Space- and time-resolved *operando* DRIFTS on NSR catalysis: Effects of precious metal and storage component

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Abstract: Spatiotemporal *operando* DRIFTS spectroscopy combined with gas phase analysis (MS and IR) was developed and utilized to study NO_x storage-reduction (NSR) catalysts. It is revealed that unique roles of each component (PGM and/or NO_x storage material) led to distinct NO oxidation activity and NO_x capture efficiency, thus resulting in very different spatial distributions of stored NO_x along the axial direction of the catalyst bed. On the other hand, the spatial distribution affects how the stored NO_x is decomposed during the reduction phase and how the spikes of quantitatively determined different nitrogen containing molecules evolved in a specific sequence during the reduction phase. This work clarifies important mechanistic insights into NSR catalysis towards zone-coated catalyst design.

Keywords: NSR, *operando*, space- and time-resolution, DRIFTS.

1. Introduction

NO_x storage and reduction (NSR) catalysis[1, 2] has become a proven complementary process to the conventional three-way catalysis (TWC) since it can efficiently convert NO_x into N_2 even when operating an internal combustion engine under lean conditions (i.e. oxygen rich; A/F > 14.7) which are beneficial for fuel economy and naturally arising for diesel engines. In NSR, the difficult reduction of NO_x to N_2 is enabled by unsteady-state operation, namely by switching between (i) a fuel-lean phase where NO_x storage takes place over a catalyst and (ii) a fuel-rich (reductive) phase where stored NO_x is converted to N_2. Due to the nature of the unsteady-state operation, the catalytic processes take place and vary dynamically within reactor. For this reason, space-resolved information of surface chemical species and their relation to the effluent gas evolution are mandatory to understand the complex NSR chemistry. This works aims at elucidating these impacts exerted by Pt/Rh or Ba through holistic understanding of NSR chemistry by the space- and time-resolved *operando* DRIFTS.

2. Experimental

Space-resolved measurements were carried out in order to understand the effects of precious metal and also Ba as the storage component along catalyst bed, thus four catalysts were evaluated (Pt/Al_2O_3, Rh/Al_2O_3, $Pt\text{-}Ba/Al_2O_3$ and $Rh\text{-}Ba/Al_2O_3$). Catalyst bed length was ca. 6 mm (66 mg) and time-resolved DRIFT spectra (250 ms time resolution) were recorded at 4 different positions (2 mm distance to the next) along the axial direction of the catalyst bed. Catalytic performance and mechanistic studies were performed under unsteady-state NSR conditions: (i) fuel-lean (600 ppm NO, 7 vol% O_2, balance He) & (ii) fuel-rich (3 vol% H_2, balance He) gases, both at 100 mL/min, alternately and periodically passing through the catalyst bed at a fixed time interval of 300 and 240 s for the lean and rich conditions, respectively. Surface chemical species evolved during NSR were studied by *operando* DRIFTS using an in-house designed cell mimicking the action of plug flow reactor.[3] Gas phase composition was analyzed by MS and IR.

3. Results and discussion

Figure 1 highlights the information we obtained from the space(4 positions)- and time(540 s)-resolved DRIFTS (blue and red color meaning minimum and maximum of concentration respectively) as well as the gas phase analysis (only NO_x concentrations are shown) for all studied catalysts at 350 ºC. For the NO_x storage phase (i.e. the first 300 s) evolution and spatial distribution of stored NO_x in the form of nitrates (bands arising at ca. 1560 & 1730 cm^{-1}) were uniquely determined by the type of precious metal and the presence/absence of Ba. Comparing Pt/Al_2O_3 and $Pt\text{-}Ba/Al_2O_3$ or Rh/Al_2O_3 and $Rh\text{-}Ba/Al_2O_3$, it is evident that the presence of Ba component induces the formation of NO_x storage front caused by full NO_x capture along the flow direction due to enhanced catalytic activity for NO_x storage.

Looking into the NO_x reduction phase (the last 240 s) especially upon lean-to-rich switching, a large NO spike was detected for $Rh\text{-}Ba/Al_2O_3$. Such a NO_x spike in reduction phase can be detrimental for overall NSR performance and thus it is of prime importance to understand the origin of such spikes. This spike is likely caused by the spatial distribution of the stored NO_x, which is more pronounced at the upstream position for $Pt\text{-}Ba/Al_2O_3$ and at the downstream position for $Rh\text{-}Ba/Al_2O_3$, due to the higher NO oxidation activity of Pt than that of Rh.

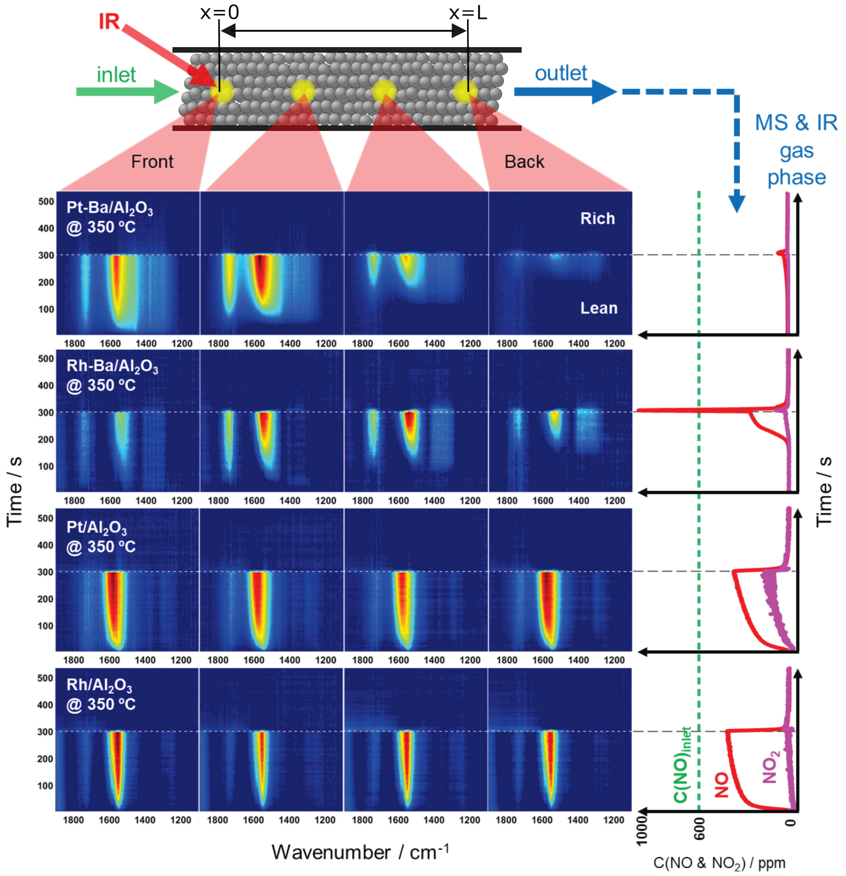

Figure 1. Space- and time-resolved DRIFTS of NSR catalysts at 350 ºC at four positions (Δx = ca. 2 mm).

4. Conclusions

Space-resolved analysis allowed to give explanation to the effluent concentration profiles as well as chemical surface species formation/consumption by thorough understanding of what, where and how the NSR processes take place along the catalyst bed. Intrinsic Ox/Red abilities of the precious metals and the presence of Ba were found to influence the surface chemistry of both NO_x storage and reduction processes and consequently the overall NSR performance.

References

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