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On the true nature of deactivation mode in methane dehydroaromatization reaction

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Abstract Text: Methane dehydroaromatization (MDA: $6 \text{ CH}_4 \rightleftharpoons \text{C}_6\text{H}_6 + 9 \text{ H}_2$) under non oxidative condition has received great interests over the past three decades. This direct route allows to decarbonize methane into benzene while simultaneously producing sustainable hydrogen, which offers great potential as future energy resource. MDA yet faces two major hurdles: (i) low activity, as the one-pass conversion into benzene is thermodynamically limited (12% at 700 °C) and (ii) rapid catalyst deactivation, as coke formation catalysed by Brønsted sites is kinetically favoured. [1] Numerous methods have been developed in the quest to mitigate the deactivation based on new chemical engineering processes (dihydrogen permeable membrane [2], O₂ pulses, ...), catalyst preparation strategies (hierarchical zeolites [3]: dealumination, desilycation, templating approaches, etc...), and optimization of the operating conditions (co-reactants : CO, CO₂, H₂..., precarburization nature: CH₄, H₂, butane,...). However, low catalytic stability still remains a major issue and is considered the major challenge to make the process viable.

In this communication, we present firstly a kinetic study of the reaction focussing on the typical deactivation period observed during the MDA reaction. From this two different phenomena could be established: (i) poisoning of molybdenum active sites by aromatics and (ii) the acting of hydrogen as scavenger, however H₂ excess would shift the reaction towards the reaction of methane.

Contact time was subsequently adjusted and MDA reaction was carried out at 700 °C with a reference catalyst constituted of 3wt% Mo on a commercial ZSM-5 zeolite (CBV 5020: Si/Al=25). Reaction products were analysed by gas chromatography. After 10 hours of reaction, the spent catalyst was recovered and characterized by thermogravimetric analysis. Surprisingly, rather unexpected results were obtained. Indeed, the carbon amount deposited on the recovered catalyst was higher at low contact time. Monitoring CO₂ intensity signals with the help of mass spectra allowed us to determine two different cokes:

- “soft” coke corresponding to the peak with lower oxidation temperature
- “hard” coke referring to higher oxidation temperature

It appeared that the “soft” coke develops independently of the contact time while the “hard” is inversely related to it (Figure. 1).

This observations arouse our curiosity on the real nature of deactivation in the MDA process. Further advanced characterizations and products distribution analysis revealed active sites inhibition by aromatics, which is attenuated in presence of hydrogen.

To support our assumption theoretical modelling was performed. Adsorption energy of benzene and naphthalene on molybdenum carbide was calculated and higher adsorption energy was revealed for aromatics with increasing number of cycles. . In the presence of hydrogen the adsorption energy is two times weaker demonstrating the scavenger effect of hydrogen (Figure2).

In conclusion we elucidated molybdenum active sites poisoning, which allows to reason why the classical strategies based on improving diffusion properties of ZSM-5 do not yield improved catalyst stability. Indeed, improving deactivation issues in MDA process should rather be focused on active site processing.

Image 1:

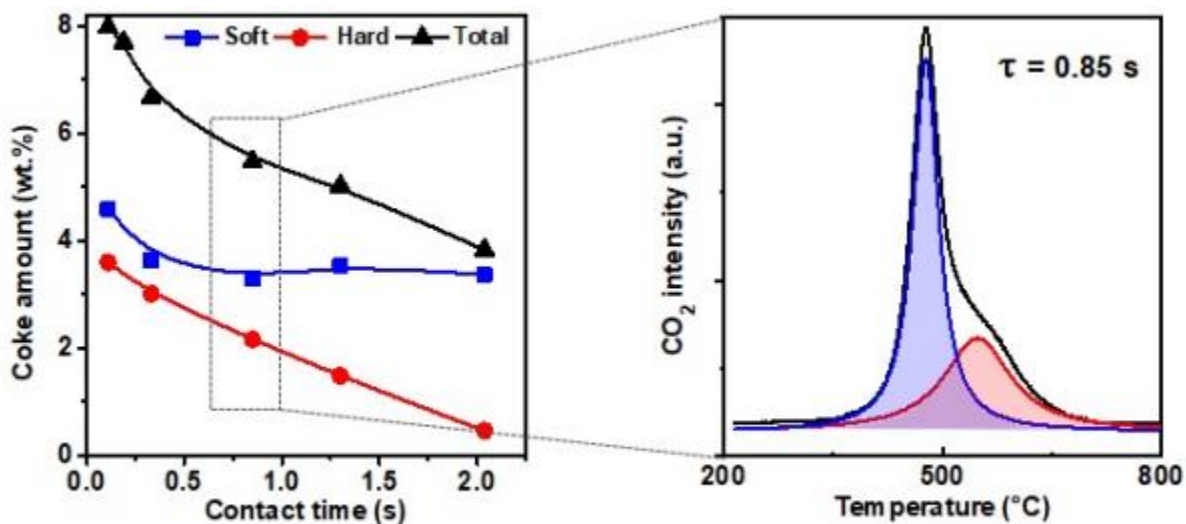
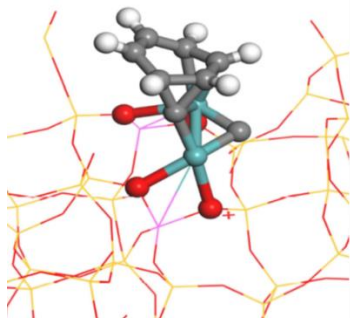


Figure.1: Coke content as function of contact time and TPO-CO₂ profile for one contact time : 0.85 s

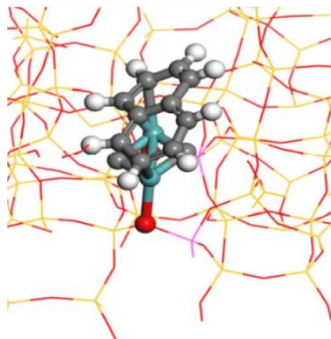
Image 2:

Benzene adsorption



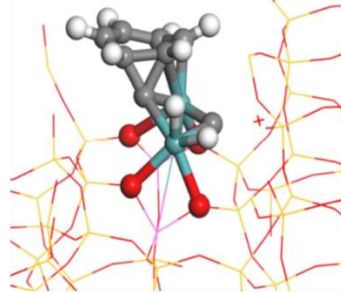
$$E_{Ads}^{C_6H_6} = 1.32 \text{ eV}$$

Naphthalene adsorption



$$E_{Ads}^{C_{10}H_8} = 2.02 \text{ eV}$$

CO-hydrogen/benzene adsorption



$$E_{Ads}^{C_6H_6} = 0.68 \text{ eV}$$

References:

1. Ma, S., Guo, X., Zhao, L., Susannah, S., and Bao, X. *Journal of Energy Chemistry* 22, 1 (2013).
2. Natesalawat, S., Means, N.C., and Morreale, B.D. *Catal. Sci. Technol* 5, 5023 (2015).
3. Van Eck, E.R.H., and Hensen, E.J.M., *Micropor. Mesopor. Mat* 203, 259 (2015).

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