Anisole hydrodeoxygenation over supported CoMo catalysts: effect of Co/Mo ratio and support on catalyst stability and activity

Chanakya Ranga,[1] Rune Lødeng,[2] Vaios I. Alexiadis,[1] and Joris Thybaut[1,]*

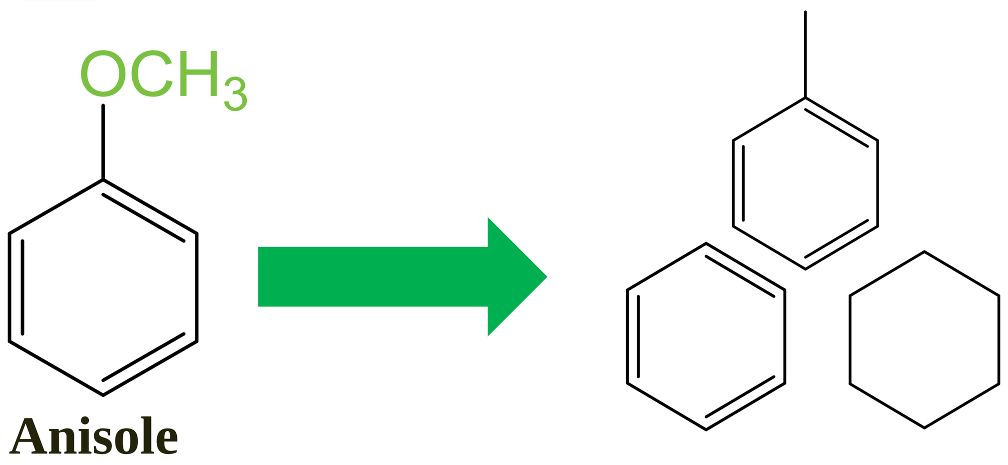
[1]Laboratory for Chemical Technology
Technologiepark 914, 9052 Ghent, Belgium
https://www.lct.ugent.be

[2]SINTEF Materials and Chemistry
Kinetics and Catalysis Research Team, N-7465 Trondheim, Norway
https://www.sintef.no/en/

Introduction

Rationale:

- ✓ Anisole is one of the most common chemical structure found in lignocellulosic biomass and challenging to perform deep HDO
- ✓ Co addition in systematic way to identify and enhance the stable & active phases of MoO_3 catalysts for oxygenate HDO

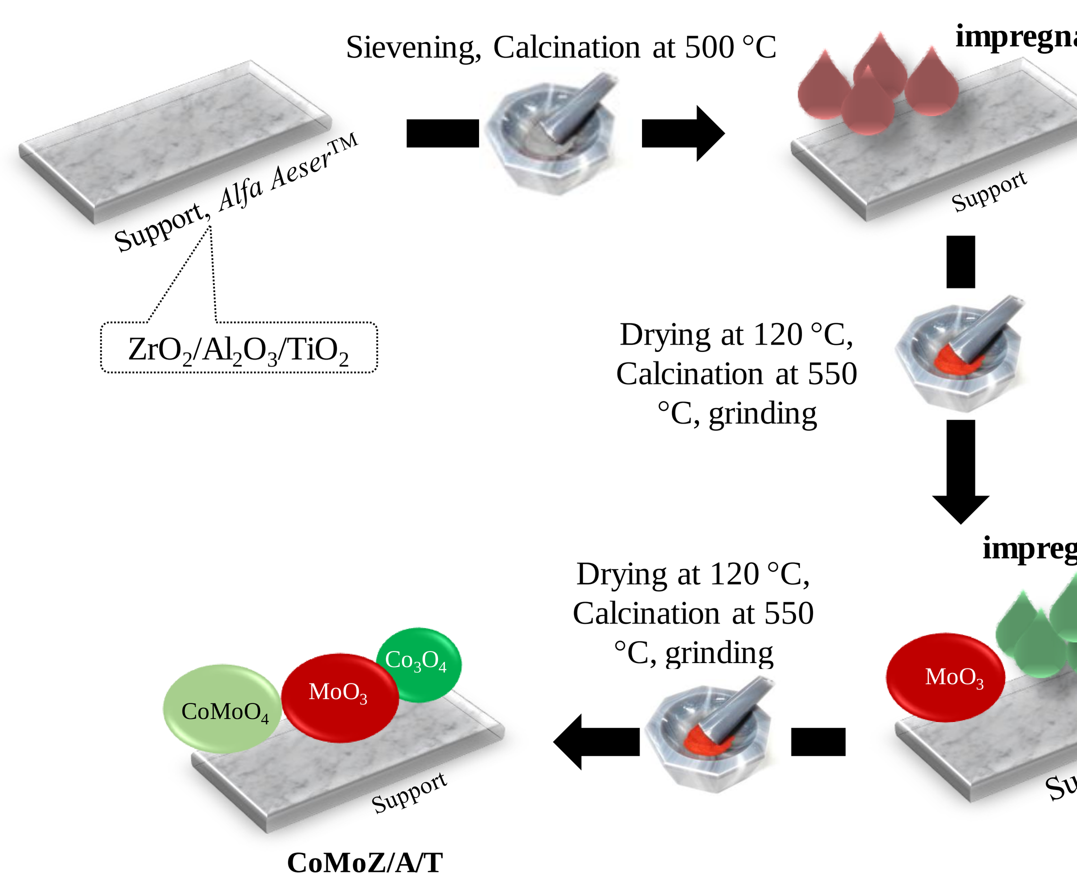


Anisole

Aim: Stable catalyst with high HDO selectivity

Catalyst Preparation

Sequential Incepient Wet Impregnation of Mo and Co

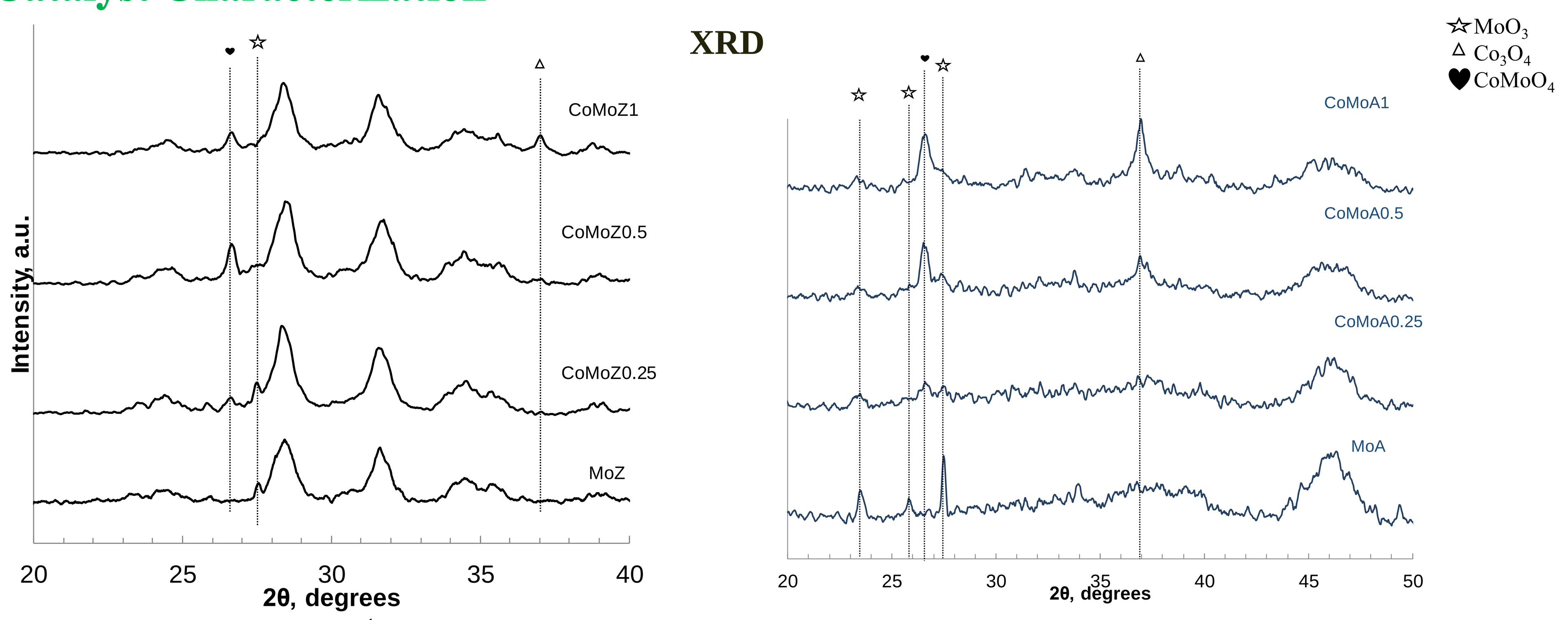


Co/Mo	ZrO_2	Al_2O_3	TiO_2
0	MoZ	MoA	-
0.25	CoMoZ0.25	CoMoA0.25	-
0.5	CoMoZ0.5	CoMoA0.5	CoMoT0.5
1	CoMoZ1	CoMoA1	-

CoMo catalysts in non-sulphided form

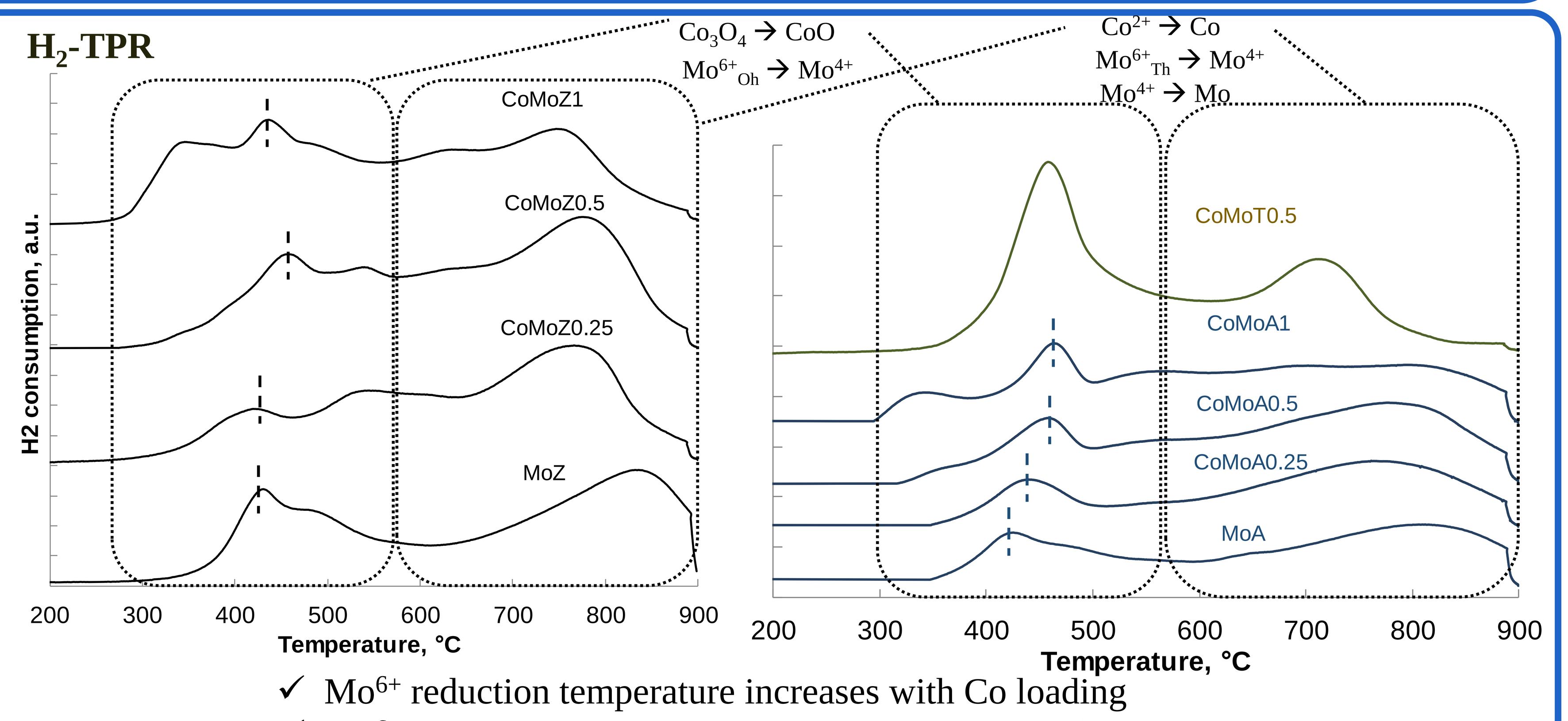
Catalyst Characterization

XRD



- ✓ MoO_3 crystallites disappear as Co loading increases
- ✓ Mixed oxide ($CoMoO_4$) crystallizes at higher Co loadings.

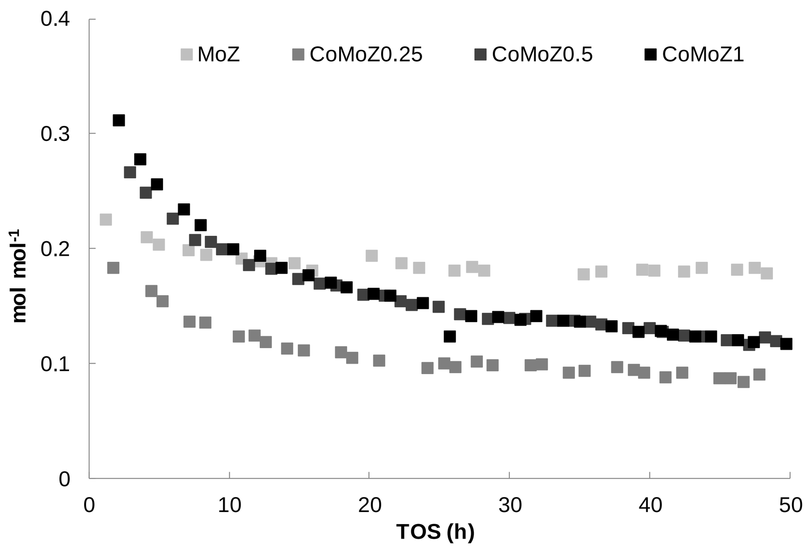
H_2-TPR



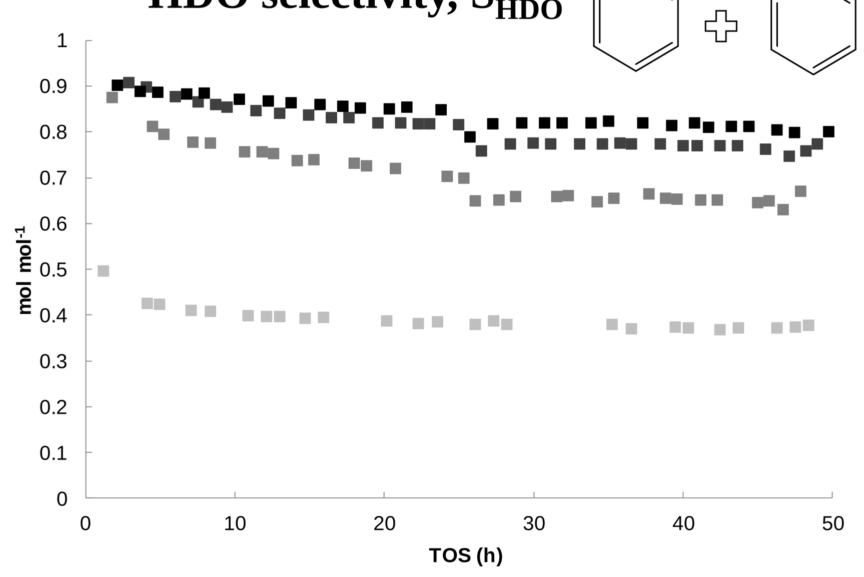
- ✓ Mo^{6+} reduction temperature increases with Co loading
- ✓ Mo^{6+} exists in MoO_3, $CoMoO_4$, and also in mixed form with support

Performance testing and Discussion

Anisole conversion



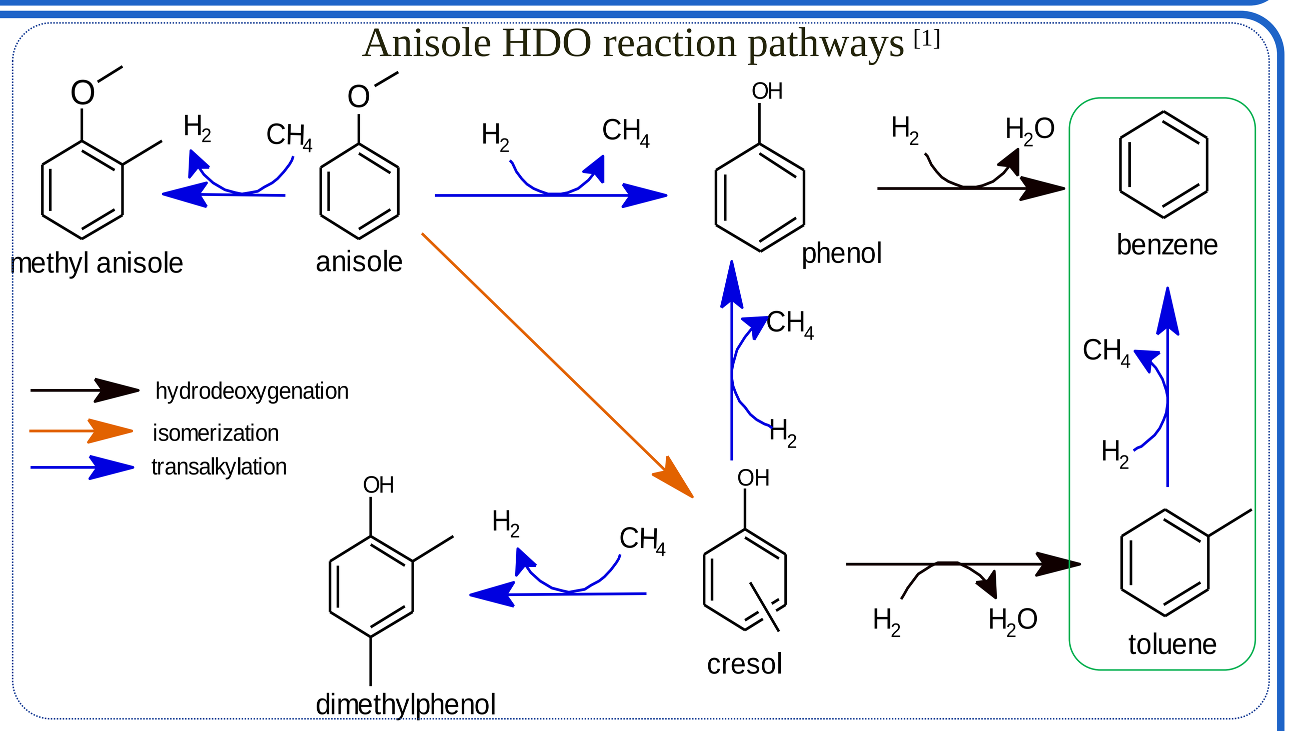
HDO selectivity, S_{HDO}



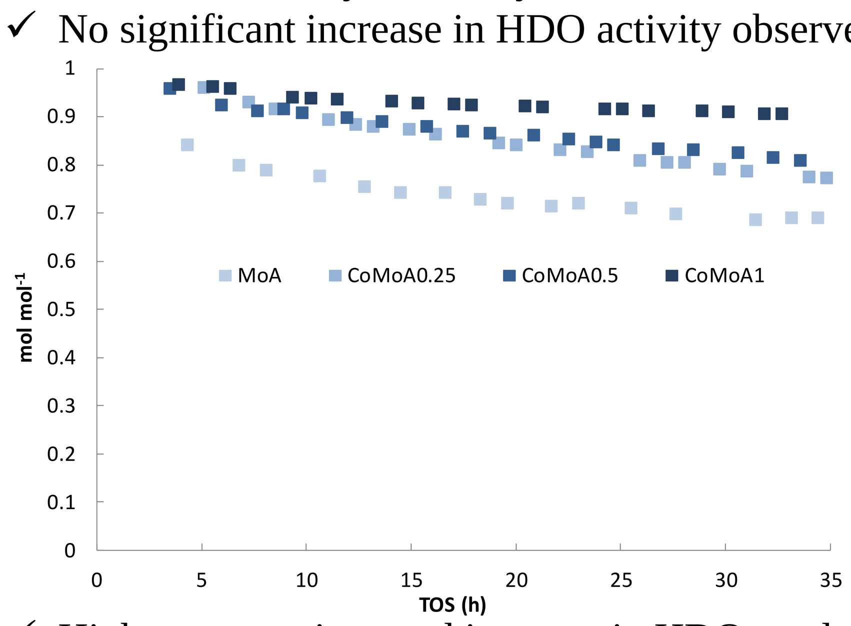
Operating conditions	
Temperature (°C)	340
Pressure (MPa)	0.5
Space time ($kg_{cat}.s/mol_{anisole}$)	20-230
H_2/anisole (mol.mol^{-1})	50

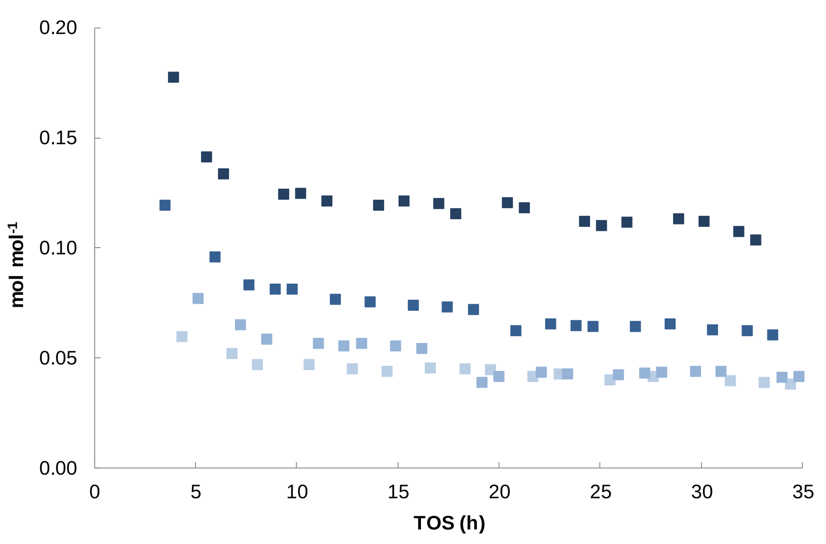
$$S_{HDO} = \frac{\sum F^{out}_{O\ free\ product}}{F^{in}_{anisole} - F^{out}_{anisole}}$$

Anisole HDO reaction pathways [1]



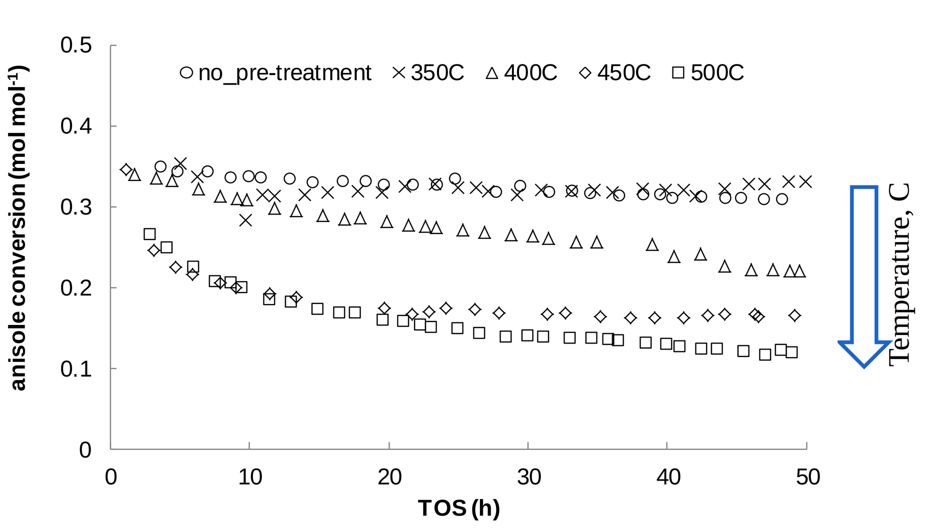
- ✓ Decrease in catalyst stability while an increase in HDO product selectivity with addition of Co
- ✓ No significant increase in HDO activity observed at Co/Mo >0.5

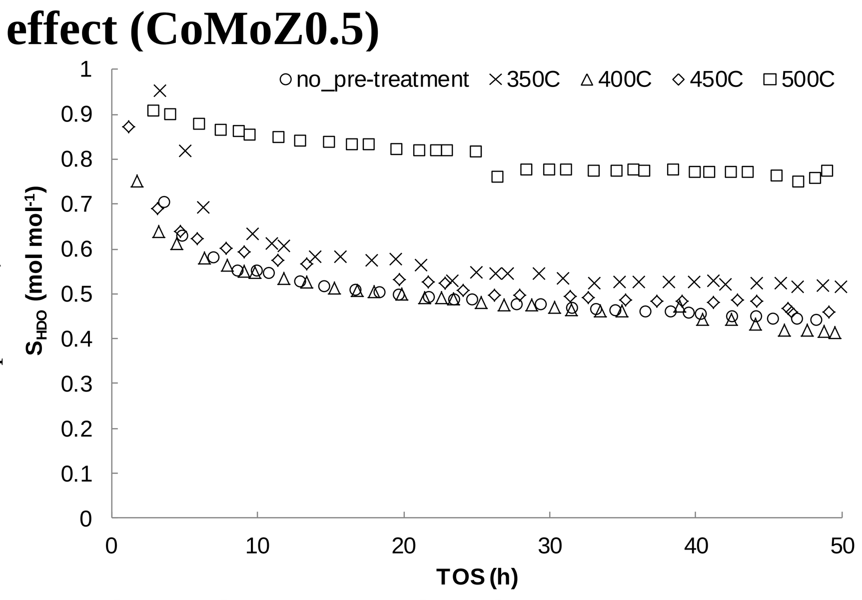




- ✓ Higher conversions and increase in HDO product selectivity with addition of Co
- ✓ Initial rapid decrease in HDO product selectivity with TOS

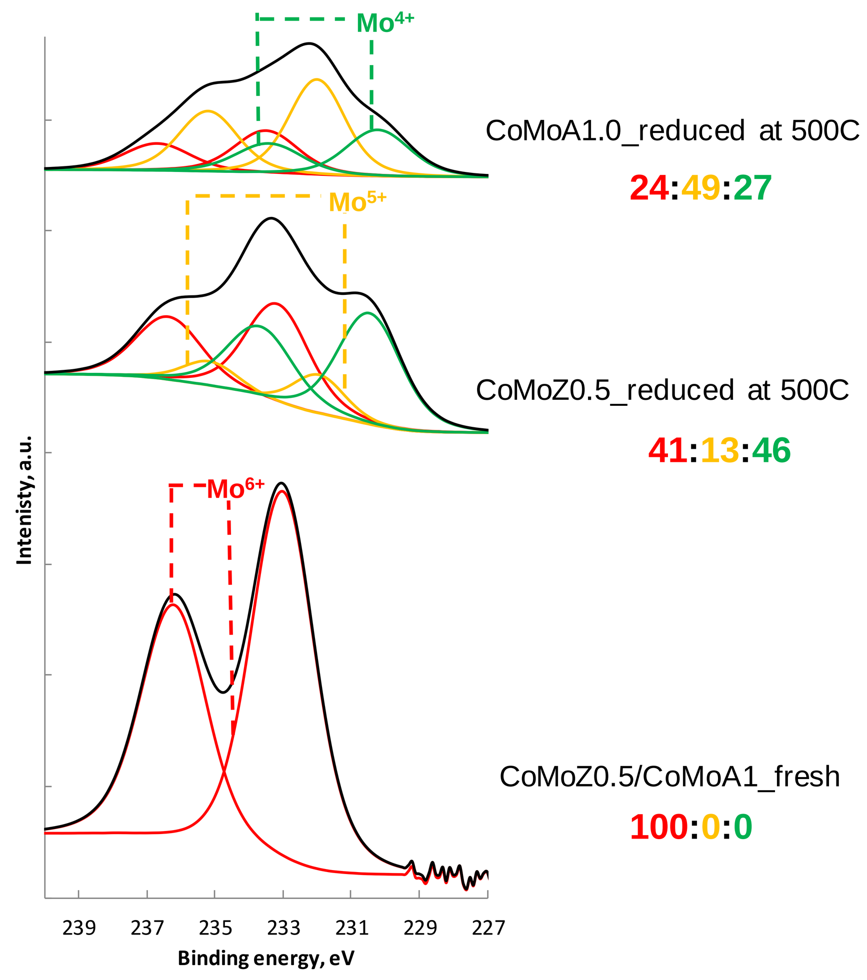
Pre-treatment effect (CoMoZ0.5)





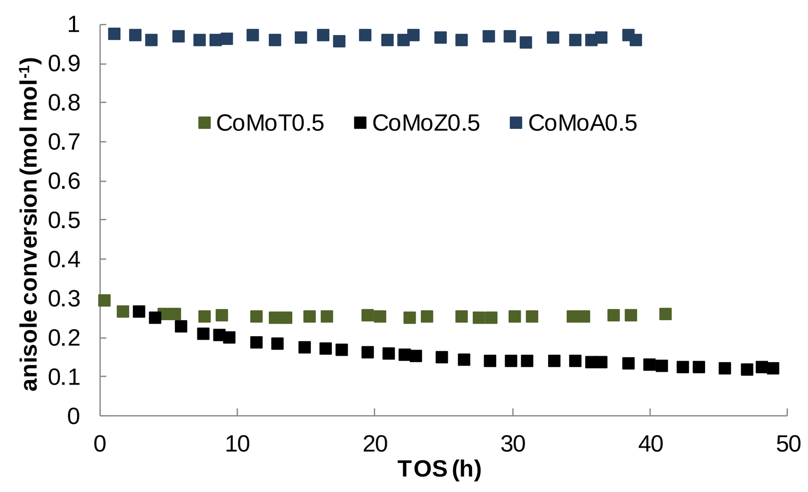
- ✓ Increase in catalyst stability while a decrease in HDO product selectivity with reduction at < 350 °C
- ✓ Reduction at higher temperatures (500 °C) → higher HDO activity, low overall conversion

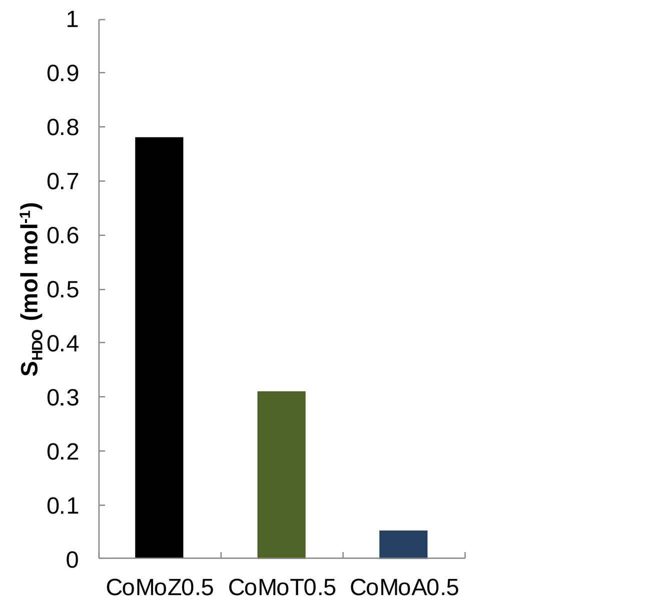
Catalyst surface composition



- ✓ Catalyst stability, Overall conversion enhanced with high Mo^{5+} quantity
- ✓ HDO selectivity enhanced with high Mo^{4+} quantity

Effect of support





- ✓ Initial anisole conversion: $Al_2O_3 > TiO_2 \approx ZrO_2$
- ✓ Total HDO selectivity: $ZrO_2 > TiO_2 > Al_2O_3$

Conclusions

- ✓ Co addition: i) Increase in the HDO activity for Mo oxide catalysts, ii) Decrease in catalyst stability and overall conversions compared to MoZ for CoMoZ catalysts, iii) Increase in catalyst stability and overall conversions compared to MoA for CoMoA catalysts
- ✓ Higher reduction temperatures favor higher HDO activity for CoMoZ catalysts
- ✓ ↑Mo^{5+} → stable catalyst and high anisole conversions, ↑Mo^{4+} → high HDO activity

Acknowledgements

This work is supported by the Innovative Catalyst Design for large-scale sustainable processes (i-CaD) project, which is an ERC consolidator grant, by the European Commission in the 7th Framework Programme (GA no 615456). It also fits in the framework of the FAST industrialization by Catalyst Research and Development (FASTCARD) project, which is a large scale collaborative project supported by European Commission in the 7th Framework Programme (GA no 604277).

[1] C.Ranga et al., Chemical Engineering Journal, 335 (2018) 120 – 132.

E-mail: chanakya.ranga@ugent.be

CatBior, Lyon, 11-15/12/2017

GHENT UNIVERSITY · LCT DRIVING CHEMICAL TECHNOLOGY · SINTEF · erc European Research Council · SEVENTH FRAMEWORK PROGRAMME · ERIC European Research Institute of Catalysis · FAST CARD