

Utilization of CO₂ in the process of propane oxidative dehydrogenation

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Introduction

The oxidative dehydrogenation (ODH) of alkanes to alkenes by molecular oxygen is a relatively new and a promising technology. The presence of O₂ may however, lead to process flammability, production of carbon oxides and over-oxidation, resulting in poor process selectivity. This can be overcome by using a safer, milder and readily available oxidant: CO₂.¹ As the issue of CO₂ emissions has become one of the main subjects in environmental chemistry, this reaction seems to serve also a great example for CO₂ utilization.² The route of this reaction may follow Mars van Krevelen mechanism, where CO₂ will dissociate on the surface of catalyst, facilitating further dehydrogenation. Catalysts with high oxygen storage capacity (OSC) and ability to dissociate CO₂ in low temperatures would be ideal for this process. One of the active metal oxides, which possess these properties, is CeO₂. Addition of ZrO₂ to CeO₂, however, increase OSC and additional presence of another metal oxide-Al₂O₃ has a positive influence on the surface area and catalyst thermal stability.³ Here, we report the oxidative dehydrogenation of propane (ODP) with the use of CO₂ and Pd/Ce-Zr-Al-O_x based catalyst. The use of temporary analysis programme (TAP) reactor for CO₂ dissociation over Pd/Ce-Zr-Al-O_x catalyst was also investigated.

Materials and Methods

Catalysts were prepared by physical grinding method. Ce, Zr, Al acacs were grinded thoroughly for 15 mins, then calcined in flowing air (500°C, 3h, 5°C/min) to give support composition Ce: Zr: Al: 1:1:2. Further Pd was wet impregnated onto calcined support following the protocol: to the aqueous solutions of Pd(NH₃)₄(NO₃)₂ requisite amount of support were added under vigorous stirring at room temperature. The solution was agitated in this way until it formed a paste, which was dried at 120°C for 12h and further calcined at 500°C for 4h. Catalytic measurements were performed using a fixed bed laboratory micro reactor at atmospheric pressure, keeping GHSV at 6385 h⁻¹ and total flow rate of 15 mL min⁻¹. Reaction mixture consisted of He, CO₂ and C₃H₈, keeping He on the level of 26% volume and using different ratio between CO₂ and C₃H₈. Reactions were explored in the temperature of 500°C. The reactants and products were analysed by a Varian 3800 online gas chromatograph using Porapak Q and Molsieve columns with TCD and FID detectors.

Results and Discussion

Pd supported catalyst were highly active for the oxidative dehydrogenation of propane. Studies with different CO₂: C₃H₈ ratio over 5%Pd/Ce_{0.25}Zr_{0.25}Al_{0.5}O_{1.75} catalyst showed that CO₂: C₃H₈ ratio > 10 resulted in highest propane as well as CO₂ conversion as it is shown in **Figure 1**. This may be attributed to the fact, that CO₂ is changing the equilibrium in the reverse water-gas shift reaction, as well as faster CO₂ dissociation over Pd supported catalyst.

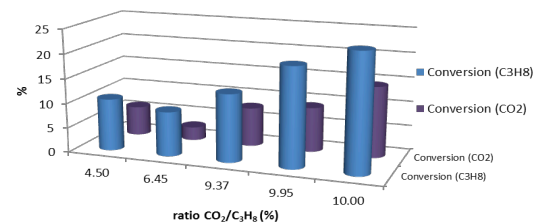


Figure 1: Comparison between CO₂: C₃H₈ ratio and C₃H₈ and CO₂ conversion. Total flow 15ml/min (25.9% He, catalyst 200mg (GHSV=6385.7h⁻¹ T=773K)

When investigating the metal loading on Ce-Zr-Al-O_x support for activity in ODP reaction, it was found that catalyst with 7% Pd loading increased the conversion of propane to more than 35% during 0.5 h reaction, as it is shown in **Figure 2**.

Studies involving TAP measurements over 5%Pd/Ce_{0.25}Zr_{0.25}Al_{0.5}O_{1.75} clearly showed CO production from CO₂ at temperature higher than 300°C. This findings indicate that CO₂ dissociate on the surface of the catalyst yielding highly oxidative O species, maintaining Ce in a highly oxidized state.⁴

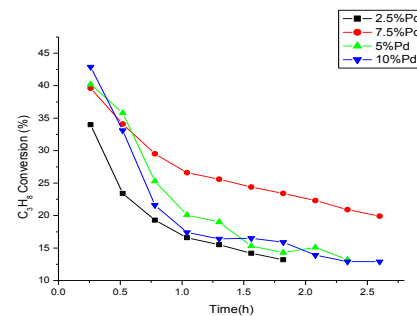


Figure 2. Conversion of C₃H₈ in ODP with Ce_{0.25}Zr_{0.25}Al_{0.5}O_{1.75}: different Pd loading. Total flow 15ml/min (25.9% He, 66.7%CO₂, 6.7% C₃H₈, catalyst 200mg (GHSV=6385.7h⁻¹ T=773K)

Significance: Pd supported catalysts displayed high activity and selectivity in the ODP with the use of CO₂. TAP measurements proved production of active oxygen species from CO₂.

References

- 1.M. B. Ansari and S.-E. Park, *Energy & Environmental Science*, 2012, **5**, 9419-9437.
- 2.K. M. K. Yu, I. Curcic, J. Gabriel and S. C. E. Tsang, *Chemsuschem*, 2008, **1**, 893-899
- 3.M. Chen, J. Xu, Y. Cao, H.-Y. He, K.-N. Fan and J.-H. Zhuang, *Journal of Catalysis*, 2010, **272**, 101-108.
- 4.O. Demoulin, M. Navez, J. L. Mugabo and P. Ruiz, *Applied Catalysis B: Environmental*, 2007, **70**, 284-293.