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Authors: Rong He, Yong Men, Jixing Liu, Jinguo Wang, Wei An, XiaoXiong Huang, Weiyu Song, Jian Liu, and Sheng Dai

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Tailoring the Selectivity of Bio-ethanol Transformation by Tuning the Size of Gold Supported on $ZnZr_{10}O_x$ Catalysts

Rong He,[a] Yong Men,*[a] Jixing Liu,[b,c] Jinguo Wang,[a] Wei An,[a] Xiaoxiong Huang,[a] Weiyu Song,[b] Jian Liu,[b] Sheng Dai[c]

Abstract: The selective bio-ethanol cascade transformation to hydrocarbons over multifunctional catalysts is a highly promising sustainable pathway to high-value chemicals and fuels. However, principles to control the selectivity of the bio-ethanol transformation using the effects of the size of nanoparticle catalysts have remained largely unexplored. Here, using bio-ethanol transformation reactions catalyzed by Au/$ZnZr_{10}O_x$ as examples, we demonstrate that changing the fashion of gold loading enables control over product distribution. Our results reveal that larger gold particles tend to show much higher selectivity for 1,3-butadiene, whereas smaller gold nanoparticles favor the formation of acetaldehyde. This study uncovers general principles for tailoring the selectivity of bio-ethanol transformation by carefully engineering the size of gold. It opens a new avenue for the rational design of multifunctional catalysts to enhance the production of desired reaction products in complex cascade reaction sequences.

Bio-ethanol has emerged as a chemical feedstock available from biomass and could provide alternative routes to producing value-added chemicals,[1] such as acetaldehyde,[2] ethyl acetate,[3] acetic acid,[4] and lower olefins[5] over various catalysts. Upgrading bio-ethanol to C4-olefins has been recognized as one of the most important strategic reactions to produce highly valuable chemicals.[6] Direct conversion of bio-ethanol into 1,3-butadiene (1,3-BD) (Lebedev process; Scheme 1) is quite complex because of the nature of the cascade reaction.[7] Mixed metal oxides with multiple catalytic functionality, in particular MgO-SiO_2 binary composite oxides, have been found to be very effective for the Lebedev process.[8] It is generally accepted that the crucial factor affecting BD formation is a subtle optimal ratio of acid-to-base sites to enhance the reactivity.[9]

Since the pioneering work showing exceptional catalytic activity of gold in low-temperature oxidation of CO by Haruta, and in hydrochlorination of ethylene by Hutchings,[10] he catalytic activity of supported nanosize gold catalysts has become a fascinating fundamental issue and attracted a great deal of attention in heterogeneous catalysis.[11] Recent progress in nanocatalysis based on sizing and shaping gold nanoparticles provides new approaches for tuning catalytic reactivity and stability.[12] Hensen et al. reported a ternary spinel ($MgCuCr_2O_4$)-supported gold catalyst for aerobic oxidation of ethanol to acetaldehyde that is capable of achieving unprecedented reactivity of ~100% ethanol conversion with ~95% acetaldehyde selectivity at 250 °C.[13] Flytzani-Stephanopoulos et al. showed that atomically dispersed nanosize gold on a $ZnZrO_x$ support was very active in achieving low-temperature ethanol dehydrogenation exclusively to acetaldehyde and hydrogen.[2] Recently, Bell et al. showed that gold supported on MgO : SiO_2 is an active catalyst for converting ethanol to 1,3-BD; and gold improved the dehydrogenation activity, resulting in increased ethanol conversion and 1,3-BD yield.[14]

In spite of tremendous advances in gold-catalyzed bio-ethanol transformation, principles for controlling the selectivity of bio-ethanol transformation by controlling the sizes of nanosize gold catalysts have remained largely unexplored. In this research, gold catalysts with well-controlled cluster sizes (3–22 nm) were prepared and investigated for their size-dependent selectivity in bio-ethanol transformation. We show for the first time how the selectivity of this reaction can be tailored toward specific cascade formation of either acetaldehyde or 1,3-BD as major products by tuning the size of gold nanoparticles.

A $ZnZr_{10}O_x$ support was prepared by a hard-template method. Au/$ZnZr_{10}O_x$ catalysts with identical gold loading of 3wt% were prepared by the anion-adsorption (AA) method[2] (3Au/ZnZr-AA) and the deposition−precipitation (DP) method[15] (3Au/ZnZr-DP_{Na}) for comparison purposes. A well-defined tetragonal phase was confirmed by x-ray diffraction (XRD) (Figure S1). The introduction of gold did not change the structure of the support.

Initially, we investigated the influence of the preparation method on the catalytic performance and the product distribution for catalysis carried out at the same reaction conditions. The product distribution observed in the continuous-flow experiments is shown as an inset in Figure 1. Ethylene was a main product of the ethanol conversion reaction on the bare $ZnZr_{10}O_x$ support (Figure S2a). Figure 1 compares the product distribution for ethanol conversion over catalysts at various reaction temperatures. For both gold-loaded catalysts, ethylene production via ethanol dehydration was suppressed by the beneficial effect of gold addition. At low temperature (200 °C), the conversion was low (28%), and the main product was acetaldehyde on 3Au/ZnZr-AA. Starting from 250 °C, 1,3-BD became the predominant product, with decreased selectivity for acetaldehyde. This finding is not consistent with Flytzani-Stephanopoulos's work, in which Au/$ZnZrO_x$ catalysts prepared by AA exhibited an extraordinary selectivity toward acetaldehyde and hydrogen from ethanol at low temperature.[2] Notably, 3Au/ZnZr-DP_{Na} exhibits a lower catalytic activity for 1,3-BD (<5%) and yields acetaldehyde as the main reaction product in the temperature range investigated. Evidently, changing the fashion of gold loading enables control over product distribution. The influence of sodium on selectivity control was effectively ruled out by performing the reaction over 3Au/ZnZr-DP samples prepared by a modified DP method using an ammonia solution.[16] The results illustrate that the 3Au/ZnZr-DP and 3Au/ZnZr-DP_{Na} catalysts show a very similar product distribution (Figure S2b).

The effects of the conversion on the product distribution were explored for a wide range of weight hour space velocity values at 300 °C over both 3Au/ZnZr-AA and 3Au/ZnZr-DP_{Na} catalysts.

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[a] R. He, Prof. Y. Men, Dr. J.G.Wang, Prof. W. An, X.X. Huang
College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, China
E-mail: men@sues.edu.cn
[b] Dr. W.Y. Song, Prof. J. Liu, State Key lab of Heavy Oil, China University of Petroleum, Changping, Beijing 102249, China
[c] J.X. Liu, Prof. S. Dai, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, USA

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As shown in Figure 2, high acetaldehyde selectivity was found on 3Au/ZnZr-AA at a low ethanol conversion rate, and 1,3-BD selectivity increased with increasing conversion at the expense of acetaldehyde. This finding suggests that acetaldehyde is a primary product that undergoes secondary reactions through aldol condensation over acidic/basic sites. It is clear that the dehydrogenation step readily takes place at low conversion, evidencing that the dehydrogenation step is the primary and also crucial step for cascade ethanol conversion. 3Au/ZnZr-AA is very selective for 1,3-BD formation within a wide conversion range of 10–75%. Interestingly, a remarkable change in product selectivity is observed over the 3Au/ZnZr-DP$_{Na}$ catalyst compared with the 3Au/ZnZr-AA catalyst. Acetaldehyde was found to be the primary product at a low ethanol conversion rate (8%) over the 3Au/ZnZr-DP$_{Na}$ catalyst; the yield was much higher (85%) than over 3Au/ZnZr-AA (only 35%). Note that acetaldehyde remained the predominant product on 3Au/ZnZr-DP$_{Na}$ when the reaction proceeded at 75% conversion of ethanol. An appreciable amount of ethyl acetate may be formed by dehydrogenative dimerization of ethanol. Our results offer firm evidence that the observed selectivity control toward either 1,3-BD or acetaldehyde over two catalysts was not governed by the conversion process.

Temperature-programmed desorption (TPD) profiles were obtained to investigate the surface acid/base properties (Figure S3). The surface acid/base properties of different materials are considered essential to catalyst performance in cascade ethanol conversion.[8b,17] In our previous work,[6a, 8a] we also concluded that the proper balance between acidic and basic components on the catalyst surface determined their catalytic activity in the conversion of ethanol into 1,3-BD and isobutene. Table S1 summarizes the basicity and acidity of each sample. The relative strengths of $Zn_1Zr_{10}O_x$, 3Au/ZnZr-AA and 3Au/ZnZr-DP$_{Na}$ in basicity/acidity were 0.55, 0.50 and 0.77, respectively. The enhanced surface basicity may facilitate the reaction step of ethanol initial dehydrogenation and sequential aldol condensation, which occurred favorably over basic sites of the multifunctional catalysts.

Transmission electron microscope (TEM) measurements were used to obtain further insights into the gold-support interaction. In TEM images (Figure S4), $ZnZr_{10}O_x$ supports in all catalysts exhibit similar polyhedral shapes. As can be clearly seen from the TEM image, the sizes of the gold nanoparticles on the $ZnZr_{10}O_x$ supports varied remarkably with the preparation method. Note that gold nanoparticles of only ~3 nm diameter were formed using DP, as opposed to large gold nanoparticles of 22 nm diameter prepared by AA. As is well documented in the literature, nanosized gold catalysts with 3~5 nm gold nanoparticles imposed distinctly different catalytic properties compared with corresponding catalysts with large gold particles.[11] This size-dependent selectivity control can also account for the different reactivities between the gold catalysts prepared in this research and Flytani-Stephanopoulos's gold catalysts prepared by AA, as chemical leaching with NaCN in the latter case would eventually lead to a nanosize gold catalyst with exceptional ethanol dehydrogenation capability. [2]

X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the chemical state of Au, Zn, and Zr in the Au/$ZnZr_{10}O_x$ catalysts (Figure 3). There are three sets of spin-orbital doublets for the Au4f$_{7/2}$ and Au4f$_{5/2}$ signals. The two Au4f$_{7/2}$ and Au4f$_{5/2}$ peaks can be split into doublets at binding energies of 87.3 for Au^{3+}, 85.6 for Au^{1+}, and 84.0 eV for metallic gold in its zero-valent state, which is consistent with the literature values.[18] The coexistence of Au^{3+}, Au^{1+}, and Au^0 can also be readily seen on all Au/$ZnZr_{10}O_x$ catalysts. Obviously, as shown in Table S2, significantly different fractions of gold species can be identified. The predominant presence of metallic gold, plus a minor fraction of oxidized Au^+ and Au^{3+} species were found on the samples prepared by AA. On the contrary, larger amounts of oxidized gold species were found on the surfaces of the DP-prepared samples. These samples exhibited high catalytic activity for the formation of acetaldehyde. Correlating the activity data, our results suggest that Au^0 species played an important role in cascade formation of 1,3-BD, while partially oxidized gold was responsible for acetaldehyde formation. This is in agreement with the results reported by Flytani-Stephanopoulos[11b] and Xu[19], that the numbers of highly dispersed ionic Au in smaller gold nanoparticles were much higher than that in larger gold particles. Accordingly, this difference in particle size and oxidation state of gold species may dictate the catalytic activity of ethanol transformation. Correlating the activity data, our results suggest that Au^0 species played an important role in cascade formation of 1,3-BD, while partially oxidized gold was responsible for acetaldehyde formation. A down-shift of the binding energy in the Zn 2p and Zr 3d spectra is also observed after gold deposition (Figure S5), which might be attributed to a strong electronic interaction between gold and $ZnZr_{10}O_x$. It is inferred that gold affects the surface properties of the composite oxides via charge transfer, in good agreement with literature reports.[11b]

Combining the results of catalytic study with those of microscopy and spectroscopy measurements, we think that the selectivity change observed over gold nanoparticles with average sizes of 3 nm and of 22 nm for gas-phase ethanol conversion is likely due to the effects of the size of the gold nanoparticles.

To ascertain the effects of the gold particle size on selectivity control over ethanol conversion, gold nanoparticles with intermediate sizes of 8 and 12 nm were synthesized by a modified DP method on $ZnZr_{10}O_x$ supports. (Figure S6) As shown in Figure 4, a clear trend of correlation of gold particle size with selectivity toward acetaldehyde or 1,3-BD can be observed; that is, the smaller the gold nanoparticle is, the more acetaldehyde will form at the expense of lower 1,3-BD generation. These results clearly confirm our hypothesis that small gold particles deposited on $ZnZr_{10}O_x$ are mainly active for acetaldehyde formation, whereas catalysts with large gold particles favor the cascade formation of 1,3-BD. A high yield of acetaldehyde or 1,3-BD can be implemented by simple tuning of the gold nanoparticles.

To further unravel the origin of the effect of gold particle size on selectivity control, kinetic studies were performed to obtain the respective activation energies of the desired intermediate and final products of acetaldehyde and 1,3-BD. (Figure 5) Our kinetic study determined that the activation energy difference between ethanol dehydrogenation and 1,3-BD formation can serve as a key selectivity descriptor. The initial dehydrogenated intermediates of acetaldehyde are the precursors for 1,3-BD formation in the course of cascade ethanol transformation. On the catalysts with large gold particles, the activation energies of acetaldehyde and 1,3-BD formation were 33.5 and 127.4 kJ/mol, respectively. On the catalysts with small gold particles, the activation energy of acetaldehyde formation was slightly lower than that on large gold particles. However, the activation energy of 1,3-BD formation on 3 nm gold nanoparticles was significantly higher than that on 22 nm gold nanoparticles, leading to a strong preference for the formation of acetaldehyde as a stabilized intermediate product. As a result, the selectivity toward acetaldehyde and 1,3-BD can be tailored by tuning the sizes of the gold nanoparticles. When the size of the gold nanoparticles was reduced to 3 nm, the gold atoms became more oxidized rather than being in a metallic state.[11b,19] Such changes could lead to significant alterations in the adsorption/desorption of the ethanol intermediates on the oxidized gold surface and gold-support interface,[10b,20] and a subsequent higher ethanol conversion rate, as well as lower selectivity toward cascade transformation of ethanol to 1,3-BD. It has been reported that the facilitated desorption of intermediates may improve the performance of catalysts in various complex cascade reactions,[21] particularly in achieving a high selectivity for the intermediates. These studies show that the adsorption strength of products plays a critical role in determining the selectivity of reaction intermediates. Likewise, the size effect of gold nanoparticles in our current work may impart the significantly weakened adsorption strength of the key intermediate acetaldehyde on various gold-containing multifunctional catalysts resulting in acetaldehyde as a stabilized product. However, the detailed reaction mechanism remains to be elucidated by future study.

In conclusion, bio-ethanol can be transformed efficiently into either acetaldehyde by initial ethanol dehydrogenation or cascade formation of 1,3-BD, depending on the fashion of the gold loading on a $ZnZr_{10}O_x$ support. Ethanol conversion studies demonstrated that catalysts with smaller gold particles tend to be selective for the acetaldehyde formation, whereas catalysts with larger gold particles favor the specific cascade formation of 1,3-BD. At this point, the implication of the different surface properties of Au/$ZnZr_{10}O_x$ catalysts as a function of the particle size may present a tentative explanation for this trend. The intrinsic impact of the gold particle sizes on ethanol transformation need to be further explored. Overall, the size of the gold nanoparticles was shown to be the key structure-selectivity indicator in cascade bio-ethanol transformation. This study highlights previously unaddressed aspects of exceptional control over catalytic product selectivity by tuning of the sizes of gold nanoparticles. It may open a new avenue for catalytic design principles of fundamental importance to enhancing the production of desired reaction products in complex cascade reaction sequences.

Experimental Section

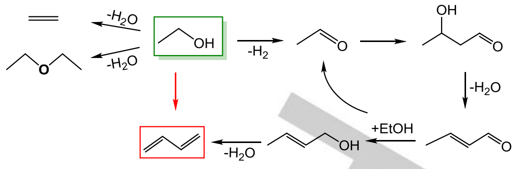
The $ZnZr_{10}O_x$ supports were synthesized by employing conductive carbon black T100 as the hard template, and the ternary Au/$ZnZr_{10}O_x$ catalysts were prepared by AA and DP methods. The actual gold contents were obtained by quantifying the residual gold ions in the precursor solution using inductively coupled plasma analysis.

The specific surface areas (S_{BET}), pore volume (V_P), and pore diameter (D_P) of the catalysts were measured by a Micromeritics ASAP 2460 using nitrogen adsorption at 77 K. The acidic and basic properties of catalysts were obtained by NH_3-TPD and CO_2-TPD using a Micromeritics Autochem II 2920.

TEM images of various samples were obtained on a field emission high-resonance TEM (HRTEM, JEOL JEM-2100).

XPS was performed on a PerkinElmer PHI 5000 to analyze the surface electronic states. All the binding energy values were calibrated using C1s=284.6eV as the reference.

Catalytic reactions were evaluated in a fixed-bed continuous-flow reactor using an online Shimadzu 2014 gas chromatograph.



Scheme 1. Generally accepted cascade reaction pathway of ethanol to 1,3-BD conversion.

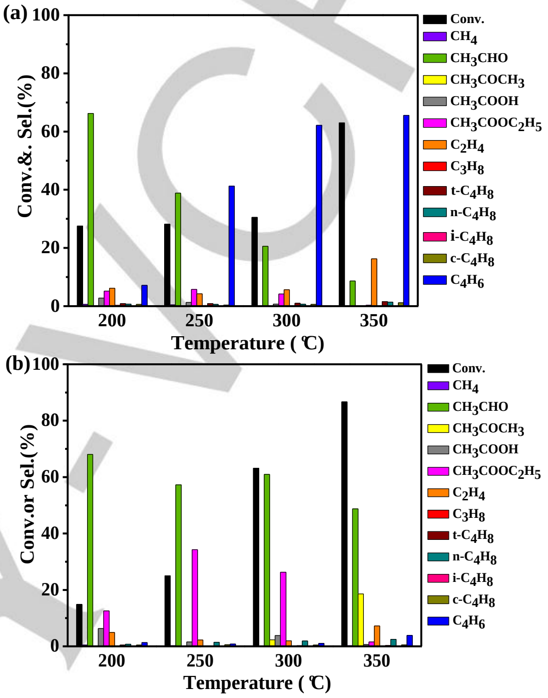


Figure 1. Temperature-dependent reactivity of the selective conversion of ethanol on (a) 3Au/ZnZr-AA and (b) 3Au/ZnZr-DP_{Na}. Reaction conditions: T=200-350 ^{o}C, $P_{ethanol}$=5.87 kPa, M_{cat}=100 mg.

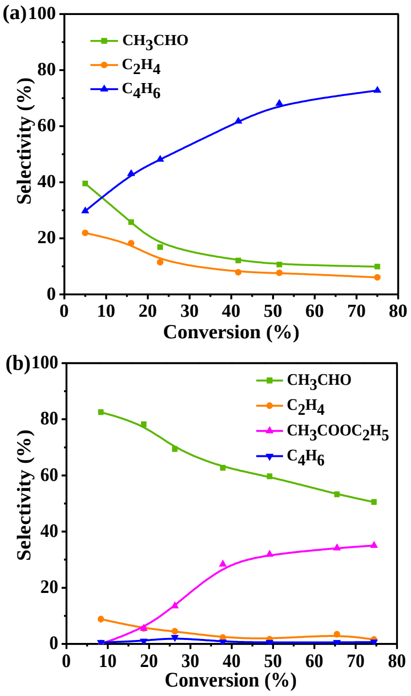


Figure 2. Conversion-dependent product selectivity of ethanol transformation over (a) 3Au/ZnZr-AA and (b) 3Au/ZnZr-DP_{Na} Catalysts. Reaction conditions: T=300 ^{o}C, $P_{ethanol}$=5.87 kPa.

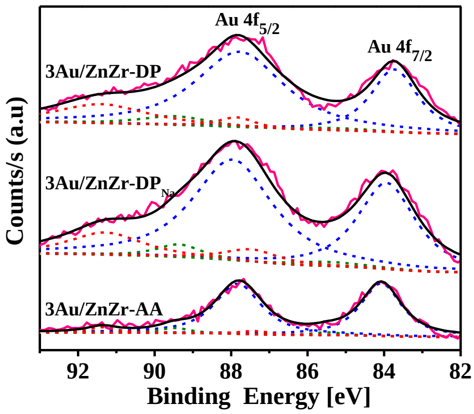


Figure 3. Au 4f XP spectra of 3Au/ZnZr-AA, 3Au/ZnZr-DP$_{Na}$, and 3Au/ZnZr-DP catalysts.

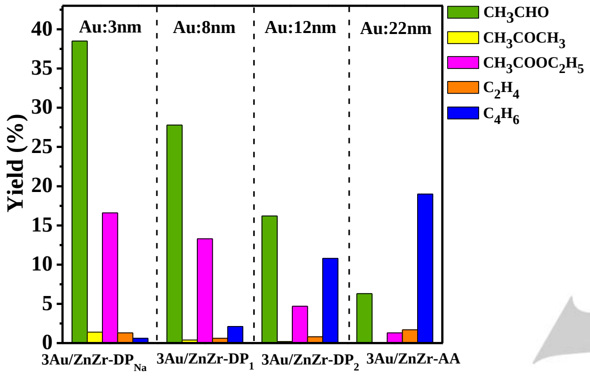


Figure 4. Product distribution at 300 °C on the 3Au/ZnZr-DP$_{Na}$, 3Au/ZnZr-DP$_1$, 3Au/ZnZr-DP$_2$, and 3Au/ZnZr-AA catalysts: smaller sizes gold (left) or larger sizes gold (right).

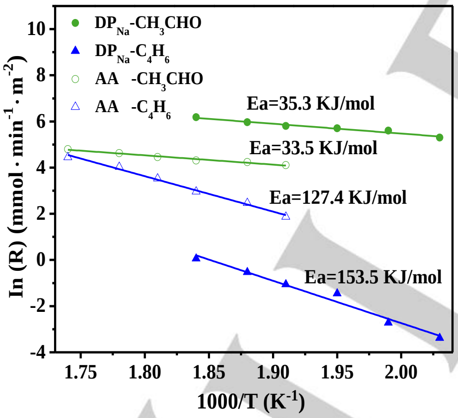


Figure 5. Arrhenius-type plot of reaction rates of 3Au/ZnZr-AA and 3Au/ZnZr-DP$_{Na}$ catalysts.

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Keywords: Bio-ethanol · 1,3-butadiene · acetaldehyde · gold catalyst · particle size effect

References

[1] a) E. V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P. A. Jacobs, B. F. Sels, *Chem. Soc. Rev.* **2014**, *43*, 7917-7953; b) G. R. M. Dowson, M. F. Haddow, J. Lee, R. L. Wingad, D. F. Wass, *Angew. Chem. Int. Ed.* **2013**, *52*, 9005-9008; c) T. N. Pham, T. Sooknoi, S. P. Crossley, D. E. Resasco, *ACS Catal*. **2013**, *3*, 2456-2473.

[2] C. Y. Wang, G. Garbarino, L. F. Allard, F. Wilson, G. Busca, M. Flytzani-Stephanopoulos, *ACS Catal.* **2016**, *6*, 210-218.

[3] K. Inui, T. Kurabayashi, S. Sato, *J. Catal.* **2002**, *212*, 207-215.

[4] X. B. Li, E. Iglesia, *Chem. Eur. J.* **2007**, *13*, 9324-9330.

[5] B. Zhao, Y. Men, A. N. Zhang, J. G. Wang, R. He, W. An, S. X. Li, *Appl. Catal.* A, **2018**, *558*, 150-160.

[6] a) F. Liu, Y. Men, J. G. Wang, X. X. Huang, Y. Q. Wang, W. An, *ChemCatChem* **2017**, *9*, 1758-1764. b) F. Collignon, G. Poncelet, *J. Catal.* **2001**, *202*, 68-77.

[7] C. Angelici, B. M. Weckhuysen, P. C. A. Bruijnincx, *ChemSusChem* **2013**, *6*, 1595-1614.

[8] a) X. X. Huang,Y. Men. J. G. Wang, W. An, Y. Q. Wang, *Catal. Sci. Technol.* **2017**, *1*, 168-180; b) C. Angelici, M. E. Z. Velthoen, B. M. Weckhuysen, P. C. A. Bruijnincx, *Catal. Sci. Technol.* **2015**, *5*, 2869-2879.

[9] a) S. H. Chung, C. Angelici, S. O. M. Hinterding, M. Weingarth, M. Baldus, K. Houben, B. M. Weckhuysen, P. C. A. Bruijnincx, *ACS Catal.* **2016**, *6*, 4034-4045; b) J. V. Ochoaa, C. Bandinelli. O. Vozniuka, A. Chieregatoa, A. Malmusi, C. Recchi, F. Cavani, *Green Chem.* **2016**, *18*, 1653-1663.

[10] a) M. Haruta, N. Yamada, T. Kobayashi S. Iijima, *J. Catal.* **1989**, *115*; b) M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, *J. Catal.* **1993**, *144*.

[11] a) G. C. Bond, D. T. Thompson, *Catal. Rev. Sci. Eng.* **1999**, *41*, 319-388; b) Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* **2003**, *301*, 935; c) L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem. Int. Ed.* **2009**, *48*, 9538-9541; d) J. L. Gong, C. B. Mullins, *J. Am. Chem. Soc*. **2008**, *130*, 16458-16459; e) M. S. Chen, D. W. Goodman, *Science* **2004**, *306*, 252-255; f) W. F. Yan, S. M. Mahurin, Z. W. Pan, S. H. Overbury, S. Dai, *J. Am. Chem. Soc.* **2005**, *127*, 10480-1048

[12] a) L. W. Guo, P. P. Du, X. P. Fu, C. Ma, J. Zeng, R. Si, Y. Y. Huang, C. J. Jia, Y. W. Zhang, C. H. Yan, *Nat. Commun*. **2016**, *7*, 13481; b) M. Murdoch, G. I. Waterhouse, M. A. Nadeem, J. B. Metson, M. A. Keane, R. F. Howe, J. Llorca, H. Idriss, *Nat. Chem.* **2011**, *3*, 489-492.

[13] P. Liu, E. J. M. Hensen, *J. Am. Chem. Soc.* **2013**, *135*, 14032-14035.

[14] S. Shylesh, A. A. Gokhale, C. D. Scown, D. Kim, C. R. Ho, A. T. Bell, *ChemSusChem* **2016**, *9*, 1462-1472.

[15] Y. J. Chen, C. T. Yeh, *J. Catal.* **2001**, *200*, 59-68.

[16] D. W. Gao, X. Zhang, Y. Yang, X. P. Dai, H. Sun, Y. C. Qin, A. J. Duan, *Nano Res*. **2016**, *9*, 985-995.

[17] W. Janssens, E. V. Makshina, P. Vanelderen, F. De Clippel, K. Houthoofd, S. Kerkhofs, J. A. Martens, P. A. Jacobs, B. F. Sels, *ChemSusChem* **2015**, *8*, 994-1008.

[18] a) A. Y. Klyushin, M. Greiner, X. Huang, T. Lunkenbein, X. Li, O. Timpe, M. Friedrich, M. Hävecker, A. Knop-Gericke, R. Schlögl, *ACS Catal.* **2016**, *6*, 3372-3380; b) X. Zhang, H. Shi, B. Q. Xu, *Angew. Chem. Int. Ed.* **2005**, *44*, 7132-7135.

[19] X. Zhang, H. Shi, B. Q. Xu, *J. Catal.* **2001**, *279*, 75-87.

[20] Y. Y. Wu, N. A. Mashayekhi, H. H. Kung, *Catal. Sci. Technol* **2013**, *3*,2881-2891.

[21] a) E. W. Shin, J. H. Kang, W. J. Kim, J. D. Park, H. M. Sang, *Appl. Catal. A*, **2002**, *223*, 161-172; b) J. L. Liu, L. J. Zhu, Y. Pei, J. H. Zhuang, H. Li, H. X. Li, M. H. Qiao, K. N. Fan, *Appl. Catal. A*, **2009**, *353*, 282-287; c) H. B. Zhao, B. E. Koel, *J. Catal.*, **2005**, *234*, 24-32.

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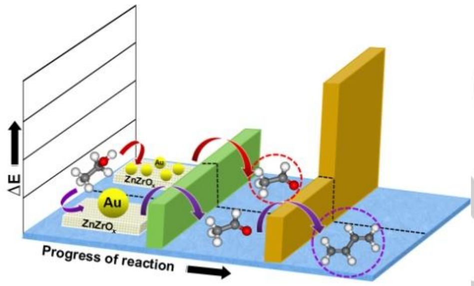

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The selective bio-ethanol cascade transformation to hydrocarbons over multifunctional catalysts is a highly promising sustainable pathway to high-value chemicals and fuels. Bio-ethanol can be transformed efficiently into either acetaldehyde by initial ethanol dehydrogenation or 1,3-BD, depending on the fashion of gold loading on a $ZnZr_{10}O_x$ support. Larger gold particles tend to show much higher selectivity for 1,3-butadiene, whereas smaller gold nanoparticles favor the formation of acetaldehyde.

Layout 2:

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