besides this, it is well known that acid catalysts can promote the dehydration reac-

Table 1

Aldol condensation of furfural with 4-heptanone over various catalysts.

Catalyst	Conversion of furfural (%)	Yield (%)		
		FH	FHF	Total
CaO	30.6	17.1	0.0	17.1
MgO	19.4	5.5	0.0	5.5
MgAl-HT	41.9	28.6	0.0	28.6
Nb_2O_5	82.2	69.1	1.7	70.8
ZrO_2	16.9	5.5	0.0	5.5
Al_2O_3	35.3	29.8	0.0	29.8

Reaction conditions: 4-heptanone (2.28 g, 20 mmol), furfural (0.48 g, 5 mmol), catalyst (0.10 g), 130 °C, 4 h.

tion, leading to the conversion of β -hydroxyketones into α,β -unsaturated carbonyl compounds.

3.2. Mechanism studies

To understand the origin of the excellent activity of Nb_2O_5 catalyst, first of all, nitrogen adsorption/desorption was carried out to measure the BET surface areas of Nb_2O_5 , ZrO_2 and Al_2O_3 . Obviously, the BET surface area of Nb_2O_5 ($207 \text{ m}^2 \text{ g}^{-1}$) is close to that of Al_2O_3 ($218 \text{ m}^2 \text{ g}^{-1}$) and higher than that of ZrO_2 ($66 \text{ m}^2 \text{ g}^{-1}$), but it is inconsistent with the trend of catalytic activity. Therefore, we can conclude that the difference of the BET surface area cannot significantly affect the catalytic activity of the catalysts in the aldol condensation.

First, we guessed that the amount of acidity was responsible for the catalytic performance and therefore NH_3 -TPD was carried out to measure the amount of acid and was shown in Fig. 1. It can be seen that Al_2O_3 catalyst has markedly higher acid amount than Nb_2O_5 and ZrO_2 , but cannot follow the sequence of catalytic activity. Interestingly, it is noticed that Nb_2O_5 has a certain amount of Brønsted acid sites but ZrO_2 and Al_2O_3 have hardly any according to the result of Py-FTIR spectra (Fig. 2). The clear difference offers a possibility, that is, the excellent performance of Nb_2O_5 catalyst may be attributed to the Brønsted acid sites on the catalyst. In order to verify this, we employed Amberlyst-15 as catalyst, which is a typical Brønsted acid catalyst, to conduct the aldol condensation under the same conditions. The results showed that the conversion of furfural and the yield of aldol adducts were 50.5% and 40.6%, respectively, significantly lower than that (82.2% and 70.8%) over Nb_2O_5 catalyst, which indicated that Brønsted acid sites are not the main origin of the excellent activity of Nb_2O_5 catalyst.

For understanding the origin of high activity, DRIFTS experiments of acetone adsorption were performed (Fig. 3) to test the activation ability of Nb_2O_5 , ZrO_2 and Al_2O_3 to C=O bond. Acetone, which is a simple biomass-derived carbonyl molecule, was chosen as the probe molecule. For acetone, the peak appeared at 1736 cm^{-1} region is ascribed to the C=O stretching vibration, the band at 1213 and 1366 cm^{-1} are attributed to C–CH₃ deformation modes. After adsorption of acetone on these three catalysts for 30 min and purging with N_2 for 30 min at 35°C , a red shift in the C=O stretching vibration was observed

Fig. 1. NH_3 -TPD profiles of various catalysts.

Fig. 2. Py-FTIR spectra collected after treatment at 100°C under vacuum of various catalysts.

in all three catalysts. But, the red shift for the Nb_2O_5 catalyst (1695 cm^{-1} , Fig. 3a) is much larger than that for ZrO_2 (1703 cm^{-1} , Fig. 3b) and Al_2O_3 catalysts (1703 cm^{-1} , Fig. 3c). The red shift of the C=O bond can be interpreted as the strong adsorption of C=O bond on catalyst, leading to weakness in the strength of the C=O bond. This result indicates that Nb_2O_5 catalyst has stronger activation ability for C=O bond than ZrO_2 and Al_2O_3 , which would be the origin of the excellent activity of Nb_2O_5 catalyst. To explore the activation behavior of the C=O bond by reaction temperature, the cell was purged with N_2 at 70 and 100°C , respectively, and the adsorption spectra of acetone were recorded. It can be seen that the red shift is more severe with the increase of temperature and the red shift on Nb_2O_5 catalyst was also more evident (1681 cm^{-1}) than that of ZrO_2 (1695 cm^{-1}) and Al_2O_3 catalysts (1700 cm^{-1}). The striking difference further confirms that Nb_2O_5 has the unique ability for C=O bond activation. It is worth noting that the intensity of a new band at 1557 cm^{-1} gradually increased over Nb_2O_5 with the rise of temperature, but it did not occur on ZrO_2 and Al_2O_3 . The band at 1557 cm^{-1} can be assigned to C=C stretching vibration. There are two possibilities for the origin of C=C stretching vibration: (1) with the activation of the C=O bond, it is gradually converted into an enolate intermediate containing a C=C bond, and thus-generated enolate can undergo nucleophilic addition with another carbonyl molecule to get target product; (2) with the increasing of temperature, the self-aldol condensation of acetone could happen over Nb_2O_5 , thus-generated adduct is a typical α,β -unsaturated carbonyl compound containing a C=C bond, so the band at 1557 cm^{-1} may be interpreted as the C=C bond of the self-aldol adduct of acetone. The two possibilities are both in good consistent with the observed catalytic activity. Meanwhile, the enolate intermediate certainly exists in every case, it is merely due to poor stability of the enolate intermediate and cannot be seized by the FT-IR spectra in the second case. Overall, the DRIFTS study of acetone adsorption reveals that Nb_2O_5 catalyst has excellent activation ability for C=O bond and thus generates an enolate intermediate for aldol condensation, leading to the high activity.

3.3. Proposed reaction mechanism

Fig. 3. DRIFTS spectra of acetone adsorption on (a) Nb₂O₅, (b) ZrO₂, and (c) Al₂O₃.

Based on the DRIFTS study of acetone adsorption, we propose a possible reaction mechanism of Nb₂O₅-catalyzed aldol condensation for two carbonyl compounds, *i.e.*, carbonyl compound **1** containing active α -hydrogen atoms with carbonyl compound **2**, as shown in Scheme 3. First, the metal center of Nb₂O₅ polarizes the C=O bond of **1**, which forms a metal enolate. Subsequently, the metal enolate undergoes nucleophilic addition to C=O bond in molecule **2** and form a new C–C bond, which affords **3**. Finally, **3** can be easily converted to an enone compound **4** by the dehydration reaction in the presence of acidic Nb₂O₅.

3.4. Extension to other biomass-derived carbonyl molecules

We were interested to extend the applicability of Nb₂O₅ to other biomass-derived carbonyl molecules-involved aldol condensation. To explore the scope of the reaction, we investigated two typical aldol condensation, the cross condensation of two different carbonyl molecules and the self-condensation of the same carbonyl molecule (for a structural analysis, see Figs. S5–S11 in the Supporting Information). Firstly, the aldol condensation of furfural with biomass-derived ketones, such as acetone, methyl isobutyl ketone (MIBK) and 2,4-pentanedione, were carried out over Nb₂O₅ catalyst under the same conditions as the probe reaction system and the results are summarized in Scheme S1. It was found that a high yield of aldol adducts was obtained in the acetone system and 2,4-pentanedione system. However, in the MIBK system, the yield (60.2%) of aldol adducts is medium, indicating steric hindrance of MIBK could be more obvious than acetone and 2,4-pentanedione. Clearly, the α -H of 2,4-pentanedione is more active than that of MIBK owing to the presence of two electron withdrawing groups in 2,4-pentanedione, which is a

Scheme 3. Proposed reaction mechanism for the aldol condensation of biomass-derived carbonyl molecules over Nb₂O₅ catalyst.

possible factor that higher yield of aldol adducts was obtained in the 2,4-pentanedione system. We tried to increase reaction time to improve the yield of aldol adducts and the results (Scheme 4) show that extending the reaction time from 4 h to 12 h significantly increased the yield of the aldol adducts of furfural with MIBK (from 60.2% to 81.7%). In addition, the self-aldol condensation of cyclopentanone over Nb₂O₅ catalyst was carried out and the result showed that a moderate yield of the aldol adducts was obtained. Inspired by the MIBK system, we extended reaction time to 12 h and achieved a high yield (87.0%) of aldol adducts (Scheme 4). The above results fully demonstrate that Nb₂O₅ is an efficient catalyst for biomass-related aldol reactions.

3.5. Recyclability test of Nb₂O₅

The recyclability of the Nb₂O₅ catalyst for the aldol condensation of 4-heptanone with furfural was investigated by reusing the catalyst in consecutive catalytic runs. After reaction, the color change of the catalyst from original white to canary yellow was observed, and the conversion of furfural and the yield of aldol adducts decreased from 55.0% to 20.3% and from 48.9% to 17.9%, respectively. To discover the reason for this catalyst deactivation, thermogravimetric analysis (TG) was performed to characterize the deactivated catalyst. The result

Scheme 4. Results of aldol condensation of other biomass-derived carbonyl molecules over Nb₂O₅.

(Fig. S12) showed that ca. 12% carbon was deposited on the deactivated catalyst, which was ascribed to polymerization of the reactants and/or products in the presence of acid catalyst [7,40]. After calcination at 400 °C for 1 h, the catalyst was re-generated and then recharged for the next run. It can be seen from Fig. 4 that no obvious change was found in the catalytic activity (58.6% conversion and 50.4% yield). Re-measurement of XRD pattern (Fig. S13) shows that there was no phase change after reaction, and N₂ sorption shows that the surface area was still high (170 m² g⁻¹). The above result clearly demonstrates the excellent reusability of Nb₂O₅ catalyst for aldol condensation.

3.6. One-pot process

Previously, our group demonstrated that metal-supported Nb-based catalysts, such as Pd/NbOPO₄, Pt/NbOPO₄, Pd/Nb₂O₅ and Pd/Nb₂O₅/SiO₂, are excellent catalysts for the total hydrodeoxygenation of biomass and biomass-derived oxygenates [48–53,60]. This is because of the abilities of noble metals for H₂ activation and dissociation, NbO_x species for C–O bond cleavage and acid sites on support for dehydration. Given this and the above results, we speculated that a one-pot process for the direct production of liquid alkanes from biomass-derived carbonyl molecules would be possible over a multifunctional metal-supported Nb₂O₅ by combining the aldol condensation with the following total hydrodeoxygenation. Therefore, we draw an experimental scheme to realize one-pot process by using Pd/Nb₂O₅ as catalyst and the detailed process is presented in the experimental section. The details of the Pd/Nb₂O₅ catalyst characterization are provided in the Supporting Information. A key in the one-pot two-step process is to change the reaction atmosphere, as the aldol condensation and the following HDO should be conducted in the atmosphere of nitrogen (as a shielding gas) and hydrogen (as a reactant gas), respectively. Firstly, furfural, 4-heptanone, cyclohexane and 2%Pd/Nb₂O₅ were transferred into the autoclave to conduct aldol condensation. The reactor was charged to 1 MPa N₂ pressure as a shielding gas. After the aldol reaction, the reactor charged to 6 MPa H₂ pressure to perform the following HDO reaction. After

Fig. 4. Recyclability test of Nb₂O₅ for aldol condensation. Reaction conditions: furfural (0.48 g), 4-Heptanone (2.28 g), Nb₂O₅ (0.1 g), 110 °C, 4 h.

the HDO reaction, the liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS and quantitatively by GC. After the one-pot two-step process, no oxygen-containing products were observed in the reaction effluent. The yield of alkanes is shown in Fig. 5. As expected, the yield of C_{12–17} alkanes reached up to 61.7%, starting from 4-heptanone and furfural. A small amount of C–C cleavage product (C₁₀ alkane) was generated by the hydrocracking of the branched C₂ alkyl groups because the hydrocracking is easier at the branched carbon atom [11]. In addition, C₇ alkanes were produced owing to incomplete reaction of 4-heptanone. The condensation product yield was 66.4% after the first step. Compare for the total yield (61.7%) of one-pot process, the above result indicates that the aldol condensation is the rate-determine step and the following hydrodeoxygenation is easy to implement, which is consistent with our previous results [48,49]. In short, the total yield of C_{10–17} alkanes reached up to 62.5% in the one-pot process. The above results integrating the aldol condensation with the total HDO over Pd/Nb₂O₅ are of interest to save considerable energy consumption and time required for intermediate separation processes, which might be an extremely promising reaction system for the industrial-scale production of liquid alkanes from biomass-derived carbonyl molecules.

Based on the above results and previous reports [51,52], Pd/Nb₂O₅ as a multifunctional catalyst plays four roles in the conversion of biomass-derived carbonyl molecules into liquid alkanes: (1) Nb₂O₅ helps to activate C=O bond of carbonyl molecules to promote aldol condensation; (2) the metal is used for H₂ activation and dissociation; (3) NbO_x species promote C–O bond cleavage; and (4) the niobium-based solid acid catalyzes the dehydration.

4. Conclusions

We have presented the exceptional activity and reusability of Nb₂O₅ catalyst for the aldol condensation of biomass-derived carbonyl compounds. Among the investigated catalysts (CaO, MgO, MgAl-HT, ZrO₂, Al₂O₃ and Nb₂O₅), Nb₂O₅ showed superior

Fig. 5. Alkanes yield obtained from the one-pot conversion of furfural and 4-heptanone over Pd/Nb₂O₅. Reaction conditions: 4-heptanone (0.57 g, 5 mmol), furfural (0.96 g, 10 mmol), cyclohexane (5.00 g), 2% Pd/Nb₂O₅ (0.3 g), 130 °C, 24 h, 1 MPa N₂ for aldol condensation; 220 °C, 24 h, 6 MPa H₂ for HDO reaction.

activity for the aldol condensation of furfural with 4-heptanone. The yield of aldol adducts over Nb_2O_5 catalyst reached about 70%, while it was lower than 30% over other catalysts. The superior activity of Nb_2O_5 catalyst for aldol condensation is found to originate from its excellent activation ability for $\text{C}=\text{O}$ bond, which plays an important role in forming a metal enolate intermediate and leading to the high performance. Meanwhile, other biomass-related aldol reactions can be efficiently conducted to produce a series of fuel precursors over Nb_2O_5 catalyst. Considering that Nb-based catalysts could effectively promote the $\text{C}-\text{O}$ bond cleavage, we provide a procedure for performing the aldol condensation and the total hydrodeoxygenation in one-pot over multifunctional $\text{Pd}/\text{Nb}_2\text{O}_5$ catalyst. This work not only provides a highly efficient catalyst for known aldol condensation, but also promotes energy-saving conversion of biomass-derived carbonyl compounds into transportation fuels.

Notes

The authors declare no competing financial interest.

Acknowledgments

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Graphical Abstract

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Highly efficient Nb_2O_5 catalyst for aldol condensation of biomass-derived carbonyl molecules to fuel precursors

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We demonstrated the exceptional activity of Nb_2O_5 catalyst for aldol condensation and provided the originate of high activity.

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氧化铈高效催化生物质衍生物的羟醛缩合反应制备燃料前驱体

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摘要: 生物质是自然界唯一可再生的有机碳来源, 其催化转化制备燃料和精细化学品受到广泛关注. 一般从生物质衍生的小分子出发制备航空煤油和柴油等高碳数燃料包括两步: 首先通过碳链增长反应如羟醛缩合和烷基化等制备目标链结构的燃料前驱体, 然后对所得燃料前驱体进行完全脱氧加氢得到燃料组分. 在目前报道的碳链增长反应中, 羟醛缩合反应应用最多, 因为生物质衍生的羰基化合物众多, 而且丙酮、糠醛及环己酮等羰基化合物已经实现了工业化生产. 羟醛缩合反应的催化剂以碱性材料为主, 但是碱性催化剂具有不抗二氧化碳、不抗水等缺点, 因此开发高活性的固体酸催化剂至关重要.

本文选择糠醛和4-庚酮的羟醛缩合反应作为模型反应, 发现氧化铈材料对该反应具有优异的催化活性, 活性明显高于常见的氧化钙、氧化镁、镁铝水滑石等固体碱和氧化铝、氧化锆等固体酸. 并采用N₂吸附-脱附、二氧化碳程序升温脱附(CO-TPD)、吡啶吸附红外光谱(Py-FTIR)、程序升温氨脱附(NH₃-TPD)和丙酮的原位吸附傅立叶变换红外光谱等表征手段

研究了氧化铝, 氧化锆和氧化铌催化性能差异的原因. 结果表明, 这三种催化剂的比表面积和酸性质与反应活性没有明显关联. 为了解释反应活性的差异, 我们采用丙酮原位吸附红外光谱探究了这三种催化剂对羰基的活化. 发现相比于氧化铝和氧化锆催化剂, 氧化铌对丙酮的C=O双键有更强的活化能力, 使C=O双键结构更容易转化为烯醇式结构, 进而促进羟醛缩合反应的进行. 基于此, 我们提出了氧化铌催化羟醛缩合的反应机理. 另外, 底物拓展实验发现, 在其他生物质相关的羟醛缩合反应体系中, 氧化铌催化依旧可以得到可观的收率. 循环套用实验表明, 由于积碳导致催化剂失活, 通过简单的煅烧即可恢复活性.

我们之前的研究发现负载金属的铌基催化剂具有很好的断裂呋喃环上碳氧键的能力, 是很好的脱氧加氢催化剂. 基于以上研究和我们之前的结论, 我们设计并制备了多功能的Pd/Nb₂O₅催化剂, 对该催化剂进行了结构表征, 并对羟醛缩合和脱氧加氢过程进行了设计整合, 一锅实现了羟醛缩合和后续的脱氧加氢.

关键词: 羟醛缩合; 氧化铌; C=O活化; 燃料前驱体; 生物燃料; 一锅过程

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