VOLVO Group Trucks Technology — RENAULT TRUCKS — IRCELYON — GRE — UPMC SORBONNE UNIVERSITÉS — IC2MP — CNRS

Biofuel impact on Diesel engine after-treatment: deactivation mechanisms and soot reactivity

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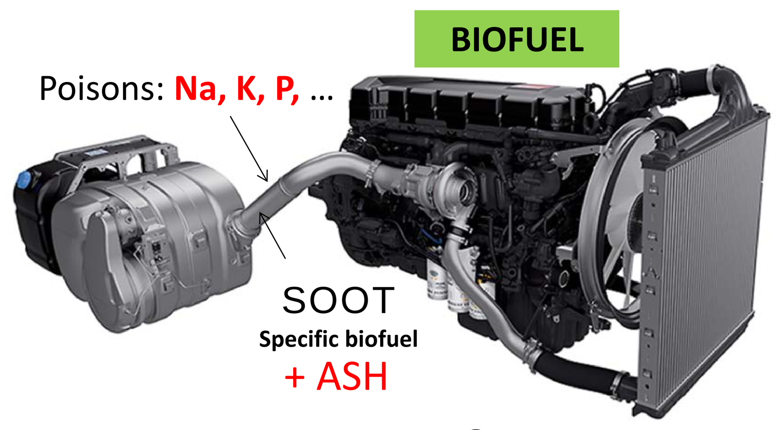
BACKGROUND: The new emission standards for diesel engines empower the need of complex and high efficient after-treatment systems, the durability being a crucial aspect. When biofuel is used, the after-treatment catalytic system is exposed to large amounts of poisons, the particles composition being as well impacted. The comprehension of the involved deactivation mechanisms as well as soot reactivity is a complex and multidisciplinary challenge.

METHODOLOGY: One focus was the study of the deactivation of the DOC and SCR catalysts through poisoning. Limited information is available about the physics and chemistry of the particles formed when biodiesel is used. The second focus was therefore devoted to the impact on soot reactivity in mechanistic and kinetic terms using model and real soot.

HOW AFTER-TREATMENT SYSTEM IS AGED USING BIOFUEL ?



HOW SOOT LOADING & REGENERATION ARE IMPACTED BY USING BIOFUEL ?

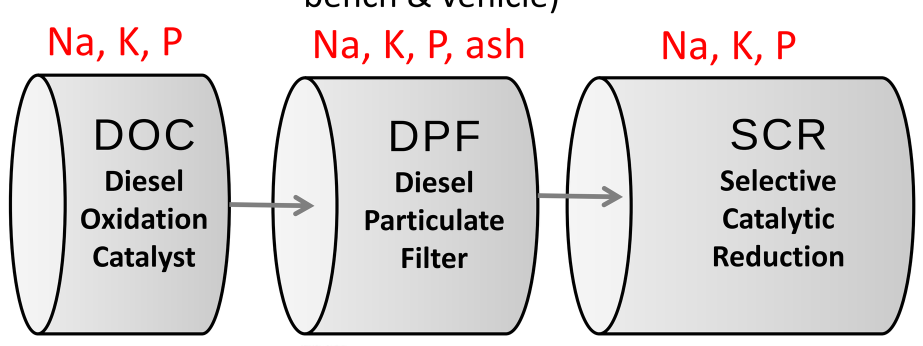
APPIBIO PROJECT

Model poisons: Na, K, P

VOLVO Group Trucks Technology

- Exhaust specification
- Catalyst benchmark
- Technical requirements
- Soot production
- Catalyst poisoning

Model SOOT
Real SOOT (engine bench & vehicle)



Global kinetic model to predict the after-treatment ageing

Reactivity – Durability/ Characterization – Mechanisms – Ageing – Regeneration

DOC Diesel Oxidation Catalyst

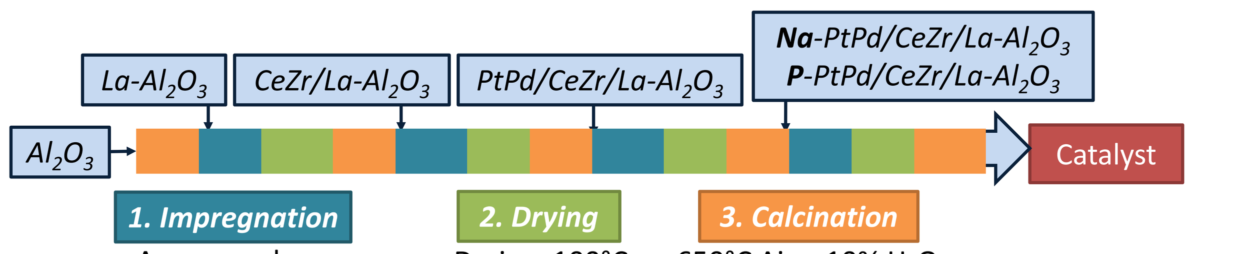
IRCELYON

The **DOC was exposed to Na and P impurities**, which are specific of the use of biofuel, being studied their impact on the catalytic performance.

BET specific surface area decreased and the total pore volume increased after addition of Na, due to the second hydrothermal treatment. In presence of P, partial blocking of the smallest mesopores decreasing pore volume was detected. TEM images showed a homogenous distribution of Na on the alumina bulk, which could modify the Al_2O_3 acid sites. On the other hand, bigger Pd-Pt particles were formed and a layer of phosphorus coated on the alumina surface was observed in the case of P-poisoned catalyst.

Catalytic results have shown that **Na have a negative impact on CO oxidation**, whereas **an improvement can be observed in presence of P**. In addition, **P poisoned catalyst enhance C_3H_6 conversion**, while **Na impurities have the contrary effect**. All elements have shown a **negative effect on NO oxidation**.

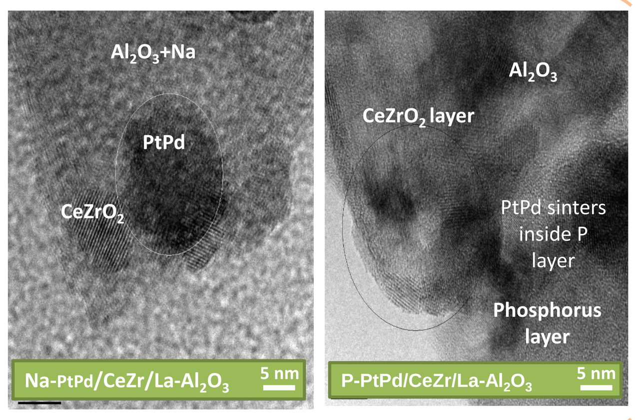
Synthesis



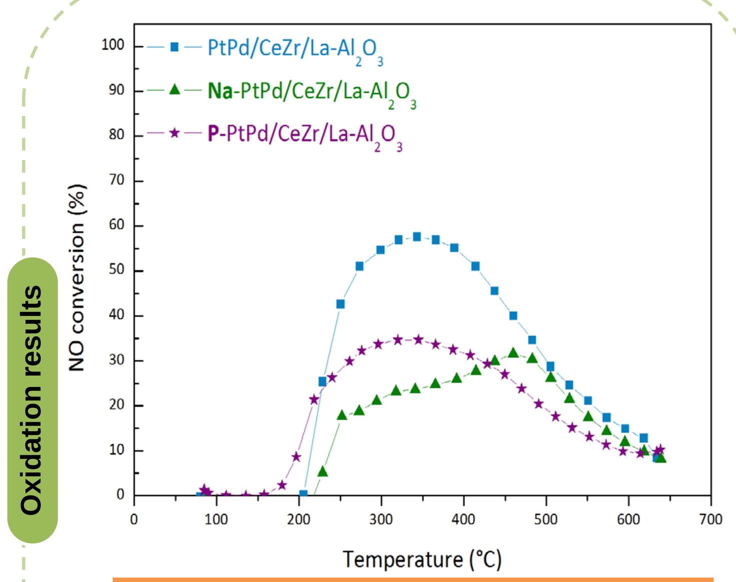
1. Impregnation — Aqueous phase, Vacuum evaporation, 90 °C, 2h
2. Drying — Drying, 100°C, 1 night
3. Calcination — 650°C Air + 10% H_2O (before and after impurities addition)

Characterization

Catalyst	S_{BET} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)	D_P (nm)
1.3% PtPd	60	0.23	14
1.3% PtPd (**x2-650ºC**)	54	0.40	31
1.6% Na – 1.3% PtPd	50	0.41	28
5.6% P – 1.1% PtPd	33	0.26	32



Oxidation results



Catalyst	r_{CO}[1]	r_{C3H6}[1]	r_{NO}[1]	NO_2/NO_X
1.3% PtPd	2.54	4.32	6.02	0.298
1.6% Na – 1.3% PtPd	1.32	0.29	5.05	0.244
5.6% P – 1.1% PtPd	5.95	7.61	4.27	0.259

[1]Reaction rate (($mol/s \cdot g_{PGM}$)$\cdot 10^5$) at 180, 210 and 250ºC for CO, C_3H_6 and NO respectively.

DPF Diesel Particulate Filter

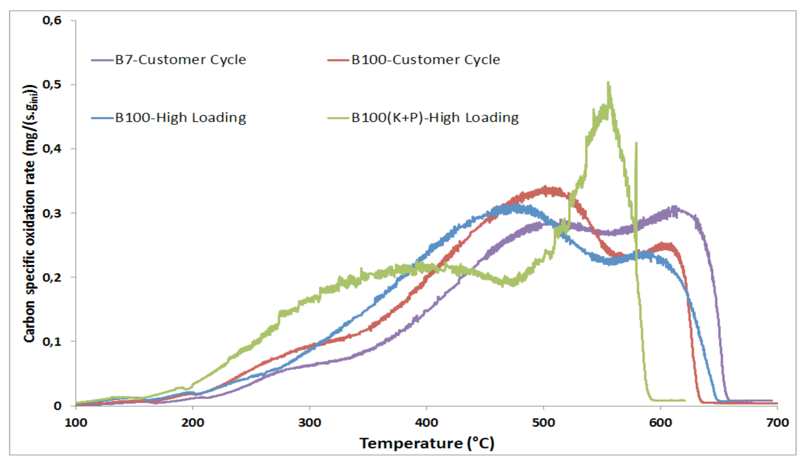
GRE — UPMC SORBONNE UNIVERSITÉS

The **real soot samples** were collected from filters operated on a **medium-duty truck in real driving conditions** or from **engine bench** using **standard** or **100% biofuel** as well as **doped biofuel**. The use of biodiesel significantly reduces the soot formation. There is no significant impact of biodiesel on the soot specific surface, the higher value being obtained for an accelerated soot loading. Experiments performed at laboratory scale showed no relationship between volatile fraction and real soot reactivity under passive regeneration conditions. Adding **alkali metals** to the real Diesel soot **enhances soot oxidative reactivity** in the whole temperature range (200 – 600 °C), regardless the cycle of production applied. Those species act as catalyst for soot oxidation process. The **kinetic of soot oxidation**, in presence of water in the feed gas, at low temperature (≤ 400 °C), **is significantly increased in the presence of phosphorus**.

Model soot were collected on a glass microfiber filter in the post flame region of an atmospheric axisymmetric co-flow diffusion flame burner. Particle size distribution and oxidative reactivity of model soot from the burner are in the same range as real soot derived from Diesel engine.

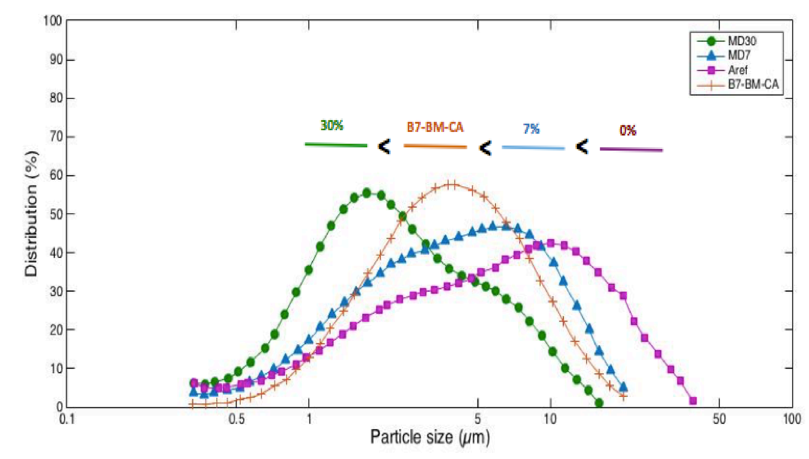
Real Soot

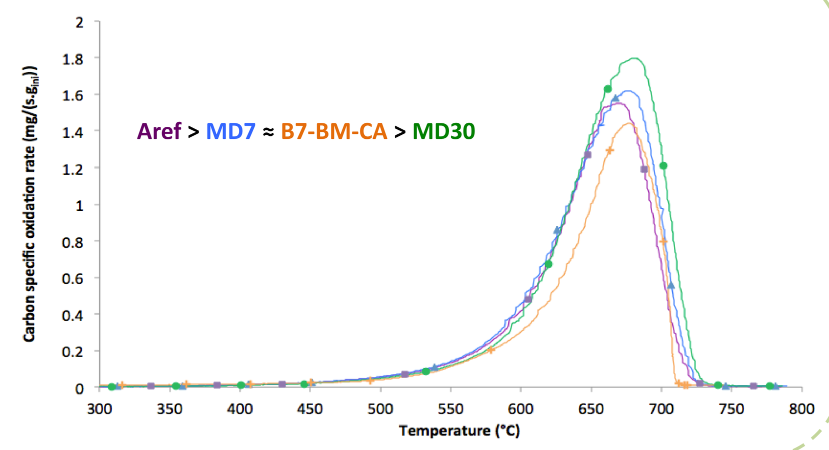
Soot Sample	Ash (%)	Volatils (%) 110 – 400 °C	P (%)	K (%)
B7-Customer Cycle	1,84	3,91	0,05	0,1
B100-Customer Cycle	7,78	5,56	0,05	0,1
B100-High Loading	1,53	0,75	0,19	0,03
B100(K+P)-High Loading	4,62	1,00	0,89	1,17



Model Soot

Soot Sample	Composition
Aref	70 mol% n-decane + 30 mol% α-methylnaphtalene
MDX	Aref + X mol% methyldecanoate





SCR Selective Catalytic Reduction

IC2MP

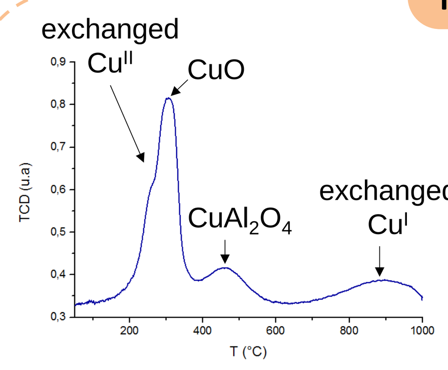
The impact of Na and P on the SCR activity of Cu/FER catalyst was studied depending on the mineral loading (until ≈2_{wt}%) and the impregnation solvent (H_2O or ethanol).

Acidity (measured by NH_3 adsorption) was poisoned after Na addition which directly affected the NOx conversion at low temperature (250°C). **Na impregnation in water led to a stronger catalyst deactivation than in ethanol, because water favors the migration of the Cu exchanged species, leading to the formation of CuO extra framework species.** It appears that the deNOx efficiency at high temperature (500°C) is clearly related to the amount of active exchanged copper.

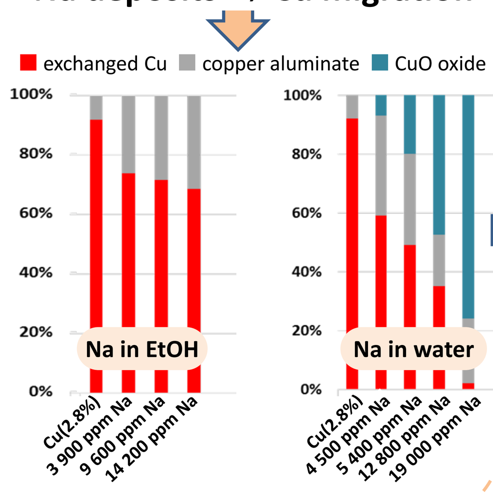
Cu-P interactions were evidenced after phosphorus addition, leading to a decrease in redox behaviors (NO oxidation and NH_3 oxidation) and consequently in the SCR activity (especially at low temperature and in Standard SCR condition). Again, lower deactivations were observed when the wet impregnations were performed in ethanol.

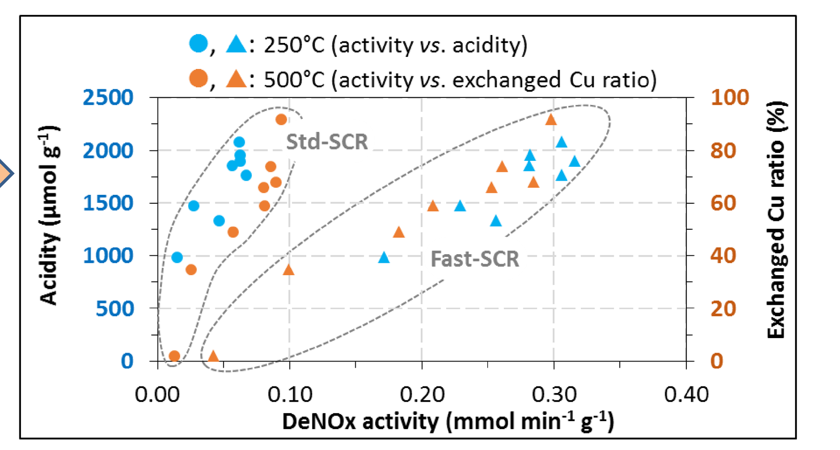
Na poisoning

H_2-TPR



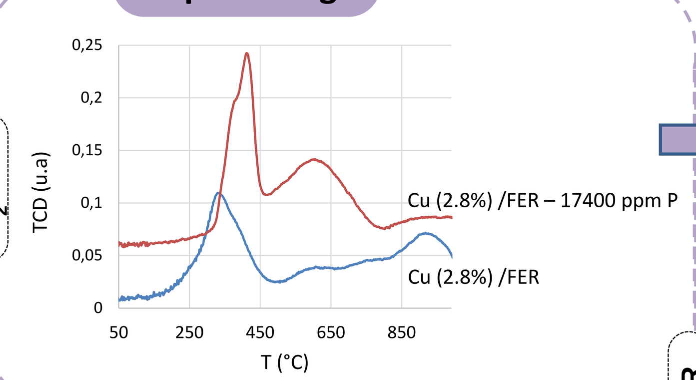
Na deposits → Cu migration



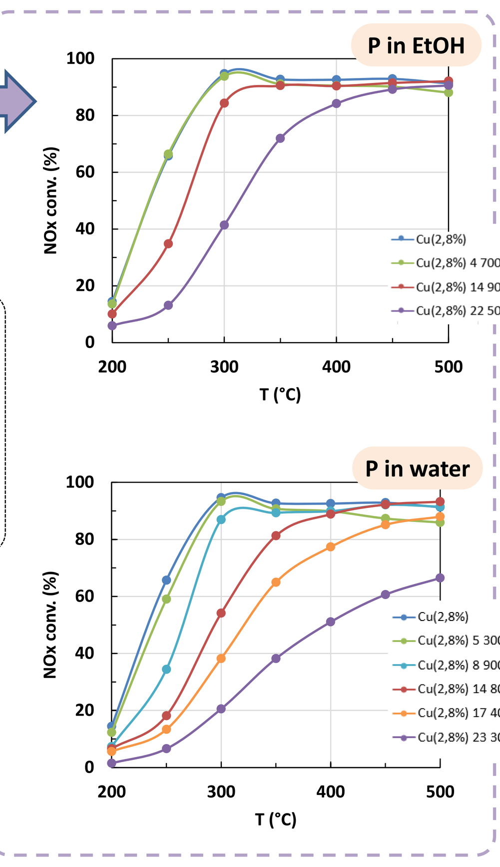


P poisoning

H_2-TPR



Standard SCR



CONCLUSIONS

Impact of biofuel poisoning elements to DOC & SCR performance has been identified, Na having the highest deactivation potential; SCR deactivation mechanism has been proposed.

Comparison between real and model soot as well as the impact of Na, K and P on soot oxidation have been successfully studied.

Biofuel use leads to more poisoning, especially due to Na, with a direct impact on DOC performance in terms of NO_2 formation which might indirectly affect soot oxidation rate and NO_x reduction.

PERSPECTIVES

Collected data by academic partners combined with results obtained on engine bench and vehicles will be used to build kinetic models that will be integrated to empower an ageing predictive model taking into account the use of biodiesel;

Adapted/innovative systems with improved poisoning resistance.

Global kinetic model - biofuel impact	AGEING PREDICTION	NO & hydrocarbon oxidation
Chemical composition of biofuel (Na, K, P, etc)		NOx, N_2O
Biofuel consumption		Soot oxidation, Ash deposit

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