

# ME-PSD IR spectroscopy to study CO Oxidation reaction under Pt/Al<sub>2</sub>O<sub>3</sub> catalyst

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#### Significance and Relevance

Applying ME-PSD IR spectroscopy shine new insights of CO oxidation reaction mechanism occurring on  $Pt/Al_2O_3$  catalyst. Based on these experiments, a new decomposition of the IR spectra of adsorbed CO is proposed.

*Preferred choice for the topic: Fundamental advances in understanding catalyst Preferred presentation*: Oral preferred or Short Oral.

### **Introduction and Motivations**

Dynamic behavior investigation of actives species involved in catalytic reaction is still highly challenging since a catalytic pathway is a combination of rapid adsorption and desorption of reactants/intermediates/products on ill-defined active surface sites.<sup>1</sup> Furthermore, the spectroscopic signal arising from non-active sites (spectators) is frequently stronger than that of actives sites, overwhelming key information on catalysis. One way to mitigate this problem is to apply Modulation Excitation Spectroscopy  $(MES)^2$  which consists in a periodic perturbation of the state of the system by the variation of external parameter such as temperature, pressure, concentration... This rapid periodic perturbation of the system state will influence only the concentration profile of the active species which will oscillate at the frequency of the periodic excitation but with a phase delay. The concentration profile of species not responding to the periodic excitation (i.e. spectator species) will remain constant making possible their removal from the global signal by a post data acquisition mathematical treatment known as PSD (Phase Sensitive Detection). In this study we aim to monitor the dynamic behavior of actives species formed on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst's surface during CO oxidation reaction by applying ME-PSD infrared (IR) spectroscopy (rapid looping from <sup>12</sup>CO to <sup>13</sup>CO while simultaneously recording time-resolved IR spectra). Indeed, although the Alumina-supported Pt catalyst (commonly used for CO and unburned hydrocarbon oxidation) has been extensively studied, the reaction mechanism of CO oxidation remains unclear and is still widely debated. Over 20 different steps have been proposed in the literature to explain this mechanism.<sup>3</sup>

### **Materials and Methods**

<u>Catalyst Synthesis</u>. Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is prepared by incipient wetness impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (specific surface area of 225 m<sup>2</sup>g<sup>-1</sup> and a pore volume of 0.76 cm<sup>3</sup>g<sup>-1</sup>) with platinum (II) acetylacetonate (Fluka) precursor salt to obtain 1 wt% metal loading. The sample was dried overnight at 85 °C, calcined 2 h under air flow at 500 °C (ramp 10 °C/min) and reduced with dihydrogen 2.5 h at 400 °C (ramp 5 °C/min).

<u>ME-experiments</u>. The catalyst is introduced in a home-made transmission IR reactor composed of 6 inlet and outlet channels (diameter 200  $\mu$ m), in form of a square pellet (~10 mg and 1.21 cm<sup>2</sup>) to perform *operando* experiments. The low dead volume of the reactor used here inferior to 0.5 cm<sup>3</sup>, a required condition to obtain more relevant kinetic data for ME application. Spectra are obtained by using a ThermoScientific Nicolet 6700 FTIR spectrometer equipped with a MCT detector enable millisecond order spectra acquisition in rapid-scan mode. The cell is connected on one side to an automatic gas distribution system (Beckhoff<sup>®</sup>) composed of 4-way pneumatic valve upstream of the transmission IR reactor in order to switch the gas phase composition in isobaric and isotherm conditions. The ME PSD IR experiments are started once the system reach its steady state, only then the switching of the reactant from <sup>12</sup>CO to its labelled counterpart <sup>13</sup>CO is performed (sending 2000 ppm of <sup>12</sup>CO + O<sub>2</sub> for 15s on the catalyst surface, then we switch to 2000 ppm of <sup>12</sup>CO + O<sub>2</sub> also for 15s,



the gas flow rate was 12ml/min), under a constant temperature of 119°C. This  $^{12}CO \rightarrow ^{13}CO$  gas switch step was repeated 100 times.

## **Results and Discussion**

"Figure 1 (top) shows IR spectra recorded during the ME-IR experiment (time domain), along with demodulated spectra obtained after PSD signal processing (Figure 1, bottom). In the 'CO adsorbed on Pt' region, the isotope peak exchange is visible in the time domain. However, in the 'carbonate and CO adsorbed on 2 Pt' regions, the isotope peaks become distinctly evident following PSD signal processing. Similar peaks between 1400 and 1900 cm<sup>-1</sup> are observed for both fundamental and harmonic frequencies. However, in the CO adsorbed on Pt region, two additional peaks appear at 2043 and 2093 cm<sup>-1</sup> in the harmonic frequency. This is clear evidence of the presence of two distinct kinetic processes. Indeed, since k3 reflects the behavior of species reacting at a higher frequency than the system's fundamental perturbation, we can conclude that carbonate species and CO bridging on two Pt atoms exhibit a slower exchange rate than CO adsorbed on a single Pt atom. Note also that the exchange between <sup>12</sup>CO and <sup>13</sup>CO is a simpler reaction when adsorbed in a bridging position between two platinum atoms, whereas it is much more complex when adsorbed on a single platinum atom (additional peaks at 2043 and 2093 cm<sup>-1</sup> for harmonic frequency).



Figure 1. Upper. IR spectra recorded during  ${}^{12}CO/{}^{13}CO$  looping experiment (time domain). Bottom. ME-IR spectra after PSD processing (demodulated spectra at  $k_1$  and  $k_3$ )

### References

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