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## Support effect on the activity and thermal stability of platinum nanoparticles for diesel oxidation

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### Abstract:

Diesel engines generate harmful gases with environmental and public health implications. Tighter emission regulations is driving the automotive industry to develop highly efficiency catalytic converter devices, where the diesel oxidation catalyst (DOC) has the crucial role of decreasing the pollution levels through the oxidation reaction of nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), unburned hydrocarbons (HC, e.g. propene) and sulfur oxides (SO<sub>x</sub>) [1].

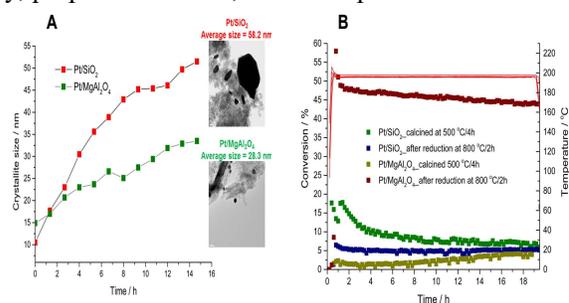
The state of the art catalysts for diesel exhaust oxidation are scarce and precious nanoparticles, eg. platinum (Pt) and palladium (Pd), supported in high surface area metal oxides (e.g. γ-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>). During the driving cycle, the active nanoparticles are prone to sintering by particle migration or Ostwald ripening mechanism [2], leading to a loss of metallic surface area and subsequent efficiency. Hydrothermal durability required up to 700-800 °C coupled with low-temperature activity (< 200 °C), is one of the main challenges of the current technology.

In this work, the activity for HC oxidation and thermal stability of platinum catalysts prepared by incipient wetness impregnation method was studied regarding the support effect (MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>). The Pt/MgAl<sub>2</sub>O<sub>4</sub> catalyst presented a remarkable stability at extreme conditions (750 °C, 10% O<sub>2</sub>) as showed in Figure 1A during *in situ* x-ray powder diffraction (XRD) measurements. Accordingly, the crystallite size of the platinum nanoparticles increased from 15 nm to 28 nm after 12 h at 750 °C in a oxygen-rich environment, whereas in the SiO<sub>2</sub> support the nanoparticles size reached the 58 nm. High resolution transmission electron microscopy images (HR-TEM) corroborated the *in situ* XRD results. As another interesting result, the Pt/MgAl<sub>2</sub>O<sub>4</sub> presented a enhance activity after a

reduction pre-treatment at 800 °C/2h with 5 % hydrogen. As visible in Figure 1B the conversion for propene oxidation increased from ca. 5 % to 45 % after the former mentioned pre-treatment. Contrary to this, the conversion for the Pt/SiO<sub>2</sub> catalyst didn't suffer any improvement. Moreover, it was possible to regenerate the activity of an aged Pt/MgAl<sub>2</sub>O<sub>4</sub> catalyst with the reduction pre-treatment (result not shown).

The MgAl<sub>2</sub>O<sub>4</sub> support is found to be a promising alternative for increasing the activity and stability of platinum nanoparticles for diesel oxidation. The obtained results are obtained within the framework of CatProDiesel project, in collaboration with Dinex (industrial partner), Danish Technological Institute (DTI) and Center for Materials Crystallography.

**Keywords:** Diesel oxidation, platinum nanoparticles, support effect, MgAl<sub>2</sub>O<sub>4</sub>, thermal stability, propene oxidation, reduction pre-treatment.



**Figure 1** – A: Crystallite size of Pt on different supports (SiO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>) determined through *in situ* XRD measurements and acquired at 750 °C with 10 % O<sub>2</sub> balanced in N<sub>2</sub> during a 15 h period. B: Stability at 200 °C of the Pt/SiO<sub>2</sub> and Pt/MgAl<sub>2</sub>O<sub>4</sub> catalyst for propene oxidation reaction, before and after a reduction pretreatment at 800 °C in 5 % H<sub>2</sub> balanced in N<sub>2</sub> for 2 h.

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