

# Deactivation as Key Factor to Understand CO<sub>2</sub> to Olefins Process over In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/SAPO-34 Tandem Catalyst

Ander Portillo\*, Onintze Parra, Arancha Saiz, Javier Ereña, Ainara Ateka

*Chemical Engineering Department, UPV/EHU, P.O. Box 644*

*48080 Leioa, Bizkaia, Spain*

*\*Corresponding author: [ander.portillo@ehu.eus](mailto:ander.portillo@ehu.eus)*

## **Highlights**

- Fast coke formation over SAPO-34 occurs regardless operating conditions
- First minutes of reaction are the key to understand the evolution of products with time on stream
- Increasing pressure leads to higher olefin yield but higher deactivation
- H<sub>2</sub>O plays a key role in deactivation attenuation

## **1. Introduction**

The effective combination of CO<sub>2</sub> to methanol and methanol to olefins (MTO) processes, known as direct CO<sub>2</sub> to olefins process, is a key to tackle on one hand, the mandatory large scale CO<sub>2</sub> valorization and on the other hand, the increasing olefin demand. In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/SAPO-34 has been proven to be a selective and suitable catalyst for direct CO<sub>2</sub> hydrogenation into light olefins. The stability of the tandem catalyst is key to check the viability of the process in a higher scale. The stability of both individual catalysts has been under the scope for methanol synthesis with In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst [1] and MTO with SAPO-34 [2], but the deactivation over each of the catalysts conforming the tandem is scarce [3]. Effect of operating conditions such as temperature, pressure, space time, catalysts configuration and feed composition are typically presented for pseudo-steady state values [4], blurring significantly the analysis of each variable. Therefore, the aim of this work is to assess the deactivation of In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/SAPO-34 tandem catalysts, delving into the effect that different operating conditions and feed composition have over deactivation.

## **2. Methods**

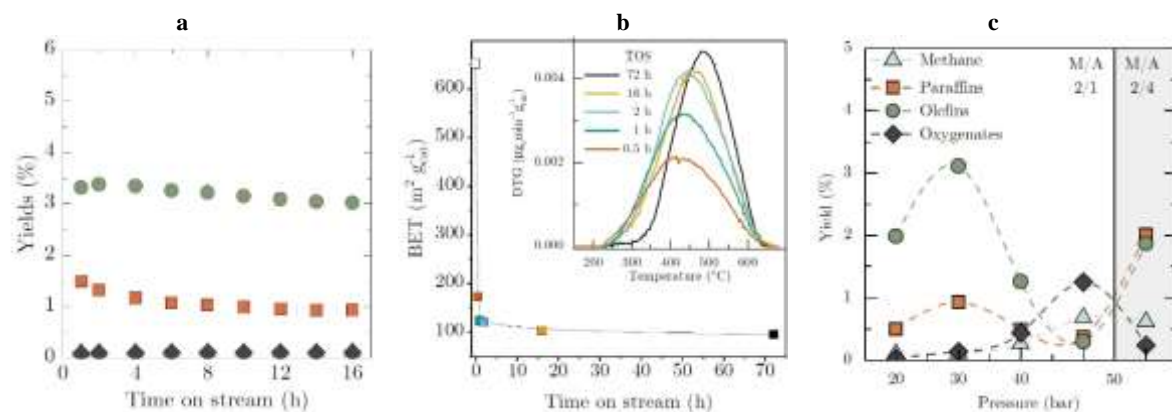
The runs were conducted in a fixed-bed reactor connected on-line to a gas-chromatograph for products analysis. The studied operating condition ranges comprise: fed CO<sub>2</sub>/(CO+CO<sub>2</sub>) molar ratio, 0-1; H<sub>2</sub>/(CO+CO<sub>2</sub>) molar ratio, 1-3; 375-425 °C; 20-40 bar; space-time, 1.25-10 g<sub>cat</sub> h (mol<sub>C</sub>)<sup>-1</sup>; time on stream, up to 300 h.

Catalysts were synthesized by coprecipitation of the metal nitrates, as thoroughly described in previous work<sup>5</sup>. Several characterization techniques were employed for fresh and deactivated catalysts, such as: N<sub>2</sub> adsorption-desorption, XRD, XRF, XPS, ICP-OES, H<sub>2</sub>-TPR, CO-TPR, CO<sub>2</sub>-TPD, NH<sub>4</sub>-TPD, TPO and HeTPD-GC/MS.

## **3. Results and discussion**

The evolution of product yields with time on stream (TOS) shows a quite steady trend for all major compounds (Figure 1a) that might indicate that deactivation is not a main character of this particular process. However, as observed in Figure 1b, the BET surface of the zeolite collapses at remarkably lower TOS and the coke amount does not change significantly (9.5 wt% at 1 h TOS and 11.8 wt% at 70 h TOS), evidencing a fast pore collapse by coke formation. Furthermore, this coke is constantly evolving (even if more coke amount is not forming) from the heterogeneous coke into a more homogeneous and harder to burn coke (black line in Figure 1b). HeTPD-GC/MS analyses of the soft coke in the zeolite (16 h TOS) evidenced that linear olefin chains with 1, 2 or 3 C=C bonds are the main coking compounds.

As a clear illustration of the relevance of the importance of deactivation to understand the operating conditions, the effect of pressure over yields at pseudo-steady state is shown in Figure 1c. The maximum



**Figure 1.** Evolution of products (a), BET surface and coke amount (b). Reaction conditions: 400 °C, 30 bar, 5  $\text{g}_{\text{cat}} \text{h mol}^{-1}$ ,  $\text{In}_2\text{O}_3\text{-ZrO}_2/\text{SAPO-34}$  (M/A) ratio 2/1. (c) Yield distribution for different operating pressure (same remaining conditions).

observed at 30 bar for the tandem catalyst conformed by a mass ratio of 2/1 ( $\text{In}_2\text{O}_3\text{-ZrO}_2/\text{SAPO-34}$ ) is not a consequence of the synergy of this ratio, but the immediate collapse of the zeolite at higher pressure due to the highest amount of methanol in the reaction medium [3]. This drawback can be avoided just by adding more SAPO-34 for the reactions with higher methanol concentration in the medium. In the case of the temperature (not shown), it is observed that 400 °C presents the best results as a direct consequence of attenuation of the deactivation, as the olefin yield is quite similar at 375 °C and 425 °C but decays with TOS. Reactions carried out varying  $\text{CO}_2/\text{CO}$  ratio also enlighten that even if CO is more active than  $\text{CO}_2$ , increasing  $\text{CO}_2$  favors the conversion as the  $\text{H}_2\text{O}$  generated by rWGS reactions attenuates deactivation in great manner.

#### 4. Conclusions

The fast and almost complete deactivation of SAPO-34 by coke formation is the main responsible of all the yields and trends observed for this particular OX/ZEO tandem catalyst. The study of any operating conditions (and even feed composition) must be carried out considering this effect. Additionally, direct  $\text{CO}_2$  to olefins process is a reaction network with many interactions that makes it difficult to dissect, forcing a complete wide study to later understand all the synergies and effects.

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#### Keywords

Deactivation, catalyst,  $\text{CO}_2$ , light olefins