Activation of O₂ on CeO₂ surfaces by electron transfer

**Motivation**

It is well known that VOCs being recognized as major responsible for the increase in global air pollution. Catalytic combustion is an efficient technology for the abatement of VOC, which are oxidized over a catalyst at temperatures much lower than those of the thermal process. Specifically, gold supported catalysts at temperatures much lower than those of the thermal process. Specifically, gold supported catalysts have shown a great performance in the oxidation of CO, MeOH, toluene, etc.

Besides, it is important to clarify the role of the support in such reaction. Ceria has the key property of high oxygen storage capacity which originates in its ability to rapidly switch from Ce to Ce oxidation states as the environment changes from reducing to oxidizing and vice versa. Its redox behaviour is influenced by the substituent lattice groups that could be incorporated during different catalyst pretreatments and could affect the oxidation of VOC. This could be understood as the influence of oxygen vacancies and/or absorbed or coadsorbed H on the actvation of oxygen molecules. The latter leads to the formation of superoxide and peroxide molecules on the surface, which could in principle be highly reactive towards oxidation of organic molecules. In this context, we study, by IR spectroscopy and mass spectrometry, the interaction of O₂ with the modified CeO₂ based material, by creating vacancies following different reduction treatments. The possible role of the vacancies and/or presence of H atoms in the electron transfer from the surface to the oxygen molecule is discussed. Using AP-XPS we are able to prove that the surface/near surface of CeOx presents a charging effect which could be due to extra charge/electrons which then transfer to O₂.

**Experimental Setup**

**Ambient Pressure XPS**

Operando DRIFT-MS

DRIFT-cell

FTIR Nicolet 8700

Mass Spectrometer

**Activated O₂ species on CeO₂ after H₂ treatments at 300 °C**

**Thermal and temporal stability of species**

MS Data:
Formation of H₂O after first contact with O₂
And then increasing with time.

At first contact of O₂ with the reduced and first pretreated sample (pretreatment with H₂ at 300 °C) some superoxide and peroxide species are formed with concomitant changes in the OH region. After the second treatment with H₂ and then contact with O₂, superoxide species are highly increased.

The stability of these species was tested against time, temperature and different ambient atmospheres. First appearance of superoxide is related to disappearance of Ce³⁺ signal and its consequent intensity decrease in the spectra is accompanied by a slight increase in the amount of peroxides.

**Conclusions**

- O₂ is readily activated on CeO₂ in the presence of vacancies.
- Transfer of one electron from cations Ce³⁺ produces superoxide species.
- Transfer of a second electron produces peroxide species.
- If vacancies are created by interaction with H₂ at moderate temperatures (200-300°C), and on already reduced materials at higher temperatures (e.g. in the presence of vacancies), more super- and per-oxides species are detected and they are more stable in various atmospheres. It is believed these treatments leave H atoms inside the material, which hold the extra charge/electrons that are later transferred to O₂.
- Using AP-XPS when performing the pretreatments with H₂ and heating the material to the set temperature, it was observed differential zones of the material charged in the surface/near surface of CeOx. This could indicate it exists a very "thin" zone or capping of CeOx where the species (possibly hydride) responsible for transferring electrons to adsorbed O₂ are located.

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**References**

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