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Direct Catalytic Conversion of Ethanol to C_{5+} Ketones: Role of Pd-Zn Alloy on Catalytic Activity and Stability

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Abstract: Ethanol can be used as a platform molecule for synthesizing valuable chemicals and fuel precursors. Direct synthesis of C_{5+} ketones, building blocks for lubricants and hydrocarbon fuels, from ethanol was achieved over a stable Pd-promoted $ZnO\text{-}ZrO_2$ catalyst. The sequence of reaction steps involved in the C_{5+} ketone formation from ethanol was determined. The key reaction steps were found to be the in-situ generation of the acetone intermediate and the cross-aldol condensation between the reaction intermediates acetaldehyde and acetone. The formation of a Pd-Zn alloy in-situ was identified to be the critical factor in maintaining high yield to the C_{5+} ketones and the stability of the catalyst. A yield of >70% to C_{5+} ketones was achieved over a 0.1% $Pd\text{-}ZnO\text{-}ZrO_2$ mixed oxide catalyst, and the catalyst was demonstrated to be stable beyond 2000 hours on stream without any catalyst deactivation.

Introduction

Growing awareness of the need for energy independence and sustainability has driven increased interest in developing energy-efficient technologies to produce renewable fuels and chemicals. As sustainable sources of small oxygenate compounds become more widely available, developing facile coupling strategies that can extend the carbon chain length would enable renewable catalytic pathways towards replacing a wider class of larger petroleum products. One promising approach is to first produce higher molecular weight ketones (C_{5+}) as intermediate precursor molecules. C_{5+} ketones possess both electrophilic and nucleophilic functionalities, as well as sufficient carbon chain length, that make them suitable building blocks, analogous to alkenes and aromatics in a petroleum refining complex, for producing infrastructure compatible hydrocarbon fuels (e.g. jet and diesel), lubricants and fuel blendstocks. C_{5+} ketones themselves also have direct applications for specialty cleaning solvents.[1]

Catalytic approaches to generate C_{5+} ketones have focused primarily on processes starting with acetone, n-butanol, and ethanol (ABE) mixtures generated from fermentation. Anbarasan et al. developed an efficient $Pd/C\text{-}K_3PO_4$ catalyst system that utilizes the nucleophilic carbonyl carbon atoms of acetone and the electrophilic α-carbon of the aldehyde intermediate, generated from the in-situ dehydrogenation of the feed alcohol, to selectively initiate the cross-aldol condensation.[1c] Several groups have followed this pathway; most recently, Wang et al. have reported ceria (Ce) -based mixed-oxide catalysts to selectively convert an ABE mixture to C_7 ketones (4-heptanone).[2] However, little work has been done on establishing an equivalent process starting from pure ethanol, which requires a modified catalytic system as it lacks an initial ketone group to dictate the reaction. Despite this, the overlap with the ABE chemistry makes ethanol a natural candidate to support the renewable production of C_{5+} ketones, particularly given its flexibility as a feedstock and ease of synthesis. In addition to accessing an established commercial infrastructure, with a US production volume near 15 billion gallons,[3] using ethanol would help diversify the potential carbon sources to include resources such as municipal solid waste, flue gas, and shale gas.[4]

Here we report a novel approach to convert ethanol in a one-pot reaction to produce long-chain ketones (C_5-C_{11}), based on the in-situ generation of both the aldehydes and acetone required for the suitable cross-aldol condensation to form longer carbon chains. This is made challenging by the nature of ethanol carbon-carbon (C-C) coupling chemistries, as they typically involve complex cascade-type reactions with multiple intermediate steps across multi-functional sites (e.g., acidic, basic, and redox).[5] The reactive nature and low thermal stability of the intermediate compounds means that parallel chemistries such as dehydrogenation, dehydration, esterification, Tishchenko reactions may occur, producing a range of products such as aldehydes, esters, alkenes, and ketones.[6] As the promoted mixed oxides catalysts typically used for these chemistries are similar in nature,[7] selective C-C coupling relies on the delicate balancing of catalyst characteristics and operating conditions to avoid activation of unwanted side reactions. As products, C_{5+} ketones are typically only observed as minor fractions in ethanol coupling reactions. However, ketones are regularly generated during the formation of *i*-butene over $ZnO\text{-}ZrO_2$ catalyst, which proceeds through an acetone intermediate formed from acetaldehyde coupling. The high reaction temperature leads to rapid self-condensation of acetone into diacetone alcohol that produces *i*-butene by decomposition,[7a, 8] but appropriate

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modification of the catalyst and conditions to instead favor acetone coupling with acetaldehyde can offer a pathway towards forming longer ketones. Literature on ABE condensation reactions has shown that promotion of Pd is particularly suitable to selectively enable the hydrogenation of α, β-unsaturated ketones to cease the undesired reactions and improve the C_{5+} ketones products.[1c, 9]

Based on these previous works, a multifunctional Pd promoted ZnO-ZrO_2 catalyst was developed to upgrade the ethanol to C_{5+} ketones in a one-pot catalytic process. (**Figure 1**) Evaluation of the operating conditions and the compositional changes in the catalyst with respect to the reaction mechanism showed this formulation to be highly active toward this chemistry, with over 70% selectivity to ketones at near complete conversion. Characterization by X-ray Absorption (XAS) and High-Angle Annular Dark Field - Transmission Electron Microscopy (HAADF-TEM) revealed the in-situ formation of a dispersed Pd-Zn alloy formation during reaction, which significantly modified the Pd functionality and was correlated with high ketone yields. Further long-term evaluation assessing the commercial viability of this catalytic system demonstrated stable catalyst performance for over 2000 hours on stream without deactivation.

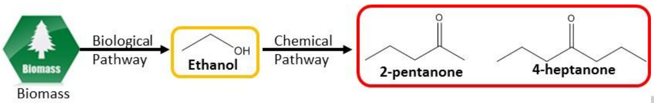

Figure 1. Overview of the production of higher ketones (C_{5+}) from biomass via a hybrid biological/chemical pathway.

Results and Discussion

Catalyst Performance and Reaction Mechanism

To develop an active catalyst and understand the reaction mechanism for the direct conversion of ethanol to C_{5+} ketones, various combinations of ZnO and ZrO_2 catalysts were synthesized with and without the Pd metal promoter. These catalyst formulations were evaluated at 370 °C temperature, 300 psig pressure, and 0.15 h^{-1} weight hourly space velocity (WHSV). The detailed results of these experiments are presented in **Table 1,** see supplementary section for the catalyst preparation, catalyst evaluation and product analysis methods.

Reactions over ZrO_2 produced primarily ethanol dehydration products, namely diethyl ether and ethylene with a combined selectivity close to 50%. Additional dehydration products were detected in the form of 1,3-butadiene (11.3%) as well as propene and pentene (27%), corresponding to aldol condensed crotyl alcohol and acetone/2-pentanone, respectively. These products can be attributed to the acid sites present in ZrO_2 that lead to unimolecular and bimolecular dehydration (**Table S4**). Combined with the lack of redox sites for ethanol dehydrogenation, this results in the preferential generation of dehydration products over ZrO_2. Next, ZrO_2 was promoted with 0.1% Pd to provide the necessary redox sites, with the results showing a minor increase in ketone formation and mild decrease in dehydration products such as ether, as well as hydrogenation of most alkenes to alkanes. At the same time, the introduction of Pd led to additional formation of carbon monoxide (CO) and methane from ethanol decomposition, presumably via sequential dehydrogenation and metal-catalyzed decarbonylation reactions.[10] Rapid deactivation of the Pd, likely due to CO poisoning as commonly reported,[11] was marked by the disappearance of these decomposition products, trending towards unpromoted ZrO_2.

Ethanol reaction over ZnO primarily produced ethyl acetate (44.5%) followed by acetone with an ethanol conversion of around 64%. Ethyl acetate can be formed via either the Tishchenko reaction from the condensation of two acetaldehydes or through the dehydrogenation of a hemiacetal formed through the ethanol-acetaldehyde interaction. The redox functionality of ZnO along with its minimal acidic sites favor the dehydrogenation of ethanol followed by either ester formation or aldol condensation over basic sites, rather than dehydration.[12] Conversion of ethanol to acetaldehyde and further condensation to acetone has been explored on different structures of ZnO, and these experimental results were consistent with those found in literature.[13] The addition of 0.1% Pd to ZnO improved the ethanol conversion to ~98% and largely eliminated ethanol dehydration products, reflecting significant improvement in dehydrogenation. Pd also contributed to greater ketone formation and condensation activity, resulting in a much higher selectivity to ketones (~58%) over esters, with a small increase to coupled alcohol products as well. However, the selectivity to acetone was quite high (~19.3%) with 2-pentanone being other major ketone product, resulting in a low average ketone carbon chain length (~4). Interestingly, very little ethanol decomposition products were detected, unlike in the reaction over the 0.1%Pd-ZrO_2 catalyst, with the increase in CO_2 directly corresponding to increased ketone formation. Furthermore, the catalyst was found be very stable in contrast to the rapid Pd deactivation observed on ZrO_2. These results indicate a significant change in the catalytic and physical nature of the Pd functionality in the presence of ZnO.

Over the mixed oxide ZnO-ZrO_2 catalyst, the conversion of ethanol was ~99% with a 25.9% selectivity toward ketones. Though the high conversion and reduced ethanol dehydration (% ethylene) signify higher dehydrogenation activity compared to the ZnO and ZrO_2, the presence of unsaturated enones such as 3-penten-2-one indicate insufficient C=C hydrogenation activity. These cross-condensed intermediates likely lead to the considerable cyclic formation, specifically 7 and 9-carbon cyclohexenones and phenols through Michael addition/ring annulation and may have contributed to an observed deactivation trend, presumably as a result of coking. Self-condensation of acetone was also observed as isobutene formation following unselective decomposition on balanced Lewis acid-base pair sites, as recognized in ZnO-ZrO_2 mixed oxides.[14] Significant dehydration rates also led to propene and pentene side products from C_3/C_5 ketones and alcohols. Accounting for these side reactions, it is evident that though condensation rates on ZnO-ZrO_2 are considerably higher compared to ZnO and ZrO_2, ketone selectivity remains limited due to insufficient redox activity.

To better assess the introduction of Pd, given the previously observed interaction of Pd with ZnO, an initial test was performed using a physical mixture of ZnO-ZrO_2 and Pd-promoted SiO_2 as a control, with the same total Pd loading. Here, as in the Pd-promoted ZrO_2 catalyst, a significant quantity of methane and CO was produced as decomposition products, with an even lower

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Head 1[a]	ZrO_2	0.1%Pd-ZrO_2	ZnO	0.1%Pd-ZnO	ZnO-ZrO_2	ZnO-ZrO_2+Pd-SiO_2[a]	0.1%Pd-ZnO-ZrO_2
Conversion	93.0	99.3	64.1	97.7	99.7	100.0	100.0
C_{5+} Ketones	0.6	5.48	4.2	38.5	12.4	7.06	65.4
Acetone	0.7	3.38	14.8	19.3	13.5	4.23	5.8
DEE/Ethane/Ethylene	49.7	23.4	15.4	2.8	13.7	13.8	2.5
C_{3+} Alkane/Alkene	36.1	37.4	2.1	1.6	24.5	36.4	9.1
CO/Methane	0.4	12.8	0.0	1.0	1.10	11.2	0.0
CO_2	5.8	14.4	6.2	8.8	18.1	19.5	14.7
Cyclics[b]	0.0	2.11	2.7	0.1	14.0	6.33	0.7
Alcohol/Aldehyde	5.2	0.49	9.5	16.0	1.51	0.38	1.7
Ester	1.0	0.56	45.1	11.6	1.29	1.10	0.0

Table 1. Ethanol conversion and product selectivity over various catalyst combinations between ZnO, ZrO_2 and Pd. Reaction conditions: Temperature 370 °C; pressure 300 psig; WHSV 0.15 h-1. The analysis results were provided for the sample collected at time on stream of 24 hour. 100% pure ethanol was used as feed. [a] Physical mix of ZnO-ZrO_2 and Pd-SiO_2 with Pd content equivalent to 0.1wt%. [b] Cyclic compounds represent compounds such as cyclohexenones,phenols etc.

selectivity toward ketones (11.3%). Though small alkene products are hydrogenated, the continued formation of cyclic compounds and as well as isobutene indicates the ineffective hydrogenation of unsaturated ketone intermediates by the physically mixed Pd, despite the presence of H_2. As with Pd-ZrO_2, rapid deactivation as measured by the decrease in CO and methane products over ZnO-ZrO_2-Pd-SiO_2 resulted in a deactivated product profile largely identical to unpromoted ZnO-ZrO_2. The Pd in a physical mixture thus does not significantly contribute to the dehydrogenation/hydrogenation activity or ketone formation, and the Pd is instead mostly active toward the unselective decomposition of ethanol.

In contrast, directly impregnating 0.1%Pd onto a ZnO-ZrO_2 catalyst resulted in the highly selective production of ketones (~71%), with a higher average carbon number (~6) and minimal acetone selectivity (<10%). A significant proportion were C_{7+} ketones, resulting from the sequential cross condensation of ketones with aldehydes. The detailed product distribution from this experiment is provided in the inset of **Figure 2a**. The stable catalyst performance and lack of ethanol decomposition products, compared to the physical mixture, again point to a significant change in the nature of Pd upon direct contact with the support, as observed with Pd-ZnO. The catalyst now proved much more effective in C=C hydrogenation, largely eliminating the formation of cyclic and isobutene products resulting from unsaturated condensed ketones intermediates.

Further study of the 0.1%Pd-ZnO-ZrO_2 catalyst was conducted across a range of temperatures from 300 to 385 °C, with the changes to carbon selectivity of the major products in presented in **Figure S8a**. Beginning at 300 °C, conversion was 74% with esters being the predominant products along with some alcohol condensation products. Raising the temperature to 340 °C results in near complete conversion and ketone selectivities above 60%, with a minor fraction of side products consisting primarily of C_{6+} aldehydes and esters. These largely disappear as ketone formation becomes more favorable with increasing temperatures, until 370 °C and above when dehydration becomes relevant. This results in a large window of temperatures where the ketone yield is considerable, with the major change being the distribution of ketone products as the average chain length grows from about 5 to 6. Comparison with the results from unpromoted ZnO-ZrO_2, in **Figure S8b** show that without Pd, ketone yield never becomes significant at lower temperatures due to the lower conversion and high ester selectivity, and remains limited by cyclic and dehydration side product formation at 370 °C. It is clear that Pd significantly improves the dehydrogenation/hydrogenation activity, and at the same time also appears to contribute to the overall selectivity of ketones over esters. To confirm this effect, ZnO-ZrO_2 catalysts with 0.05 wt% and 0.5 wt% Pd were also prepared and tested at 340 °C. Ketone formation was found to be highly dependent on the Pd concentration, as overall yield nearly doubled at 0.5 wt% loading compared to 0.05 wt%, corresponding to an improvement in ketone selectivity from 43.95 to 74.6% in conjunction with a small 8% increase in conversion. In addition, no esters were observed during reaction over 0.5 wt%, resulting in a product profile similar to that observed at 370 °C for 0.1 wt% Pd. However, the average ketone chain length remained relatively invariant to Pd loading, showing a slight increase from 5.0 to 5.1, suggesting that the effect of Pd is related the formation of the ketone moiety rather than ketone chain growth. Similar results were obtained by studying Pd concentration on ZnO catalyst, showing that added Pd could increase the total ketone yield to > 60% even at 340 °C, but had no effect on the ketone distribution with a static chain length of 4.0 (See Supplementary Section **Figure S9**). To better understand the reaction mechanism, reaction data was gathered for the 0.1wt%-ZnO-ZrO2 catalyst for lower conversions by varying space velocity. **Figure 2b and S9** shows the corresponding changes in the product distribution, where increasing WHSV corresponds to lower conversions and a large shift in selectivity away from ketones towards esters and alcohols/aldehydes, as well as a reduction in product chain lengths. The same trends were observed with decreasing reaction

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temperatures, indicating the in-situ formation of acetone was a slower secondary process. The rates of formation of key compounds as a function of contact time is shown in **Figure 2b**. Lower contact times (i.e. < 20 min) were not tested due to the cyclic compound formation from unsaturated condensations. Importantly, we note that the total ketone production is approximately one-to-one by moles to CO_2. This is consistent with a decarboxylation pathway for the production of intermediates, or through water gas shift from CO generated from a decarbonylation pathway.[15]

These experimental results demonstrate that a sequential C-C coupling pathway can be used to efficiently build long chain ketones up to C_{13} starting from ethanol in a single catalyst bed. The regular distribution of ketone products at odd carbon number intervals is consistent with the preferential cross-condensation of aldehydes with acetone formed in-situ, which limits excess CO_2 byproduct formation (see SI for details). Though other major side products can form from the numerous intermediate steps along the reaction pathway, as shown in **Figure 2c**, they were found to be largely mitigated upon the introduction of Pd, specifically those promoted on zinc containing catalysts. Elevated dehydrogenation activity suppressed dehydration reactions while effective hydrogenation of α,β-unsaturated ketone intermediates prevented potential subsequent decomposition or cyclic products. Pd was found to directly increase ketone formation over esters and alcohols. and exhibited a wide operating reaction temperature regime without catalyzing unselective ethanol decomposition. This surprising effectiveness of Pd towards achieving high ketone selectivity over ZnO-ZrO$_2$ catalysts warranted further investigation. Supplementary section includes the detailed discussion on the reaction steps involved in the formation of acetone (**Figure S6**) and experimental details on the intermediate feed experiments to demonstrate the evidence for the cross-aldol condensation between acetaldehyde and acetone to form 2-pentanone (**Figure S7 and Table S4**).

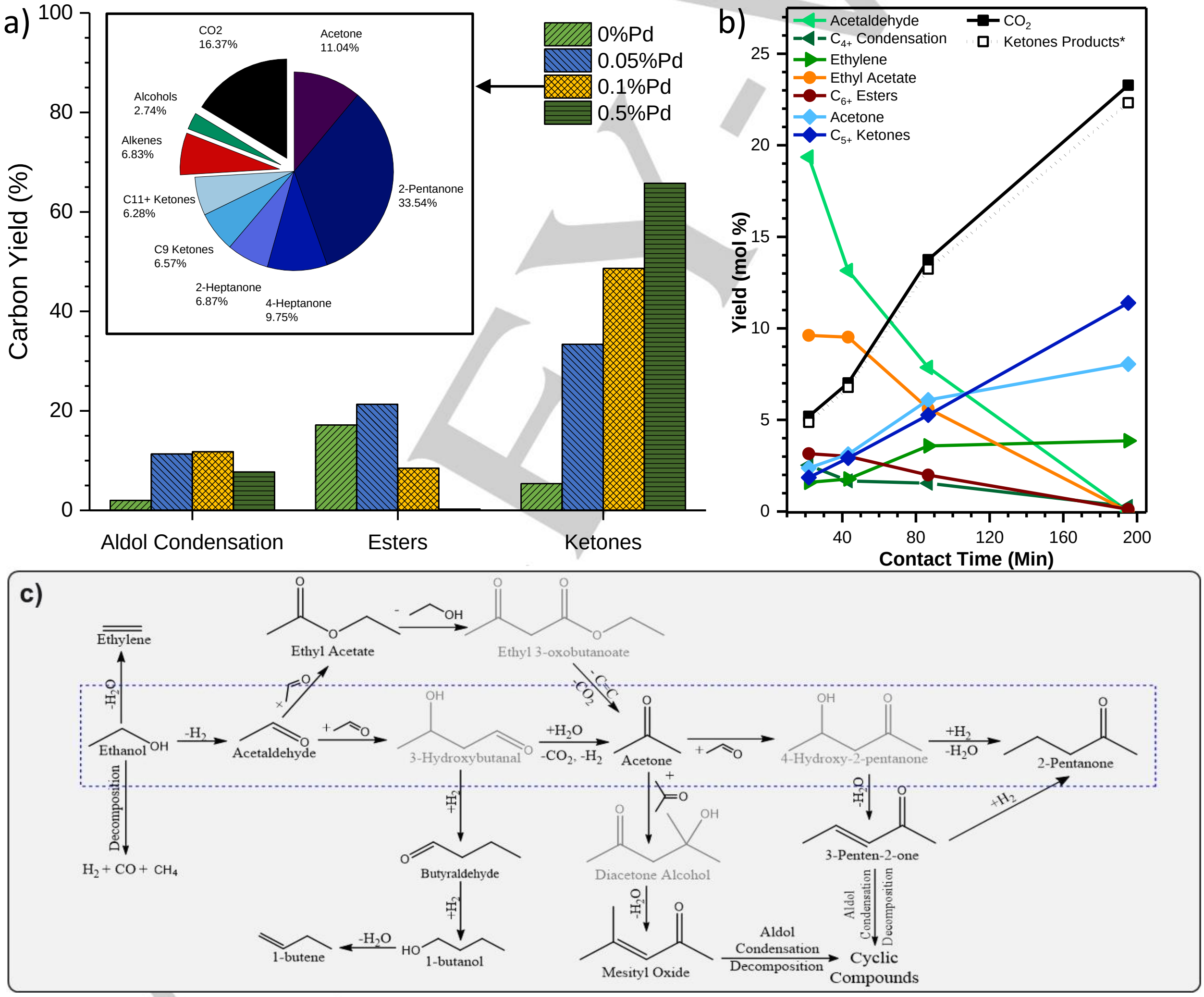

Figure 2. (a) Carbon yield distribution of major product groups with varying Pd loading on ZnO-ZrO$_2$ at 340 °C, 0.21 MPa EtOH, 1.86 MPa N_2 and 0.15 h^{-1}, inset showing detailed product carbon selectivity from the ethanol conversion over 0.1%Pd-ZnO-ZrO$_2$ at 370 °C, 0.21 MPa EtOH, 1.86 MPa N_2 and 0.15 h^{-1}; (b) Molar yield of key products as a function of contact time conducted by varying catalyst loading for ethanol conversion over 0.1%Pd-ZnO-ZrO$_2$ at 370 °C, 0.21 MPa EtOH, 1.86 MPa N_2 and 0.15 h^{-1}. *Denotes the sum of products including all ketones such as acetone, 2-pentanone and 3-penten-2-one, their respective alcohols such as isopropanol and 2-pentanol, their respective dehydration products such as propene and trans-2-pentene, as well as isobutene from acetone self-condensation (c) Simplified reaction mechanism for the ethanol conversion to C_{5+} ketones and the potential side reactions (compounds shown in gray are not found in product stream.

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Catalyst Characterization

The catalyst evaluation results demonstrate that intimate contact is required between Pd and ZnO, as well as between ZrO_2 and ZnO. To understand the intrinsic reasons for the site requirements, we undertook an extensive catalyst characterization studies using X-ray Absorption Spectroscopy (XAS), Temperature Programmed Reduction (TPR), and Transmission Electron Microscopy (TEM), experimental details listed in the supplementary section. Wang et al. researched the interaction of ZnO and ZrO_2. In their study, which focused on the aldol condensation reaction to convert ethanol to isobutene, they reported that the incorporation of ZnO into the ZrO_2 promotes the formation of new Lewis acid-base active structures (i.e., Zr-O-Zn) on the catalyst surface, which play a critical role in the activity of the cascade aldol-condensation chemistry.[16] The TPD and Py-IR results from our studies on the ZnO-ZrO_2 catalyst show a similar trend in the acid–base characteristics (**Figure S2, Table S3**). The addition of 0.1% Pd to the ZnO-ZrO_2 results in a further increase in the number of Lewis acid and base sites. However, this did not significantly impact the cross-condensation chemistry, as experiments reacting acetone and butanal over Pd-promoted and unpromoted ZnO-ZrO_2 resulted in largely identical product profiles of primarily 4-heptanone. (**Figure S8**) Further investigation of the incorporation of Pd over the ZnO-ZrO_2 matrix and the resulting effect on its redox characteristics was thus necessary to explain the higher catalyst activity of Pd-ZnO-ZrO_2 compared to the other catalyst compositions tested.

The Pd K-edge X-ray Absorption Near Edge Structure (XANES) spectra of the 0.1%Pd-ZnO-ZrO_2 catalyst suggest that under ambient conditions the Pd in the catalyst exists predominately as PdO. Upon heating to 370 °C in the presence of ethanol, the Pd in the catalyst reduced to the metallic state (PdO→Pd). (**Figure S3a**) The ambient-condition Extended X-Ray Absorption Fine Structure (EXAFS) spectrum fit is consistent with a four-coordinated Pd-O species. (**Figure S3b**) In the R-space of the operando scan at 370 °C in the presence of ethanol (**Figure 3a**), we observe scattering at distances shorter than the expected Pd-Pd scattering. This suggests the presence of a scattering atom other than Pd as nearest neighbor to Pd. Based on the relative atomic sizes, we fit the EXAFS spectrum using Pd-Pd scattering at 2.733Å and Pd-Zn scattering at 2.565Å. To achieve a meaningful fit without high correlations, we used the Debye-Waller factors from our previous work on Pd-Cu alloys.[17] The small coordination numbers obtained (**Table S2**) suggest small nanoparticles of Pd-Zn alloy.

This picture is also consistent with the results of TPR experiments (**Figure S4**). Two reduction peaks may be observed for the 0.1%Pd-ZnO-ZrO_2 catalyst: a small peak at 80 ºC and a larger one at 340 ºC. We tentatively attribute these to the reduction of PdO to Pd and to the formation of a Pd-Zn alloy as a result of Zn reduction, respectively. We observe no peaks under 500 ºC for the temperature-programmed reduction of ZnO, leading us to conclude that hydrogen spillover from Pd to ZnO is responsible for the formation of the Pd-Zn alloy. The as-prepared and spent 0.1% Pd-ZnO-ZrO_2 catalysts were further analyzed using STEM imaging and EDS mapping. Consistent with the requirement for intimate contact between ZnO and ZrO_2, the catalyst support material was confirmed to be predominately a mixture of the two oxides.

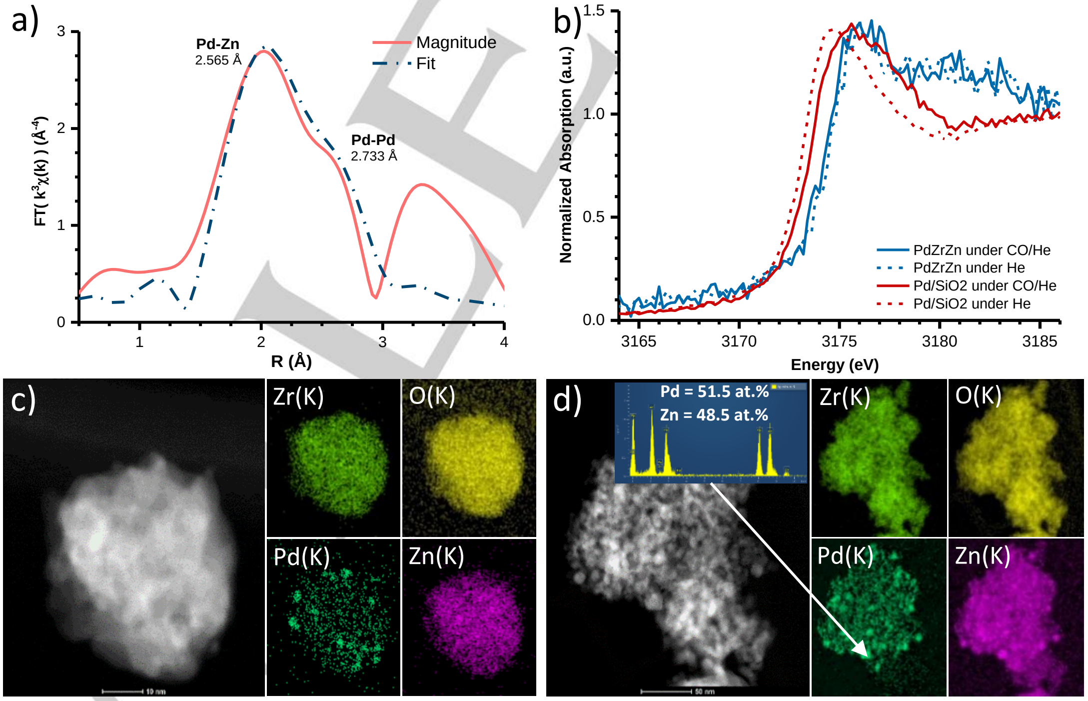

Figure 3. (a) Pd K-edge EXAFS *in operando* under ethanol flow and 370 °C and atmospheric pressure; (b) Normalized Pd L_{III}-edge XANES spectra of reduced 0.1% Pd on ZnO-ZrO_2 catalyst compared to reduced Pd on SiO_2 control, and under CO flow; (c) HAADF-STEM and corresponding Zr, Zn, and Pd EDS mapping on fresh 0.1% Pd loaded on ZnO-ZrO_2 catalyst; and (d) HAADF-STEM and corresponding Zr, Zn, and Pd EDS mapping on spent 0.1% Pd loaded on ZnO-ZrO_2 catalyst after >100 hours on stream.

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This can be seen in the results from energy dispersive spectroscopy (EDS) mapping (**Figure 3c, 3d**), which shows both Zn and Zr uniformly distributed throughout the oxide phase. In the as-synthesized sample, individual Pd nanoparticles of ~2.7 nm in diameter were identified in the EDS maps (**Figure 3c**); the HAADF imaging provided only minimal contrast. In the spent sample (collected after 100 hours on stream at 370 °C and 300 psig), shown in **Figure 3d**, we find that the Pd nanoparticles are enriched in Zn with an average Pd/Zn ratio of approximately 1 with the measured average particle size of 10.2 nm. This TEM analysis supports the results of the EXAFS analysis indicating the formation of the Pd-Zn alloy phase in the presence of ethanol at the reaction temperature. This is consistent with the work of Waele et al., who have noted the activity of Pd-Zn alloys in ethanol dehydrogenation.[18] These results point to the possible role of Zn as a modulator for the Pd reactivity, much like the role of Cu in PdCu alloys in alcohol dehydrogenation reactions.[11b]

Pd L_{III}-edge XANES was also performed to clarify the associated changes in Pd after alloy formation. Prior to reduction, the catalyst is oxidized. The oxidation is evidenced by the height of the white line. Consistent with the TPR results, there is a reduction of the strength of the white line between the 80 and 130 ^{o}C scans, suggesting a reduction of the Pd. (**Figure S5a**) Furthermore, at higher temperatures, the edge shifts to higher energies, suggesting that there is an electronic modification of the Pd. This could be ascribed to alloying with Zn. (**Figure S5b**) Further evidence for that can be found by comparison of the reduced 0.1%Pd-ZnO-ZrO_2 catalyst with a Pd-SiO_2 standard; the edge is shifted by about 0.7 eV, consistent with alloying.[19] Moreover, there is a feature approximately 15 eV above the edge position similar to that reported by Tew, et al. for the bonding of Pd and H;[20] this suggests bonding between Pd and a heteroatom, in this case Zn. with the shift corresponding to charge transfer of the PdZn alloy. Furthermore, the XANES spectra showed no changes under the presence of CO, indicating weak CO binding characteristics that differ from bulk Pd.[21] These results offer a direct explanation for the absence of the decarbonylation products observed during EtOH conversion over Pd-Zn catalysts.

It has been reported elsewhere that intermetallic alloying between Pd and Zn offers an improved dispersion of Pd in the catalyst matrix in addition to the unique and homogeneous collaborative active sites, providing improvement in a variety of reactions such as alkyne hydrogenation[22] and steam reforming [23]. In this work, for the first time we report the formation of a Pd-Zn alloy on a ZnO-ZrO_2 catalyst and the role of the alloy in the tandem dehydrogenation-aldol condensation chemistry. The alloy formation makes this catalyst both highly active, stable, and selective to producing C_{5+} ketones from ethanol. In general, Pd in metallic form is known to decompose ethanol and produce methane, CO, and hydrogen[23] which is clearly evident in our experiments with both the Pd impregnated ZrO_2 catalyst and the physical mix of Pd-SiO_2 plus ZnO-ZrO_2 catalysts. However, in the case of Pd impregnated on ZnO and the Pd impregnated on ZnO-ZrO_2 catalyst, the selectivity to the methane and CO is negligible. We attribute that to the in-situ formation of Pd-Zn alloy by hydrogen spillover from Pd to the ZnO on the 0.1%Pd impregnated on ZnO-ZrO_2 catalyst matrix, consistent with a PdO→Pd→Pd-Zn reductive process.

The formation of Pd-Zn alloy modulates the role of Pd in the catalyst matrix in several ways. First, the alloy increases the rate of ethanol dehydrogenation to form acetaldehyde selectively [18]. Second, the alloy selectively hydrogenates α,β-unsaturated ketone intermediates such as 3-penten-2-one to avoid the formation of undesired cyclic compounds. Finally, the Pd-Zn alloy creates a balanced environment between the redox, acid and base active sites to selectively form the C_{5+} ketones from ethanol via the complex cascade reaction mechanism.

Catalyst Stability

To assess the stability of the 0.1%Pd-ZnO-ZrO_2 catalyst, a long-term experiment was conducted for a period over 2000 hours in a plug flow reactor arrangement. **Figure 4** represents the detailed product selectivities from the samples collected at periodic intervals over the 2000-hour experiment. The ethanol conversion was consistently ≥ 99% for the duration of the experiment. During this study, extreme fluctuations in the operating conditions occurred periodically due to incidents such as power outages. These fluctuations included temperature, pressure, ethanol feed flow rate, and carrier gas flow rate. The catalytic activity quickly returned to its normal level once the operating conditions were restored every time these fluctuations occurred. Throughout the duration of the experiment, the catalyst did not show any deactivation towards the ethanol conversion and the product selectivity. The formation of Pd-Zn alloy can be seen to play a key role in the high level of stability of the Pd-ZnO-ZrO_2 catalyst over time and its robustness across wide operating windows.

Typical deactivation mechanisms for ZnO-ZrO_2 and other catalysts, such as TiO_2, hydroxyapatite and basic metal oxides during gas-phase aldol condensation chemistry were reported to be due to the strong adsorption of high molecular weight compounds over the active sites, and this was demonstrated through facile regeneration by calcination in air.[14, 24] Pd metal can also be easily deactivated from particle growth for various reasons such as coke deposition and coke transformation, modification of the Pd surface and the variations of physical properties, as well as chemical poisoning and leaching.[25] The interaction of Pd with Zn prevents the Pd from sintering and mitigates coke deposition and chemical poisoning, stabilizing the catalyst for more than 2000 hours of time on stream, even at temperature regimes where Pd diffusion would otherwise be high and sintering likely

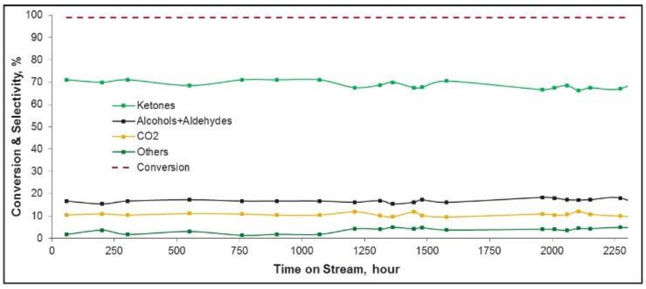

Figure 4. Product selectivity snapshot at various points time on stream during the 2000 hour catalyst stability experiment. Experiment was conducted at 370 °C temperature, 300 psig pressure, 0.15 hr^{-1} WHSV with nitrogen carrier gas and ethanol feed solution.

Conclusion

In summary, we have developed a new Pd-promoted ZnO-ZrO_2 catalyst to convert ethanol to C_{5+} ketones in a one-pot reaction with ketones selectivity >70% at 100% ethanol conversion, with catalyst stability >2000 hours of time on stream at 370 °C. We also showed that (1) the reaction mechanism includes the in-situ generation of acetone followed by the cross condensation between acetaldehyde and acetone to generate C_{5+} ketones from ethanol and (2) the formation of an intermetallic Pd-Zn alloy in-situ during the reaction is essential for the activity, selectivity, and stability of the catalyst.

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Keywords: Mixed oxide catalyst, Ethanol upgrading, Aldol condensation

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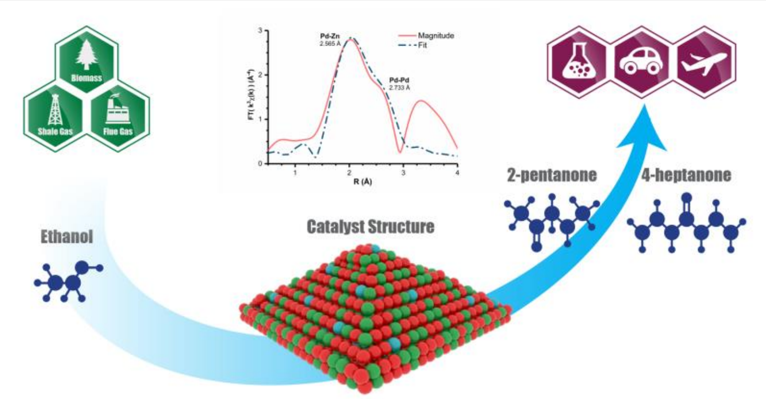

The **formation of Pd-Zn** alloy on a Pd-ZnO-ZrO$_2$ results in the modification of the Pd electronic structure and enables the highly selective formation of C$_{5+}$ ketones from renewable ethanol (>70%yield) for extended catalysts lifetimes above 2000 hours

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