Coke formation in low temperature Methanol-to-DME reaction: the effect of zeolites channel topology

Massimo Migliori,[a,]* **Giuseppe Bonura,**[b] **Luis Gómez-Hortigüela,**[c,] **Alfredo Aloise,**[a] **Enrico Catizzone,** [a] **Francesco Frusteri,**[b] **Girolamo Giordano,** [a]

[a] *University of Calabria - Department of Environmental and Chemical Engineering, Via P. Bucci, Cubo 42a, I–87036 Rende (CS), Italy*

[b] *CNR–ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via S. Lucia sopra Contesse 5, I–98126 Messina, Italy*

[c] *Instituto de Catálisis y Petroleoquímica-CSIC, c/Marie Curie 2, Madrid, Spain*

**Corresponding author: Fax +39 0984 496655, massimo.migliori@unical.it*

Abstract: In this contribution, methanol dehydration to DME over zeolites was investigated, focusing on the role of channel system on activity, selectivity, lifetime and coke deposition. A theoretical approach was also adopted in order to deeply investigate about the location of coke molecules deposited during the reaction (the main cause of deactivation).

Keywords: Zeolites, Dimethyl-ether, coke.

1. Introduction (11-point boldface)

Catalytic dehydration of methanol represents, so far, the most common way to obtain dimethyl ether ether (DME), a chemical compound representing either a promising alternative to both LPG and diesel fuel or a valuable chemical intermediate. Selective methanol dehydration to DME is usually carried over γ-Al_2O_3, whose catalytic activity is strongly inhibited by adsorption of water produced during the reaction. Zeolites might be used as alternative catalysts because of its higher resistance in presence of water[1]. Nevertheless, zeolites usually favor formation of hydrocarbons promoting deposition of coke that causes deactivation of the catalyst. In this concern, it is of paramount importance to obtain new insights about the role of zeolite structure on coke deposition and deactivation during methanol-to-DME reaction[2].

2. Experimental (or Theoretical)

In this work, MOR-, FER- and MFI-type zeolites were home-synthesized and characterized in terms of the main physicochemical properties by using common techniques such as XRD, SEM, N_2 adsorption, NH_3-TPD and FT-IR. Methanol dehydration reaction was carried out over the investigated samples assessing initial methanol conversion, DME selectivity, coke deposition and deactivation. In particular, the coke formation and location was deeply investigated and discussed by using both experimental and theoretical approaches. In this concern, the deposition of coke was monitored via TG/DTA while coke composition was analyzed via GC-MS technique. Moreover, both textural analysis and Monte-Carlo simulations allowed having more insights about the location of carbonaceous molecules formed during the reaction. Spent catalysts were subjected to regeneration and stability of both textural and acid characteristics was assessed after that.

3. Results and discussion

The initial catalytic activity follows the order FER≈MOR>MFI, especially at lower temperature as showed in Figure 1-a). FER and MFI structures offer the best performances in terms of resistance of catalyst towards coke deposition, whilst a fast deactivation was observed on 1–D MOR-type structure (see Figure 1-b)), resulting from a higher carbon deposition as external clusters blocking the access of reactants to internal pores. A kinetic analysis about coke deposition permitted to compare the catalysts revealing that FER shows the lowest tendency to deposit coke, despite its higher acidity.

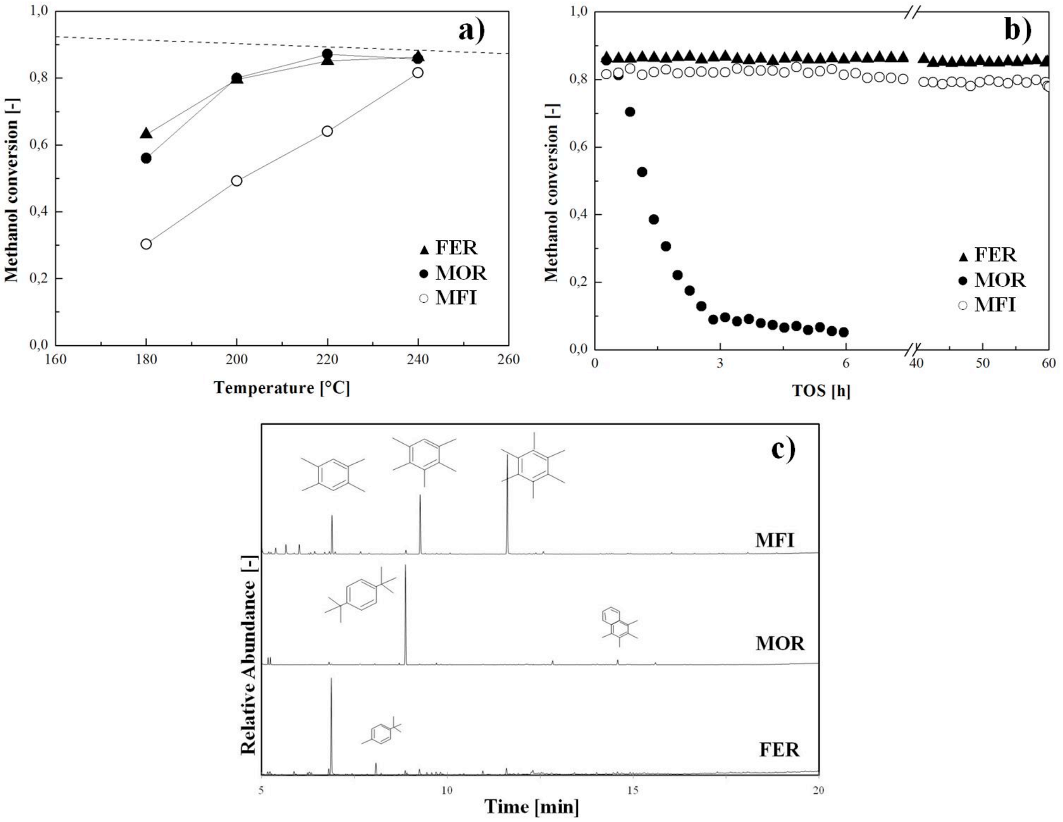

Figure 1. Methanol conversion vs reaction temperature (a), stability tests at 240 °C (b) and GC-MS spectra of deposited coke (c).

Figure 1-c) shows GC-MS spectra of coke deposited during the reaction at 240 °C and extracted for spent catalysts. Coke mainly consists of poly-methyl benzenes (poly-MB) with a grade of substitution depending on channel system. In particular, tetra-MB is preferably formed over FER while MFI is also able to form penta- and hexa-MB. Bulkier molecules (such as 1,4-ditetrtbuthylbenzene and naphthalenes) are deposited over MOR. Monte-Carlo simulations suggest that tetra-MB can be located in FER cages while hexa-MB is too bulky to be accommodating inside the channels of MFI and then it is located on the external surface. Furthermore, 1,4-ditetrtbuthylbenzene is located in 1-D channels of MOR causing pore blocking and fast deactivation while naphthalenes form clusters on external surface. Regeneration process caused an important acidity loss on MOR structure, whilst acid sites concentration was almost preserved on MFI and FER structures after carbon burning treatment, even though a weakening effect of the Lewis acid strength was observed.

4. Conclusions

In this contribution, the effect of channel-system of zeolite catalysts on dimethyl ether production by methanol dehydration reaction was studied. Compared with MOR and MFI, FER-type zeolite showed the best catalytic performances in terms of activity, selectivity, resistance, coke deposition and stability during regeneration. Furthermore, both experimental and theoretical data allowed obtaining new insights about the role of zeolite channel system on coke deposition and location.

References

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