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Supplementary Information

High-Efficiency CO₂ Utilization in Isobutane Dehydrogenation over ZnAl Hydrotalcite Derivatives: Optimizing Calcination Temperature and Unlocking Reaction Mechanism

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Figure S1. XRD patterns of the reduced ZA-T-R catalysts (T = 550, 600, 650, 700).



Figure S2. EDX elemental mapping of the representative ZA-600 catalyst.



Figure S3. EPR signal of the reduced ZA-T-R catalysts (T = 550, 600, 650, 700).

Electron paramagnetic resonance (EPR) serves as a powerful tool for probing paramagnetic species containing unpaired electrons, particularly in elucidating defect structures within catalytic materials. In order to further evaluate the oxygen vacancies evolution, the EPR analysis was conducted on the fresh ZA-T-R (T = 550, 600, 650,

700) catalysts, and the results are shown in Figure S3. Among all ZA-T-R catalysts, a significant signal emerged at g = 2.003, indicative of the surface oxygen vacancies, while a weaker signal at g = 1.960 corresponds to bulk oxygen vacancies. Notably, the signal intensities at both g=2.003 and 1.960 values exhibit an inverse correlation with calcination temperature (ZA-550-R > ZA-600-R > ZA-650-R > ZA-700-R), confirming that the lower calcination temperature favor oxygen vacancies formation, which is consistent with XPS data in Table 2.



Figure S4. The selectivities of by-products over the reduced ZA-T-R catalysts (T = 550, 600, 650, 700) under the dehydrogenation conditions of reaction temperature = 600 °C, GHSV = 2100 mL h⁻¹ g_{cat} ⁻¹, CO₂: i-C₄H₁₀ molar ration = 2:1, catalyst mass = 0.5 g.



Figure S5. Dehydrogenation performance of $i-C_4H_{10}$ over the representative ZA-600-R catalyst under different reaction atmospheres: (a) $i-C_4H_{10}$ conversion, (b) $i-C_4H_8$ selectivity, (c) $i-C_4H_8$ yield, (d) by-products selectivity. The feed gas composition was controlled under different atmospheres: ZA-600-R-C with a CO₂/i-C₄H₁₀ molar ratio of 2:1 (CO₂-ODHB) and ZA-600-R-N with a N₂/i-C₄H₁₀ ratio of 2:1 (DH).

To investigate the influence of CO_2 on the oxidative dehydrogenation of $i-C_4H_{10}$ (ODHB) reaction, the DH performance of $i-C_4H_{10}$ was also evaluated under CO_2 -free over the representative catalyst ZA-600-R. The conversion of $i-C_4H_{10}$, the selectivity and yield of $i-C_4H_8$ along with by-products selectivity vs time on stream are depicted in Figure S5. The initial conversion of $i-C_4H_{10}$ on the catalyst ZA-600-R under CO_2 free is higher than that under the presence of CO_2 , indicating that the presence of CO_2 is negative to the dehydrogenation of $i-C_4H_{10}$. It is attributed to the greatly reduced $i-C_4H_{10}$ adsorption capacity due to the competition of CO_2 ¹. Under the absence of CO_2 in the feed, the initial $i-C_4H_{10}$ conversion can be kept at high level, but a rapid deactivation can be observed after reaction of 50 min, and even the conversion of i C_4H_{10} is lower than that in the presence of CO_2 after 105 min on stream. This indicates that the presence of CO_2 is beneficial for improving the durability of catalyst in the i- C_4H_{10} dehydrogenation reaction, arising from the inhibiting effect of CO_2 on carbon deposition. In addition, the target product i- C_4H_8 and by-products (CH_4 , C_2H_6 , C_2H_4 , C_3H_8 and C_3H_6) are formed during the dehydrogenation process of i- C_4H_{10} regardless of the presence of CO_2 . However, the by-products selectivity in the presence of CO_2 is lower than those in the absence of CO_2 (see Figure S5). It is thought that the CO_2 , as a mild oxidant, can promote the dehydrogenation of i- C_4H_{10} preferentially and weaken the cracking and hydrocracking reactions, thereby increasing the selectivity of the target product i- C_4H_{10} compared with the situation in the absence of CO_2 . This observation further supports the hypothesis that the CO_2 -ODHB over ZA-600-R follows a Mars-van Krevelen (MvK) mechanism, rather than a combination of DH and the reverse water-gas shift reaction (RWGS) mechanism.



Figure S6. i- C_4H_{10} conversion and i- C_4H_8 selectivity as function of time for the representative ZA-600-R catalyst after regeneration and activation (regeneration conditions: T = 600 °C, oxidation in air for 1 h, sequencing purge with N₂ for 30 min and then reduction in 5 vol% H₂/N₂

for 2 h; reaction conditions: reaction temperature = 600 °C, GHSV = 2100 mL h⁻¹ g_{cat}⁻¹, CO₂: i-C₄H₁₀ molar ratio = 2:1, catalyst mass = 0.5 g).

The regeneration behavior of the representative catalyst ZA-600-R is shown in the Figure S6. After each cycle, the $i-C_4H_{10}$ conversion and $i-C_4H_8$ selectivity can be basically restored to the level before regeneration. It indicates that the deposited carbon can be removed by a simple oxidation process.



Figure S7. XRD patterns of the used ZA-T-R catalysts (T = 550, 600, 650, 700) after 250 min of reaction.

The XRD patterns of the used ZA-T-R catalysts (T = 550, 600, 650, 700) after reaction are shown in the Figure S7. It can be observed that the samples still exhibit diffraction peaks corresponding to ZnO and ZnAl₂O₄ phases. However, no diffraction peaks corresponding to carbon-containing species can be detected in any of the samples, speculating that the carbon deposits are too little to be detected or are likely to be in an amorphous state.



Figure S8. TG-DTG curves of the used ZA-T-R catalysts (T = 550, 600, 650, 700) after 250 min of reaction.

During the dehydrogenation process, the carbon deposition resulting from alkane dramatic cracking and the Boudouard reaction (CO₂ disproportionation) is a significant cause of catalyst deactivation due to the coverage of active sites^{1-4.} Therefore, it is essential to investigate the carbon deposition on the catalyst using TG-DTG experiments, the curves are shown in Figure S8.

The TG steps and DTG peaks of catalysts exhibit four mass loss regions below 700 °C. The initial mass loss at 100 °C is attributed to the removal of physically adsorbed water. Between 100 °C and 300 °C, the second mass loss corresponds to the removal of chemically bound water and organic species. The third significant mass loss starting at 300 °C is due to the combustion of carbon deposits. The last stage above 600 °C is likely associated to the decomposition of the residual CO_3^{2-} anions, resulting in an extended emission of product CO_2 across a broad temperature range ⁵. It is noted

that the fourth mass loss stage is absent in sample ZA-700-R. This is due to the sample having been pretreated at 700 °C, which eliminating any residual CO_3^{2-} anions.

The amount of carbon deposits decreases gradually from ZA-600-R (7.9%) to ZA-650-R (7.5%), ZA-550-R (7.4%), and ZA-700-R (5.1%). And the trend in carbon deposition correlates with the S_{BET} value and dehydrogenation performance, which suggests that a higher S_{BET} value and catalytic conversion leads to the more carbon deposition. In fact, all catalysts exhibit limited carbon deposition, which is attributed to the carbon suppression effect exerted by weak surface acidity and CO₂ oxidation ⁶. This corroborates the structural insights obtained from XRD analysis of the used catalysts.

Additionally, the temperature of the DTG maximum signal, arising from the removal of carbon deposits, increases from 446 °C of ZA-550-R to 471 °C of ZA-600-R and then decreases to 466 °C of ZA-650-R and to 446 °C of ZA-700-R. It can be found the combustion temperature of carbon deposition is inversely proportional to the average pore size of catalyst. Namely, the combustion temperature of carbon deposition should be controlled by the average pore size. Once the carbon species are deposited in the narrow pore channels, they become difficult to interact with oxygen, resulting in an elevated combustion temperature. However, the higher the combustion temperature of carbon deposition generally means the more difficult regeneration for the corresponding used catalyst, and vice versa ⁷. Considering the minimal carbon deposition on the surface of catalyst and the constrained pore volume, it is speculated that the carbon accumulation after a long reaction time should have a negligible impact on regeneration, and relevant issues need to be further studied in detail.



Figure S9. XPS spectra of (a) Zn 2p3/2 and (b) O 1s regions and (c) EPR signal for the used ZA-T-R catalysts (T = 550, 600, 650, 700).

Table S1. XPS data of Zn 2p3/2 and O 1s regions in the used ZA-T-R catalysts (T = 550, 600, 650, 700).

Used catalysts	BE (eV)				Chemical state distribution (%) ^a			AOS
	Zn ⁰	Zn^{2+}	O _{latt}	O _{ads}	Zn ⁰	Zn^{2+}	O _{ads}	
ZA-550-R	1021.5	1022.1	530.4	531.7	61	39	65	0.78
ZA-600-R	1021.5	1022.1	530.6	531.9	50	50	57	1.00
ZA-650-R	1021.5	1022.2	531.6	532.9	45	55	48	1.20
ZA-700-R	1021.5	1022.1	531.6	532.9	39	61	42	1.22

^a The fitted peak to total peak area ratio (%).

The XPS spectra of the used ZA-T-R catalysts were analyzed to investigate the evolution of Zn and O chemical states (Figure S9). The deconvolution of the asymmetric Zn 2p3/2 and O 1s spectral envelopes gives two distinct contributions,

and the quantified parameters are summarized in Table S1. Notably, the binding energy (BE) values of the Zn⁰, Zn²⁺, lattice oxygen (O_{latt}) and surface adsorbed oxygen (O_{ads}) species in the used catalysts remain consistent with those of the fresh ones. However, the used catalysts exhibit an increased content of Zn⁰ and O_{ads} and a shrinkage of calculated AOS values of the surface Zn species compared to their fresh counterparts, likely attributed to reaction-mediated reduction processes. This observation suggests enhanced oxygen vacancies formation ability on the catalyst surface after the reaction.

The EPR analysis of the used catalyst display the complete disappearance of the bulk oxygen vacancy signal (g = 1.960), whereas the surface vacancy signal (g =2.003) is retained and even the proportion of oxygen vacancies relative to lattice oxygen has been enhanced slightly, based on the XPS data in Table 2 and Table S1. It can be deduced that there must exist oxygen migration in the CO₂-ODHB process. The driving force should come from the consumption of lattice oxygen by i-C₄H₁₀ and replenishment by CO₂, along with the formation and consumption of oxygen vacancies in the reaction process.



Figure S10. TPSR-MS signals of m/z = 28, 44 and 18 over the representative ZA-600-R catalyst under continuous flow He, CO₂, He, i-C₄H₁₀, He, CO₂ and He at 600 °C. The first CO₂ treatment stage: 30-90 min, i-C₄H₁₀ treatment stage: 120-180 min, the second CO₂ treatment stage: 210-270 min.

In order to understand the role of oxygen vacancies (Vo) in CO_2 -ODHB, the temperature-programmed surface reaction-mass spectrometry (TPSR-MS) experiments were carried out on the representative ZA-600 catalyst.

During the first CO₂ treatment stage, a strong and gradually declining CO₂ signal (m/z = 44) was observed, accompanied by a weaker but relatively stable m/z = 28 signal (subtle changes cannot be ruled out due to its low intensity). Notably, a transient m/z = 28 peak emerged within the initial 5 minutes. Upon switching to He, the m/z = 28 signal rapidly vanished (<10 minutes), while the CO₂ signal (m/z = 44) decayed more slowly. The distinct trends of the m/z = 44 and 28 signals confirm that the m/z = 28 signal originates from CO molecular ions rather than CO₂ fragment peaks, demonstrating that CO₂ interacts with oxygen vacancies on the catalyst surface

to generate CO via the reaction: $CO_2 + Vo \rightarrow CO + O^-$. The transient CO peak in the first 5 min followed by stabilization suggests that CO_2 preferentially reacts with highly active surface oxygen vacancies initially, followed by slower interactions with the deeper oxygen vacancies.

In the i-C₄H₁₀ treatment stage, both m/z = 44 and 28 signals reappeared, but the m/z= 44 signal was significantly weaker than the m/z = 28 signal. Transient peaks for both signals were observed within the first 10 min, with the m/z = 28 peak intensity being twice that of the first CO_2 treatment stage. A weak spike in the m/z = 28 signal also occurred in the final 10 min of i-C₄H₁₀ treatment. Upon switching to He, both signals returned to baseline, while a distinct H₂O signal (m/z = 18) emerged, indicating H_2O production during i-C₄H₁₀ treatment. This implies that i-C₄H₁₀ undergoes oxidative dehydrogenation via lattice oxygen (O⁻): i-C₄H₁₀ + O⁻ \rightarrow C₄H₈ + $H_2O + CO + Vo$. The weak H_2O signal is attributed to its strong adsorption on the catalyst surface, while the persistent m/z = 28 signal arises from CO generation (though contributions from dehydrogenation byproducts like propane, ethane, and ethylene cannot be entirely excluded). Critically, the consumption of lattice oxygen regenerates Vo. The transient m/z = 28 peak at the beginning of the i-C₄H₁₀ stage likely reflects rapid oxidation of i-C₄H₁₀ by highly reactive lattice oxygen, while the late-stage m/z = 28 spike may result from newly formed Vo promoting trace CO generation (e.g., via carbon gasification: $C + O^- \rightarrow CO$).

During the second CO₂ treatment stage, the m/z = 28 signal exhibited a trend similar to the first CO₂ stage, but the CO₂ signal (m/z = 44) gradually increased. Upon switching to He, asynchronous decay of the m/z = 28 and 44 signals was observed, along with a pronounced H₂O signal. These results confirm that regenerated oxygen vacancies on the catalyst surface are consumed by CO₂. The strong H₂O signal during He purging suggests substantial H₂O accumulation from the i-C₄H₁₀ stage, which may oxidize surface carbon deposits during the second CO₂ treatment via the reaction: C + $2H_2O \rightarrow CO_2 + 2H_2$, potentially contributing to the enhanced CO₂ signal.

The differing CO_2 signal trends between the two stages may also stem from variations in the sources of oxygen vacancies, leading to time-dependent changes in surface basicity or oxygen transport rates, thereby altering CO_2 adsorption/desorption behavior. This observation highlights the tunable nature of the catalyst, opening new avenues for future research.

In conclusion, the TPSR-MS results provide evidence for the MvK mechanism:

(1) CO Generation Linked to Oxygen Vacancies, namely the CO signals during CO_2 and i-C₄H₁₀ treatments are consistent with oxygen vacancies-mediated reactions:

 CO_2 activation: $CO_2 + Vo \rightarrow CO + O^-$ (oxygen vacancy consumption).

i-C₄H₁₀ activation: i-C₄H₁₀ + O⁻ \rightarrow C₄H₈ + H₂O + CO + Vo (oxygen vacancy regeneration).

The rapid disappearance of CO signal upon He purging confirms its reactive origin, ruling out physical adsorption and CO₂ fragment signal.

(2) Oxygen Vacancy Regeneration:

The similar signal vary for m/z = 44, 28 and 18 during the first and second CO₂ treatments (44 signal increase) indicates oxygen vacancies were regenerated after i-C₄H₁₀ consumption of lattice oxygen.

(3) H₂O Signal Dynamics:

The H₂O (m/z=18) signal increased during He purging after i-C₄H₁₀ treatment, suggesting H₂O formation from dehydrogenation (i-C₄H₁₀ + O⁻ \rightarrow C₄H₈ + H₂O + CO + Vo) and subsequent desorption. This aligns with the MvK pathway, where lattice oxygen participates in H₂O formation.

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