Low-Temperature Direct Dehydrogenation of Propane over Binary Oxide Catalysts: Insights into Geometric Effects and Active Sites

Yingmin Qu, Ganggang Li, Ting Zhao, Zhongshen Zhang,* Mark Douthwaite, Jing Zhang, and Zhengping Hao*

ABSTRACT: Binary ZnZrxOy catalysts were prepared and employed to catalyze propane dehydrogenation at relatively low temperatures. The evaluation of these materials for propane dehydrogenation was supplemented by material characterization and density functional theory calculations, to provide molecular insights into the nature of the catalytic active sites. Combined, these experiments suggested that coordinatively unsaturated Zn cations (Zn\(\text{cus}\)) in Zn\(\text{cus}\)-O-Zr\(\text{cus}\) were the active sites for the first step of propane dehydrogenation, and coordinatively unsaturated Zr cations (Zr\(\text{cus}\)) in Zn\(\text{cus}\)-O-Zr\(\text{cus}\) were active sites for the second step. This synergistic effect, derived from both these components, led to significant enhancements in activity. Furthermore, the combination of Zn and Zr species resulted in notable changes to the structure of the catalysts, leading to both the formation of the Zr\(\text{cus}\) active site and improved oxygen mobility. ZnZr2 exhibited relatively high activity.

KEYWORDS: propane direct dehydrogenation, low temperature, synergy effect, reaction mechanism, binary ZnZrxOy catalysts

INTRODUCTION

Propene (C\(\text{3}\)H\(\text{6}\)) is one of the most important petrochemicals and is commonly used to produce polymers and rubber.1 The continuously increasing demand for C\(\text{3}\)H\(\text{6}\) has led to the development of alternative, nonoxidative approaches for propane (C\(\text{3}\)H\(\text{6}\)) dehydrogenation (PDH) reaction, compared to traditional methods such as the cracking of naphtha.2 At present, PDH is predominantly catalyzed by supported Pt-based3-9 and CrO\text{x}-based catalysts.8 However, some problem-atic limitations associated with the use of these materials must not be overlooked. For instance, Pt-based catalysts are costly and CrO\text{x}-based catalysts are toxic to the environment.20,25 It is of great importance to develop an effective catalyst that is cheap and environmentally friendly. A variety of materials, such as carbon-based materials,11-14 Ga-based catalysts,15,16 V-based catalysts,17 Zn-based catalysts,18-20 Co-based catalysts,21 and Zr-based catalysts,22 were found to be active for this reaction. Some progress has been made in this field, but in some areas, there remains room for development: (1) catalytic performance (activity and selectivity) must be enhanced; (2) high reaction temperatures are often employed, which favor undesirable side reactions such as cracking forming C\(\text{2}\)H\(\text{4}\) and CH\(\text{4}\), coking, and hydrogenolysis generating C\(\text{3}\)H\(\text{6}\) and CH\(\text{4}\); and (3) the reaction mechanism is still under debate, due to high reaction temperatures hindering the application of operando characterization techniques.

Among the aforementioned materials, Zr-based catalysts, which are cheap and environmentally friendly, exhibit relatively good catalytic performance for PDH. A previous study by Otroshchenko et al. proposed that coordinatively unsaturated Zr cations (Zr\(\text{cus}\)) were the active sites for PDH.22 The authors demonstrated that the activity of the catalysts increased with decreasing strength of the metal–oxygen bond. This was attributed to the high oxygen mobility and the easy removal of lattice oxygen forming oxygen vacancy (Ov) and Zr\(\text{cus}\).22 Zhang et al. also proposed that Zr\(\text{cus}\) sites in ZrO\text{2} were responsible for the breaking of C–H bonds in PDH.23 The phase composition and crystallite size of ZrO\text{2} was demonstrated to influence the ability of ZrO\text{2} to release lattice oxygen upon reduction of catalysts, influencing the formation of Zr\(\text{cus}\) sites. Zr-based catalysts have therefore shown promise for PDH, but most examples require a high reaction temperature (ca. 570 °C) to reach a favorable substrate conversion. It has been suggested that the utilization of reductive methods or doping with lower valence metals can lead to improved activity of Zr-based...
Doping of these Zr catalysts has also been demonstrated to have a positive effect on C₃H₆ selectivity. However, a limited number of studies have focused on deriving a mechanism for PDH over Zr-based bimetallic oxides, especially regarding the role of metal species in the reaction. There is some debate on the role of the metals in this reaction. For instance, in some reports, Zr₃ sites have been proposed to be the active sites, with the secondary metal serving as a promoter. On the contrary, other studies have suggested that Zr species are promoters for the secondary metal ions, which are considered to be the active sites. For example, Han et al. reported that supported ZnOₓ species participated in the PDH reaction, while ZrO₂ enhanced the activity of Zn-containing ZrO₂-based catalysts. The byproducts formed in this research, which were also important, were not found in a systematic study. However, the formation of byproducts over these catalysts should also be investigated to design catalysts with high catalytic activity and C₃H₆ selectivity. It has been claimed in other works that the acidity of catalyst influences the product selectivity. With this in mind, it is important to develop an effective Zr-based bimetallic oxides catalyst, which can exhibit both a good activity and selectivity at relatively low temperatures. Further efforts are also required to determine the nature of the active sites and the role of metal species. To better understand and design catalysts for this process, it is critical to further study the reaction mechanism and the formation of byproducts.

It is known that ZnO is a weak base and ZrO₂ is a weak acid. Considering acid–base properties and their influence on the product selectivity, a series of binary ZnZrₓOᵧ catalysts (denoted as Zn–Zr catalysts) were prepared and investigated for PDH at relatively low temperatures (400–500 °C). Experiments were designed to get insight into the active sites present in these materials and understand the synergistic relationship between Zn and Zr species. These investigations included probing the materials using a variety of characterization techniques and correlating their physicochemical properties with kinetic experiments and density-functional theory (DFT) calculations. These investigations revealed that the Znₓₓ and Zrₓₓ sites present in Znₓₓ–Oₓₓ–Zrₓₓ are active sites for the first and second steps of C₃H₆ dehydrogenation. By conducting these investigations, a reaction pathway for PDH over bimetallic ZnZrₓOᵧ catalysts was proposed.

**RESULTS AND DISCUSSION**

**Catalyst Characterization.** X-ray powder diffraction (XRD) patterns of the Zn–Zr catalysts (referred to as ZnZrₓ, where x represents Zr/Zn mole ratio) are presented in Figure 1. Both tetragonal (t-ZrO₂) and monoclinic (m-ZrO₂) phases were identified in pure ZrO₂. However, upon the addition of Zn, diffraction peaks associated with m-ZrO₂ phase disappeared. This suggests that doping ZrO₂ with transition metals, which have different oxidation states and/or atomic radii, can lead to phase transformation from m-ZrO₂ to t-ZrO₂. Previously, this has been attributed to the formation of Oₓ and Zrₓₓ. The disappearance of the monoclinic phase in the Zn–Zr catalysts indicates the successful substitution of Zn into the ZrO₂ crystalline phase and the formation of Zrₓₓ. For pure ZnO, a hexagonal ZnO phase was observed. Upon increasing the Zr/Zn mole ratio, the intensity of diffraction peaks associated with ZnO decreased and eventually disappeared in the ZnZrₓ material. The dramatically diminished intensity of diffraction peaks associated with ZnO in the Zn–Zr catalysts decreased and eventually disappeared in the ZnZrₓ material. The dramatically diminished intensity of diffraction peaks associated with ZnO in the Zn–Zr catalysts.
compared with pure ZnO is likely to be indicative of the incorporation of Zn ions into ZrO\(_2\) lattice. In addition, the XRD patterns of the used ZnZr\(_2\) catalyst were similar to the fresh. The specific surface area and pore structure parameters of the Zn–Zr catalysts were determined by N\(_2\) adsorption–desorption isotherms (shown in Figure S2 and Table S1). The Zn–Zr catalysts all exhibited a type IV isotherm with an H4-type hysteresis loop, indicating that all of the Zn–Zr catalysts possessed mesoporous structures.

X-ray photoelectron spectra (XPS) of the Zr 3d and Zn 2p regions for each of the catalysts are shown in Figures 2 and S3. The peaks at 184.0 ± 0.2 and 1044.0 ± 0.2 eV can be assigned to Zr\(^{4+}\) and Zn\(^{2+}\), respectively. This suggests that only Zr\(^{4+}\) and Zn\(^{2+}\) species are present on the surface of the catalysts. It was noteworthy that as the Zr/Zn mole ratio increased from 1:1 to 2:1, the Zr 3d\(_{5/2}\) peaks shifted to a lower binding energy (BE) and the Zn 2p\(_{3/2}\) peaks moved toward a higher BE, and then the BE of both species changed indistinctively when the Zr/Zn mole ratio increased further. This implies that the interactions between ZrO\(_2\) and ZnO become stronger as the Zr/Zn mole ratio is increased, which gives further evidence of the replacement of Zr by Zn in the ZrO\(_2\) lattice. Furthermore, the corresponding O 1s spectra of Zn–Zr catalysts have been deconvolved into three peaks as shown in Figure 2. The peaks at 529.9, 531.4, and 532.4 eV can be ascribed to lattice oxygen (O\(^2–\)), O\(_v\), and chemically adsorbed oxygen species (O\(_\alpha\)), respectively.\(^{29}\) The relative areas of O\(_v\)/O for the samples are summarized in Table S2. It can be observed that ZnZr2 has the highest O\(_v\). This result is also proved by EPR shown in Figure S4. It is rational to suggest that as the Zr/Zn ratio increased, a greater quantity of Zn–O–Zr bonding and Zr\(_{\text{cus}}\) will be present. This is further supported by the fact that the electron-withdrawing nature of Zr is known to weaken the Zn–O bonds.\(^{30}\) The determined atomic ratios of Zr/Zn on the catalyst surface were 1.5, 2.5, and 3.9 for ZnZr, ZnZr2, and ZnZr5, respectively (Table S2). These values were close to the corresponding nominal values, which again suggests that Zn was successfully incorporated into the ZrO\(_2\) structure.

H\(_2\)-TPR profiles of the Zn–Zr catalysts are displayed in Figure 3. The temperatures associated with the maximal consumption of hydrogen (T\(_{\text{max}H_2}\)) are listed in Table S3. Only small quantities of H\(_2\) were consumed in the experiment over pure ZnO; this material exhibited a T\(_{\text{max}H_2}\) at ca. 522 °C, which is ascribed to the reduction of Zn\(^{2+}\) to Zn\(_{\text{cus}}\). However, there was a large hydrogen uptake at ca. 620 °C in the H\(_2\)-TPR experiment over ZrO\(_2\), which has previously been attributed to an interaction between lattice oxygen and H\(_2\).\(^{31}\) Compared to
Zn$_2$Zr$_2$ possessed the highest amount of H for the Zn−Zr catalysts, generating Zn$_{\text{cus}}$ and Zr$_{\text{cus}}$ of Zn$_{\text{cus}}$−O−Zr$_{\text{cus}}$. In brief, the oxygen mobility of Zn−Zr catalysts increased due to the synergy effect of ZnO and ZrO$_2$. The $T_{\text{maxH}_2}$ value for the Zn−Zr catalysts shifted to a higher temperature as the Zr/Zn mole ratio was increased; this was true for all of the bimetallic catalysts screened, apart from ZnZr$_2$, which exhibited the lowest $T_{\text{maxH}_2}$ due to the more Zn−O−Zr species. Quantitative measurements in relation to hydrogen consumption are presented in Table S3. ZnZr$_2$ possessed the highest amount of H$_2$ consumed among the Zn−Zr catalysts, which was ascribed to more Zn−O−Zr species.

The acid−base properties of the Zn−Zr catalysts were determined by NH$_3$−TPD (Figure S5), CO$_2$−TPD (Figure S6), and IR-Py (Figure S7). For all samples, only a broad desorption peak of NH$_3$ was observed in a temperature range between 80 and 300 °C, indicative of weak- and medium-strength acid sites. It was found that an increase in acid strength was in direct correlation with an increase in the Zr content. On the contrary, CO$_2$−TPD indicated that the quantity of basic sites in the material decreased as the Zr content increased; the strength of the basic sites was however enhanced. Figure S7 displays the IR-Py spectra determined by adsorbing pyridine at 400 and 500 °C. The bands at 1443 and 1595 cm$^{-1}$ are indicative of pyridine adsorbed on Lewis acid sites (LA). A band at 1486 (1495) cm$^{-1}$ is indicative of pyridine adsorbed on Bronsted acid sites (BA) and LA sites. The amounts of LA sites, BA sites, and basic sites for each of the catalysts are listed in Table S1. Among the bimetallic catalysts, ZnZr$_2$ possessed the lowest quantity of acid sites. This was attributed to the low content of Zr$^{4+}$ and total metal ions on the surface of the ZnZr$_2$ catalyst as determined by XPS results.

Activity of Zn−Zr Catalysts and Determination of Active Sites for C$_3$H$_6$ Formation. The catalytic performances of a series of Zn−Zr catalysts for the PDH were investigated at 400 and 500 °C (Table 1), respectively. Zn−Zr catalysts displayed remarkably improved catalytic performance compared to the monometallic counterparts (ZnO and ZrO$_2$). As the reaction temperature was increased from 400 to 500 °C, the C$_3$H$_8$ conversion over the Zn−Zr catalysts increased significantly, but the C$_3$H$_6$ selectivity declined drastically. The ZnZr$_2$ catalyst was determined to be superior to the other Zn−Zr catalysts, in terms of both the C$_3$H$_8$ conversion and C$_3$H$_6$ selectivity; 21% of C$_3$H$_8$
conversion and 92% of $\text{C}_3\text{H}_6$
selectivity were obtained over ZnZr2 at 450 °C. When the
C₃H₈ feed concentration was increased to 21 vol %, the
conversion and the C₃H₆ selectivity were 26 and
86% with space-time yield of C₃H₆ of 1.32 kg₃H₆·kg⁻¹h⁻¹,
respectively, at 500 °C. The catalytic activity was higher
than that of Zn(4 wt %)/TiZrOₓ (1.25 kg₃H₆·kg⁻¹h⁻¹ at 550
°C) with respect to space-time yield of C₃H₆. Interestingly, under
these conditions, the C₃H₈ conversion and C₃H₆ selectivity were only 20 and 81% over the industrial 0.5
wt % Pt/Al₂O₃, and 17 and 85% over commercial K-
CrO₃/Al₂O₃ catalysts, respectively. This illustrated that
ZnZr2 provided a better catalytic activity than 0.5 wt %
Pt/Al₂O₃. The TOF for C₃H₆ formation, normalized by the
amount of consumed H₂, is illustrated in Figure 4a, and the correlation between \( r_{C₃H₆} \) and
dehydrogenation consumption is also shown in Figure 4b. It
found that \( \frac{r_{C₃H₆}}{r_{C₃H₆}} \) had almost linear correlation with
the hydrogen consumption. This confirms that the active
sites

were Znₐct and/or Zrₐct. Furthermore, it was observed
that the TOFs for all of the Zn–Zr catalysts were comparable. All of these were however notably higher than TOFs calculated from the reactions over the Znₐ, ZrO₂, and physically mixed ZnO + ZrO₂ catalysts. It can be concluded that the active sites in the Zn–Zr catalysts

for C₃H₆ dehydrogenation to C₃H₆ are likely different
from those in the Znₐ (with single Znₐct) and ZrO₂ (with
single Zrₐct) catalysts. It can be postulated that both Zrₐct
and Znₐct of Znₐct−O–Zrₐct were the active sites in the

bimetallic Zn–Zr catalysts, and a synergistic relationship can be observed through combining both
Zr and Zn species.

Arrhenius plots for C₃H₆ formation over each of the catalysts are shown in Figure 5, and the corresponding \( E_a \) are listed in Table 2. It is clear that the \( E_a \) values of C₃H₆ formation over ZnZr2 was much lower than that for Znₐ, ZrO₂, ZnO + ZrO₂, and other Zr-based catalysts reported
by other works. This provides further evidence that the
active sites for C₃H₆ dehydrogenation to C₃H₆ are not
the single Znₐct as in ZnO or the single Zrₐct as in
ZrO₂, but Znₐct−O–Zrₐct derived through a combination of Zrₐct and Znₐct. The high \( E_a \) observed for catalysts that are not exposed to a pre-reductive treatment gives evidence that additional energy is required for the formation of Znₐct and Zrₐct in situ. The comparable \( E_a \) for ZnZr2 before and after reduction confirms that ZnZr2 could be reduced in situ easily. It is therefore important to note that ZnZr2 catalyst can be employed without reduction while maintaining a high catalytic performance; the performance of this material is either comparable to or higher than other reduced catalysts at lower reaction temperatures in the literature, which are examined at temperatures up to ca. 600
°C. The good catalytic performance of ZnZr2 is due to the

presence of both Zn and Zr species; this evidently

influence the structure of the catalyst and leads to the observed

synergistic effect.

To determine whether Znₐct, Zrₐct, and neighboring lattice

oxygen O²⁻ were involved in breaking the C–H bonds in

C₃H₈, additional C₃H₈ dehydrogenation experiments

over ZnZr2 catalyst were conducted in the presence of

CO₂ (1 vol %) and O₂ (1 vol %), respectively. It is known that under these conditions, CO₂ can react with O²⁻ to form carbonates while O₂ can react with Ov to reduce the number of Znₐct and Zrₐct species. At 500 °C, the rate of C₃H₆ formation over the reduced ZnZr2 catalyst dropped from 0.18 to 0.15 mmol₃H₆·g⁻¹·min⁻¹ in the presence of CO, and to 0.08 mmol₃H₆·g⁻¹·min⁻¹ in the presence of O. These results confirmed

that Znₐct, Zrₐct, and species in Znₐct−O–Zrₐct were

O²⁻ responsible for C₃H₆ dehydrogenation to C₃H₈.

To confirm the above hypothesis in which the

combination of Zn and Zr species resulted in notable changes to the structure of the catalysts and Znₐct−O–Zrₐct were the active sites, a series of DFT calculations were performed. The optimized geometry structures of ZrO₂(101), Zn-substituted ZrO₂, and Zn–Zr catalysts are displayed in Figure S8. For pure ZrO₂, the length of the Zr–O bond was 2.32 Å. For the optimized structure of Zn–Zr catalysts, the formation energy

<table>
<thead>
<tr>
<th>catalyst</th>
<th>( X_{C₃H₆} )</th>
<th>( S_{C₃H₆} )</th>
<th>( X_{C₃H₆} )</th>
<th>( S_{C₃H₆} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Znₐ</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>66</td>
</tr>
<tr>
<td>ZnZr</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>77</td>
</tr>
<tr>
<td>ZnZr₂</td>
<td>6</td>
<td>98</td>
<td>44</td>
<td>73</td>
</tr>
<tr>
<td>ZnZr₃</td>
<td>4</td>
<td>96</td>
<td>45</td>
<td>61</td>
</tr>
<tr>
<td>ZnZr₄</td>
<td>4</td>
<td>95</td>
<td>51</td>
<td>44</td>
</tr>
<tr>
<td>ZnZr₅</td>
<td>3</td>
<td>≥ 99</td>
<td>22</td>
<td>84</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>ZnO + ZrO₂</td>
<td>0</td>
<td>0</td>
<td>13</td>
<td>77</td>
</tr>
<tr>
<td>ZnZr₂</td>
<td>2</td>
<td>99</td>
<td>26</td>
<td>86</td>
</tr>
</tbody>
</table>

| Table 1. Catalytic Activity for PDH over Various Mono- and Bimetallic Catalysts Comprising Zn and Zr³⁺ |

*Reaction conditions: 5 vol % C₃H₈ in N₂ at a flow rate of 25.0
mL·min⁻¹, 0.1 g of catalyst. Mechanical mixture of ZnO and
ZrO₂ with Zr/Zn mole ratio of 2:1. Reaction conditions: 21 vol
% C₃H₈ in N₂ at a flow rate of 25.0 mL·min⁻¹, 0.1 g of catalyst,
WHSV C₃H₈ of 5.88 h⁻¹.*
Figure 4. (a) TOF over the reduced catalysts at a reaction temperature of 500 °C, Zn–Zr catalysts were reduced under 550 °C, others under 600 °C. (b) Dependence of the rates of \( \text{C}_3\text{H}_6 \) formation over the Zn–Zr catalysts at 500 °C on the amount of consumed \( \text{H}_2 \).
of the surface Ov was $-1.36 \text{ eV}$, indicating that Ov can form spontaneously in the Zn–Zr catalysts. This result was consistent with the XRD results. Compared with Zn–O (1.99 Å) in ZnO and Zr–O in ZrO$_2$, the bond lengths of Zn–O (2.08 Å) and Zr–O (2.43 Å) of Zn–O–Zr in Zn–Zr catalysts were long, which could result in the weakening of Zn–O and Zr–O. This would ultimately lead to an increase in oxygen mobility, which was in agreement with the results acquired from H$_2$-TPR experiments (Figure 3). These results further confirmed that the incorporation of Zn led to the formation of Zr$_{\text{cus}}$ and increased the oxygen mobility, while neighboring Zr led to weakened Zn–O bonds, compared to those present in pure ZnO.

To gain further insight into the nature of the active sites present, reaction pathways for C$_3$H$_8$ dehydrogenation to C$_3$H$_6$ were computed over the Zn–Zr catalyst. The optimized structures of intermediates and transition states are displayed in Figure 6. Furthermore, minimum-energy pathways on different sites are displayed in Figure 7. For the dehydrogenation of C$_3$H$_8$ on the single Zr$_{\text{cus}}$ sites in Zn–Zr catalysts (scheme a in Figure 6), the rate-determining step (RDS) was estimated to be the first step ($\text{C}_3\text{H}_8 + * \rightarrow *\text{C}_3\text{H}_7 + *\text{H}$), an energy barrier ($E_a$) of 1.65 eV was determined. For the second step ($*\text{C}_3\text{H}_7 = \text{C}_3\text{H}_6 + *\text{H}$), it was estimated to be 0.95 eV. For comparison, over the single Zn$_{\text{cus}}$ site in the Zn–Zr catalysts (scheme b in Figure 6), the calculated $E_a$ values were 0.61 and 0.67 eV for the first and second steps of C$_3$H$_8$ dehydrogenation, respectively. Therefore, over the single Zn$_{\text{cus}}$ site, the second step is rate-determining. The $E_a$ on the single Zn$_{\text{cus}}$ sites for both steps is much lower than that on the single Zr$_{\text{cus}}$ sites, indicative of that C$_3$H$_8$ dehydrogenation is more efficient over the Zn$_{\text{cus}}$ sites. This is consistent with the experimental results in Table 2. However, the path by which the first step occurs on Zn$_{\text{cus}}$ sites in Zn$_{\text{cus}}$–O–Zr$_{\text{cus}}$ and then
the second step occurs on $Z_{\text{cus}}$ sites in $Zn_{\text{cus}}-O-Zr_{\text{cus}}$ (scheme c in Figure 6) shows $E_a$ values of 0.61 and 0.52 eV for the first and second steps, respectively. However, the pathway by which the first step occurs on $Z_{\text{cus}}$ sites in $Zn_{\text{cus}}-Ov-Zr_{\text{cus}}$ and then the second step occurs on $Zr_{\text{cus}}$ sites in $Zn_{\text{cus}}-Ov-Zr_{\text{cus}}$ (scheme c in Figure 6) shows $E_a$ values of 0.70 and 0.74 eV for the first and second steps, respectively. These calculations therefore suggest that over Zn–Zr catalysts, the lowest-energy barriers are observed when the first step occurs on $Z_{\text{cus}}$ sites in $Zn_{\text{cus}}-Ov-Zr_{\text{cus}}$ and then the second step occurs on $Zr_{\text{cus}}$ sites. Therefore, through consideration of the experimental and theoretical results, it concludes that $Zn_{\text{cus}}$ sites and $Zr_{\text{cus}}$ sites in $Zn_{\text{cus}}-O-Zr_{\text{cus}}$ have a synergy effect on the dehydrogenation of $C_3H_8$ to $C_3H_6$ that the first dehydrogenation step occurs on $Zn_{\text{cus}}$ sites and that the second step occurs on $Zr_{\text{cus}}$ sites in $Zn_{\text{cus}}-O-Zr_{\text{cus}}$, decreasing $E_a$ further compared with the single $Zn_{\text{cus}}$ and $Zr_{\text{cus}}$. This result is different from the results reported by Han et al. that Zn species were the active sites for PDH.27

From the above conclusions and H$_2$-TPR experiments (Figure 3), the Zn–Zr catalysts cannot be reduced at 400 °C. Therefore, the differences in activity of the catalysts at 400 °C must be attributed to the presence of intrinsic $Zn_{\text{cus}}-O-Zr_{\text{cus}}$. However, at a higher temperature of 500 °C, whereby Zn–Zr catalysts can be reduced by H$_2$ in situ, these active sites could be generated during the reaction. Therefore, at higher temperatures, the better catalytic performance of the ZnZr2 catalyst can be ascribed to the more intrinsic and generated $Zn_{\text{cus}}-O-Zr_{\text{cus}}$. In brief, regardless of the reaction temperature, the more $Zn_{\text{cus}}-O-Zr_{\text{cus}}$ a catalyst possesses, the higher the dehydrogenation activity observed.

Formation of Byproducts. As discussed previously, the formation of byproducts often limits the viability of catalysts for this reaction. In addition, to understand how $C_3H_6$ is formed over these materials, it is also important to consider how byproducts are formed, to further aid catalyst design. It is known that the product selectivity and $C_3H_8$ conversion in this reaction are not only affected by the physicochemical of catalysts but also by the reaction conditions. According to the results acquired from BET measurements (Figure S2 and Table S1), Py-IR experiments (Figure S7 and Table S1), CO$_2$-TPD experiments (Figure S6 and Table S1), and NH$_3$-TPD experiments (Figure S5 and Table S1), the specific surface area, acidity, and basicity of catalyst had no significant influence on $C_3H_8$ conversion at low reaction temperatures. Other studies have confirmed that the product selectivity is also influenced by $C_3H_8$ conversion.32 To identify which parameter influenced the product selectivity over these catalysts, experiments were performed on the different catalysts

https://doi.org/10.1021/acssuschemeng.1c03074
under identical reaction conditions. Product selectivity and C$_3$H$_8$ conversion at 500 °C over various catalysts are shown in Figure 8. When the C$_3$H$_8$ conversion was almost same, the coke selectivity over ZnZr was higher than that over ZnZr5, ascribed to the more BA amount of ZnZr. To further confirm the effect of BA on coke at 500 °C, the amount of ZnZr2 was halved to ensure the C$_3$H$_8$ conversion is comparable to that of ZnZr (Figure 8). It was found that C$_3$H$_8$ conversion was 30%, and the coke selectivity was 8%, which was lower than that over ZnZr and ZnZr5 (determined in Figure 8). These results further illustrated that BA favored the formation of coke. To further explore and detect the difference of coke type and coke amount, Raman spectra (Figure S9) and TGA (Figure S10) were employed. The calculated $I_D/I_G$ ratios of Zn–Zr catalysts
Table S4) were in the range of 0.27−0.39. Additionally, when C3H8 conversions were comparable, the amounts of coke on the spent ZnZr2 (0.7%) and ZnZr5 (0.9%) were lower than that on ZnZr, ascribed to the more amount of BA of ZnZr. This suggested that BA favored the formation of coke.

The influence of the reaction’s conditions on product selectivity, such as the amount of catalyst and reaction temperature, was also investigated. For ZnZr2, when the catalyst amount was increased (Figure 8), C3H8 conversion, coke selectivity, and C2H6 selectivity all increased dramatically. This may be attributed to the increased active sites and quantity of acid sites, which promotes both side reactions such as the consecutive reaction of C3H6 and hydrogenolysis. The result also indirectly confirmed that a sequential reaction...
Involving C₆H₆ occurs. It was also found that, upon increasing the reaction temperature from 500 to 550 °C, the cokeselectivity over ZnZr2 increased from 20 to 37%. Therefore, over this catalyst, the lower the reaction temperature, the higher the C₆H₆ selectivity.

To further investigate the formation of byproducts, the Eₐ values of the cracking product (C₃H₆) and coke were derived from Arrhenius plots, where C₃H₆ was used as substrate (Figure S11 and Table 3). Evidently, the Eₐ values for both C₃H₆ and coke formation over ZnZr2 were much higher than those over ZnO and ZrO₂. This implies that the formation of these byproducts is inhibited over the ZnZr2 catalyst. The reduced ZnZr2 exhibited a much higher Eₐ for C₃H₆ formation and a lower rate of C₃H₆ formation (0.0017 mmol C₃H₆·g⁻¹·cat⁻¹·min⁻¹) than that over ZnZr2 (C₃H₆ formation rate of 0.016 mmol C₂H₄·g⁻¹·cat⁻¹·min⁻¹) at 550 °C. These results indicate that H₂ reduction may inhibit this undesirable cracking reaction. Therefore, it could be inferred that the active sites for the cracking reaction, which are different from the active sites of dehydrogenation, were the coordinatively saturated Zn and/or Zr sites, the quantities of which are reduced after catalyst reduction. By comparing the Eₐ values for coke formation over the different catalysts, it is evident that coke is more easily generated over ZrO₂ and ZnO than over ZnZr₂. This is further underlined by the fact that Eₐ for C₃H₆ conversion over ZnZr2 was higher than that over ZnO and
ZrO$_2$. The results ultimately suggest that the ZnZr2 catalyst inhibits the undesirable side reactions. From these experiments, it could also be concluded that ZnO promoted these side reactions compared to ZrO$_2$.

**Reaction Mechanism.** In light of the aforementioned results, Zn$_{\text{clus}}$ and Zr$_{\text{clus}}$ in Zn$_{\text{clus}}$–O–Zr$_{\text{clus}}$ are the active sites for propane dehydrogenation. For this reason, the catalytic activity of Zn–Zr catalysts should improve after reduction by H$_2$.$^{21,23,25}$ To improve the catalytic performance of ZnZr2, it was reductively (5 vol % H$_2$ in N$_2$) treated at 500 °C for 30 min before use. Surprisingly, the initial C$_3$H$_8$ conversion was less than that observed over ZnZr2 in the corresponding experiment without pre-reduction. This behavior was inconsistent with the results presented previously by others.$^{24}$ It was also observed that the C$_3$H$_8$ conversion over reduced ZnZr2 increased first and then decreased, which was different from that over ZnZr2 with C$_3$H$_8$ conversion decreasing monotonously. This behavior can be attributed to the decreased adsorption amount of C$_3$H$_8$ on reduced ZnZr2 because of the competitive adsorption of H$_2$, which is adsorbed during the reduction step.

To validate this, additional diffuse reflectance Fourier transform spectroscopy (DRIFTS) experiments were conducted on the fresh ZnZr2 (Figure 10a) and pre-reduced ZnZr2 (Figure 10b), respectively. For the fresh ZnZr2 catalyst (Figure 10a), the peaks at 2962 and 1445 cm$^{-1}$ are indicative of $\nu_{as}$(CH) stretching and $\delta_{as}$(CH) bending of $-\text{CH}_3$ in C$_3$H$_8$, respectively. These peaks were almost unchanged after 2 min. The peaks at ca. 1472 and 1696 cm$^{-1}$ can be assigned to $\delta_{as}$(CH) of $-\text{CH}_3$ and the stretching vibration of C–C in C$_3$H$_6$, respectively, which appear at 2 min. These bands first increased and then decreased with a peak indicative of coke (1560 cm$^{-1}$) appearing.$^{33}$ This behavior further evidences that C$_3$H$_8$ reacts sequentially to form coke and is consistent with the experiment results discussed previously. This phenomenon also confirmed that the formation of coke is the main reason for the deactivation of the catalysts.

A similar experiment was subsequently conducted on the pre-reduced ZnZr2 sample (Figure 10b). The intensity of the peaks indicative of C$_3$H$_6$ increased over time. This illustrates that the initial adsorption of C$_3$H$_8$ decreased after reduction of ZnZr2, confirming our hypothesis that hydrogen competes with C$_3$H$_8$ for active sites. This correlation is supported by...
1547 cm$^{-1}$ over reduced ZnZr2 was similar to that over fresh ZnZr2.

Based on all of the work presented herein, reaction pathways for C$_3$H$_8$ dehydrogenation over Zn–Zr catalysts were proposed (Figure S12). We propose that C$_3$H$_8$ first adsorbs on the surface of catalysts and then dehydrogenates one H on Zn$_{\text{cus}}$ in Zn$_{\text{cus}}$–O–Zr$_{\text{cus}}$ forming C$_3$H$_7^*$; the C$_3$H$_7^*$ further dehydrogenates H on neighboring Zr$_{\text{cus}}$ in Zn$_{\text{cus}}$–O–Zr$_{\text{cus}}$ to generate surface-adsorbed C$_3$H$_6$. The adsorbed C$_3$H$_6$ subsequently either desorbs or partakes in further reactions, forming CH$_4$, C$_2$H$_4$, C$_2$H$_6$, and coke. It has however other paths for C$_3$H$_8$ conversion that adsorbed C$_3$H$_8$ can also crack to CH$_4$ and C$_2$H$_4$ on coordinatively saturated Zn and/or Zr sites and convert to CH$_4$ and C$_2$H$_6$ via hydrogenolysis reaction and coke.

To better understand the active sites and the difference between ZnZr2 without reduction and pre-reduction, the time-on-stream (TOS) plot of ZnZr2 is provided in Figure S13. It could be found that the ZnZr2 without reduction had a lower rate of C$_3$H$_6$ formation than that over the pre-reduction ZnZr2 in the initial due to the formation of active sites during reduction. However, the highest rate of C$_3$H$_6$ formation over the former is higher than that over the latter at 15 min due to the competitive adsorption of H$_2$, which is adsorbed during the reduction step. This was consistent with the above results.

Stability of ZnZr2. Besides catalytic activity and selectivity, the stability of the catalyst is also important. To assess the stability of the superior catalyst ZnZr2 in this reaction, a series of cycling experiments were conducted (shown in Figure 11). After each reaction, the ZnZr2 catalyst was regenerated.

Figure 11. Rate of C$_3$H$_6$ formation after several regeneration cycles; reaction condition: 0.05 g of catalyst, 5 vol % C$_3$H$_8$ in N$_2$ at a flow rate of 25.0 mL·min$^{-1}$, 450 ºC.
through calcination of the material in flowing air (25 mL·min⁻¹) at 550 °C for 20 min. The initial rate of C₃H₆ formation was 0.106 mmol C₃H₆·g⁻¹·min⁻¹, which decreased to 0.05 mmol·g⁻¹·min⁻¹ after 120 min on stream. The diminished catalytic activity was ascribed to the coke formation. After three regeneration cycles, the initial rate was 0.104 mmol C₃H₆·g⁻¹·min⁻¹, and as such, the catalyst can be fully and repeatedly regenerated to its initial rate. As the XRD patterns of used ZnZr2 catalyst were almost the same as the fresh, it also illustrated that the catalyst was stable.

Dehydrogenation of Isobutane over Zn–Zr Catalysts. To investigate the universality of catalysts, the series of Zn–Zr catalysts were also investigated for isobutane dehydrogenation (Table S5). The reactivity of the catalysts was similar to that observed in C₃H₆ dehydrogenation. An isobutane conversion of 11% and isobutene selectivity of 98% were observed in reactions over the ZnZr2 catalyst at 400 °C. Furthermore, isobutane conversion and isobutene selectivity reached 46 and 91% with space-time yield of isobutene of 0.79 mmol·h⁻¹·g⁻¹·cat at 500 °C, respectively, which is superior or comparable in performance to other Zn-based, Zr-based catalysts and carbon materials reported for this reaction with respect to space-time yield of isobutene and reaction temperature.⁴⁻⁵ The main byproducts formed in these reactions were CH₆, C₂H₆, C₂H₄, C₂H₅, C₃H₆, cis-2-butene, trans-2-butene, and coke.

CONCLUSIONS

The binary oxide Zn–Zr catalysts synthesized herein exhibit good activity for PDH even at low temperatures. Through evaluating various propane dehydrogenation reactions and conducting DFT calculations, we propose that Zn₃cus and Zr₃cus present in Zn₃cus–Zr₃cus are the active sites for the first and second steps of C₃H₆ dehydrogenation, respectively. The combination of Zn and Zr species led to dramatic changes in the structure and properties of the material, which led to the observed synergistic enhancement in activity, compared to the monometallic counterparts. The incorporation of Zn led to the formation of Zr₃cus and improved oxygen mobility; Zn₃cus–Zr₃cus are formed in situ under dehydrogenation conditions. Kinetic experiments illustrated that the coordinatively saturated Zn and/or Zr were the active sites for cracking reaction, which were inhibited over the Zn–Zr catalysts.

The ZnZr2 catalyst presented herein is displayed superior catalytic performance to other examples of ZnZrₓ at low temperature; 92% C₃H₆ selectivity was observed at 21% C₃H₈ conversion at 450 °C. These materials are also demonstrated to perform well in the dehydrogenation of isobutane; anisobutene selectivity of 91% was observed at an isobutane conversion of 46% at 500 °C. Evidently, these catalytic materials possess great potential for direct alkane dehydrogenation. We hope that the proposed activation mechanism study into product formation will serve as a foundation to further improve the reactivity of Zn–Zr catalysts for such applications.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03074.

Detailed procedures of catalyst preparation, catalyst characterization, catalyst tests, and DFT calculations; Madon–Boudart test; nitrogen adsorption–desorption isotherms; physicochemical properties of catalysts; XPS, EPR, and NH₃-TPD profiles; CO₂-TPD profiles; IR-Py spectra; structural models of DFT calculation; Raman spectra; TGA tests; additional kinetic tests; and catalytic performance for isobutane dehydrogenation (PDF)
Authors

Yingmin Qu – National Engineering Laboratory for VOCs Pollution Control Material & Technology, Research Center for Environmental Material and Pollution Control Technology, University of Chinese Academy of Sciences (Yanqihu Campus), Beijing 101408, China

Ganggang Li – National Engineering Laboratory for VOCs Pollution Control Material & Technology, Research Center for Environmental and Pollution Control Technology, University of Chinese Academy of Sciences (Yanqihu Campus), Beijing 101408, China; Key Laboratory of Environmental Nanotechnology and Health Effects, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Ting Zhao – National Engineering Laboratory for VOCs Pollution Control Material & Technology, Research Center for Environmental Material and Pollution Control Technology, University of Chinese Academy of Sciences (Yanqihu Campus), Beijing 101408, China

Mark Douthwaite – Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, U.K.

Jing Zhang – National Engineering Laboratory for VOCs Pollution Control Material & Technology, Research Center for Environmental Material and Pollution Control Technology, University of Chinese Academy of Sciences (Yanqihu Campus), Beijing 101408, China

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the R&D Program of Beijing Municipal Education Commission (KJZD20191443001), the Beijing Municipal Science & Technology Commission (Z1811000018003), the National Natural Science Foundation of China (21707152, 22176189).
and the Fundamental Research Funds for the Central Universities (E0E48977, E1E46001).

REFERENCES


(17) Liu, Q.; Yang, Z.; Luo, M.; Zhao, Z.; Wang, J.; Xie, Z.; Guo, L. Vanadium-containing dendritic mesoporous silica nanoparticles:


(32) Otroshchenko, T. P.; Rodemerck, U.; Linke, D.; Kondratenko, E. V. Synergy effect between Zr and Cr active sites in binary CrZrO$_2$.
or supported CrOx/LaZrOx: consequences for catalyst activity, selectivity and durability in non-oxidative propane dehydrogenation. *J. Catal.* 2017, 356, 197–205.


