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# Effect of $Ga_2O_3$ content on the activity of $Al_2O_3$-supported catalysts for the $CO_2$-assisted oxidative dehydrogenation of propane

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## INTRODUCTION & AIM

Propylene ($C_3H_6$) is one of the most important building blocks of the petrochemical industry as it is essential for the production of a wide range of chemicals such as polypropylene, acrylonitrile and propylene oxide. In recent years, the catalytic oxidative dehydrogenation of propane ($C_3H_8$) using a mild oxidant such as $CO_2$ has gained interest as an efficient and eco-friendly process for $C_3H_6$ production because it not only produces propylene but also utilizes the $CO_2$ emissions, thus contributing to the mitigation of the greenhouse effect. Furthermore, adding $CO_2$ in the gas stream can shift the equilibrium towards $C_3H_6$ production by consuming the produced $H_2$ via the RWGS reaction, while simultaneously can inhibit coke deposition by promoting the reverse Boudouard reaction, thus preventing catalyst deactivation. However, depending on the catalyst and reaction conditions employed, the reactions of propane hydrogenolysis and propane or propylene decomposition may also take place, resulting in a decrease of propylene yield and possibly coke formation, which has a significant impact on the lifetime of catalyst. Thus, the physicochemical characteristics of catalyst and operating conditions should be properly selected.

## METHOD

### Catalyst preparation

**Wet impregnation** **x%$Ga_2O_3$/$Al_2O_3$ (x : 0,10,20,30,40 wt.%)**

### Catalyst characterization

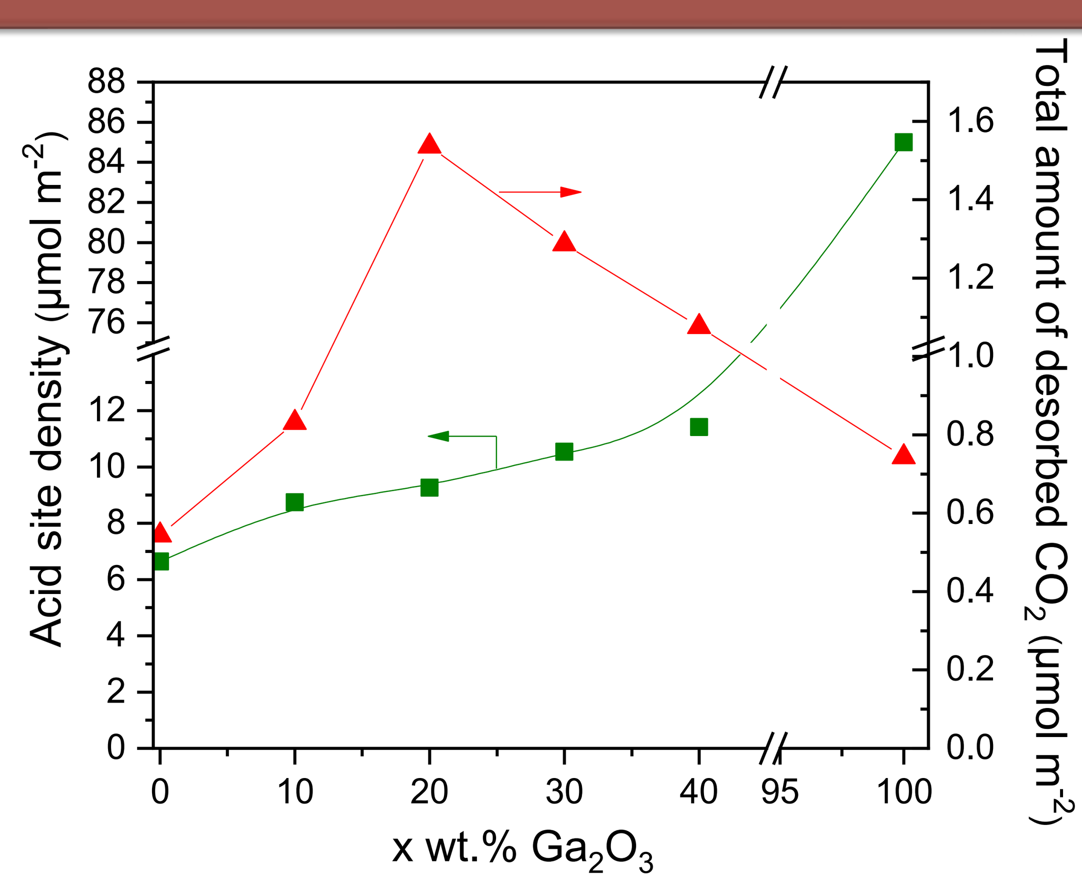
- BET
- XRD
- TEM
- SEM
- $CO_2$-TPD
- FTIR
- Pyridine adsorption/desorption
- Potentiometric titration method
- $H_2$-TPR

### Catalytic performance tests

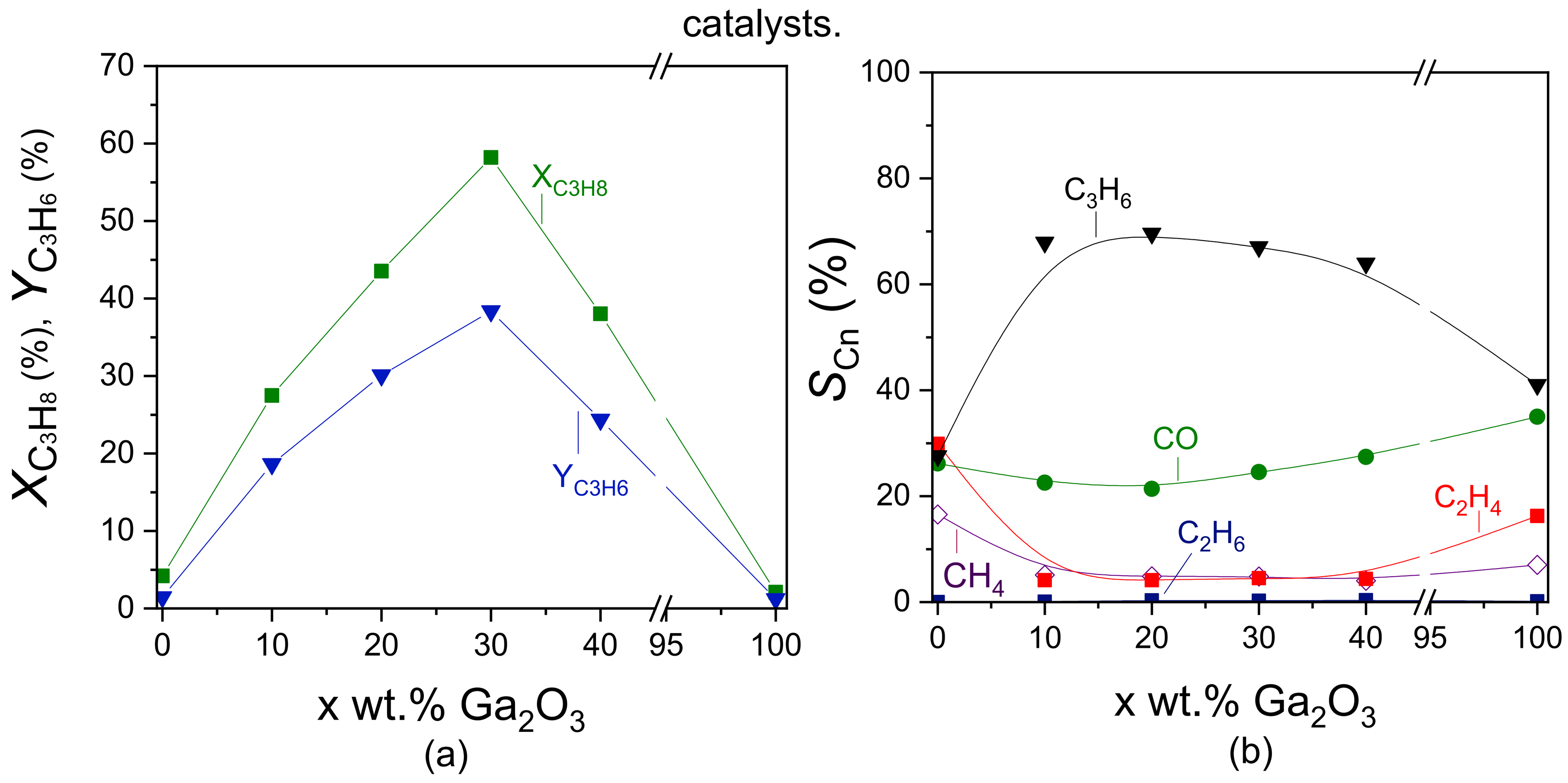
**Temperature range** 450- 750 °C

**Feed composition** 5%$C_3H_8$ + 25%$CO_2$/He

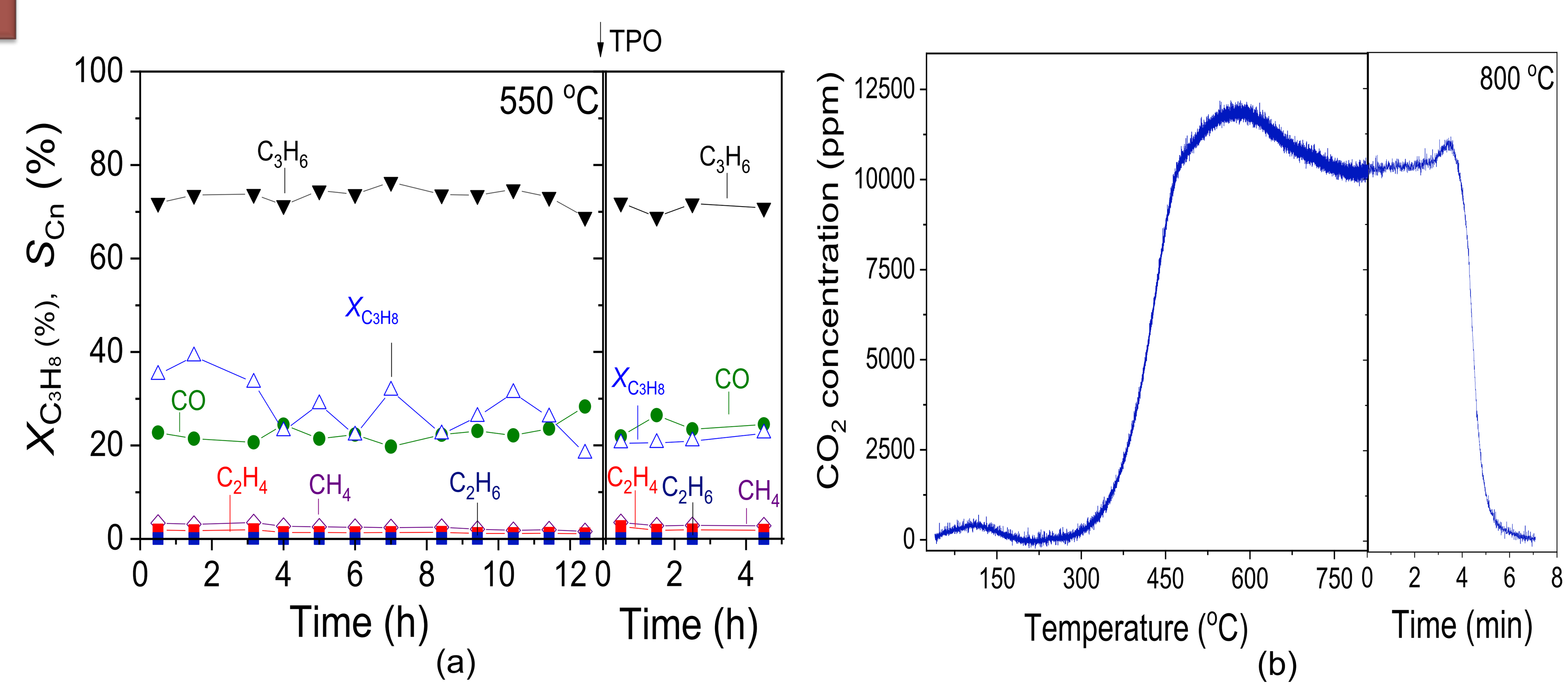
## RESULTS & DISCUSSION



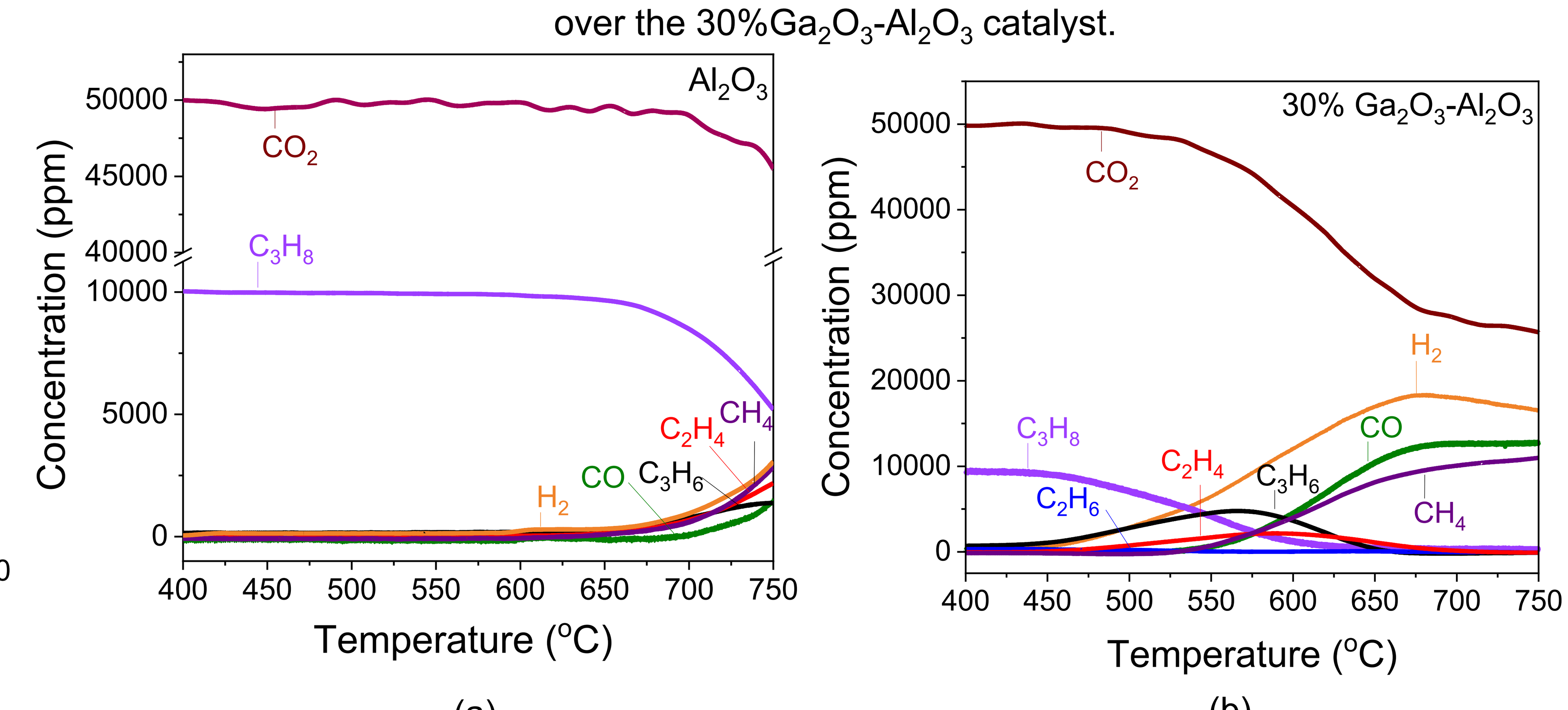

Effect $Ga_2O_3$ content on the surface basicity estimated by $CO_2$-TPD experiments and the acid site density estimated by the potentiometric titration experiments of the synthesized catalysts.




Effect $Ga_2O_3$ content on the (a) propane conversion and propylene yield, and (b) selectivities towards reaction products measured at 600 °C for the $CO_2$-ODP reaction.




(a)TOS stability test conducted at 550 °C under $CO_2$-ODP conditions over the fresh and spent 30%$Ga_2O_3$-$Al_2O_3$ catalyst following TPO experiment and (b) Responses of $CO_2$ produced during TPO experiment occurred after the TOS stability tests conducted at 550 °C presented over the 30%$Ga_2O_3$-$Al_2O_3$ catalyst.




Transient-MS spectra obtained over the (a) $Al_2O_3$ and (b) 30%$Ga_2O_3$-$Al_2O_3$ catalysts following interaction with the reaction mixture 1% $C_3H_8$ + 5% $CO_2$ (in He) at 25 °C and subsequent linear heating at 750 °C.

## CONCLUSION

- Surface basicity was maximized for the sample containing 20wt.% $Ga_2O_3$, whereas surface acidity was monotonically increased with increasing the $Ga_2O_3$ loading.
- A volcano type correlation was found between catalytic performance and acid/base properties according to which propane conversion and propylene yield exhibited optimum values for intermediate surface basicity and acidity, which both correspond to the sample containing 30wt.% $Ga_2O_3$.
- The 30%$Ga_2O_3$-$Al_2O_3$ catalyst exhibited very good stability at 550°C where byproducts formation and carbon deposition were limited.
- Mechanistic studies indicated that the reaction proceeds through a two-step oxidative route with the participation of $CO_2$ in the abstraction of $H_2$, originated by propane dehydrogenation, through the RWGS reaction shifting the thermodynamic equilibrium towards propylene generation.

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