

# Stabilizing Oxygen Vacancies in ZrO<sub>2</sub> by Ga<sub>2</sub>O<sub>3</sub> Boosts the Direct Dehydrogenation of Light Alkanes

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**ABSTRACT:** The conversion of light alkanes to olefins (e.g., ethylene, propylene, or butylene) is crucial to the chemical industry.  $ZrO_2$  with oxygen vacancies has recently been regarded as a promising catalyst for the direct dehydrogenation of light alkanes. However, the intrinsic mechanism of the effect of oxygen vacancies on catalytic performance has not been completely understood yet, and  $ZrO_2$  without promoters generally displays poor activity toward the direct dehydrogenation of light alkanes. In this work, we demonstrate that the oxygen vacancies in  $ZrO_2$  can be poisoned by H atoms during the dehydrogenation of light alkanes, and we report a strategy for stabilizing the oxygen vacancies in  $ZrO_2$  with oxygen vacancies is responsible for dehydrogenation, while  $Ga_2O_3$  prevents the poisoning of oxygen vacancies by dissociated hydrogen atoms which, in the absence of the  $Ga_2O_3$  component, blocks further dehydrogenation.



 $Zr_{0.26}Ga_1$  catalyst exhibits superior propane dehydrogenation performance to the industrial Pt–Sn catalyst, the state-of-the-art catalyst for the direct dehydrogenation of light alkanes. We anticipate this work may shed light on both the fundamental research of catalysis and the chemical industry.

**KEYWORDS:** light alkanes, light olefins, low-coordinated ZrO<sub>2</sub>-Ga<sub>2</sub>O<sub>3</sub>, oxygen vacancies, H diffusion

## 1. INTRODUCTION

The conversion of light alkanes to olefins (e.g., ethylene, propylene, or butylene) is crucial to the chemical industry.<sup>1-3</sup> Traditionally, light olefins are produced by catalytic cracking of oil fractions and byproducts (e.g., naphtha). The fast-growing demand for light olefins and the limited petroleum reserves have motivated the search for alternative olefin production methods. Shale gas that mainly consists of light alkanes is considered an important economical substitute of crude oil. The catalytic dehydrogenation of light alkanes to generate the corresponding olefins is therefore of tremendous significance.<sup>4–7</sup> Pt-based catalysts are widely used for the catalytic dehydrogenation of light alkanes,<sup>8–13</sup> and Pt–Sn catalyst has been industrialized for propane dehydrogenation (PDH). However, the Pt-Sn catalyst suffers the disadvantages of high cost and sintering.<sup>14-18</sup> Replacing Pt-based catalysts with cheap catalysts for the dehydrogenation of light alkanes is therefore of significance, yet remains a great challenge.

Recently,  $ZrO_2$  has been deemed as a promising catalyst for PDH. It has been widely reported that H<sub>2</sub> treatment will produce oxygen vacancies in  $ZrO_2$ , resulting in the formation of low-coordinated Zr active sites for significantly enhancing the dehydrogenation activity.<sup>19–23</sup> Despite the experimental observation and theoretical prediction of oxygen vacancies in

 $ZrO_2$  for PDH, the intrinsic mechanism of the effects of oxygen vacancies on PDH performance has not been completely understood yet, and  $ZrO_2$  without promoters generally displays poor activity toward the direct dehydrogenation of light alkanes. For instance, amorphous (or highly dispersed)  $ZrO_2$  displays poor activity for PDH, even though it has plenty of oxygen vacancies.<sup>24</sup> Composting  $ZrO_2$  with other promoters, such as Cr, La, Y, and Zn,<sup>19–23</sup> can significantly promote the PDH activity, nevertheless, the PDH performance of cheap oxide catalysts is inferior to those of Pt-based catalysts.

Inspired by those reports, we speculate that the active sites of defective  $ZrO_2$  might be poisoned during dehydrogenation in the absence of promoters. Herein, we demonstrate an efficient promoter (Ga<sub>2</sub>O<sub>3</sub>) for stabilizing the oxygen vacancies in ZrO<sub>2</sub>. Density functional theory (DFT) calculations show that 4-coordinated Zr atoms at the  $ZrO_2-Ga_2O_3$  interface are the energetically favorable sites for the adsorption of propane

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molecules. The subsequent successive C–H bond activations are then catalyzed by the low-coordinated (4-coordinated) Zr atoms.  $Ga_2O_3$  promotes the diffusion of dissociated hydrogen atoms from vacancies to regenerate the low-coordinated Zr atoms. Moreover,  $Ga_2O_3$  strongly suppresses coke formation during PDH. Consequently, the optimal  $Zr_{0.26}Ga_1$  catalyst exhibits superior PDH performance to the industrial Pt–Sn catalyst, the state-of-the-art catalyst for the direct dehydrogenation of light alkanes. Additionally, the suppression of coke deposition of  $Ga_2O_3$  has been further validated by other Mo<sup>-</sup>, W<sup>-</sup>, Co<sup>-</sup>, Ni<sup>-</sup>, Y<sup>-</sup>, and Fe<sup>-</sup> modified Ga oxide composites.

## 2. METHODS

**2.1. Materials.**  $Zr(NO_3)_4$ :  $SH_2O$ ,  $Ga(NO_3)_3$ ,  $Fe(NO_3)_3$ :  $9H_2O$ ,  $Ni(NO_3)_2$ :  $6H_2O$ ,  $Co(NO_3)_2$ :  $6H_2O$ ,  $(NH_4)_6Mo_7O_{24}$ :  $4H_2O$ ,  $SnCl_2 \cdot 2H_2O$ ,  $KNO_3$ ,  $Y(NO_3)_3 \cdot 6H_2O$ ,  $(NH_4)_6H_2W_{12}O_{40}$ ,  $Cr(NO_3)_3$ :  $9H_2O$ , and  $Al_2O_3$  were obtained from Sinopharm Chemical Reagent Co., Ltd.  $H_2PtCl_6$ :  $6H_2O$  was purchased from Aldrich. The reference materials of  $ZrO_2$  (99%) and  $Ga_2O_3$  (99.99%) were purchased from Aladdin (China). The aluminosilicate supports of SIRAL10 (SiO\_2/Al\_2O\_3 = 10/90, weight percentage) and SIRAL30 (SiO\_2/Al\_2O\_3 = 30/70, weight percentage) were obtained from Sasol as gifts. The industrial  $Al_2O_3$ -supported Pt-Sn catalyst (Pt-Sn(I)) was provided by UOP.

**2.2. Catalyst Preparation.** All catalysts were prepared using the wet impregnation method, and the loading percentage of the catalyst was kept at 4% in weight. To prepare  $Zr_{0.26}Ga_1$ , for instance, stoichiometric  $Zr(NO_3)_4$ ·SH<sub>2</sub>O and  $Ga(NO_3)_3$  were dissolved in deionized water, and then the solution was dropwise added into the support to form a slurry. After that, the slurry was aged at 60 °C for 1 h, followed by drying at 100 °C for 12 h. The obtained powder was calcinated in air under 800 °C for 2 h. The  $CrO_x/Al_2O_3$  catalyst was prepared using a wet impregnation process. Specifically, stoichiometric  $Cr(NO_3)_3$ ·9H<sub>2</sub>O dissolved in deionized water was added into a commercial  $Al_2O_3$  support (purchased from Sinopharm Chemical Reagent Co., Ltd) dropwise, and the slurry was dried for 12 h at 100 °C. After that, the catalyst was heated to 600 °C in air for 2 h.

2.3. Catalyst Characterization. The compositions of different catalysts were determined by inductivity-coupled plasma optical emission spectrometry (Variance, VISTA-MPX). X-ray diffraction (XRD) patterns were collected on a PANalytical Empyrean machine. The surface area of the catalysts was measured by the Brunauer-Emmett-Teller method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. X-ray photoelectron spectroscopy (XPS) spectra were collected on a KRATOS Analytical-KRATOS AXIS Ultra DLD spectrometer (Kratos Analytical-A Shimadzu group company) using a monochromatic Al K $\alpha$  source (1486.6 eV). The binding energy scale was calibrated according to the C 1s peak (284.8 eV) of adventitious carbon on the analyzed sample surface. Transmission electron microscopy images were collected on a FEI-Tecnai G2 F20 (200 kV) microscope equipped with energydispersive X-ray spectroscopy (EDX) functionality. Electron paramagnetic resonance (EPR) spectra were obtained by using the JEOL machine (JES-FA200) with the microwave frequency range of 8750-9650 MHz (X-band). H<sub>2</sub> temperatureprogrammed reduction (H2-TPR) was performed using a TPR analyzer equipped with a thermal conductivity detector (TCD) detector. The catalyst sample (40 mg) was flushed

with argon and heated to 150 °C for 60 min. After that, the sample was heated to 900 °C at a heating rate of 10 °C/min under a flow of 10% H<sub>2</sub>/Ar (50 mL/min). Temperatureprogrammed oxidation (TPO) was performed on an automatic chemical adsorption instrument (FINESORB-3010). 100 mg of the catalyst was put in a U-shape quartz tube and pretreated by  $H_2/Ar$  (50 mL/min) at 600 °C for 2 h, followed by flushing with Ar (50 mL/min) at 600 °C for 0.5 h. Afterward, the sample was cooled to 30  $^{\circ}$ C in the same Ar flow. O<sub>2</sub>/Ar (20 mL/min, 2 vol % in Ar) was introduced into the U-shape quartz tube, and the sample was heated to 600 °C with a heating rate of 10 °C/min. The temperature and current of TCD were 60 °C and 70 mA, respectively. Coke deposition was determined by using thermogravimetry (Mettler Toledo, TGA1). Specifically, the preweighted catalyst sample (about 100 mg) was flushed with Ar for 1 h at 150 °C and then cooled to room temperature. After that, the sample was heated to about 800 °C in air with the heating rate of 10 °C/min. The coke deposition was determined by the weight loss in the temperature range of 300-650 °C. Synchrotron experiments were conducted at beamline BL01C1 at the National Synchrotron Radiation Research Centre, Hsinchu, Taiwan. The storage ring was operated at 1.5 GeV with a current of 300 mA; further measurements were also conducted at beamline BL14W1 at the Shanghai Synchrotron Radiation Facility. The storage ring was operated at 3.5 GeV with a current of 250 mA. The Zr K-edge and Ga K-edge were measured using the same configuration. The samples were pressed into pellets and sealed with Kapton tape. The thicknesses of the pellets were adjusted to reach the optimum absorption thickness. All spectra were recorded at room temperature in a transmission mode. The spectral analysis was performed following the standard procedure using ATHENA and IEFFIT software package.<sup>25</sup> The extended X-ray absorption fine structure (EXAFS) function,  $\chi$ , was obtained by subtracting the postedge background from the overall absorption and then normalizing with respect to the edge jump step.

EXAFS fitting over the Zr K-edge was performed on ZrO<sub>2</sub> on the Zr<sub>0.26</sub>Ga<sub>1</sub> catalysts (before and after H<sub>2</sub> treatment) and on the metallic Zr reference over a k-range of 2–15 Å<sup>-1</sup> and an R-range of 1–5 Å. The fitting was performed in the R-space with a k-weight of 2. Fitting of ZrO<sub>2</sub> was performed using monoclinic ZrO<sub>2</sub> (space group  $P2_1/c$ ) as a model. Monoclinic ZrO<sub>2</sub> features Zr coordinated by seven O atoms, all with unique bond lengths. Since many of these bond lengths differ by less than 0.05 Å (essentially the resolution of EXAFS), we simplified the model by grouping the O atoms into three coordination shells. Reassuringly, the fit was excellent (*r*-factor 0.044) and the bond lengths were within error of those in the reported monoclinic crystal structure.

Because the Zr EXAFS of the Zr–Ga catalysts is almost the same as that of ZrO<sub>2</sub> and because the features in the Fourier transformed EXAFS of the Zr–Ga catalysts are aligned with those in ZrO<sub>2</sub>, to fit the EXAFS from the Zr–Ga catalysts, we constrain the bond lengths, energy shift ( $E_0$ ), and amplitude reduction factor ( $S_0^2$ ) to those obtained from fitting the ZrO<sub>2</sub> EXAFS, and instead we allow the coordinate number (previously fixed for ZrO<sub>2</sub>) to be fitted. The Debye–Waller disorder factor is fitted for all cases. Because we do not expect H<sub>2</sub> treatment to remove Zr atoms, we also constrain the Zr–Zr coordination number to be consistent with the EXAFS of the Zr–Ga catalysts before and after H<sub>2</sub> treatment. The fitting space, range, and *k*-weight were kept constant with those for

 $ZrO_2$ . The fit was good (*r*-factor 0.075 for simultaneously fitting the spectra from catalysts before and after H<sub>2</sub> treatment), although better *r*-factors could be obtained by changing the variables that were fit. This procedure often resulted in unphysical fitted values. As our present approach results in physically valid parameters that suggest a structural model in agreement with the EXAFS and is closely tied to the  $ZrO_2$  reference fit, we believe our approach is the most appropriate method for studying this system.

EXAFS fitting over the Ga K-edge was performed on Ga<sub>2</sub>O<sub>3</sub> on both Zr<sub>0.26</sub>Ga<sub>1</sub> catalysts (before and after H<sub>2</sub> treatment) and the metallic Ga reference over a *k*-range of 2-15 Å<sup>-1</sup> and an *R*range of 1-5 Å. The fitting was performed in the *R*-space with a k-weight of 2. Fitting of ZrO<sub>2</sub> was performed using monoclinic  $Ga_2O_3$  (space group C2/m) as a model. Monoclinic Ga<sub>2</sub>O<sub>3</sub> has two distinct Ga sites, one of which is 4-coordinated and one of which is 6-coordinated. In principle, this presents a difficulty for EXAFS fitting as each site may have a distinct onset energy. However, because both Ga sites are expected to be Ga<sup>3+</sup>, and as model full-potential, allelectron calculations suggest that the difference in the X-ray absorption onset for the two sites is only around 0.1 eV, we simplify and use only a single energy shift  $E_0$  in our fitting. We also simplify the structure by grouping atoms with very similar bond lengths into a single coordination shell and fixing the coordination number of these shells as the average between the two Ga sites. The fit was excellent (r-factor = 0.037). The fitted bond lengths were generally slightly larger than those of the ideal crystal structure but not by much. This may be due to the simplifications employed in our model mentioned above (forming approximate coordination shells, treating both Ga sites as having identical onset energies) or may simply be due to local heating by the X-ray beam expanding the Ga<sub>2</sub>O<sub>3</sub> lattice.

For the Ga EXAFS of the Zr-Ga catalysts, we again constrained the amplitude reduction factor  $(S_0^2)$  to those obtained from the Ga<sub>2</sub>O<sub>3</sub> reference fitting. The k- and r-ranges and the fitting space are the same as used for Ga2O3. We also constrained the Debye-Waller disorder parameters (we employ one for scattering from O and one for scattering from Ga) to those obtained from Ga<sub>2</sub>O<sub>3</sub> fitting. This choice was motivated by simplifying the fitting model; as the resulting fit is quite good and provides physically reasonable parameters, we believe this simplification was justified. We further reduce the number of scattering paths as the EXAFS transform from the Zr-Ga catalysts has fewer features than that from Ga<sub>2</sub>O<sub>3</sub>. However, for the Zr–Ga catalysts, we fit both the coordination number and the bond length as the Fourier transform (FT) suggests small shifts in bond length compared to Ga<sub>2</sub>O<sub>3</sub>. We also fit the  $E_0$  as the EXAFS for the Zr–Ga catalysts features a noticeably different absorption onset compared to  $Ga_2O_3$ .  $E_0$ and the bond lengths are, however, fitted simultaneously for both Zr-Ga catalysts. The fitted energy shift places the absorption onset  $1.3 \pm 0.6$  eV lower than in Ga<sub>2</sub>O<sub>3</sub>, consistent with what we expect from the EXAFS. The fit was excellent (*r*factor = 0.039) for simultaneous fitting of spectra from before and after H<sub>2</sub> treatment.

**2.4. Catalytic Evaluation.** All catalysts were evaluated in a fixed quartz reactor with the inner diameter of 10 mm. The flow rates of  $C_3H_{8}$ ,  $N_2$ , and  $H_2$  were controlled by mass flow controllers. The outlet gases were detected by two online gas chromatographs (GCs). Hydrocarbons were analyzed by a GC with flame ionization detector using a capillary column

(model: TM-Al<sub>2</sub>O<sub>3</sub>/S), and N<sub>2</sub> and H<sub>2</sub> were detected by a GC with TCD using a packed column (model: TDX-01). Catalytic performance was evaluated using eqs 1-7. 0.4 g of the catalyst with a size of 60-80 mesh mixed with 1.2 g of quartz glass (60-80 mesh) was fixed in the middle of the reactor. Each ethane dehydrogenation (EDH) test consisted of (i) a 15 min reduction step at 600 °C (heating rate: 10 °C/ min) using a  $H_2/N_2$  flow (volume ratio: 10:90%), (ii) a 15 min EDH step at 650 °C using a  $C_2H_6/H_2/N_2$  flow (flow rate: 12:12:100 mL/min) without specific note, and (iii) a 15 min dry air treatment step at 750 °C; each PDH test consisted of (i) a 15 min reduction step at 600 °C (heating rate: 10 °C/ min) using a  $H_2/N_2$  flow (volume ratio: 10:90%), (ii) a 15 min PDH step at 600 °C using a  $C_3H_8/H_2/N_2$  flow (flow rate: 12:12:100 mL/min) without specific note, and (iii) a 15 min dry air treatment step at 750 °C; each i-butane dehydrogenation (BDH) test consisted of (i) a 15 min reduction step at 600 °C (heating rate: 10 °C/min) using a  $H_2/N_2$  flow (volume ratio: 10:90%), (ii) a 15 min *i*-BDH step at 550 °C using a *i*- $C_4H_{10}/H_2/N_2$  flow (flow rate: 12:12:100 mL/min) without specific note, and (iii) a 15 min dry air treatment step at 750 °C. The propane conversion and propylene selectivity were measured three times to get the mean values. A series of blank experiments were performed by using only quartz glass to study the possible cracking of light alkanes. It should be pointed out that no conversion of alkanes was obtained during one cycle (15 min). The propane conversion and propylene selectivity were obtained in 15 min without specific note.

2.5. Definition of Conversion, Selectivity, and Yield.

$$C_{3}H_{8} \text{ con. } (\%) = \frac{n(C_{3}H_{8})_{\text{in}} - n(C_{3}H_{8})_{\text{out}}}{n(C_{3}H_{8})_{\text{in}}} \times 100\%$$
(1)

$$i-C_4H_{10} \text{ con.} (\%) = \frac{n(i-C_4H_{10})_{\text{in}} - n(i-C_4H_{10})_{\text{out}}}{n(i-C_4H_{10})_{\text{in}}}$$

$$\times 100\%$$
(2)

$$C_{2}H_{6} \text{ con. } (\%) = \frac{n(C_{2}H_{6})_{\text{in}} - n(C_{2}H_{6})_{\text{out}}}{n(C_{2}H_{6})_{\text{in}}} \times 100\%$$
(3)

$$C_{3}H_{6} \text{ sel. } (\%) = \frac{n(C_{3}H_{6})_{out}}{n(C_{3}H_{8})_{in} - n(C_{3}H_{8})_{out}} \times 100\%$$
(4)

$$i-C_4H_8$$
 sel. (%) =  $\frac{n(i-C_4H_8)_{out}}{n(i-C_4H_{10})_{in} - n(i-C_4H_{10})_{out}} \times 100\%$ 
(5)

$$C_2H_4 \text{ sel. } (\%) = \frac{n(C_2H_4)_{\text{out}}}{n(C_2H_6)_{\text{in}} - n(C_2H_6)_{\text{out}}} \times 100\%$$
(6)

$$C_{3}H_{6} STY = \frac{m(C_{3}H_{6})}{m_{Cat.} \times t}$$
(7)

$$i-C_4H_8 STY = \frac{m(i-C_4H_8)}{m_{Cat.} \times t}$$
(8)

$$C_2 H_4 STY = \frac{m(C_2 H_4)}{m_{Cat.} \times t}$$
(9)

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**Figure 1.** (a) EPR spectra of the  $Zr_{0.26}Ga_1$  catalyst before (black line) and after (red line)  $H_2$  treatment. In situ IR spectra for PDH on  $ZrO_2$  (b),  $Ga_2O_3$  (c), and  $Zr_{0.26}Ga_1$  catalysts (d). In situ IR measurements were performed in the mixture of  $C_3H_8$ ,  $N_2$ , and  $H_2$ . IR conditions:  $V_{\text{total}} = 3 \text{ mL}$ ,  $P_{\text{total}} = 0.12 \text{ MPa}$ , T = 600 °C, and  $m(Zr_{0.26}Ga_1) = 50 \text{ mg}$ .

where *n* and *m* represent the mole and mass, respectively. For example,  $n(C_3H_8)_{in}$  and  $n(C_3H_6)_{out}$  represent the mole of propane introduced and the mole of propylene produced, respectively. The mole of propylene was obtained through the division of the peak area of propylene in the GC pattern and that of the standard (propylene with a different volume fraction). N<sub>2</sub> was used as a standard to calibrate the volume changes for PDH  $(C_3H_6 \rightarrow C_3H_6 + H_2)$ .

2.6. DFT Calculations. All DFT calculations were carried out using the Vienna Ab Initio Simulation code.<sup>28,29</sup> The interaction between the valence electrons and the ions were described with the project-augmented-wave<sup>30</sup> scheme and a planewave energy cutoff of 400 eV. The exchange-correlation interactions were treated within the generalized gradient approximation in the form of Perdew-Burke-Ernzerhof functional.<sup>31</sup> The van der Waals interactions were described using the empirical correction in Grimme's scheme (DFT-D3).<sup>32</sup> As  $Ga_2O_3$  and  $ZrO_2$  are both semiconductors, the Gaussian smearing with a width of 50 meV was used for the occupation of electronic levels. The climbing-image nudged elastic band<sup>33</sup> calculations and the dimer method<sup>34</sup> were employed to determine the configurations of transition states. In all calculations, the surfaces were modeled with periodic slabs consisting of a vacuum region of 15 Å and several atomic layers. The two bottom layers of atoms were kept fixed, while the rest of atoms were fully relaxed until the atomic force was less than 0.02 eV/Å. The convergence threshold of selfconsistent filed iterations was set to  $10^{-4}$  eV. Taking the experimental conditions into consideration, the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>(100) and m-ZrO<sub>2</sub>( $\overline{1}11$ ) were selected to represent the surfaces of Ga<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. The parameters are listed in Tables S10 and S11. The optimized lattice constants for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and *m*-ZrO<sub>2</sub> are in good agreement with the previous theoretical calculations and experimental measurements. The atomic simulation environment was used to calculate all thermodynamic properties.<sup>35</sup> The Gibbs free energy G was calculated at

the reaction temperature (823.15 K) and ambient pressure according to the following equation

$$G = H - T\Delta S = E_{\text{DFT}} + E_{\text{ZPE}} + \int_0^{873} C_v \, \mathrm{d}T - T\Delta S$$

where  $E_{\rm DFT}$  is the DFT-optimized energy,  $E_{\rm ZPE}$  is the zeropoint energy,  $\int_{0}^{873} C_{\rm v} \, dT$  is the heat-capacity, T is the temperature, and  $\Delta S$  is the entropy. The ideal gas model was used when calculating the thermodynamic properties of gas-phase molecules like H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>3</sub>H<sub>6</sub>, while adsorbates on surfaces were treated using harmonic approximation.

## 3. RESULTS AND DISCUSSION

Zr-Ga catalysts with different molar ratios of Zr and Ga were impregnated into an alumina or an aluminosilicate support (Tables S1 and S2 and Figures S1 and S2). Moreover, we characterized the Zr-Ga catalyst by using (EDX, Figure S3), (XPS, Figure S4), X-ray absorption near edge structure (XANES), and the FT of the EXAFS (Figures S5 and S6) measurements. XPS and XANES also confirmed the oxidation nature of the Ga and Zr constituents. EDX elemental mapping clearly shows that both Zr and Ga were well dispersed on the support (Figure S3). We thus concluded that the catalysts consist of oxides with an extremely small grain size. No obvious H<sub>2</sub> consumption peak was observed in the H<sub>2</sub>-TPR profile (Figure S7), which was in good agreement with the results from the XPS measurement. The intensities of the EPR signals are proportional to the free electron density, indicating the formation of oxygen vacancies. The EPR signal intensities for both ZrO<sub>2</sub>/SIRAL10 and Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 catalysts strongly increase after H<sub>2</sub> treatment, suggesting that the H<sub>2</sub>treated catalyst contains a significant amount of oxygen vacancies (Figures 1a and S8). In contrast, Ga<sub>2</sub>O<sub>3</sub> seems to be stable under H<sub>2</sub> treatment, and its EPR signal before and after H<sub>2</sub> treatment is weak (Figure S8). This indicated that the oxygen vacancies in the Zr–Ga catalysts were formed in the  $H_2$ -treated ZrO<sub>2</sub> component.<sup>19,21</sup> XANES further substantiated



**Figure 2.** PDH performance over Zr–Ga/SIRAL10 catalysts. (a) Propane conversion and propylene selectivity and (b) STY using different Zr–Ga/SIRAL10 catalysts. The PDH conditions were  $C_3H_8/H_2/N_2 = 12:12:100 \text{ mL/min}$ ,  $T = 600 \degree C$ ,  $P_{total} = 0.12 \text{ MPa}$ , and WHSV = 3.5 h<sup>-1</sup>.



**Figure 3.** PDH performance over Pt–Sn(I), 20 wt %  $CrO_x/Al_2O_3$ , and  $Zr_{0.26}Ga_1/SIRAL10$  catalysts. (a) Propane conversion, (b) propylene selectivity, and (c) STY of propylene. The PDH conditions were  $C_3H_8/H_2/N_2 = 12:12:100 \text{ mL/min}$ , T = 500-625 °C,  $P_{total} = 0.12$  MPa, and WHSV = 3.5 h<sup>-1</sup>. (d) Long-term stability in 300 cycles using the  $Zr_{0.26}Ga_1/SIRAL10$  catalyst for PDH. The PDH conditions were  $C_3H_8/H_2/N_2 = 12:12:100 \text{ mL/min}$ , T = 600 °C,  $P_{total} = 0.12$  MPa, and WHSV = 3.5 h<sup>-1</sup>.

this observation showing a much stronger intensity change of Zr K-edge than Ga K-edge in the H<sub>2</sub>-treated  $Zr_{0.26}Ga_1/$  SIRAL10 sample (Figure S5). EXAFS confirmed the lack of a complete second shell around Zr in the catalyst and the decrease of Zr–O coordination number after H<sub>2</sub> treatment (Figure S6 and Table S3).

We used in situ infrared (IR) spectrometry to monitor the PDH performance over ZrO<sub>2</sub>/SIRAL10, Ga<sub>2</sub>O<sub>3</sub>/SIRAL10, and Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 catalysts The characteristic peaks associated with C-H vibrations of C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> could be easily distinguished in the IR spectrum (Figure 1b). The characteristic C-H vibration positions in the IR spectra were determined by injecting propane (2920-2980  $\text{cm}^{-1}$ ) and propylene (3015 cm<sup>-1</sup>) separately into the in situ IR cell (Figure S9). When ZrO<sub>2</sub>/SIRAL10 was used as the catalyst, only the characteristic peaks corresponding to the C-H vibrations of propane were observed in the range of 2920-2980 cm<sup>-1</sup>, suggesting that ZrO<sub>2</sub>/SIRAL10 was not active for the dehydrogenation reaction. In comparison, a small peak at about 3015 cm<sup>-1</sup> corresponding to the C-H vibrations of propylene was observed after 20 min when pure Ga<sub>2</sub>O<sub>3</sub>/ SIRAL10 was used as the catalyst (Figure 1c), indicating that

 $Ga_2O_3$  was active for the PDH reaction. In a striking contrast, a rapid evolution of the propylene characteristic signals was observed when the optimized  $Zr_{0.26}Ga_1/SIRAL10$  was used. The intensity of peaks in the range of 2920–2980 cm<sup>-1</sup> (Figure 1d) rapidly decreased after 3 min, while the intensity of the peak at 3015 cm<sup>-1</sup> increased accordingly. These results indicated that the synergy between  $ZrO_2$  and  $Ga_2O_3$  strongly contributed to the improved PDH performance.

The catalytic performance of the Zr–Ga catalysts supported on SIRAL10 with varying Zr/Ga molar ratios was measured in a lab-scale reactor. The molar ratio of Zr/Ga was found critical to PDH performance (Figure 2a,b). When  $ZrO_2/SIRAL10$  was used as the catalyst, only 1.8% of propane was converted with a low selectivity (74.3%). Both the conversion of propane and the selectivity of propylene increased significantly with the addition of Ga<sub>2</sub>O<sub>3</sub> (Figure 2a). The propane conversion reached 50.1% at a propylene selectivity of 95.1% for a Zr/Ga molar ratio of 0.26/1 (e.g.,  $Zr_{0.26}Ga_1/SIRAL10$ ). A further increase of the amount of Ga<sub>2</sub>O<sub>3</sub> led to a decrease of the catalytic activity. The propylene yield showed a similar dependence on the ratio of Zr/Ga. As depicted in Figure 2b, the space time yield (STY) of propylene was 0.045 kg kg<sub>Cat</sub><sup>-1</sup>



**Figure 4.** (a) *i*-BDH performance using the Pt-Sn(I), 20 wt %  $CrO_x/Al_2O_3$ , and  $Zr_{0.26}Ga_1/SIRAL10$  catalysts. The *i*-BDH conditions were *i*-C<sub>4</sub>H<sub>10</sub>/H<sub>2</sub>/N<sub>2</sub> = 12:12:100 mL/min, *T* = 550 °C, *P*<sub>total</sub> = 0.12 MPa, and WHSV = 3.5 h<sup>-1</sup>. (b) EDH performance using the Pt-Sn(I), 20 wt %  $CrO_x/Al_2O_3$ , and  $Zr_{0.26}Ga_1/SIRAL10$  catalysts. The EDH conditions were  $C_2H_6/H_2/N_2$  = 12:12:100 mL/min, *T* = 650 °C, *P*<sub>total</sub> = 0.12 MPa, and WHSV = 3.5 h<sup>-1</sup>.

 $h^{-1}$  for ZrO<sub>2</sub>/SIRAL10, which increased to 1.61 kg•kg<sub>Cat.</sub><sup>-1</sup>  $h^{-1}$  for the optimized Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10. It should be noted that the PHD activity of Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 surpassed that of the industrial Pt–Sn catalyst [noted as Pt–Sn(I) and obtained from UOP] and most of the reported catalysts for PDH (Table S4).

Moreover, home-made Pt–Sn and  $CrO_r/Al_2O_3$  were used as another reference (Figures S10-S13 and Table S5). It was found that Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL 10 yielded a larger improvement of the PDH performance with respect to Pt-Sn(I) and 20 wt %  $CrO_x/Al_2O_3$  under different temperatures (Figure 3a-c). Similar superior PDH properties of Zr<sub>0.26</sub>Ga<sub>1</sub> with respect to Pt-Sn(I) and 20 wt %  $CrO_{y}/Al_{2}O_{3}$  were observed when PDH was performed under different weight hourly space velocities (WHSVs) (Figures S14). Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 initiated a propylene STY of 1.61 kg kg<sub>Cat.</sub><sup>-1</sup>•h<sup>-1</sup>, while Pt-Sn(I) and 20 wt %  $CrO_x/Al_2O_3$  catalysts produced lower propylene STYs (1.33 kg kg<sub>Cat.</sub><sup>-1</sup>  $\dot{h}^{-1}$  for Pt–Sn(I) and 1.04 kg kg<sub>Cat.</sub><sup>-1</sup>  $h^{-1}$  for 20 wt %  $CrO_r/Al_2O_3$ ) when the temperature and WHSV were 600 °C and 3.5 h<sup>-1</sup>, respectively (Figure 3c). In order to highlight the long-term stability, Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 was tested for PDH in 300 consecutive dehydrogenation-regeneration cycles. The propane conversion decreased to about 38.9% after 75 cycles (Figure 3d) and then was almost constant within the next 225 cycles, indicating the high stability of  $Zr_{0.26}Ga_1/$ SIRAL10 for PDH. Note that the Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 catalyst requires only calcination in air to remove the deposited coke, while the industrial Pt-Sn catalyst requires additional oxychlorination.<sup>4,13</sup> This is expected to significantly reduce the cost of PDH when using Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 [in addition to the reduction due to the much cheaper cost of  $Zr_{0.26}Ga_1/$ SIRAL10 with respect to Pt-Sn(I)]. Moreover, additional EPR measurements were performed on other Zr-Ga catalysts to further verify the effects of vacancies on PDH. It was found that the areas of the EPR peak of different catalysts were strongly correlative with the propane conversion (Figure S15). Additionally, TPO measurements were employed to quantificationally measure the vacancies, which further confirmed the significance of vacancies on PDH (Figure S16 and Table S6). Moreover, kinetic studies show that the reaction order and apparent activation energy  $(E_a)$  of PDH over  $Zr_{0.26}Ga_1/$ SIRAL10 are 1.06 and 65.1 kJ/mol, respectively (Figure S17).

 $H_2$  was used in Oleflex PDH process to suppress coke deposition on Pt–Sn catalysts.<sup>36</sup> In the present work, we found that  $H_2$  was quite important for activating the  $Zr_{0.26}Ga_1/$  SIRAL10 catalyst in the  $H_2$  reduction stage (preceding PDH) and reducing coke formation in the PDH stage. The initial propane conversion was about 29.9% when no  $H_2$  treatment

stage was used and no H<sub>2</sub> was fed during the PDH stage (Table S7). The conversion increased to 46.9% when the  $H_2$ treatment was performed at 600 °C and further increased to 50.1% after the  $H_2$  treatment and the addition of  $H_2$  to the PDH feeding gas (Figure S18a). The observed enhancement in activity after H<sub>2</sub> treatment might be attributed to the formation of O vacancies at the ZrO<sub>2</sub>-Ga<sub>2</sub>O<sub>3</sub> interface leading to 4coordinated Zr active sites. The effect of H<sub>2</sub> introduction to the PDH feeding gas may be associated with the reported ability of H<sub>2</sub> to retard the coke formation during dehydrogenation.<sup>37,38</sup> Our experiments have indeed confirmed that the coke deposition on various Zr-Ga catalysts significantly decreased after the addition of  $H_2$  to propane (Table S8). Furthermore, similar results of suppression of coke deposition due to  $H_2$  feeding gas were observed on the 20 wt %  $CrO_x/$ Al<sub>2</sub>O<sub>3</sub> and Pt-Sn(I) catalysts (Figure S18b,c and Table S9).

In addition to PDH, the Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 catalyst was a universal catalyst for the catalytic dehydrogenation of light alkanes to light olefins. The present work also studied the properties of Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 for *i*-BDH and EDH reactions. As shown in Figure 4, Zr<sub>0.26</sub>Ga<sub>1</sub> exhibited a superior catalytic performance for the EDH reaction compared to the Pt-Sn(I) and  $CrO_x/Al_2O_3$  catalysts. For example,  $Zr_{0.26}Ga_1/$ SIRAL10 allowed a 95.9% selectivity to ethylene at 37.8% ethane conversion, while the Pt-Sn(I) catalyst allowed a 96.2% ethylene selectivity at 33.9% ethane conversion. When  $CrO_x/Al_2O_3$  was used as the catalyst, the ethane conversion and ethylene selectivity were 30.1 and 92.4%, respectively. Similarly, Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 presented a higher *i*-butane conversion and comparable *i*-butylene selectivity in *i*-BDH (Figure 4b). In addition, the  $Zr_{0.26}Ga_1$  catalyst was tested for 20 consecutive dehydrogenation-regeneration cycles for both EDH and *i*-BDH. No decay in conversion, selectivity, and yield was observed, indicating the applicability of Zr<sub>0.26</sub>Ga<sub>1</sub>/ SIRAL10 to dehydrogenations of a variety of different alkanes (Figures S19 and S20).

Considering the existence of  $H_2$  in both reactants and products, the surface of  $Zr_{0.26}Ga_1/SIRAL10$  might be hydroxylated during PDH. We thus performed additional experiments to check the surface state of  $Zr_{0.26}Ga_1/SIRAL10$ . As shown in Figure S21, typical peaks corresponding to OH appeared at 3180–3400 cm<sup>-1</sup> in the IR spectrum of  $Zr_{0.26}Ga_1$ at 100 °C, and the peaks completely disappeared when the treatment temperature was further increased to 300 °C, which could be attributed to the dehydration under high temperature. Moreover, we synthesized  $ZrO(OH)_2^{39}$  and GaOOH,<sup>40</sup> two typical compounds with abundant surface OH, to further confirm this assumption. Thermogravimetric analysis indicated



**Figure 5.** Energy profile for PDH over the Zr–Ga catalyst. The calculated energy profile of the C–C bond activation (a), first C–H bond activation (b), second C–H bond activation at the carbon radical (c), and the second C–H bond activation at the methylene group (d). The active site is a 4-coordinated Zr atom. Starting from an adsorbed propane molecule, the C–H bond activation (b) has a much lower reaction barrier (1.11 eV) than the C–C bond activation (2.78 eV) shown in (a), indicating that the first preferential reaction path is to form  $CH_3CH_3CH_3^*$  (in red). Once the first C–H bond activation is occurring, the production of propylene (d) has a very low activation barrier (0.10 eV), suggesting that the second preferential reaction path is to form propylene rather than over dehydrogenation. The energetically preferred reaction pathways are marked in red. Note that the dissociated H in the FS of (b,d) is attached to the O lattice atom adjacent to the four-coordinated Zr atom, so that the further C–H activation is blocked. Removal of the dissociated H atom is necessary for further activation. Indeed, the dissociated H atom was removed from the O lattice atom in the IS of (b,d) to allow C–H activation.

that both  $ZrO(OH)_2$  and GaOOH suffered dehydration at 300–400 °C (Figure S22). No weight loss was observed when the temperature is higher than 450 °C, suggesting the complete dehydration. XRD patterns show that both  $ZrO(OH)_2$  and GaOOH are converted into  $ZrO_2$  and  $Ga_2O_3$  after thermal treatment at 500 °C (Figure S23). Consequently, the Zr and Ga species presented as the oxidation state on the surface of catalysts during dehydrogenation.<sup>41</sup>

Based on the above results from experiments and characterizations, DFT calculations were performed to elucidate the reaction pathway of the selective dehydrogenation of propane molecules at the ZrO2-Ga2O3 interface and at the ZrO2 and Ga<sub>2</sub>O<sub>3</sub> surfaces (Tables S10 and S11). The calculations refer to the different physical-chemical aspects relevant to the dehydrogenation process which include (i) the nature of the surface and the different activation sites involved, (ii) the adsorption energies of the different species participating (propane, propylene, dissociated H, and intermediate radicals), and (iii) the C-H and C-C activation barriers at the different stages of the dehydrogenation process. We first studied the PDH process at the  $ZrO_2-Ga_2O_3$  interface which was modeled with an adsorbed  $Zr_4O_8$  cluster on the  $Ga_2O_3(100)$ surface [a simple configuration which we assume to be sufficient to describe the PDH properties since they are determined (as a first order approximation) by the atoms in the neighborhood of the active site]. This model contains (Figure S24) two different types of Zr atoms: (i) a 4coordinated Zr atom (bonded to O atoms coming from the ZrO<sub>2</sub>) and (ii) a 5-coordinated Zr atom bonded to an O atom coming from the  $Ga_2O_3(100)$  surface. The number of 4coordinated Zr atoms is 3 times larger than that of the 5coordinated Zr atoms. The PDH active site is marked by a circle in Figure S24a (containing a 4-coordinated Zr cation

plus an O lattice atom plus a Ga lattice atom). It is similar to the active Zr site for PDH (coordinatively unsaturated Zr cations) reported by Otroshchenko et al.,<sup>21</sup> which is well consistent with our EXAFS fitting results (Table S3). The PDH process on a 4-coordinated Zr site as derived from DFT calculations is presented in Figure 5. The initial states (ISs) of Figure 5a,b show the propane molecule adsorbed on the 4coordinated Zr atom. The first C-H activation (1.11 eV, Figure 5b) is energetically much more favorable than the C-Cactivation (2.78 eV, Figure 3a). The scission of C-H bonds is thus much faster than that of C-C bonds, resulting in the propyl radical as the major product. Note that the dissociated H atom is adsorbed on the nearby O lattice atom [final state (FS) in Figure 5b and has to be removed to allow further C-H activation (note that it is absent in the IS of Figure 5c,d). The second C-H activation may occur either at the first carbon atom or at the second (central) carbon atom of the propyl radical. The calculated energy profiles show that the dissociation of H atom from the second carbon atom of the propyl group to produce the propylene molecule is a highly exothermic reaction, with a very small activation barrier of 0.10 eV and a large energy drop of 1.87 eV. By contrast, the C-H activation on the first carbon atom is an endothermic reaction with a much larger energy barrier of 0.91 eV. Again, the dissociated H atom generated via the second C-H activation is trapped by the nearby O lattice atom and must be removed to facilitate further C-H activation. The removal of the dissociated H atom eliminating poisoning of the active sites and facilitating further dehydrogenation is feasible by diffusion of the dissociated H atom to the Ga<sub>2</sub>O<sub>3</sub> surface. The diffusion barrier (calculated by DFT) is 0.33 eV (Figure S25).

The full energy and Gibbs profiles of PDH (Figure S26, Tables S12 and S13) show a similar trend. A DFT analysis of



**Figure 6.** Catalytic performance for PDH over different M-Ga/SIRAL10 catalysts. (a) Propane conversion, (b) propylene selectivity, (c) propylene STY, and (d) catalytic performance in 20 cycles. The PDH conditions were  $C_3H_8/H_2/N_2 = 12:12:100 \text{ mL/min}$ ,  $T = 600 \degree C$ ,  $P_{total} = 0.12 \text{ MPa}$ , and WHSV = 3.5 h<sup>-1</sup>.

the 5-coordinated Zr atom reveals that in accordance with the 4-coordinated Zr atom, the first C-H activation is energetically much more likely than the C-C activation and the second C-H activation occurs at the second C atom of the propyl radical. The C-H energy barriers are about the same as for the 4-coordinated Zr (1.18 and 0.12 eV) (Figure S27). Similar to the 4-coordinated Zr system, the dissociated H atom should be removed to allow further PDH. The H diffusion barrier to the Ga<sub>2</sub>O<sub>3</sub> in the 5-coordinated system is larger than for the 4-coordinated system (0.87 vs 0.33 eV, Figure S25). Moreover, the diffusion of H in the 5-coordinated system is reversible (the transition state and the FS have the same energy), so that the 5-coordinated Zr is more vulnerable to poisoning. We also calculated the adsorption energies of propane and propylene on 4- and 5-coordinated Zr (Figure S28). The 4-coordinated Zr has a lower absorption energy of propylene (i.e., less over dehydrogenation or other side reactions). In conclusion, both the 4-coordinated and 5coordinated Zr atoms at the ZrO<sub>2</sub>-Ga<sub>2</sub>O<sub>3</sub> interface are active for PDH. The 4-coordinated Zr atom is, however, a better PDH active site. This theoretical analysis is indeed in accordance with our experimental findings. H<sub>2</sub> involvement generates O vacancies which increase the number of 4coordinated Zr atoms, enhancing the number of active sites and improving the PDH catalytic performance.

Additional DFT calculations probed the PDH activity of  $Ga_2O_3$  (Figure S29). The first C–H activation barrier of  $Ga_2O_3$  is slightly higher than that of  $ZrO_2-Ga_2O_3$  (1.35 compared to 1.11 and 1.18 eV for the 4- and 5-coordinated Zr in the  $ZrO_2-Ga_2O_3$  system). The competing C–C activation reaction is very unlikely with an activation barrier of 3.67 eV. The C–H activation barrier of the central C atom leading to propylene production is low (0.25 eV). As for Zr at the  $ZrO_2-Ga_2O_3$  interface, the dissociated H atom sticks to the O lattice atom in both the first and second C–H activation and must be removed to facilitate further PDH. The diffusion energy barrier needed to remove the dissociated H atom is 1.19 eV (Figure

S30), significantly larger than that of the  $\text{ZrO}_2/\text{Ga}_2\text{O}_3$  system (0.33 eV, Figure S25). Note that O vacancies do not improve the PDH catalytic properties of  $\text{Ga}_2\text{O}_3$  [the first C–H activation barrier of defective  $\text{Ga}_2\text{O}_3$  is 1.46 eV (Figure S31) compared to 1.35 eV (Figure S29) for pristine  $\text{Ga}_2\text{O}_3$  (Figure S32)]. This is in accordance with the experimental data which shows that H<sub>2</sub> involvement does not affect the PDH activity of  $\text{Ga}_2\text{O}_3$ .

Additionally, DFT calculations were also used to investigate the pure  $ZrO_2$  system (Figure S33). Pristine *m*-ZrO<sub>2</sub>(111) surface (containing 6- and 7-coordinated Zr atoms) has a very large C-H activation barrier (1.73 eV) which explains its very low propane conversion (Figure S34). Defective m-ZrO<sub>2</sub>( $\overline{1}11$ ) with 5- and 6-coordinated Zr sites (Figure S33c) possesses a very low C-H activation barrier of 0.01 eV (Figure S35). The poisoning of the active site by strong adsorption of the dissociated H however blocks the further PDH process. The trapping of the dissociated H by the adjacent O lattice atom is very strong and requires at least 2.64 eV for its removal (Figure \$36). Moreover, DFT calculations were conducted to evaluate the feasibility of H<sub>2</sub> formation by two dissociated H atoms. The calculated activation barrier is up to 2.15 eV, suggesting that the H<sub>2</sub> recombination near the active site is a very slow step compared to the H diffusion (Figure S37). Note that our energy profile of the PDH process of the m-ZrO<sub>2</sub>(111) system is similar to that of Zhang et al.<sup>24</sup> They show that the PDH of the defective m-ZrO<sub>2</sub>( $\overline{111}$ ) catalyst has a very low energy barrier, but the final desorption of H<sub>2</sub> required for completion of the PDH process is endothermic by 1.40 eV.<sup>24</sup>

The Zr–Ga system indicates that one can design a binary component catalyst in which  $Ga_2O_3$  suppresses poisoning and coke formation. To generalize this strategy and confirm it to components different than Zr, we first checked the PDH performance and coke formation of single-component materials.  $Ga_2O_3$  obviously has a very low coke formation rate, orders of magnitude lower than that of the other catalysts (Table S14). The PDH performance of the single component

catalysts is very low (high coke rate formation leading to low yield), except Ga<sub>2</sub>O<sub>3</sub> (low coke rate formation and medium yield). The addition of Ga2O3 to the other metallic components (Fe, Y, Ni, Co, W, Mo, and Zr) indeed suppresses coke formation and enhances PDH performance (Figures \$38-\$43 and Tables \$15-\$20). The exact nature of the processes occurring in the Zr<sub>0.26</sub>Ga<sub>1</sub> nanocomposite catalyst was thoroughly investigated in the present work. In contrast, the other M-Ga oxide catalysts may differ for different components and should be checked in future studies (both experimentally and by DFT calculations). However, the rational catalyst strategy was validated. All M-Ga composite catalysts surpass the activity of Ga<sub>2</sub>O<sub>3</sub>, and Mo<sub>0.2</sub>Ga<sub>1</sub>/SIRAL10 even compares well with Pt-Sn(I), though it is still inferior with respect to Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10. These optimized catalysts exhibited an excellent catalytic performance in terms of propane conversion (31.8-43.2%), propylene selectivity (>89%), and stability (Figure 6). It is well known that ironbased materials are poor catalysts for nonoxidative dehydrogenation of alkanes because they can activate the C-C bond and form coke quickly, leading to low selectivity and short life times.<sup>41</sup> We show herein that a Fe-based catalyst can however also activate the C-H bond. so that it can be used to modify Ga<sub>2</sub>O<sub>3</sub> and form a good alkane dehydrogenation catalyst. Indeed, the Fe-Ga catalyst shows a good catalytic performance with a propane conversion of 31.8%, a propylene selectivity of 91.1%, and a propylene STY of 0.98 kg kg<sub>Cat</sub> $h^{-1}$ , further confirming our proposed catalytic scheme (Figure 6). The modification of  $Ga_2O_3$  by metal/metal oxides is thus a universal and versatile approach for preparing inexpensive and highly efficient catalysts for conversion of alkanes to olefins.

### 4. CONCLUSIONS

In summary, we have demonstrated the stabilization of oxygen vacancies in defective  $ZrO_2$  with the assistance of  $Ga_2O_3$ . Ga<sub>2</sub>O<sub>3</sub> suppressed active site poisoning and coke formation and enabled efficient dehydrogenation. Our most efficient (Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10) catalyst showed superior catalytic activity of conversion of alkanes to olefins compared with the industrial Pt-Sn catalyst. DFT calculations of the Zr-Ga system provided insight into its improved PDH performance, emphasizing the role of oxygen vacancies (and low coordinated Zr atoms) in the  $ZrO_2$  part of the  $ZrO_2$ -Ga<sub>2</sub>O<sub>3</sub> interface. The optimum dehydrogenation activity is achieved by the interplay between the number of low-coordinated Zr sites at the ZrO<sub>2</sub>- $Ga_2O_3$  interface and the availability of  $Ga_2O_3$  to provide a low energy channel for removal by diffusion of the dissociated H atoms which otherwise block the reaction sites. The optimized Zr<sub>0.26</sub>Ga<sub>1</sub>/SIRAL10 displayed a higher propylene STY by 21% compared to the industrial Pt-Sn catalyst. The promising catalytic performance for the dehydrogenation of light alkanes over the cheap  $ZrO_2-Ga_2O_3$  catalyst is expected to have a significant impact on the chemical industry.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c02621.

Experimental details, material characterization data, and computational details (PDF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors. Y.X., X.W., D.Y., and Z.T. contributed equally.

#### Notes

The authors declare no competing financial interest.

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