Heterogeneous Catalysis

International Edition: DOI: 10.1002/anie.201508731
German Edition: DOI: 10.1002/ange.201508731

ZrO_2-Based Alternatives to Conventional Propane Dehydrogenation Catalysts: Active Sites, Design, and Performance

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Abstract: *Non-oxidative dehydrogenation of propane to propene is an established large-scale process that, however, faces challenges, particularly in catalyst development; these are the toxicity of chromium compounds, high cost of platinum, and catalyst durability. Herein, we describe the design of unconventional catalysts based on bulk materials with a certain defect structure, for example, ZrO_2 promoted with other metal oxides. Comprehensive characterization supports the hypothesis that coordinatively unsaturated Zr cations are the active sites for propane dehydrogenation. Their concentration can be adjusted by varying the kind of ZrO_2 promoter and/or supporting tiny amounts of hydrogenation-active metal. Accordingly designed Cu(0.05 wt %)/ZrO_2-La_2O_3 showed industrially relevant activity and durability over ca. 240 h on stream in a series of 60 dehydrogenation and oxidative regeneration cycles between 550 and 625 °C.*

Propene, used in the chemical industry for the manufacture of polymers, solvents, dyes, resins, fibers, and drugs is mainly produced from crude oil. In view of finite petroleum reserves but growing demand for this olefin, vast reserves of shale gas consisting predominantly of methane and of lower amounts of ethane and propane[1] could provide an economical alternative to crude oil.[2]One way to convert propane to propene is the non-oxidative propane dehydrogenation (PDH), which is a successful example of raw-material change in the chemical industry.[3] Propene production via PDH in 2012 amounted to about 5 million metric tons (mmt) from the total 80 mmt production.[3d] The share is expected to grow because several PDH plants are under construction.[4] Consequently, demand for PDH catalysts will also increase. Commercial catalysts with CrO_x or Pt–Sn species typically supported on Al_2O_3[3] are either toxic or have a limited availability of the active components. For several decades, researchers have attempted to design suitable alternatives based on supported V_2O_5, Ga_2O_3, or MoO_3.[3d] Recently, Weckhuysen and co-workers[5] developed an active Al_2O_3-supported catalyst consisting of two typical propane dehydrogenation components, that is, Pt and Ga_2O_3. The noble metal was assumed to participate directly in PDH through assisting in the recombination of hydrogen atoms thus helping the active Ga^{3+} sites to recover. In a long-term test over 150 PDH/regeneration cycles, this catalyst, however, lost around 30 % of its initial activity during the first twenty sequences and then operated at a stable level. Thus, the traditional concept of active sites in supported noble metals or transitional metal oxides has only resulted in limited progress in developing novel catalysts.

Herein, we elucidated and provide general fundamentals for designing alternative catalysts composed of unconventional PDH components, in which lattice defects of the support are the catalytically active sites. Our working hypothesis was that oxides of metals which usually have an unchangeable oxidation state but a high oxygen mobility can generate the required defects under PDH conditions. ZrO_2 promoted with other metal oxides is a typical representative of such materials[6] and has actually been used as a support for catalytically active Pt, CrO_x, or GaO_x species.[3d] However, the loading was too high to test the intrinsic support activity. Our mechanistic analysis led us to the conclusion that coordinatively unsaturated Zr cations (Zr_{cus}, where cus = coordinatively unsaturated) are the active sites possessing PDH activity and selectivity comparable to those of an industrially relevant CrO_x-containing catalyst. Thus, this study further supports the importance of coordinatively unsaturated cations in heterogeneous catalysis including alkane dehydrogenation.[3d,7] We also established basic principles for tuning the concentration of such defect sites. Importantly, dispersed ZrO_x species supported on SiO_2 or Al_2O_3–SiO_2 are significantly less active than Zr_{cus} on the surface of bulk ZrO_2-based catalysts. The derived knowledge will aid in the optimization of such catalysts and motivate the exploration of other materials with high surface reducibility for PDH application.

We initially selected metal oxides differing in oxygen surface mobility,[8] that is, SiO_2, Al_2O_3, 10Si90AlO_x (10 wt % SiO_2 in Al_2O_3), 40Si60AlO_x (40 wt % SiO_2 in Al_2O_3), and LaZrO_x (10 wt % La_2O_3 in cubic ZrO_2). To increase their reducibility, they were impregnated with pre-formed Pt, Rh, or Ru nanoparticles (NPs).[9] The NPs were between 1.1 and 1.5 nm diameter with a narrow size distribution (Figure S1 in the Supporting Information). The loading of Pt was set to 0.1 wt %, while that of Rh or Ru was 0.05 wt % to ensure similar surface area of each metal (ca. $0.2\ m^2_{metal}/g_{support}$ calculated according to Ref. [10]). Figure 1 A presents the rate of propene formation over supported catalysts and pristine supports. To assure the metallic state of Pt, Rh, and Ru, the catalysts (as well as the pristine supports) were pre-treated in a flow of H_2 at 550 °C before the reaction. The supports were significantly less active than the corresponding catalysts but their activity increased as the strength of the

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201508731.

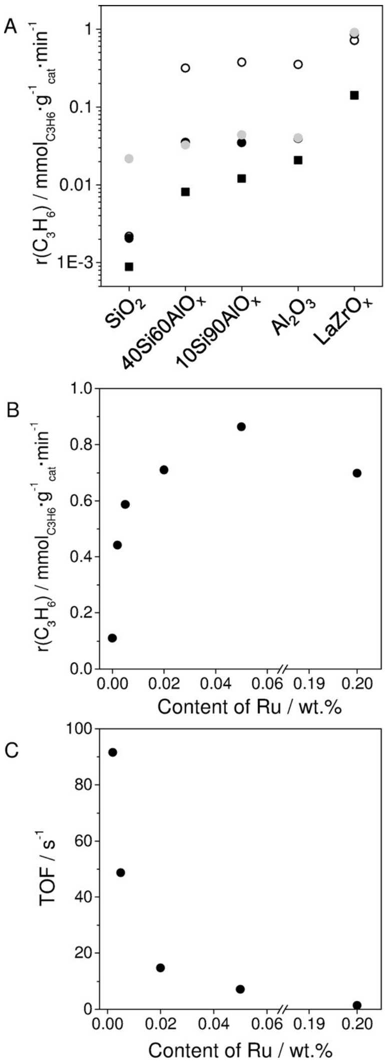

Figure 1. A) Propene formation rate ($r(C_3H_6)$) over pristine supports (■) and with supported Pt (○), Rh (gray filled circles) or Ru (●) NPs. B) The rate and C) TOF as a function of Ru content in Ru/LaZrO$_x$. Test conditions: 550 °C, $C_3H_8:N_2 = 40:60$, weight hourly space velocity (WHSV) of 23.6 h^{-1}.

metal–oxygen bond decreased. The catalysts based on SiO$_2$–Al$_2$O$_3$ with Rh or Ru NPs showed lower rates than their Pt-containing counterparts. The activity order, however, changed when the metals were supported on LaZrO$_x$. Remarkably, pristine LaZrO$_x$ with the weakest metal–oxygen bond gave an even higher rate than the catalysts with Ru or Rh NPs on SiO$_2$–Al$_2$O$_3$ and slightly lower than Pt/SiO$_2$–Al$_2$O$_3$. To understand the origins of the high activity of LaZrO$_x$-based materials, we tested additional catalysts with Ru content between 0.002 and 0.2 wt %. The rate of propene formation (Figure 1 B) and propene selectivity (Figure S2) passed over a maximum on the catalysts with 0.05 and 0.005 wt % Ru respectively.

Essentially, the apparent turnover frequency (TOF) of propene formation, that is, the activity related to one surface Ru atom, decreased with Ru loading (Figure 1 C). Since the catalysts had the same 1.1 nm Ru NPs, any effects of the metal–support interaction(s) and/or particle size on TOF are excluded. Therefore, Ru is not directly responsible for the high PDH activity of Ru/LaZrO$_x$. Thus, we postulate that Zr$_{cus}$, that is, zirconium cations located near anion vacancies, are catalytically active sites. We put forward that Ru NPs participate in the formation of adsorbed hydrogen species, which remove lattice oxygen from LaZrO$_x$ thus yielding Zr$_{cus}$. This assumption is indirectly supported by the fact that the initial activity of oxidized catalysts was lower but increased with time on stream compared with their reduced counterparts (Figure S3).

The formation of anion vacancies (a direct indicator of Zr$_{cus}$ existence) in the lattice of LaZrO$_x$ after reduction in H$_2$ at 550 °C was experimentally demonstrated by electron paramagnetic resonance (Figure S4). To quantify the concentration of anion vacancies, O$_2$-pulse experiments with catalysts reduced at 550 °C were performed in the temporal analysis of products (TAP) reactor.[11] Having a minimal pulse size of around 0.1 nmol, this technique is perfectly suitable for such purposes. Based on the amount of O$_2$ consumed (Figure S5), we calculated the concentration of anion vacancies assuming that one O$_2$ molecule fills two vacancies. The corresponding values for LaZrO$_x$ without Ru and with 0.002, 0.005, or 0.05 wt % Ru were $2.4\cdot10^{16}$, $4.6\cdot10^{16}$, $1.2\cdot10^{18}$, and $1.0\cdot10^{19}$ sites per gram. It cannot be completely excluded that bulk vacancies also participated in this process to some extent. Control experiments with Ru/40Si60AlO$_x$ which has the same Ru NPs but on a non-reducible support showed that gas-phase O$_2$ was not consumed for oxidation of Ru to RuO$_2$.

To further validate our hypothesis about the kind of PDH active sites, we measured the rate of propene formation over LaZrO$_x$, Ru/LaZrO$_x$, and Rh/LaZrO$_x$ at different reaction temperatures. The purpose was to check if apparent activation energy (E_a) of propene formation depends on the presence and the type of noble metal. In the first series of experiments, the catalysts were reduced at 575 °C before determining the rate between 525 and 575 °C. This experiment was important to exclude temperature effects on the concentration of Zr$_{cus}$ sites formed upon catalyst reduction. Figure 2 shows that E_a determined from the Arrhenius plots was around 170 kJ mol^{-1} for all catalysts and did not depend on the kind of noble metal and its concentration. This result strongly suggests that the catalysts have the same kind of PDH sites, which should be Zr$_{cus}$ but not Ru or Rh.

Significantly higher E_a values were obtained in a second series of tests (Figure 2), when the catalysts were reduced at the same temperature, at which the rate of propene formation was measured, that is, at 525, 550, and 575 °C. This is because E_a in the second series additionally includes the energy required for formation of Zr$_{cus}$ sites upon catalysts reduction. As seen in Figure 2, the difference in E_a for a given catalyst between the two series of experiments depends on the catalyst composition. The largest difference of 80 kJ mol^{-1} was determined for pristine LaZrO$_x$ and became lower when Ru or Rh NPs were present on this support because these metals catalyze the reduction of the support. Based on the results presented above and mechanistic studies on alkane dehydrogenation over CrO$_x$-containing[12] and GaO$_x$-containing[7d,13] catalysts, we postulate that Zr$_{cus}$ and neighboring lattice oxygen participate in the C−H bond activation resulting in the

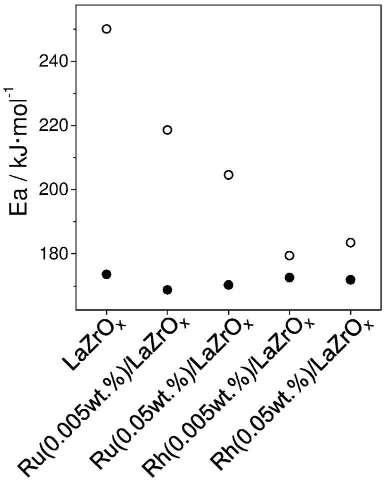

Figure 2. Apparent activation energy of propene formation over different catalysts. The catalysts were either pre-reduced at the corresponding (525, 550, and 575 °C) reaction temperature (○) or at 575 °C (●) before testing at this and lower temperatures.

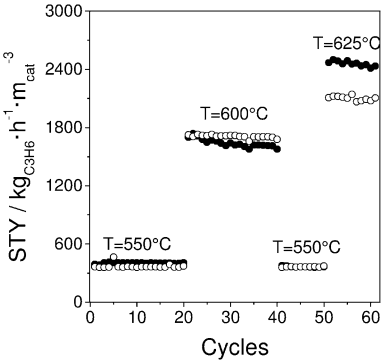

Figure 3. Space time yield (STY) of propene over Cu(0.05 wt %)/LaZrO$_x$ (●) and Cr(19.6 wt %)–K(0.9 wt.%)/Al$_2$O$_3$ (○) in a series of 60 PDH/regeneration cycles at 550, 600, and 625 °C with WHSV of 1.57, 6.26, and 9.42 h^{-1}, respectively.

formation of Zr$_{cus}$–C$_3$H$_7$ and O–H surface species. After the elimination of the β-hydrogen, propene and hydrogen are formed. According to theoretical calculations,[14] the excess electron density is mainly localized in the anion vacancy. Thus, Zr$^{4+}_{cus}$ and not Zr$^{3+}_{cus}$ should participate in propane activation. Furthermore, control experiments with ZrO$_x$/SiO$_2$ and ZrO$_x$/SiAlO$_x$ revealed that the surface Zr$^{4+}_{cus}$ of bulk LaZrO$_x$ are significantly more active than supported ZrO$_x$ species (Figure S6).

If the role of Rh or Ru is to promote the formation of Zr$_{cus}$ sites on the surface of LaZrO$_x$, any other hydrogenation-active metal can also be used for this purpose. As a proof of concept, we prepared additional catalysts with Cu, Ni, or Co species supported on LaZrO$_x$. Note that these metals have never been reported to be active in the PDH reaction. All these catalysts revealed up to five-times higher rate of propene formation than LaZrO$_x$, with Cu(0.05 wt %)/LaZrO$_x$ showing the highest rate among them (Figure S6). Importantly, the Cu(0.05 wt %)/LaZrO$_x$ catalyst was only two-times less active than the Ru(0.05 wt %)/LaZrO$_x$ catalyst. The difference between the catalysts with different supported metals should be due to the dissimilar ability of the metals to generate the surface hydrogen species required for LaZrO$_x$ reduction during H$_2$ pre-treatment. The practical relevance of Cu(0.05 wt %)/LaZrO$_x$ was demonstrated over approximately 240 h on stream in a series of 60 PDH/oxidative regeneration cycles at 550, 600, and 625 °C (Figure 3). No reductive pre-treatment was performed because the catalyst can be reduced in situ. The conversion of propane at 550 °C and 600 °C initially increased and then decreased within each 30 min DH cycle but continuously decreased at 625 °C.

Figure 3 shows the highest space–time yield (STY) of propene obtained over Cu(0.05 wt %)/LaZrO$_x$ and Cr(19.6 wt %)–K(0.9 wt %)/Al$_2$O$_3$[9] in each cycle between 550 °C and 625 °C. It is clear that Cu(0.05 wt %)/LaZrO$_x$ give a similar or even superior STY than the industrially relevant reference material and did not significantly change its performance from cycle to cycle. It also showed propene selectivity above 90 % (Figure S7). The main side products were light hydrocarbons and coke. The coke could be completely removed within only 5 min by an air stream at the PDH temperature.

Finally, we demonstrate how the derived fundamental knowledge about the nature of active sites can be applied to tailor ZrO$_2$-based catalysts without using supported metals. The concentration of anion vacancies and accordingly the number of Zr$_{cus}$ in ZrO$_2$ can be increased through promoting with a metal of lower than Zr^{4+} oxidation state.[6] Doping with other metals causing distortion in the ZrO$_2$ lattice can also enhance the reducibility of ZrO$_2$ and thus the concentration of Zr$_{cus}$ upon reductive treatment. Bearing this in mind, we prepared ZrO$_2$ doped to various degrees with TiO$_2$ (TiZrO$_x$), CeO$_2$ (CeZrO$_x$), or Y$_2$O$_3$ (YZrO$_x$) and tested them for their PDH activity. Figure 4 shows that YZrO$_x$, TiZrO$_x$, and CeZrO$_x$ outperformed LaZrO$_x$. Importantly, the rate of propene formation over YZrO$_x$ was very close to that over the most active Ru (0.05 wt %)/LaZrO$_x$ catalyst. The results further support our conclusion about the PDH role of Zr$_{cus}$ thus demonstrating generality of our concept for designing novel catalysts. Our preliminary results revealed that such

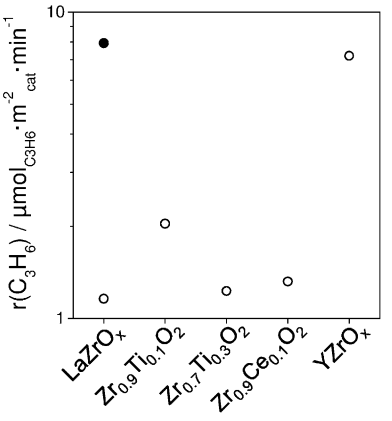

Figure 4. Propene formation rates over pristine supports (○) and over Ru (0.05 wt %)/LaZrO$_x$ (●).

catalysts could even find their application for dehydrogenation of *iso*- or *n*-butanes to generate corresponding olefins or dienes, which are also important building blocks of the chemical industry.

In this study, we revisited the fundamentals of catalyst design for the non-oxidative dehydrogenation of alkanes to olefins. Compared to conventional supported PDH catalysts, alternative catalysts are bulk metal oxides with lattice defects on their surface functioning as active sites. The concept was verified for propane dehydrogenation over ZrO_2-based catalysts, where Zr_{cus} cations were identified to be the PDH active sites. Such sites can be created by promoting ZrO_2 with metal oxides, which induce formation of structural anion vacancies or enhance ZrO_2 reducibility. Their concentration can also be increased by depositing tiny amounts of hydrogenation-active metals catalyzing ZrO_2 reduction in situ under dehydrogenation conditions or during reductive catalyst treatment.

Experimental Section

Nanoparticles (NPs) of Ru, Rh, and Pt were synthesized by a modified ethylene glycol method. Supported catalysts were prepared by adding dropwise NPs solution in ethanol to support suspensions in ethanol at room temperature. Further details on preparation of NPs, supports, catalysts and their characterization are provided in Section A1 in the Supporting Information.

Catalytic tests were performed in an in-house developed setup consisting of 15 continuous-flow fixed-bed reactors. The feed components and the reaction products were analyzed by an on-line gas chromatograph (Agilent 7890). A more detailed description of catalytic tests is provided in Section A2 in the Supporting Information.

Acknowledgements

We thank Anja Simmula for the ICP OES analysis, Dr. Matthias Schneider for the XRD analysis, Jacqueline Priebe and Ulrich Marx for the EPR spectra and Dr. Marga-Martina Pohl for the TEM images. T.O. acknowledges support from DAAD (German Academic Exchange Service) and the Ministry of Education and Science of the Russian Federation.

Keywords: active sites · heterogeneous catalysis · propane dehydrogenation · propene · zirconia

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 15880–15883
Angew. Chem. **2015**, *127*, 16107–16111

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[1] a) E. McFarland, *Science* **2012**, *338*, 340–342; b) U. S. Energy Information Administration, Annual Energy Outlook, **2013**; c) BP Energy Outlook 2015, **2014**.

[2] a) E. V. Kondratenko, M. Baerns in *Handbook of Heterogeneous Catalysis*, *Vol. 6* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3010–3023; b) P. Tang, Q. Zhu, Z. Wu, D. Ma, *Energy Environ. Sci.* **2014**, *7*, 2580–2591.

[3] a) K. J. Caspary, H. Gehrke, M. Heinritz-Adrian, M. Schwefer in *Handbook of Heterogeneous Catalysis*, *Vol. 7* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3206–3228; b) J. C. Bricker, *Top. Catal.* **2012**, *55*, 1309–1314; c) B. V. Vora, *Top. Catal.* **2012**, *55*, 1297–1308; d) J. J. H. B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, B. M. Weckhuysen, *Chem. Rev.* **2014**, *114*, 10613–10653.

[4] C. Boswell, ICIS Chemical Business, April 16, 2012.

[5] J. J. H. B. Sattler, I. D. Gonzalez-Jimenez, L. Luo, B. A. Stears, A. Malek, D. G. Barton, B. A. Kilos, M. P. Kaminsky, T. W. G. M. Verhoeven, E. J. Koers, M. Baldus, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2014**, *53*, 9251–9256; *Angew. Chem.* **2014**, *126*, 9405–9410.

[6] R. J. D. Tilley, *Defects in Solids*, Wiley, **2008**.

[7] a) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Ferey, *Angew. Chem. Int. Ed.* **2008**, *47*, 4144–4148; *Angew. Chem.* **2008**, *120*, 4212–4216; b) P. D. C. Dietzel, V. Besikiotis, R. Blom, *J. Mater. Chem.* **2009**, *19*, 7362–7370; c) J. H. Kwak, J. Z. Hu, D. Mei, C. W. Yi, D. H. Kim, C. H. F. Peden, L. F. Allard, J. Szanyi, *Science* **2009**, *325*, 1670–1673; d) C. Coperet, *Chem. Rev.* **2010**, *110*, 656–680; e) D. Teschner, G. Novell-Leruth, A. K.-G. Ramzi Farra, R. Schlögl, L. Szentmiklosi, M. Gonzalez Hevia, H. Soerijanto, R. Schomäcker, J. Pérez-Ramírez, N. Lopez, *Nat. Chem.* **2012**, *4*, 739–745; f) D. J. Xiao, E. D. Bloch, J. A. Mason, W. L. Queen, M. R. Hudson, N. Planas, J. Borycz, A. L. Dzubak, P. Verma, K. Lee, F. Bonino, V. Crocella, J. Yano, S. Bordiga, D. G. Truhlar, L. Gagliardi, C. M. Brown, J. R. Long, *Nat. Chem.* **2014**, *6*, 590–595.

[8] D. Martin, D. Duprez, *J. Phys. Chem.* **1996**, *100*, 9429–9438.

[9] Materials, methods, and supporting data are available as Supporting Information online.

[10] T. Abe, M. Tanizawa, K. Watanabe, A. Taguchi, *Energy Environ. Sci.* **2009**, *2*, 315–321.

[11] a) J. Pérez-Ramírez, E. V. Kondratenko, *Catal. Today* **2007**, *121*, 160–169; b) J. T. Gleaves, G. Yablonsky, X. L. Zheng, R. Fushimi, P. L. Mills, *J. Mol. Catal. A* **2010**, *315*, 108–134.

[12] a) S. Lillehaug, K. J. Børve, M. Sierka, J. Sauer, *J. Phys. Org. Chem.* **2004**, *17*, 990–1006; b) S. Lillehaug, V. R. Jensen, K. J. Børve, *J. Phys. Org. Chem.* **2006**, *19*, 25–33.

[13] B. Zheng, W. Hua, Y. Yue, Z. Gao, *J. Catal.* **2005**, *232*, 143–151.

[14] M. V. Ganduglia-Pirovano, A. Hofmann, J. Sauer, *Surf. Sci. Rep.* **2007**, *62*, 219–270.

Received: September 17, 2015
Revised: October 13, 2015