



## Simultaneous coking and dealumination of zeolite H-ZSM-5 during the transformation of chloromethane into olefins†

M. Ibáñez,<sup>a</sup> M. Gamero,<sup>a</sup> J. Ruiz-Martínez,<sup>b</sup> B.M. Weckhuysen,<sup>b</sup> A.T. Aguayo,<sup>a</sup> J. Bilbao,<sup>a</sup> P. Castaño<sup>\*a</sup>

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The deactivation pathways of a zeolite H-ZSM-5 catalyst, containing bentonite and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as binder material, have been studied during the transformation of chloromethane into light olefins, which is considered as a possible step to valorize methane from natural gas. The reactions have been carried out in a fixed bed reactor, feeding pure chloromethane at 400, 425 and 450 °C; 1.5 bar and with a space-time of 5.4 (g<sub>catalyst</sub>) h (mol<sub>CH<sub>2</sub></sub>)<sup>-1</sup> during 255 min. The properties of the fresh and spent catalysts have been assessed by several techniques, such as N<sub>2</sub> physisorption, adsorption/desorption of NH<sub>3</sub>, XPS and <sup>29</sup>Si NMR. Additional measurements of the spent catalysts have been performed to study the nature of the deactivating coke species: TG-TPO, SEM, FT-IR and UV-vis spectroscopies. With the results in hand, two deactivation mechanisms were proposed: irreversible dealumination at temperatures higher than 450 °C by HCl and reversible coke fouling, while coke formation results from the condensation of poly-alkylbenzenes, which are also intermediates for olefin production. The coke deposits grow in size with the addition of Cl to the carbonaceous structure.

### 1. Supporting information

Table S1 displays the selectivity of products at 400 °C as an example. This conditions corresponds with chloromethane conversions of 78 and 60 % (Figure 1a), at 15 and 255 min, respectively. Methane selectivity increases with time due to the higher predominance of the thermal cracking of chloromethane. Light olefin selectivity increases with time (Figure 1b), and this increase is due to the higher selectivity of the butenes (heavier fraction) at the price of lower selectivities of ethylene and propylene. The selectivity of C<sub>5+</sub> aliphatics increases over time due to the higher prevalence of oligomerization reactions, while the selectivities of light paraffins and aromatics decrease severely with TOS due to the deactivation of the hydrogen transfer pathways.

Figure 1S shows a FT-IR spectra as an example of one of the deactivated catalyst at 450 °C and 255 min time on stream. It has been represented the two regions of coke: region a) corresponding to aliphatic compounds (-CH<sub>2</sub> or -CH, and -CH<sub>3</sub> groups) and region b) PAH, dienes and chlorinated species.

Figure 2S shows the UV-Vis spectra of fresh and deactivated catalyst, after being used for 0, 5, 45 and 120 min. This figure also shows the Gaussian deconvolution bands over time.

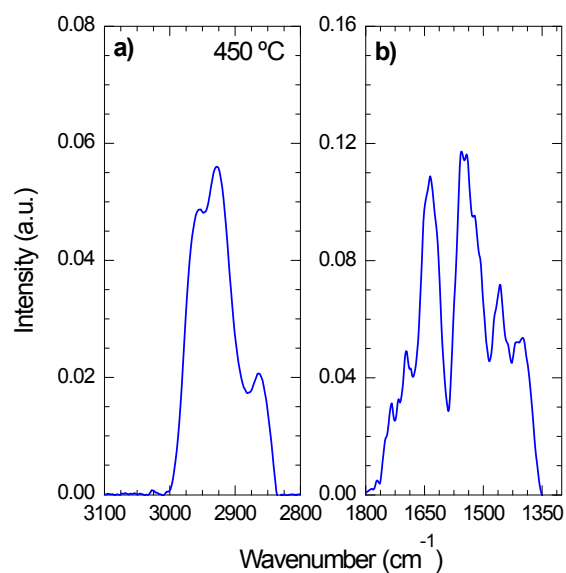
**Table S1.** Product selectivity at 400 °C and 15 and 255 min on stream.

	400 °C	
	15 min	255 min
Methane	0.81	1.41
Light olefins	40.61	43.80
Ethylene	4.16	3.55
Propylene	12.14	9.88
Butene	24.31	28.72
C <sub>5+</sub> aliphatics	32.74	44.70
Light paraffins	20.30	6.60
Aromatics	4.59	3.43

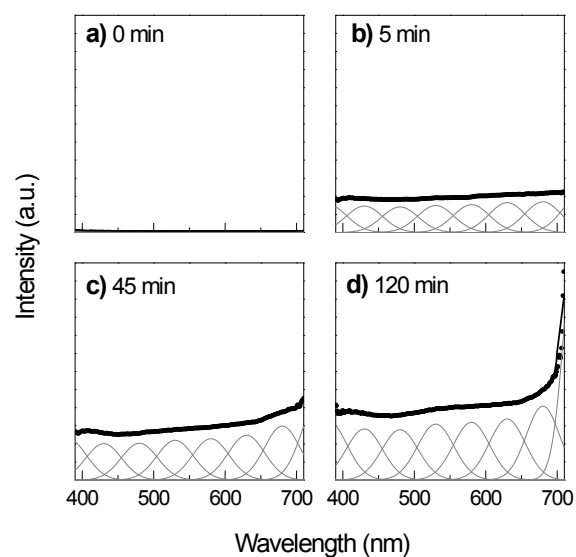
<sup>a</sup> Department of Chemical Engineering, University of the Basque Country (UPV/EHU). P.O. Box: 644, 48080. Bilbao (Spain)

<sup>b</sup> Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Faculty of Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht (the Netherlands)

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**Figure S1.** IR spectra of spent catalyst at 450 °C after 255 min on stream (a) aliphatic region and (b) chlorinated, PAH and dienes region.



**Figure S2.** Deconvolution in different aromatic species of the UV-Vis spectra of used catalyst at 450 °C after 0, 5, 45 and 120 min on stream.