Structured Pt catalysts for hydrogen release from LOHCs: Monolith and open-cell foam reactors for methylcyclohexane dehydrogenation

Pol Fernandez[1], Peter Surjo [1], Isa Pettersson Haag [1], Efthymios Kantarelis[1]*

1 KTH Royal Institute of Technology, Chemical Engineering, Stockholm, Sweden

**Corresponding author: polfir@kth.se*

Highlights

- Pt + S/Al_2O_3 monolith exhibits a 3.8-fold activity increase compared to fixed bed
- $Pt/MgAl_2O_4$ exhibits lower coke formation per unit time and coke with higher H/C ratio
- Multiple regeneration cycles allowed for Pt+S catalysts at 500 °C in 1% O_2

1. Introduction

One of the main barriers to the development of a hydrogen economy is the need for an efficient large-scale storage and supply infrastructure. Liquid organic hydrogen carriers (LOHCs) have emerged as a promising technology for hydrogen storage, consisting of organic molecules capable of undergoing multiple catalytic hydrogenation–dehydrogenation cycles to store and release H_2. The compatibility of LOHC systems with existing fuel transport and storage infrastructure represents a key advantage for large-scale implementation. However, the dehydrogenation step requires high LOHC conversion and high selectivity toward the desired products, while minimizing coke formation to prevent severe catalyst deactivation. Conventional packed-bed reactors often limit conversion and exhibit high coking rates due to mass-transfer limitations and non-uniform temperature distributions. Reducing diffusion lengths and improving heat and mass transfer rates can significantly enhance the performance of such systems. Structured catalysts remain largely unexplored for LOHC dehydrogenation but offer the potential to improve heat and mass transfer characteristics, thereby enhancing selectivity and catalyst stability.

2. Methods

In the present study, structured reactors (ceramic monoliths and aluminum open-cell foams) were investigated as alternatives to conventional fixed-bed reactors for the dehydrogenation of the LOHC methylcyclohexane (MCH) over Pt-based catalysts. The monoliths were made of cordierite (square-shaped channels, 400 cpsi), while the Al open-cell foams had a pore density of 40 ppi. Both structures had a diameter of 15 mm and a height of 3 cm. The fixed-bed reactors contained the same amount of catalyst, and the same bed volume was achieved by dilution with SiC. The performance of the catalytic structures was evaluated by comparing their effects on catalyst utilization, selectivity, stability, and regeneration for the state-of-the-art catalyst for this reaction, $Pt+S/\gamma\text{-}Al_2O_3$, and a previously studied alternative, $Pt+S/MgAl_2O_4$ [1,2]. The structured catalytic reactors were prepared by dip-coating of the ball-milled catalysts using polyvinyl alcohol (PVA) as a binder. The catalysts were first prepared by dry impregnation using $Pt(NH_3)_4(NO_3)_2$ and $(NH_4)_2SO_4$ as precursors. Prior to coating, the aluminum foams were anodized to enhance coating adhesion. Catalytic performance was evaluated at 320 °C, 1.5 bar, a WHSV of 11.0 h^{-1}, and a GHSV of 76,210 h^{-1}. For catalyst regeneration studies, the oxidation kinetics of Pt catalysts deactivated in a fixed-bed configuration were investigated by temperature-programmed oxidation (TPO) using 1% O_2 in Ar in a Micromeritics AutoChem 2910 coupled with a mass spectrometer (MS). This analysis was used to determine coke oxidation kinetics and differences in coke characteristics, such as the H/C ratio of the deposited coke, for both catalysts. Based on these results, catalyst regeneration was performed in situ in the reactor at 500 °C.

3. Results and discussion

The experiments performed with alternative catalytic structures using $Pt+S/\gamma\text{-}Al_2O_3$ showed that the monolithic structure produced higher H_2 than the equivalent fixed-bed configuration of the ball-milled catalyst (Figure 1). The improved catalyst utilization in the monolith is attributed to reduced diffusion resistance in the thin washcoat layer and more uniform gas flow through the channels.

In contrast, the open-cell foam exhibited lower H_2 production than the equivalent fixed bed, which may be attributed to the significantly thicker washcoat layer observed on the foam and backmixing induced by the open-cell structure. The thicker washcoat cannot be explained solely by the lower surface area of the foam compared to the monolith and is instead suggested to result from less uniform catalyst deposition, leading to localized washcoat thickening due to slurry droplet accumulation in some cells.

Furthermore, evaluation of Pt catalysts deactivated in a fixed-bed configuration on different supports (Al_2O_3 and $MgAl_2O_4$) showed lower coke formation rates and a higher H/C ratio of the deposited coke for Pt/$MgAl_2O_4$ (Figure 2, inset), which is attributed to the lower acidity of the $MgAl_2O_4$ support.

The obtained data were used to estimate the kinetic parameters of coke oxidation (activation energy, Ea, and pre-exponential factor, A) [3]. Regeneration of Pt+S/γ-Al_2O_3 was tested in a fixed-bed configuration and demonstrated the possibility of multiple regeneration cycles (Figure 2), with higher activity recovery than Pt/γ-Al_2O_3, which is attributed to the effect of sulfur on the characteristics of the deposited coke.

Ongoing experiments aim to evaluate the performance of structured catalytic reactors at lower WHSV, providing additional insight into the effect of reactor structure on selectivity and catalyst deactivation by coke deposition, and to investigate regeneration of the structured catalysts for both catalytic systems.

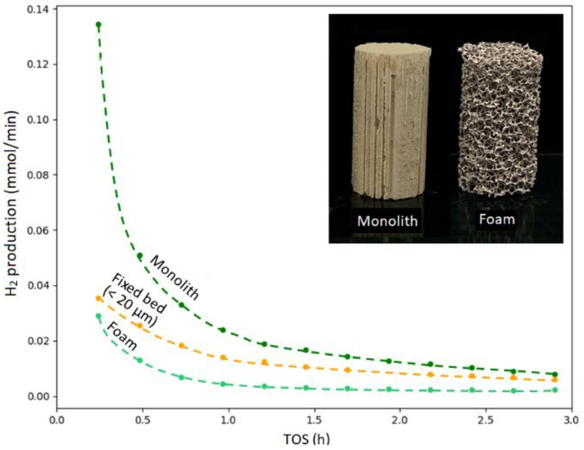

Figure 1. Effect of catalytic structure selection on H_2 produced for Pt + S / Al_2O_3, Trendlines for visual guide only

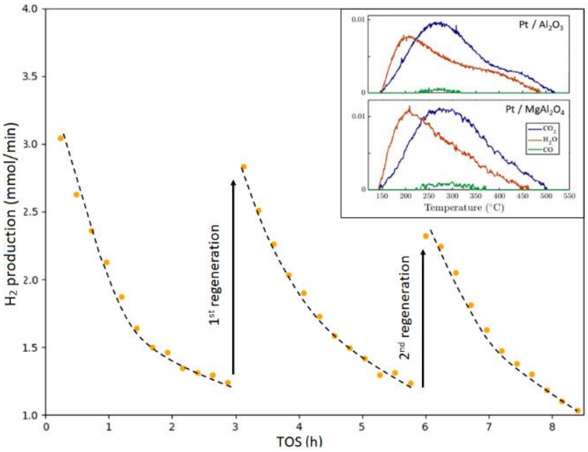

Figure 2. Regeneration of Pt+S/Al_2O_3, at WHSV= 5.5 h^{-1} and 500 °C for 4 h and TPO -MS of deactivated catalysts

4. Conclusions

The results demonstrate that the catalytic structure significantly influences the performance of MCH dehydrogenation. The Pt+S/γ-Al_2O_3 monolithic structure showed higher H_2 production than the equivalent fixed-bed configuration of the ball-milled catalyst, which is attributed to improved catalyst utilization resulting from the thin washcoat layer and uniform gas flow through the channels. In contrast, the open-cell foam exhibited lower H_2 production, likely due to back mixing and non-uniform catalyst deposition leading to thicker washcoat regions and increased diffusion limitations.

References

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Keywords

Monoliths; foams, hydrogen; LOHCs.