On the true nature of deactivation mode in methane dehydroaromatization reaction

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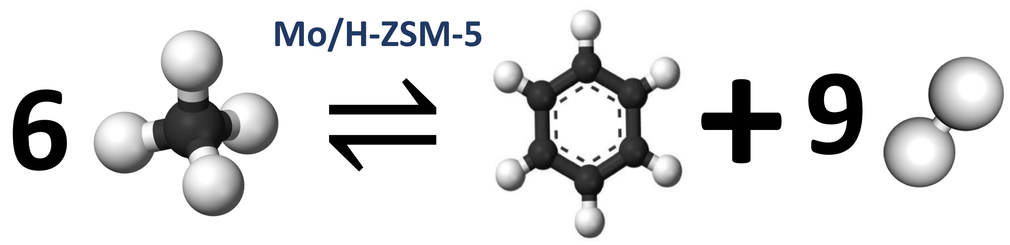
Introduction



Methane dehydroaromatization under non oxidative conditions over bimetallic catalyst : Mo/H-ZSM-5

Reaction properties

Products valorization

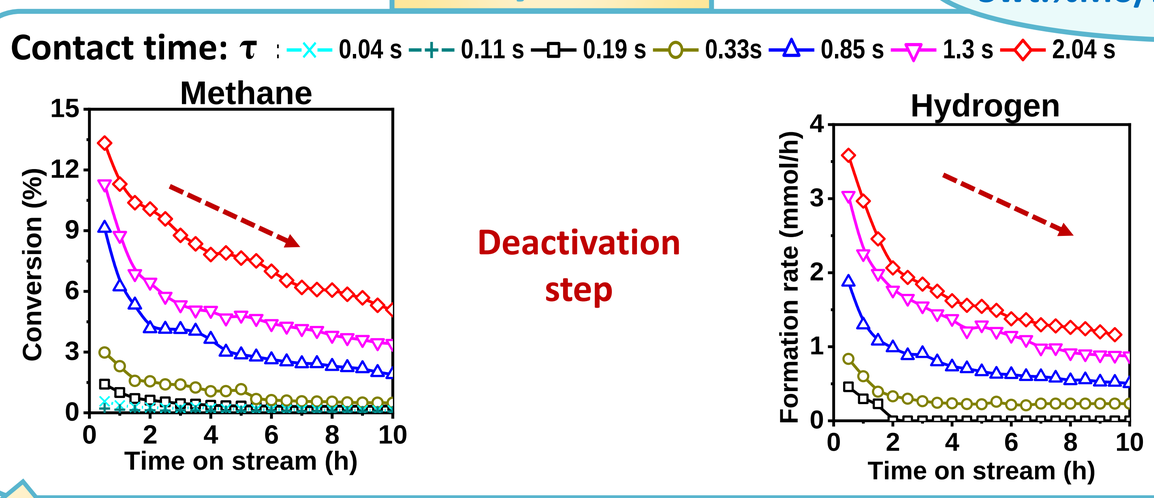
- Highly selective towards benzene ~70%
- Sustainable hydrogen production without any CO_2 emission

2 major hurdles

- Thermodynamic equilibrium ~12.5% at 700 °C
- Fast deactivation ~ 10 hours

Catalytic tests

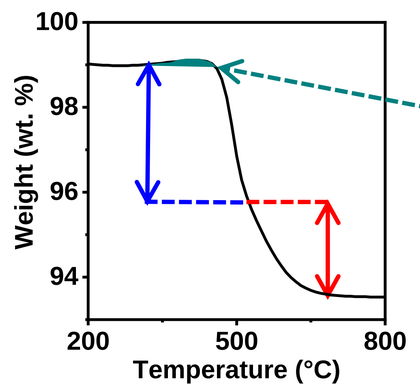
Fresh catalyst 3wt.%Mo/H-ZSM-5 (Si/Al=25)



Deactivation step

Spent catalysts characterisation

Thermogravimetric analysis

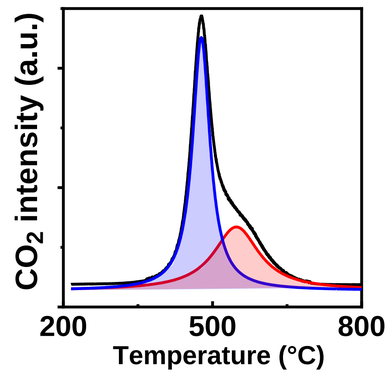


1 weight gain

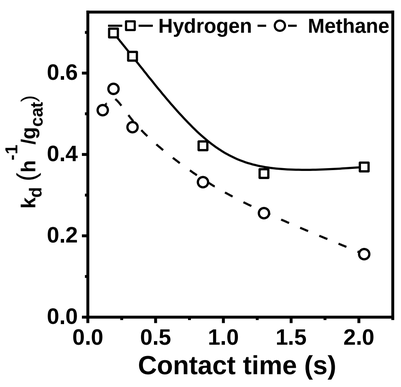
Carbide oxidation

2 weight losses

"soft" coke **"hard" coke**

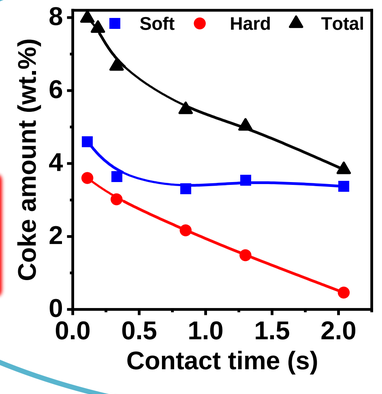


K_d calculated considering a pseudokinetic order of 1



Unconventionnal behavior

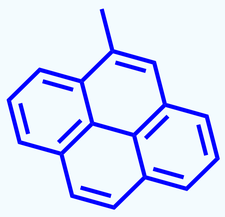
Contact time increases ➔ Lower coke amount, Better catalyst stability



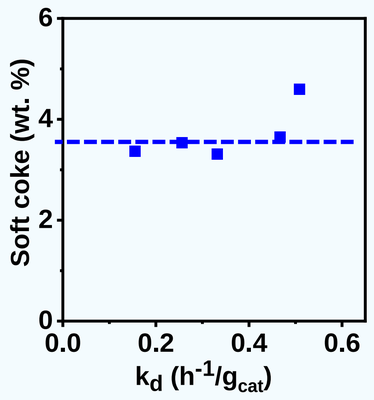
- Total coke content decreases with τ
- Coke amount independent of τ
- Coke amount inversely related with τ

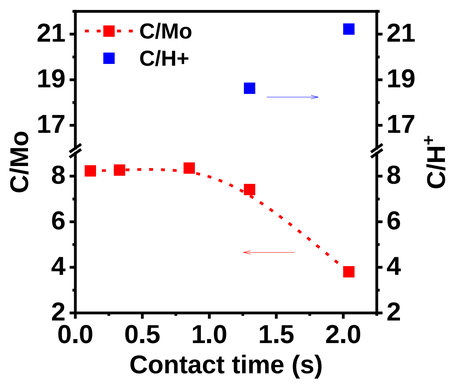
"soft" coke = non toxic coke

- Non toxic type of coke



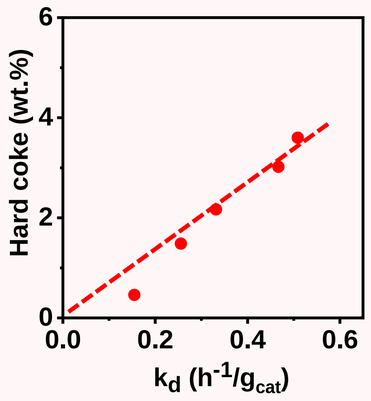
Spectator





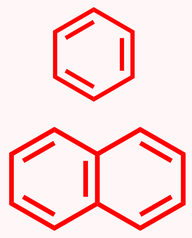
Values estimated from pyridine IR acidity mesurement

"hard" coke = toxic coke

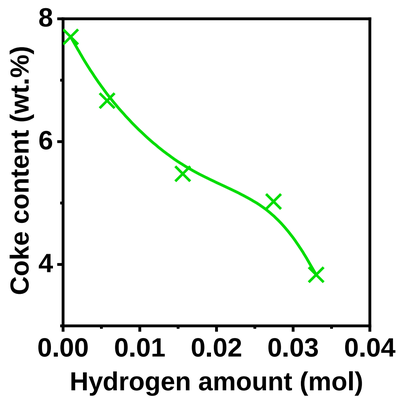


- Toxic type of coke ➔ inhibit the active species

Actor



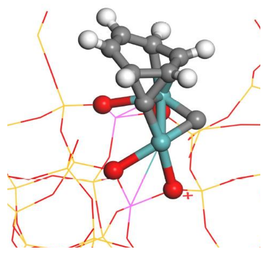
Hydrogen production



- The higher the H_2 production, the lower the total coke amount

"auto-immune" effect owed to the presence of hydrogene

Benzene adsorption

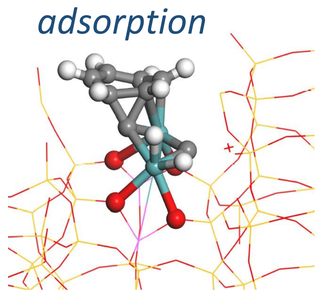


$E_{Ads}^{C_6H_6} = 1.32\ Ev$

Naphthalene adsorption

$E_{Ads}^{C_8H_{10}} = 2.02\ Ev$

CO-hydrogen/benzene adsorption



$E_{Ads}^{C_6H_6} = 0.68\ Ev$

Presence of hydrogen reduces strength of the benzene adsorption on active sites

Conclusion

- **Contact time was subsequently adjusted and methane dehydroaromatization was carried out. The catalyst deactivates in about 10 hours**
- **Two different type of coke were identified thanks to TGA/TDA analysis: « soft » and « hard » coke**
- **Soft coke is considered as a non toxic type of coke whereas « hard » coke inhibits the active species**
- **Autogenous hydrogen prevents the formation of "hard" coke, which is the cause of deactivation**

References

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