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Summer School Catalysis: from understanding to applications
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Evaluation of the performance of catalytic oxidation of VOCs by a mixed oxide at pilot scale

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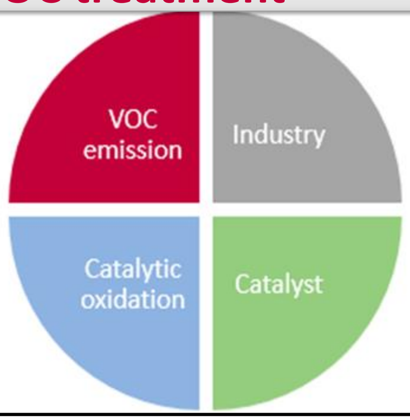
VOC treatment

- Ozone layer depletion
- Ground level smog

- Low operation temperature



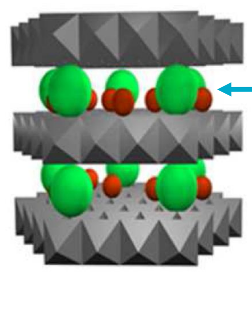
- Main source (coating processes)

- Noble metal
- Mixed oxide

Objective: Test new materials in a pilot scale

Hydrotalcite precursor (Layered Double Hydroxide) **Co-precipitation method**

Metal hydroxide



Anions
Water
molecules

Materials

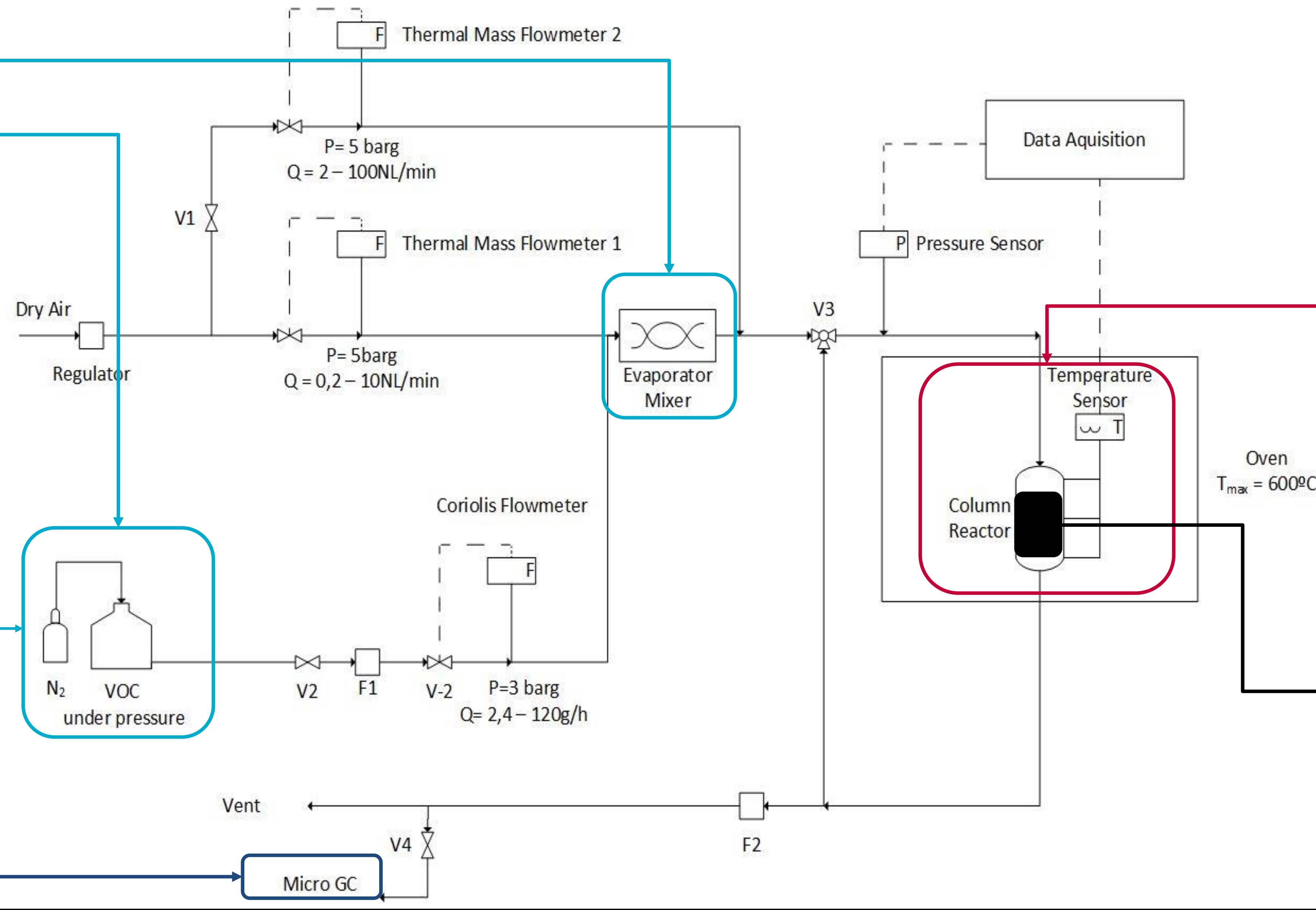
Catalyst	Co-Al-Ce [1]
Pellets	
Diameter (mm)	3
Lenght (mm)	5
S_{BET} (m^2/g)	92
V_{pores} (cm^3/g)	0.358

Experimental Methods

- The VOC solvent is mixed with dry air in the Evaporation Controller Mixer (CEM) at 200°C.
- Air flowrates are controlled by two thermal mass flowmeters and the VOC flowrate is controlled by a mass Coriolis flowmeter (all provided by Bronkhorst).

VOCs tested: n-Butanol/Toluene

The VOC concentration is measured by a gas phase micro chromatograph - 490 micro GC (Varian). It is equipped with two columns:
- CP-Wax 52CB
- CO/CO_2- CP-COX



- Column reactor (internal diameter of 5 cm and height between 20 and 50 cm).
- Temperature is measured by three thermocouples placed at different heights inside the reactor, (top, middle and bottom)

Catalyst	Co-Al-Ce [1]
Volume of Catalyst (cm^3)	569
Bed Height (cm)	29
Mass of catalyst (g)	400.7

Experimental conditions
Flowrate: 22-44 NL/min
VOC concentration: 1000, 1500, 2000 ppmv

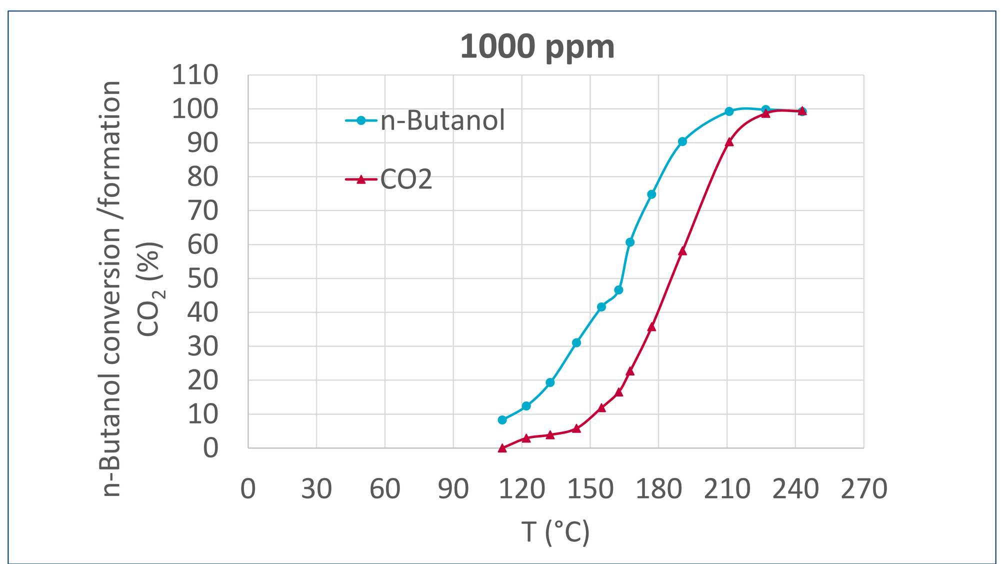
Results and Discussion

Light off curves – Single Component

$$X_{VOC} = \frac{C_{in,VOC} - C_{out,VOC}}{C_{in,VOC}} * 100$$

$$X_{CO_2} = \frac{C_{out,CO_2}}{n.C_{in,VOC}} * 100$$

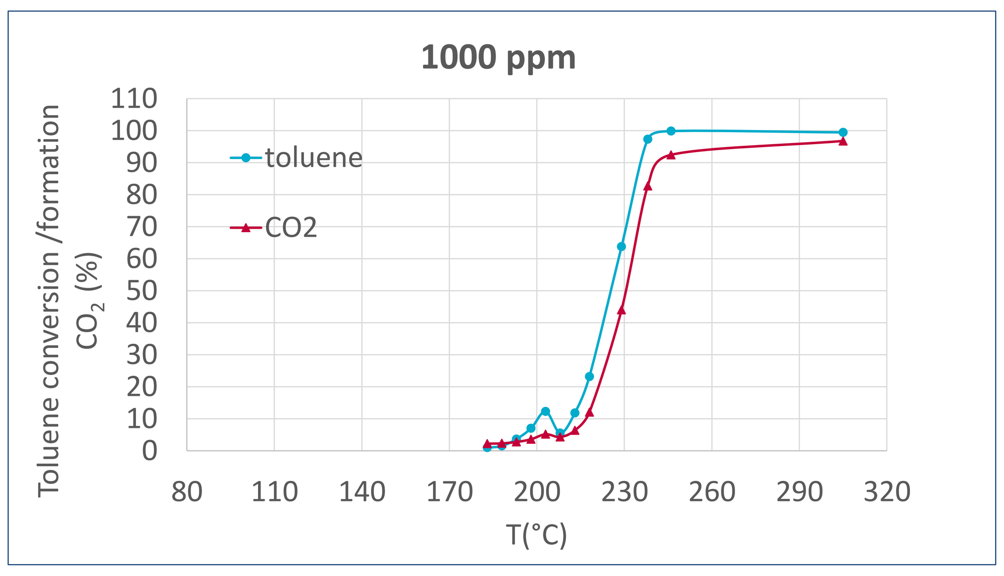
n-Butanol



n-Butanol's oxidation takes place at low temperature (230°C). However there is some by-product formation, showed by the gap between the two curves.

Toluene's oxidation requires higher temperatures, but the catalyst provides a good selectivity.

Toluene



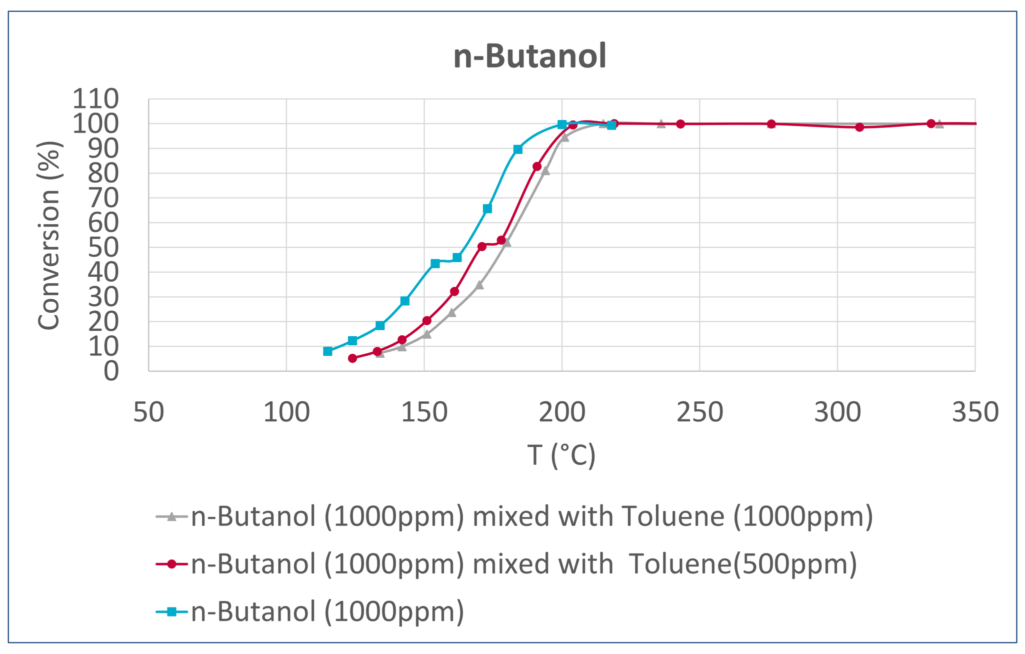
Air flowrate – 22 NL/min			
n-butanol	1000 ppm	1500 ppm	2000 ppm
conversion	ΔT	ΔT	ΔT
10%	34	25	30
50%	25	26	19
90%	16	23	10

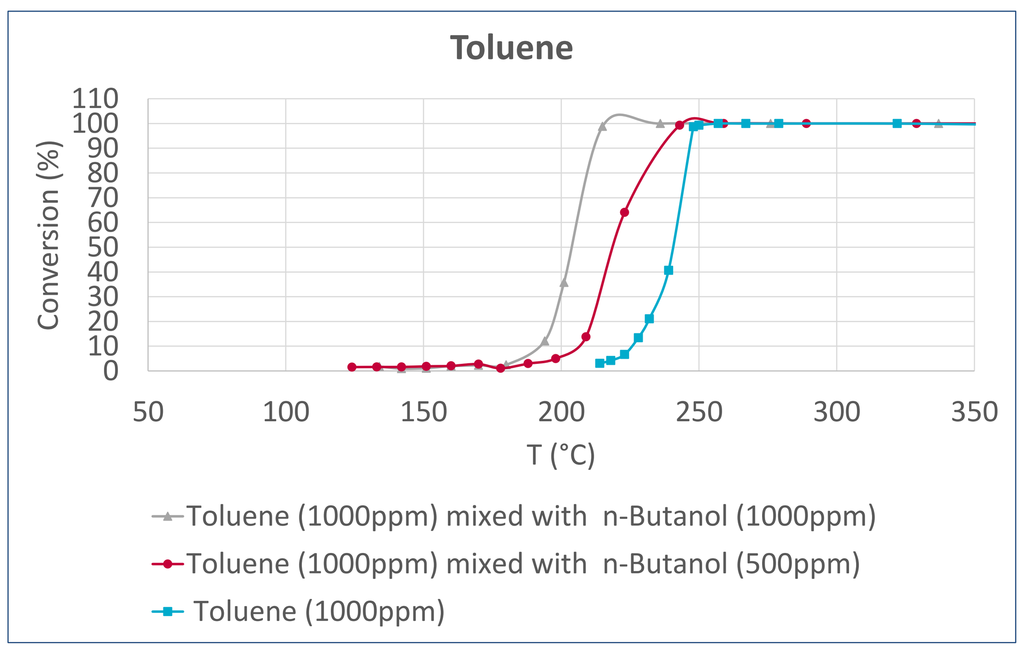
ΔT between the curves of VOC conversions and CO_2 formation: The smaller the value the better the catalyst selectivity towards the VOC

Air flowrate – 22 NL/min			
Toluene	1000 ppm	1500 ppm	2000 ppm
conversion	ΔT	ΔT	ΔT
10%	2	3	4
50%	5	3	1
90%	5	10	6

Light off curves – Mixtures

The presence of Toluene slightly increases the temperature required for the oxidation of n-Butanol.





When mixed with n-Butanol, Toluene's light off curve is displaced towards lower temperatures.

Air flowrate – 44 NL/min					
n-Butanol	Mixture 1	Mixture 3	n-Butanol (1000 ppm)	T_{S-M1}	T_{S-M3}
$T_{10\%}$	142	138	120	22	18
$T_{50\%}$	180	171	165	15	6
$T_{90\%}$	198	195	185	13	10

1000 ppm of Toluene and 1000 ppm of n-Butanol (Mixture 1)
1000 ppm of Toluene and 500 ppm of n-Butanol (Mixture 2)
500 ppm of Toluene and 1000 ppm of n-Butanol (Mixture 3)

Air flowrate – 44 NL/min					
Toluene	Mixture 1	Mixture 2	Toluene (1000 ppm)	T_{S-M1}	T_{S-M2}
$T_{10\%}$	191	207	225	-34	-18
$T_{50\%}$	203	219	240	-37	-21
$T_{90\%}$	212	236	246	-34	-10

Conclusion

A promising mixed oxide catalyst previously tested at micro-pilot scale was therefore tested for the oxidation of n-Butanol and Toluene, for single component and mixture experiments at a pilot scale unit in several conditions. These could then be extrapolated for industrial scale conditions. This catalyst enables complete oxidation of n-Butanol at low temperatures (230°C), while also providing a very good selectivity for the oxidation of Toluene (the average difference between the curves of conversion of Toluene and CO_2 formation is below 10°C). Furthermore, it was found that, for this catalyst, the presence of n-Butanol has a promoting effect on the oxidation of Toluene.

Acknowledgements

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[1] J. Brunet *et al.*, "Co-Al-Ce Mixed Oxide Materials Prepared by Hydrotalcite Way for VOCs Total Oxidation in Micro- and Semi-Pilot Scale," *Mater. Today Proc.*, vol. 3, no. 2, pp. 188–193, 2016.