

## STUDY OF THE DEACTIVATION OF CARBON-SUPPORTED MONO- AND BIMETALLIC CATALYSTS USED IN THE AQUEOUS PHASE REFORMING OF BREWERY WASTEWATER

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### Introduction

Aqueous phase reforming (APR) has gained much attraction since the pioneer work by Cortright *et al.*<sup>1</sup> that showed the possibility of obtaining H<sub>2</sub> and alkanes from organic oxygenated compounds in water under mild reaction conditions (473-523 K, 15-50 bar) using supported metal catalysts. Since then, great efforts have been made, mostly focused on APR of model compounds such as glycerol, glucose, sorbitol, among others. A recent and promising application for APR is the treatment and valorisation of wastewater<sup>2</sup>. So far, the obtained results allow considering APR as an environmentally good candidate for this application in the case of brewery industrial wastewater. However, catalyst deactivation in APR is a common feature for all the systems investigated in the literature, which could affect the success and competitiveness of this recent application. In this work, the stability of carbon-supported Pt and PtRe catalysts was evaluated in the APR of brewery wastewater. Likewise, the influence of porous texture of the support, space velocity and carrier gas flow were studied.

### Materials and Methods

3%Pt/C catalyst was prepared by incipient wetness impregnation using a commercial activated carbon (MER) and a modified MER (MER+40RES) as support. This last was prepared by the addition of 40 wt% resol phenolic resin, calcination at 403 K and pyrolysis at 973 K under N<sub>2</sub> flow in order to reduce microporosity. 3%PtRe/C catalyst was also prepared by sequential incipient wetness impregnation with a metal ratio of 1:1, 1:2 and 2:1 using MER as support. APR experiments were carried out using a fixed bed reactor: 498 K, 28 bar, weight hour space velocity (WHSV) = 0.03-0.48 h<sup>-1</sup>, Ar flow (carrier) = 5-40 mL/min. The monitored variables were: TOC, COD, carbon conversion to gas and H<sub>2</sub> production. Fresh and used catalysts were characterized by N<sub>2</sub> adsorption/desorption and TG-TPD/TPO.

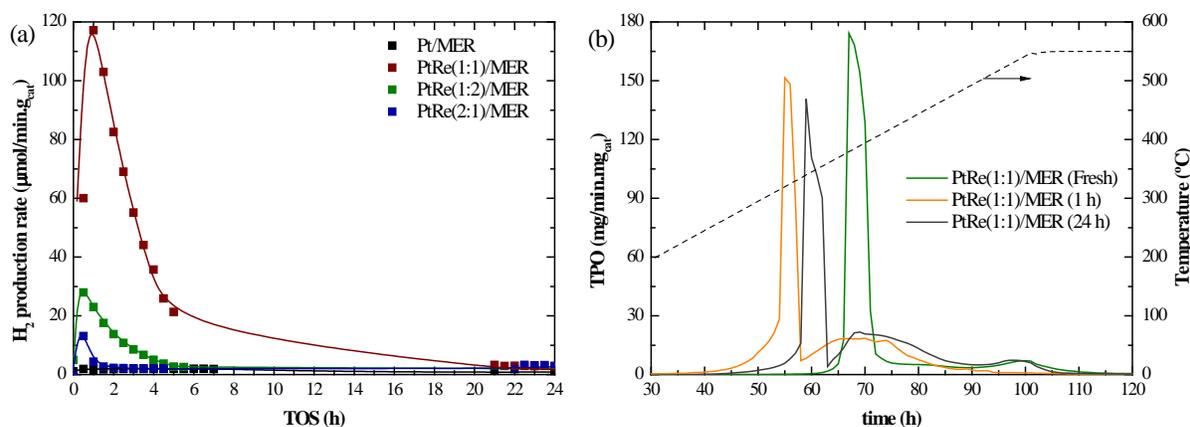
### Results and Discussion

MER support exhibited high S<sub>BET</sub> (930 m<sup>2</sup>/g), basic pH slurry and significant contribution of micropore volume (0.38 cm<sup>3</sup>/g). In MER+40RES support S<sub>BET</sub> and both micro and mesopore decreased significantly (S<sub>BET</sub> = 490 m<sup>2</sup>/g, micropore vol. = 0.20 cm<sup>3</sup>/g) due to pore filling by carbonized resol. Impregnation did not lead to significant porous texture variation and pH slurry.

Catalysts suffered deactivation after a time-on-stream (TOS) of 2-4 hours, however they showed a stable behaviour for 24 h after this initial deactivation. Bimetallic catalysts presented a better

performance, in particular PtRe(1:1)/MER (Figure 1 (a)). The use of MER+40RES support improved H<sub>2</sub> production in the first hours, however TOC and COD removal was lower. TOC and COD removal changed significantly with TOS, mainly at low Ar flows. At the highest Ar flow (40 mL/min) TOC removal was more stable (around 25%) and H<sub>2</sub> production rate was higher, possibly due to the reduction of its consumption in secondary reactions. TOC and COD removal, CC gas and H<sub>2</sub> production decreased at high WHSV, due to shorter contact times. In contrast, at higher WHSV, the percentage of H<sub>2</sub> in the gas fraction was higher (around 90%), presumably because H<sub>2</sub>-consuming reactions have lower contribution.

After 24 hours of TOS, the catalysts almost lost all S<sub>BET</sub> due to deposition of carbonaceous deposits (coke). At high WHSV the loss of S<sub>BET</sub> was faster increased. The final S<sub>BET</sub> was around 30 m<sup>2</sup>/g regardless the type of support and the Ar flow. TG-TPO profiles of used catalysts showed a combustion peak below 350 °C that can be attributed to coke precursor species or reagents/products physically adsorbed on the catalysts surface. MER+40RES support decreased the deposition of coke and related species. The catalyst showing the highest production of H<sub>2</sub>, i.e. PtRe(1:1)/MER, also exhibited a remarkable increase of deposited coke and a clear coke aging with TOS (Figure 1 (b)).



**Figure 1. (a) H<sub>2</sub> production rate of bimetallic and monometallic catalysts and (b) TG-TPO profiles of PtRe(1:1)/MER catalysts fresh and used at different TOS**

## Conclusions

Catalysts deactivation is a challenge in wastewater treatment by APR. Coke deposition on catalysts has an important role in deactivation, but may not be the only reason. High carrier gas flows, bimetallic PtRe catalysts and non-microporous supports can reduce deactivation.

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## References

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2. Oliveira, A. S., Baeza, J. A., Calvo, L., Alonso-Morales, N., Heras, F., Rodriguez, J. J. and Gilarranz, M. A. (2019). Production of hydrogen from brewery wastewater by aqueous phase reforming with Pt/C catalysts. *Applied Catalysis B: Environmental* 245, 367–375.