

On the deactivation of Zr-loading P-containing mesoporous carbon catalyst during methanol dehydration

Javier Torres-Liñán, Miguel García-Rollán*, Juana María Rosas-Martínez, José Rodríguez-Mirasol and Tomás Cordero

Universidad de Málaga, Andalucía Tech, Facultad de Ciencias, Dto. Ingeniería Química, Campus de Teatinos s/n, 29071 Málaga, España.

*mgarciarollan@uma.es

Abstract

Dimethyl ether (DME) has received much attention in the last few years due to its potential use as a diesel substitute, specially because it can be obtained from dehydration of biomass-based methanol. γ -Alumina, ZSM-5 and HPAs have been tested as catalyst. Nevertheless, only a few authors have evaluated the use of acid activated carbons as catalyst for this reaction¹. Catalyst deactivation is a main issue in this reaction, so its detailed study can be crucial to improve the properties and stability of the catalyst while operating under severe conditions. A carbon-supported zirconium phosphate catalyst has been synthesized and tested for methanol dehydration reaction in a high temperature range.

Carbon matrix was produced by olive stone waste activated with phosphoric acid (mass acid to olive stone ratio of 2:1) at 800°C for 2 h. Then, after washing with distilled water and sieving between 100-300 μ m, the obtained carbon was impregnated with $ZrO(NO_3)_2$ and thermal treated at 250°C for 2 h. Reaction was performed in a fixed-bed reactor at a space time of 75 g_{cat}·s/mmol_{CH₃OH}, a partial pressure of 0.04 atm of methanol and temperatures between 450-600°C. Deactivated samples were exposed to air at 350°C for 100 min to study the catalyst regeneration.

The catalyst has shown a high selectivity to DME ($\geq 95\%$) and an acceptable conversion at temperatures lower than 400°C without noticeable deactivation. At temperatures higher than 400 °C, deactivation has been detected (Fig. 1) due to coke deposition, whose rate increases with operating temperature. However, a high selectivity to DME was observed (above 65%) even at very long times on stream (tos).

N₂ adsorption results pointed out that deposition of coke took place mainly on the surface of the narrow micropores of the catalyst, blocking much of this narrow porosity at long tos. According to XPS analysis, superficial concentration of phosphorus and zirconium were also diminished with coke deposition, although zirconium was decreased to a larger extend. A kinetic model was developed for the catalyst deactivation during methanol dehydration under different reaction conditions, based on coke deposition.

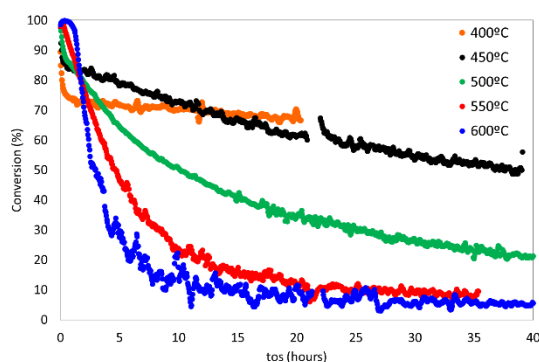


Fig. 1. MeOH conversion as a function of tos of the fresh catalyst (0.04 atm_{MeOH}, 75 g_{cat}·s/mmol_{MeOH})

Table 2. Atomic surface concentration of the fresh catalyst, the catalyst used after reaction at 450°C and 550°C for 15h and used after regeneration in air treatment (75 g_{cat}·s/mmol_{MeOH}, 0.04 atm_{MeOH})

Sample	C _{1s}	O _{1s}	P _{2p}	Zr _{3d}
Fresh catalyst	61.24	30.45	4.42	3.89
450°C 15h	78.38	16.05	2.82	2.53
450°C 15h+OX350	49.83	37.54	8.25	4.38
550°C 15h	86.03	10.46	2.32	1.18
550°C 15h+OX350	57.43	30.93	8.09	3.54

Acknowledgements

We gratefully thank MINECO (Project CTQ2015-68654-R) for financial support. J.T.L. thanks MINECO for FPI grant (BES-2016-079237). M.G.R. thanks Universidad de Málaga for financial support.

References

[1] Valero-Romero, M.J., Calvo-Muñoz, E.M., Ruiz-Rosas, R., Rodríguez-Mirasol, J., Cordero, T. (2019). Industrial and Engineering Chemistry Research, 58, 4042-4053.