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One-pot synthesis of 2-alkyl cycloketones on bifunctional Pd/ZrO₂ catalyst

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ABSTRACT

2-Alkyl cycloketones are essential chemicals and intermediates for synthetic perfumes and pesticides, which are conventionally produced by multistep process including aldol condensation, separation and hydrogenation. In present work, a batch one-pot cascade approach using aldehydes and cycloketones as the raw materials, and a bifunctional Pd/ZrO₂ catalyst was developed for the synthesis of 2-alkyl cycloketones, e.g., cyclohexanone and cycloheptanone. Very high aldehydes (except for paraldehyde with large steric hindrance) conversion and high yields for 2-alkyl cycloketones (e.g., 99 % of conversion for n-butanal and 76 wt.% of yield for 2-butyl cyclohexanone) were obtained at mild temperature of 140 °C. After 10 cycles of reuse, Pd/ZrO₂ catalyst showed slight deactivation (ca. 5 % conversion and 10 % yield losses), due to the coke on the catalyst. However, the performance of the catalyst was completely recovered after an oxidative regeneration.

1. Introduction

Heterogeneous catalysis has several advantages compared to homogenous catalysis in terms of product separation, catalyst recycle, equipment corrosion, and environment pollution, etc [1,2]. It is attractive to develop novel heterogeneous processes and catalysts for chemicals traditionally produced through homogenous processes. Besides, the application of multifunctional catalysts makes it possible to integrate those sophisticated multistep reactions into one-pot cascade processes, which eliminates intermediates separation and other tedious operations [3–6]. Although it is difficult to optimize efficient multifunctional groups that selectively or cooperatively work at specific steps onto single catalyst, as so far, fruitful one-pot processes have been developed in bulk chemistry, fine chemistry and biochemistry [4,7–10].

Aldol condensation is a fundamental pathway for C = C bond formation, which conventionally applies liquid acid-base catalysts. Recently, attentions have been drawn by using heterogeneous catalysts, such as solid alkali hydroxide, carbonates, metal oxides, metal-organic framework and supported KF [11–15]. Unsaturated C = C hydrogenation is also an important reaction in petrochemistry and fine chemistry, which is mainly catalyzed by e.g., Pd, Pt, Ru, and Ni supported catalysts [16,17]. One-pot process cascading aldol condensation and hydrogenation have been applied to synthesize methyl isobutyl ketone (MIBK)

[4,18–20], 2-heptyl cyclopentanone [21] and biofuel [22–24]. In these processes, ZrO₂, Al₂O₃, aluminum silicates, and zeolites are the most popular supports due to their suitable acid-base property for aldol condensation and interaction with noble metals for hydrogenation [19, 25–27].

2-Alkyl cycloketones are essential products or intermediates for synthetic perfumes and pesticides, which are traditionally produced through multistep method including aldol condensation, separation and hydrogenation. For example, 2-Butylcyclohexanone (2BCH) is the essential intermediate for synthesis of 5(6)-decenoic acid, a widely used milk-like spice in cream, yogurt, strawberry, etc., through the successive Baeyer-Villiger oxidation, saponification and dehydration (Route I, Scheme 1) [28,29]. Aldol condensation between n-butanal and cyclohexanone is firstly catalyzed by NaOH aqueous. After acidification, extraction, and distillation, the separated 2-butenylcyclohexone (2BCH⁺) is sequentially hydrogenated by Pd/C catalyst to produce 2BCH. The disadvantages of this process, such as vast wastewater emission (about 15 tons wastewater per ton of 2BCH), severe equipment corrosion, sophisticated operation, and low conversion and yield, have afflicted enterprises for a long time. Therefore, the development of green and simplified synthesis of 2BCH, e.g., by using the one-pot heterogeneous system, is necessary.

Herein, a bifunctional heterogeneous Pd/ZrO₂ catalyst was prepared

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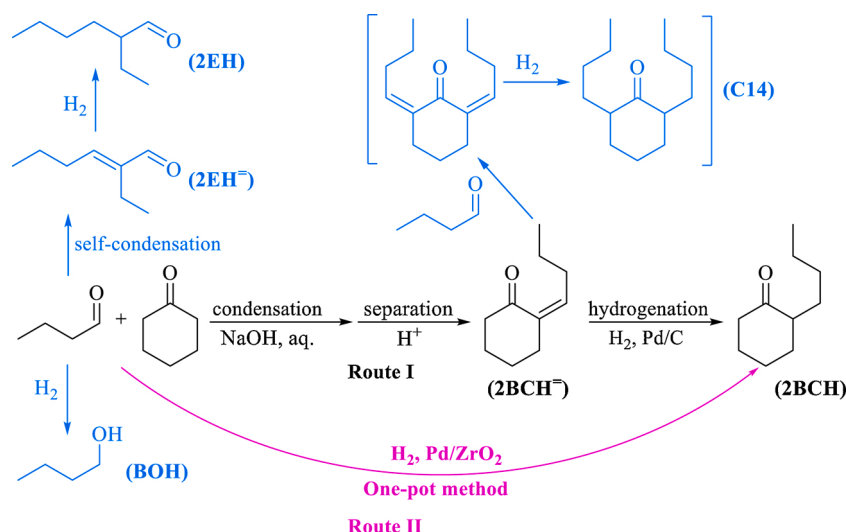
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Scheme 1. The conventional homogeneous (**Route I, black**) and the one-pot cascade heterogeneous (**Route II, magenta**) synthesis for 2BCH and the side reactions (**blue**).

and applied for 2BCH synthesis through one-pot cascade process (Route II, Scheme 1), where ZrO₂ provided acid-base sites for aldol condensation and Pd was active for C = C hydrogenation. The synergistic effect between ZrO₂ and Pd was investigated. Furthermore, the established process and catalyst were extended to synthesis of other 2-alkyl cycloketone homologs and isomers.

2. Experiments

2.1. Materials

Hexachloroplatinic acid hexahydrate (H₂PtCl₆(H₂O)₆, 37.5 wt.% Pt), nickel chloride hexahydrate (NiCl₂(H₂O)₆), ruthenium chloride (RuCl₃(H₂O)_x, 37 wt.% Ru), and palladium chloride (PdCl₂, 58 wt.% Pd) were used as metal precursors. γ -Al₂O₃ and ZrO₂ were obtained from commercial pseudoboehmite and zirconium hydroxide by calcination at 600 °C for 4 h. Aluminium silicate, magnesium oxide (MgO), ceria (CeO₂), zinc oxide (ZnO), calcia (CaO), titanium oxide (TiO₂) and all organic reagents were purchased from Macklin Co., Ltd., which are analytical grade and used without any treatment.

2.2. Preparation of catalysts

Pd based catalysts were prepared via a wet impregnation method. Typically, 10 g powdered carrier was dispersed in 25 mL aqueous solution of stoichiometric PdCl₂ and stirred at room temperature for 3 h, followed by filtration and washing with deionized water for three times. xPd/Y catalysts were obtained after drying at 80 °C overnight and calcination at 450 °C for 4 h, where x refers to the weight percentage (wt.%) of Pd and Y represents the carrier. Besides, another three ZrO₂ supported catalysts containing 0.2 wt.% of Pt, 0.2 wt.% of Ru, and 5.0 wt.% of Ni were also prepared by following the above procedure and using the corresponding metal salts.

2.3. Characterizations

Powder X-ray diffraction (PXRD) was recorded on PANalytical X'Pert PRO X-ray diffractometer with Cu K α radiation (40 kV and 40 mA).

Transmission electron microscopy (TEM) images were taken on JEOL JEM-2100 microscopy at an accelerating voltage of 200 kV equipped with an energy dispersive X-ray (EDX) detector.

Thermogravimetric analyses (TGA) were performed on Netzsch STA 449 F3 at a heating rate of 10 °C min⁻¹ in air.

The contents of Pd in the catalysts were measured by inductively coupled plasma mass spectrometry (ICP-MS) on PerkinElmer NexION 300D apparatus under the Kinetic Energy Discrimination mode (KED).

¹H and ¹³C NMR spectras of 2BCH isolated by vacuum distillation and dissolved in CDCl₃ solution were analyzed on 400 MHz Bruker Avance III.

N₂ physisorption was obtained at 77 K on Quantachrome Quadrasorb SI. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure (P/P₀) of ca. 0.98.

CO₂ or NH₃ temperature programmed desorption (CO₂/NH₃-TPD) was measured on Micromeritics AutoChem 2910 with mass spectrometry detector. Catalysts were saturated by 100 % CO₂ or 10 vol% NH₃/He (at 50 °C and 100 °C, respectively) and desorbed at a heating rate of 10 °C min⁻¹.

The H₂ temperature programmed reduction (H₂-TPR) was measured on a Finesorb-3010 under the condition of 10 vol% H₂ balanced with Ar.

2.4. One-pot synthesis of 2-alkyl cycloketones from aldehydes and cycloketones

Take 2BCH as example, 18 g (0.25 mol) n-butanal, 54 g (0.55 mol) cyclohexanone, and 3.7 g catalysts were added into a 250 mL autoclave. Oxygen in autoclave was displaced thrice by 0.2 MPa N₂ and 0.5 MPa H₂ in sequence. Then, 3.5 MPa H₂ was charged into the autoclave at room temperature. The reaction was carried out at 140 °C for 400 min under stirring at 400 rpm followed by cooling to room temperature naturally. The other 2-alkyl cycloketones were synthesized with the same cycloketone/aldehyde molar ratio.

For comparison, 2BCH⁻ was also synthesized by conventional homogeneous method. Briefly, 60 mL 1 wt.% NaOH aqueous and 24 g of cyclohexanone were added into a 250 mL flask at room temperature. Then, 8 g n-butanal was slowly dropped into the flask during 10 min under violent stirring. After stirring for another 1.5 h and settling for 12 h, the organic phase was obtained by separation, extraction with ethyl acetate, and drying with anhydrous sodium sulfate.

The liquid products were filtrated and analyzed on Agilent 7890A gas chromatograph (GC) equipped with HP-5 ms ((5%-phenyl)-methylpolysiloxane, 30 m) capillary column, flame ionization detector (FID), and mass spectrometry detector (MS).

n-Butanal conversion (X), products selectivities (S_i) and 2BCH yields (Y_i) were calculated as follows:

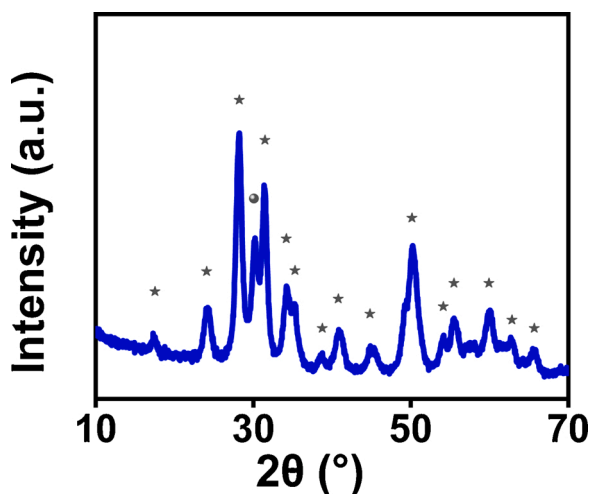


Fig. 1. XRD patterns of fresh 0.2Pd/ZrO₂ catalyst.

$$X_{n\text{-butanal}}(\%) = \frac{n_{n\text{-butanal}}^i - n_{n\text{-butanal}}^f}{n_{n\text{-butanal}}^i} \times 100\%$$

$$S_i(\%) = \frac{x \cdot n_i}{n_{n\text{-butanal}}^i - n_{n\text{-butanal}}^f} \times 100\%$$

$$Y_i(\%) = \frac{X_{n\text{-butanal}} \times S_i}{100}$$

Where $n_{n\text{-butanal}}^i$ and $n_{n\text{-butanal}}^f$ are the initial and final contents of n-butanol, respectively; n_i is the final molar quantity of product i and x refers to the number of n-butanol molecules needed for yielding one i molecule.

3. Results and discussion

3.1. Performance of Pd/ZrO₂

The actual Pd loading of 0.2Pd/ZrO₂ determined by ICP-MS was 0.216%, which was very close to the theoretical value. The XRD pattern of fresh 0.2Pd/ZrO₂ catalyst was displayed in Fig. 1, which showed primary diffraction peaks of monoclinic ZrO₂ at $2\theta = 28.2^\circ$, 31.4° and 50.1° [30] as well as a weak diffraction peak of tetragonal ZrO₂ at $2\theta = 30.3^\circ$ [31]. No diffraction peaks of Pd or PdO were observed due to the relatively low Pd content. TEM images of 0.2Pd/ZrO₂ catalyst (Fig. 2) showed no visible Pd nanoparticle or cluster. These results indicated that Pd species were highly dispersed on ZrO₂, which was probably due to the strong metal-support interaction (SMSI) between Pd and ZrO₂ [32]. As reported [33,34], highly dispersed Pd species are highly selective and active for C = C hydrogenation.

The reducibility of Pd/ZrO₂ was measured by H₂-TPR and shown in

Fig. 3. Two H₂-consumption peaks were observed at 123°C and 249°C, respectively. The former was ascribed to PdO and the latter was attributed to Pd species of Pd-O-Zr, which evidenced the existence of SMSI on Pd/ZrO₂ [35].

0.2Pd/ZrO₂ catalyst was applied to synthesize 2BCH through a one-pot method, where ZrO₂ provided suitable acid-base sites for

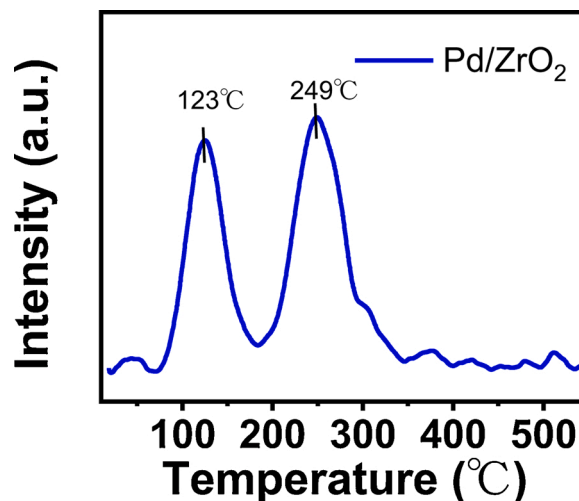


Fig. 3. H₂-TPR curve of 0.2Pd/ZrO₂.

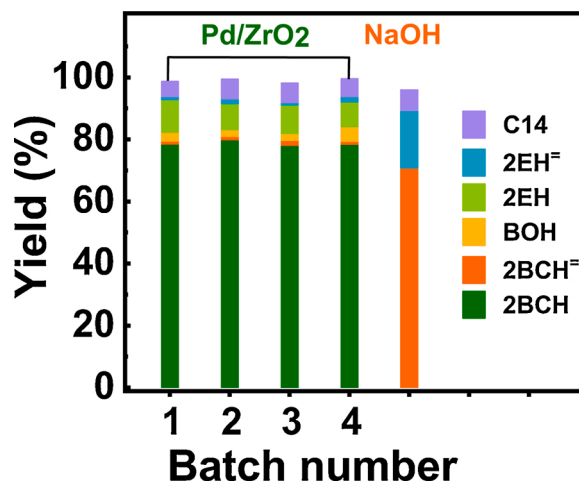


Fig. 4. Product distributions for one-pot (Pd/ZrO₂) and homogenous (NaOH) syntheses. Repeated results for 2-butyl cyclohexanone synthesis via one-pot cascade approach over 0.2Pd/ZrO₂ catalyst of different batch. Conditions: 0.25 mol n-butanol, 0.55 mol cyclohexanone, 3.7 g 0.2 wt.%Pd/ZrO₂, 3.5 MPa H₂, reaction temperature of 140 °C, reaction time of 400 min.

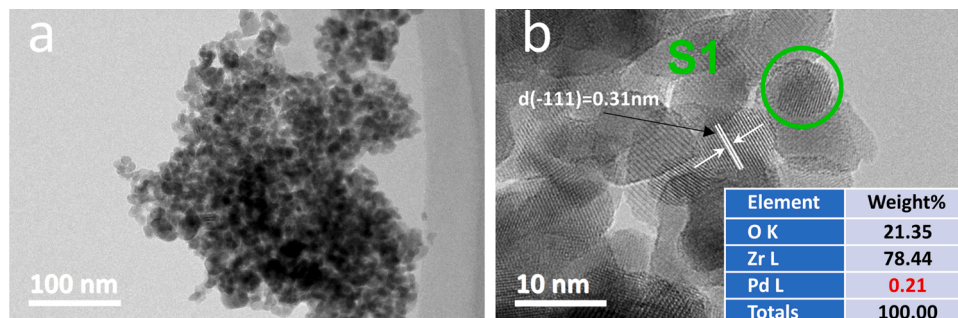


Fig. 2. TEM images and EDX results (at S1 sites) of fresh 0.2Pd/ZrO₂ catalyst.

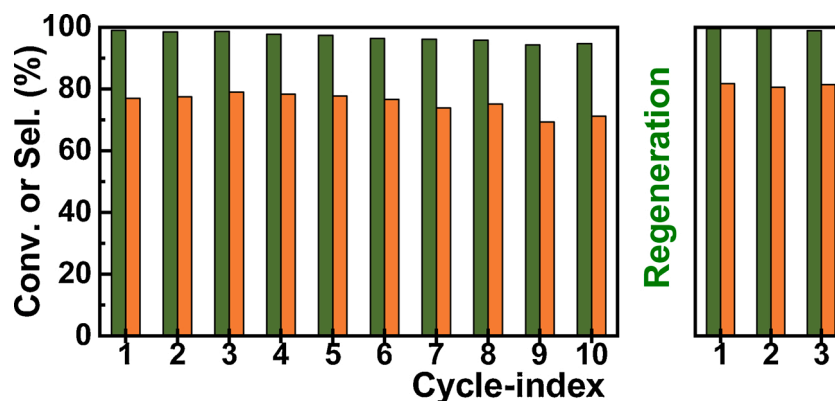


Fig. 5. Stability and regeneration of Pd/ZrO₂ (green: n-butanol conversion, orange: 2BCH selectivity). Conditions: 0.25 mol n-butanol, 0.55 mol cyclohexanone, 3.7 g 0.2 wt.%Pd/ZrO₂, 3.5 MPa H₂, reaction temperature of 140 °C, reaction time of 400 min (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

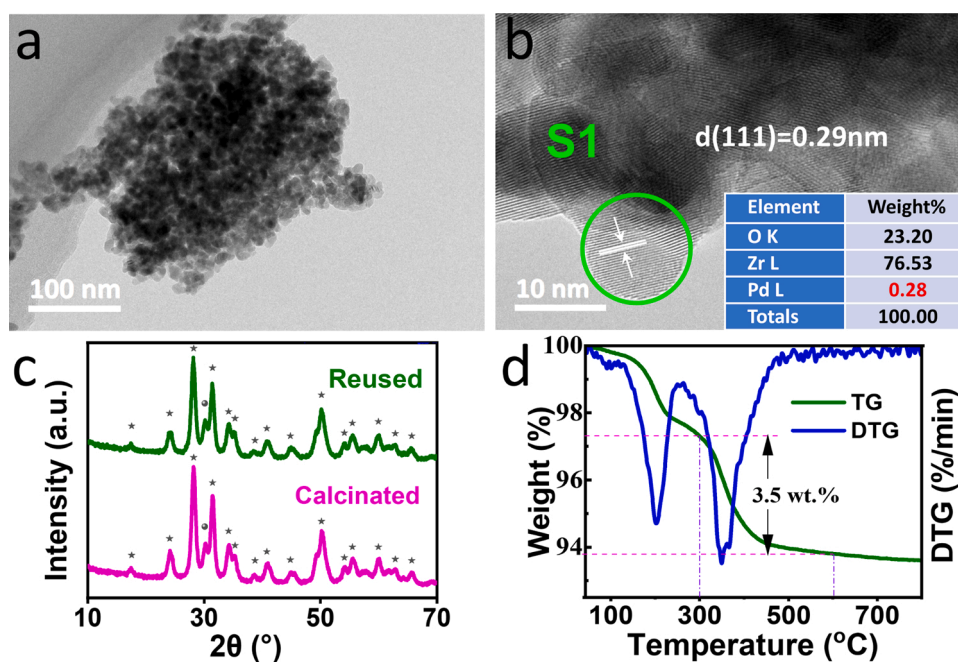


Fig. 6. TEM images and EDX results (at S1 sites) (a and b), XRD (c) and TG-DTG curves (d) of spent 0.2Pd/ZrO₂ catalyst after 10 cycles.

condensation and Pd was responsible for selective hydrogenation of as-formed C = C bond. Experiment was repeated four times (Fig. 4), which showed excellent repeatability. As shown in Fig. 4, 99 % of n-butanol conversion and 76 % of 2BCH yield were achieved under reaction temperature of 140 °C and catalyst dose (the weight ratio of catalyst to total feeding of organics) of 5 wt.%. Trace amount (< 2%) of 2BCH[−] still existed, which was not completely hydrogenated. Side reactions, such as n-butanol hydrogenation to 1-butanol (BOH), self-condensation of n-butanol to 2-ethylhexaldehyde (2EH) and 2-ethylhexenal (2EH[−]), and further condensation to 2,6-dibutyl/dibutenyl cyclohexanone (C₁₄) were inevitable. However, they were dramatically suppressed in the one-pot synthesis. In comparison, conventional multistep method (labeled as NaOH in Fig. 4) gave n-butanol conversion of 95 % and 2BCH[−] yield of 68 %. So, the yield of 2BCH through further hydrogenation of the latter by Pd/C would be even lower, which was thus considerably lower than that obtained from the one-pot cascade method in present study.

3.2. Stability and regeneration of Pd/ZrO₂

Stability of 0.2Pd/ZrO₂ catalyst was studied by a 10 times of reuse experiment. After each reuse, the used 0.2Pd/ZrO₂ catalyst was separated by sedimentation only and reused without any treatment. As shown in Fig. 5, in the first six reuses, the catalyst showed benign stability with negligible decay of n-butanol conversion and 2BCH yield. Afterward, a slight deactivation occurred, leading to 95 % of n-butanol conversion and 67 % of 2BCH yield after 10 times of reuse.

The TEM images (Fig. 6a and b) of deactivated catalyst showed that Pd species were not aggregated, which indicated the good stability of 0.2Pd/ZrO₂ catalyst. XRD pattern of the used catalyst (Fig. 6c) indicated that the crystallization of the catalyst was well kept. The Pd content of deactivated catalyst measured by ICP-MS was 0.204 %, which was comparable to fresh catalyst (0.216 %) by taking experimental error in consideration. All above results indicated the good structural stability of 0.2Pd/ZrO₂ catalyst. Therefore, the deactivation of 0.2Pd/ZrO₂ was most likely related to the Pd coverage by organic impurities rather than the intrinsic structure change of the catalyst [36]. This speculation is evidenced by TG analysis (Fig. 6d), showing that 3.5 wt.% of coke was

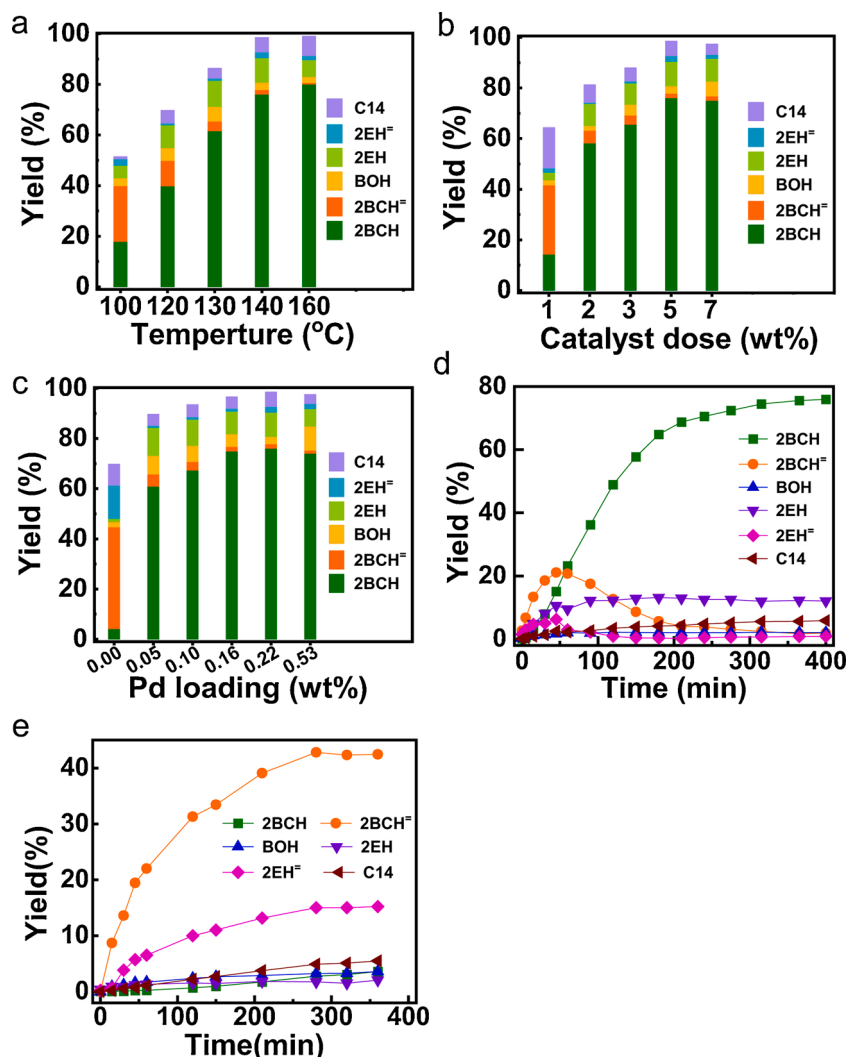


Fig. 7. Product yields over Pd/ZrO₂ with respect to reaction temperature (a), catalyst dose (b), Pd loading (c), reaction time (d) and product yields over pure ZrO₂ versus reaction time (e).

formed on the used catalyst. Notably, the soft coke could be removed by an oxidative regeneration at a low temperature of ca. 450 °C.

The deactivated 0.2Pd/ZrO₂ catalyst was then regenerated at 450 °C in air for 4 h. After the removal of coke, the activity of Pd/ZrO₂ was completely recovered [37], showing an excellent regenerability of this heterogeneous catalyst. The good stability and excellent regenerability of Pd/ZrO₂ catalyst would lower the cost of one-pot cascade process, even though more reaction-regeneration cycles are still needed to be considered.

3.3. Optimizations of reaction conditions

The temperature dependence results (Fig. 7a) showed that n-butanol conversion and 2BCH yield were positively related to the reaction temperature. At stage of temperature from 100 °C to 140 °C, n-butanol conversion and 2BCH yield were almost linearly increased with the reaction temperature. When reaction temperature reached 140 °C, n-butanol was nearly completely (> 99 %) converted. Further increasing temperature to 160 °C made little change for n-butanol conversion, while a slightly increased 2BCH yield (from 76 % to 80 %) was obtained. However, higher reaction temperature could lead to higher energy consumption and severer equipment requirement.

The effect of catalyst dosage was also investigated and displayed in Fig. 7b. In the case of 1% catalyst dosage, n-butanol conversion and

2BCH yield were relatively low (64 % and 14 %, respectively) due to the deficient active sites for both condensation and hydrogenation processes. The high amount of 2BCH⁻ suggested that Pd sites were inadequate. By increasing catalyst dosage, both n-butanol conversion and 2BCH selectivity were improved, accompanied with the dramatically decreased 2BCH⁻. n-Butanol conversion and 2BCH yield were linearly increased with catalyst dosage from 2% to 5%. Further increasing catalyst dosage made negligible change for 2BCH yield.

The effect of Pd loading on catalytic activity was further investigated and showed in Fig. 7c. Over the ZrO₂ carrier without loading Pd, 70 % of n-butanol was converted. However, 2BCH yield is only 4%. Instead, 2BCH⁻ showed a very high yield of 41 %. These results indicated that ZrO₂ was mainly responsible for aldol condensation but not active for hydrogenation. Interestingly, by loading trace amount (0.05 wt.%) of Pd on ZrO₂, the 2BCH yield remarkably rose to 61 %, along with an increased n-butanol conversion to 90 % and a significantly decreased 2BCH⁻ yield to 5%. With loading more Pd, e.g., 0.05–0.2 wt.%, n-butanol conversion and 2BCH yield rised proportionally. However, excess Pd loading (0.53 wt.%) improved the side reaction, e.g., self-hydrogenation of n-butanol to 1-Butanol (BOH, Scheme 1), leading to a slight decrease of 2BCH yield.

Product distribution with respect to reaction time on Pd/ZrO₂ catalyst and ZrO₂ carrier were studied (Fig. 7d and e). As shown in Fig. 7d, during the first 50 min, the condensation on Pd/ZrO₂ was very fast due

Table 1
reaction results of catalysts with varied active metals and supports.

Entry	Catalysts	$S_{\text{BET}}/$ $\text{m}^2 \text{g}^{-1}$	$V_t/\text{mL g}^{-1}$	Conv. /% n-butanol	Yield/%					
					2BCH	2BCH ⁻	BOH	2 EH	2 EH ⁻	C14
1	Pt/ZrO ₂	37	0.15	97	36	23	8	1	10	17
2	Ru/ZrO ₂	25	0.13	98	16	43	9	1	6	20
3	Ni/ZrO ₂	32	0.14	99	8	46	1	1	5	33
4	Pd/Al ₂ O ₃	160	0.66	97	55	2	18	16	1	4
5	Pd/MgO	203	0.59	97	50	4	13	16	0	12
6	Pd/CaO	8	0.04	100	52	3	26	2	1	8
7	Pd/ZnO	4	0.01	100	10	1	80	1	0	2
8	Pd/TiO ₂	8	0.05	86	55	2	4	14	6	4
9	Pd/CeO ₂	2	0.01	87	52	12	5	6	0	11
10	Pd/Al ₂ SiO ₅	52	0.23	49	14	14	7	8	0	5

Conditions: 0.25 mol n-butanol, 0.55 mol cyclohexanone, 3.7 g catalyst (0.2 wt.% metal loading), 3.5 MPa H₂, reaction temperature of 140 °C, reaction time of 400 min. ^a The active metal content is 5 wt.%.

Table 2
NH₃ and CO₂ TPD results.

Catalysts	NH ₃ (TPD)		CO ₂ (TPD)	
	Top peak (°C)	NH ₃ uptake (μmol/g)	Top peak (°C)	CO ₂ uptake (μmol/g)
Pd/ZrO ₂	212.7	296.3	79.5	20.2
Pd/Al ₂ O ₃	178.2	674.4	94.1	31.7
Pd/Al ₂ SiO ₅	150.4	675.7	94.0	4.8
Pd/MgO	n.d.	n.d.	120.5	31.8

to the high concentration of n-butanol and cyclohexanone, resulting in rapid increase of 2BCH⁻ yield, while the formation of 2BCH was hysteretic. With the proceeding of reaction, the concentration of n-butanol decreased along with the accumulation of 2BCH⁻, the reaction rate of hydrogenation became higher than that of condensation. Thereafter, the yield of 2BCH⁻ gradually decreased to a relatively low level. Similar trend was also observed for 2 EH and 2 EH⁻ although their total yields were much lower than 2BCH⁻ and 2BCH. On the contrary, yields of unsaturated 2BCH⁻ and 2 EH⁻ increased steadily on pure ZrO₂ in the first 300 min and then keep unchanged (Fig. 7e). In this case, the final yield of 2BCH⁻ (42 %) was twice as the highest value on Pd/ZrO₂ but still was lower than the 2BCH yield. Therefore, compared with multistep approach, the one-pot cascade process improved the yield of 2BCH,

Table 3
One-pot synthesis of 2-alkyl cycloketones from cycloketone and aldehyde.

Entry	ketone	R of 2	Conv. ^[a] /%	Yield ^[a] of 3a or 3b/%
1	1a	i-C ₃ H ₇ -	92	76
2		n-C ₄ H ₉ -	99	84
3		tert-C ₄ H ₉	10	<1
4		n-C ₅ H ₁₁ -	99	84
5		n-C ₆ H ₁₃ -	99	86
6		n-C ₇ H ₁₅ -	99	88
7		n-C ₈ H ₁₇ -	98	87
8		i-C ₃ H ₇ -	84	65
9		n-C ₄ H ₉ -	98	70
10		tert-C ₄ H ₉	29	1
11		n-C ₅ H ₁₁ -	95	75
12		n-C ₆ H ₁₃ -	96	71
13		n-C ₇ H ₁₅ -	96	74
14		n-C ₈ H ₁₇ -	97	76

Conditions: 0.25 mol aldehyde, 0.55 mol ketone, 3.7 g 0.2 wt.%Pd/ZrO₂, 3.5 MPa H₂, reaction temperature of 140 °C, reaction time of 400 min. ^[a] Conversion and yield were calculated by area normalization method of GC. 2-alkyl cycloketones were determined by the molecular ion peak detected by GC-MS.

which was atomic economic.

3.4. Effects of active metals and supports

Pt, Ru and Ni, the commonly-used metals for hydrogenation, were also loaded on ZrO₂ carrier for this study (Entry 1–3 in Table 1). Pt/ZrO₂, Ru/ZrO₂ and Ni/ZrO₂ catalysts showed excellent n-butanol conversion (> 97 %). However, the yield of 2BCH over these catalysts are much lower than that over Pd/ZrO₂. Products distributions show that large amount of 2BCH⁻ are produced on Pt/ZrO₂, Ru/ZrO₂ and Ni/ZrO₂, related to the insufficient C = C hydrogenation. Notably, with the increase of 2BCH⁻ yields, the yields of C₁₄ are simultaneously increased in the order of Pd/ZrO₂ (6%)<Pt/ZrO₂ (17%)<Ru/ZrO₂ (20%)<Ni/ZrO₂ (33 %). This is ascribed to the more active α-H of 2BCH⁻ than 2BCH to further condense with n-butanol and higher thermodynamic stability of 2,6-dibutenyl cyclohexanone [1]. In brief, Pd has great superiority over other metals for selective synthesis of 2BCH through one-pot method [34].

For the bifunctional catalyst, support is as important as metals, which provides the acid-base sites for aldol condensation [1]. Therefore, in order to understand the effect of supports, commonly used supports, such as acidic Al₂O₃ [38], strong basic MgO, CaO [39,40] and weak basic ZnO [41], TiO₂ [42], CeO₂ [43] and amorphous alumina silicate (Al₂SiO₅) [44], were also studied. As shown in Table 1 (Entry 4 to 7), Pd/Al₂O₃, Pd/MgO, Pd/ZnO and Pd/CaO showed comparable n-butanol

conversion with Pd/ZrO₂, while the 2BCH yields (< 55 %) on these catalysts were much lower than that on Pd/ZrO₂. This was due to the high selectivities of side reactions like self-condensation and n-butanol hydrogenation on these catalysts. On the contrary, much lower n-butanol conversions were obtained on Pd/TiO₂, Pd/CeO₂ and Pd/Al₂SiO₅, owing to their lower intrinsic activity than Pd/ZrO₂. So, in this system, ZrO₂ was the most suitable support, which was probably due to its suitable acid-base properties. In order to demonstrate this, NH₃-TPD and CO₂-TPD measurements were applied for Pd/ZrO₂, Pd/Al₂O₃, Pd/Al₂SiO₅ and Pd/MgO (Table 2). Quantities of weak or medium basic sites were observed on Pd/ZrO₂, Pd/Al₂O₃ and Pd/MgO, while those on Pd/Al₂SiO₅ was much lower. Considering the fact that n-butanol conversions were higher than 97 % on the formers but only 49 % on the latter, we could conclude that the condensation step was primarily catalyzed by base sites. However, higher amount of base site also partially contributed to higher self-condensation of n-butanol, which leads to lower 2BCH yield on Pd/Al₂O₃ and Pd/MgO than that on Pd/ZrO₂. No obvious correlations between acid sites and catalytic performance were observed on these catalysts, so the hydrogenation of C=C bond might be influenced by the Pd metal only. Therefore, we could conclude that active metal (Pd) and suitable support (ZrO₂) [36] cooperatively resulted in the high performance of Pd/ZrO₂ catalyst.

3.5. Universality

The above success of one-pot synthesis of 2BCH had inspired us to further extend the application of the bifunctional 0.2Pd/ZrO₂ catalyst for other 2-alkyl cycloketone homologs and isomers (**3a** or **3b**) syntheses. Encouragingly, satisfactory aliphatic aldehyde (**2**) conversion and 2-alkyl cycloketone (**3a/3b**) yield were obtained (Table 3), showing good universality of present one-pot approach. Cyclopentanone was slightly lower reactive than cyclohexanone, which favored the side reactions of aldehyde, such as self-condensation and C = O hydrogenation of aldehyde. Therefore, selectivity and yield of **3b** were relatively lower than **3a**. On the other hand, the reactivity of iso-aldehyde (Entries **1** and **8**) was lower than that of linear ones due to its larger steric hindrance. However, this hindrance effect restrained main reaction and side reactions synchronously, leading to their similar selectivity of corresponding **3a** or **3b**. For tert-aldehyde (Entries **3** and **10**), the much larger steric hindrance lead to sharp decrease of conversion of **2** and yield of **3a** and **3b**.

4. Conclusions

2-Alkyl cycloketones were synthesized through one-pot cascade process using a Pd/ZrO₂ catalyst. The cooperative effect between ZrO₂ support and high dispersed Pd provided suitable acid-base sites for aldol condensation and metal sites for selective C = C hydrogenation, resulting in a superb performance. The activity of the deactivated catalyst could be completely recovered by an oxidative regeneration, showing excellent catalyst regenerability. Besides, the one-pot cascade process could also be extended to synthesize a series of 2-alkyl cycloketones. These results were of significant relevance for the industrial application, in terms of replacing the present homogeneous synthesis protocol.

Author statement

Huiling Wu: Conceptualization, Formal analysis.
 Mengyang Liu: Conceptualization, Data curation.
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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcata.2021.118107>.

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