# Mechanistic analysis of active site formation and reaction mechanism of non-oxidative propane dehydrogenation over bare $ZrO_2$

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**Abstract:** The non-oxidative dehydrogenation of propane (PDH) to propene was investigated over alternative-type catalysts composed of bare $ZrO_2$. The ability of zirconia for formation of anion vacancies and accordingly coordinatively unsaturated Zr cations ($Zr_{cus}$) through removal of lattice oxygen was concluded to play an important role for the PDH activity. Such defect sites are responsible for breaking C-H bonds in propane to yield propene. Preparation method of $ZrO_2$ and the kind of reducing agent used for catalyst treatment before PDH determine the concentration of $Zr_{cus}$. $ZrO_2$ treated in CO revealed higher activity in comparison with a commercial like K-$CrO_x$/$Al_2O_3$.

**Keywords:** Propane dehydrogenation, propene, zirconia, reaction mechanism.

## 1. Introduction

Non-oxidative dehydrogenation of propane (PDH) is one of the most important processes for on-purpose propene production. Pt or $CrO_x$-based catalysts are applied in industry, which are, however, either expensive or toxic [1]. To account for these drawbacks, alternative non-toxic and low-cost $ZrO_2$-based catalysts promoted with some metal oxides have been recently developed by some of the present authors [2-4]. Coordinatively unsaturated Zr cations ($Zr_{cus}$) and neighboring lattice oxygen were suggested to be catalytically active sites. However, fundamental factors affecting the activity and formation of such sites were not thoroughly investigated. Thus, the present work was focused on bare $ZrO_2$ to exclude any effect of dopant on catalyst performance. We synthesized several $ZrO_2$ samples possessing different phase compositions and textural properties and tested them in PDH. For elucidating the reaction mechanism and the formation of active sites on a level as elementary as possible, we combined catalytic tests with in-depth catalyst characterization by complementary techniques including DFT calculations.

## 2. Experimental and Theoretical

$ZrO_2$ materials were prepared by sol-gel, precipitation, hydrothermal methods and simple thermal decomposition of zirconium salts. Furthermore, for each method, several parameters were varied, which were the kind of $ZrO_2$ precursor, its concentration, crystallization temperature, crystallization time and calcination duration. Finally, $ZrO_2$ materials with different phase composition, crystallite size and surface area were obtained as concluded from the results of catalyst characterization by XRD, TPR with $H_2$ or CO, BET, SEM, TEM, $NH_3$-TPD and Raman spectroscopy. Their activity, selectivity, on-stream stability and durability in PDH were determined between 550 and 625°C using a feed containing 40 vol% $C_3H_8$ in $N_2$.

## 3. Results and discussion

The results of catalytic tests indicate that high surface area of $ZrO_2$ does not automatically guarantee high PDH activity thus suggesting that some other factors determine the activity. For example, $ZrO_2$ exclusively composed of the monoclinic phase showed higher activity than their counterparts stabilized in the tetragonal phase. However, when comparing samples composed of both monoclinic and tetragonal phases, no direct correlation between the activity and the content of the monoclinic phase could be established. Therefore, the phase composition is not the only factor determining dehydrogenation activity of $ZrO_2$. On the basis of our previous studies with doped $ZrO_2$, we put forward that the ability of zirconia for formation of anion vacancies through removal of lattice oxygen plays an important role for the activity. To check this hypothesis, we investigated the effect of CO and $H_2$ used as reducing agents for catalyst treatment before the PDH reaction on the rate of propene formation. In comparison with oxidized $ZrO_2$ samples, their reduced counterparts showed higher activity. However, the treatment in CO resulted in an increase in the rate by at least a factor of 3 in comparison to the treatment with $H_2$ (Fig. 1(a)). Moreover, bare $ZrO_2$ reduced in CO performed superior to the most active $ZrO_2$-based catalysts from our previous studies [2-4] and revealed even higher activity than a commercially like K-$CrO_x/Al_2O_3$ (Fig. 1(a)). The distinctive effects of CO and $H_2$ treatments on the rate of propene formation was explained by the fact that CO removes easier lattice oxygen from $ZrO_2$ and this amount is higher in comparison with $H_2$ as concluded from TPR tests with CO and $H_2$ (Fig. 1(b)). The consumption of CO and $H_2$ is 1.57 and 0.066 μmol/m$^2$, respectively. As a consequence, a higher concentration of catalytically active $Zr_{cus}$ sites was formed after CO treatment. In addition to the activity, propene selectivity was also improved when $ZrO_2$ was pretreated with CO, while the selectivity to cracking products decreased.

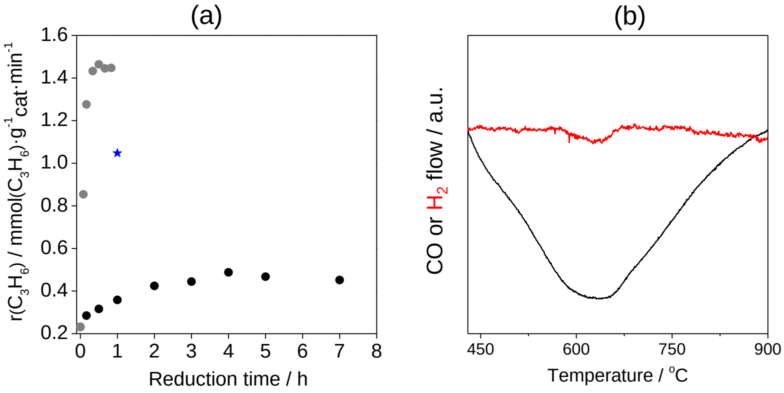

**Fig. 1** (a) The rate of propene formation over monoclinic $ZrO_2$ at 550°C versus reduction time in 57 vol.% CO (●) or $H_2$ (●) in $N_2$. ★ stands for K-$CrO_x/Al_2O_3$; (b) CO-TPR (—) and $H_2$-TPR (—) profiles of this sample.

To derive deeper fundamental insights into the role of $Zr_{cus}$ sites in the reaction mechanism of propene formation, DFT calculations were performed. The (-111) facet of monoclinic $ZrO_2$ with or without oxygen vacancies was used as a model for calculating the elementary pathways leading from propane to propene. In comparison with the non-defect Zr-O-Zr site, the activation barrier for the dissociation of the first C-H bond on Zr-$O_v$-Zr defect sites ($O_v$ stands for oxygen vacancy) was established to be lower. Further transformations of isopropyl bonded to Zr into gas-phase propene also proceed easier on the defect surface.

## 4. Conclusions

In summary, the activity of bare $ZrO_2$ is affected by phase composition, crystallite size, and particularly, by the ability of zirconia for removal of lattice oxygen upon reductive catalyst treatment to create catalytically active $Zr_{cus}$ sites. Such sites are easily generated upon catalyst treatment in CO thus enabling to increase catalyst activity up to 3 times in comparison with $H_2$ treatment and to outperform commercially like K-$CrO_x/Al_2O_3$. DFT calculations suggest that $Zr_{cus}$ lowers the activation barrier for C-H bond dissociation of $C_3H_8$ and opens an alternative pathway of propene formation in comparison with non-defect surface.

## References

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