Effect of support material Al_2O_3 vs ZrO_2-TiO_2 on the Ba availability for NSR catalyst: an *in situ* and *operando* IR study

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Introduction

NOx storage and reduction (NSR) is an essential technology for removal of nitrogen oxides (NO and NO_2 or NOx) from exhaust gases of Diesel or gasoline lean-burn engine. This technology is based on catalytic formulations comprising 3 major components: 1) a platinum group metal (PGM); 2) a NOx storage material; and 3) a support. The commonly studied NSR catalyst is Pt-Ba/Al_2O_3, however no viable solution was found to its main causes of deactivation, being sulfur-poisoning and/or thermal deterioration [1]. One way to improve the sulfur tolerance, consists in replacing the support by titanium dioxide (TiO_2). This support offers lower sulfates decomposition temperature than the original Al_2O_3 support. Moreover, the thermal stability of the catalytic formulation can be increased by the incorporation of ZrO_2 to TiO_2 [2] .

Goals

The present investigation aims at elucidating the interaction between the barium storing phase and the oxide support (Al_2O_3 or ZrO_2-TiO_2), in order to understand the distinct dynamic behaviors observed during the lean storing period.

Tools

Operando IR spectroscopy in combination with isotopic labeling is a powerful technique that allow us determining the superficial modification under duty conditions

Conclusions

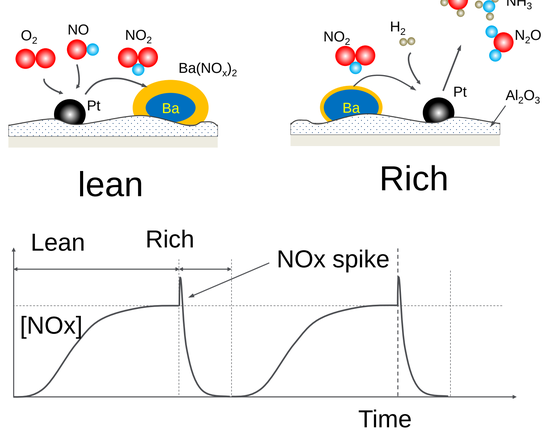
The interaction of Ba phase with different oxide supports provokes different Ba particles morphologies and as consequence changes of the properties during dynamic storage of NOx.
The higher concentration of the 'anchoring' sites for the ZT oxide support leads to a higher amount of more finely dispersed Ba when compared to Al_2O_3. The full storage capacity for both formulations is thus similar but under realistic NSR cyclic conditions the Pt/Ba/ZrO_2-TiO_2 will lead to a higher NOx adsorption efficiency related to a higher (faster) availability of the whole Ba sites.

References

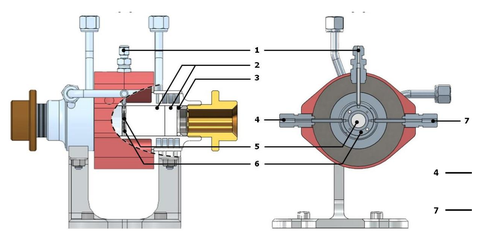
[1] A. William, S. Epling, L.E. Campbell, N.W. Currier and J.E. Parks, Catal. Rev. Sci. Eng. 46, 2004, 1–72

[2] N. Hachisuka, I. Yoshida, T. Ueno and H. Takahashi, SAE Tech. Pap. 2002

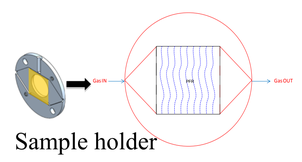
NO_x storage and reduction (NSR)



IR *operando* experiments



1 – Thermocouple location
2 – KBr windows
3 – Joint
4 – Gas In
5 – Pellet
6 – Sample holder
7 – Gas out.

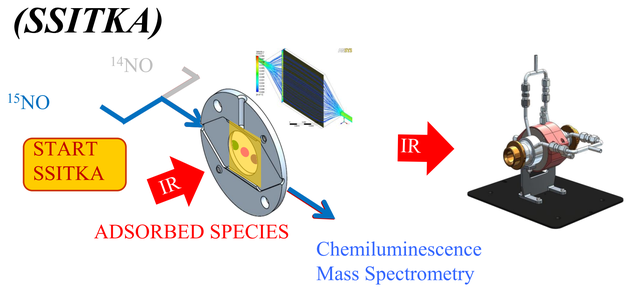


Sample holder

2D Decomposition of the catalytic zone in PFR reactor

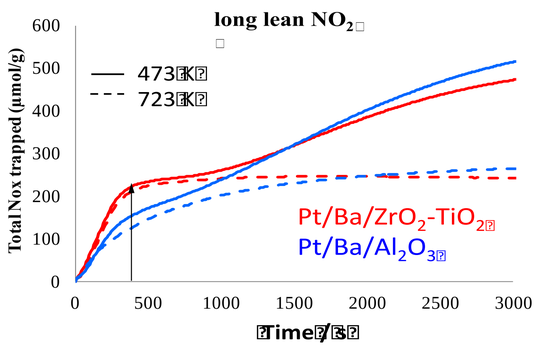
No vertical concentration gradients

Steady state isotopic transition kinetic analysis (SSITKA)



Long nitration experiments

Lean Period: 400 ppm NO_2/1% O_2 in Ar/$GHSV_{eq\ mono}$ = 100,000 h^{-1}



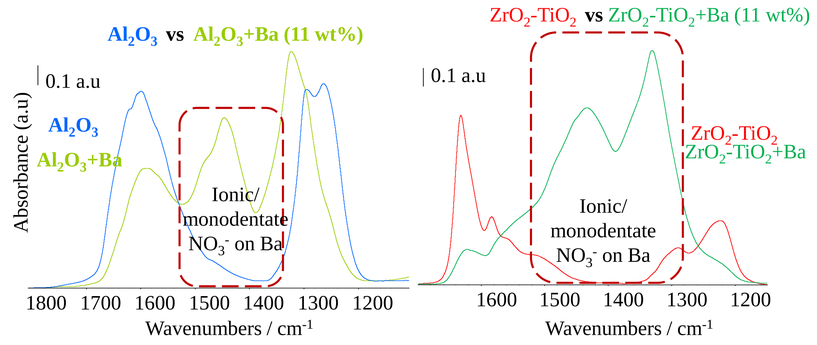
At both low and high T :
short TOS => ZT traps more than Al
high TOS => similar full trapping capacity

Samples composition
1% wt. Pt/11%wt. Ba/ Al_2O_3
1% wt. Pt/ 11%wt. Ba/ZrO_2-TiO_2 (70% ZrO_2 -30% TiO_2)
provided by Toyota company.

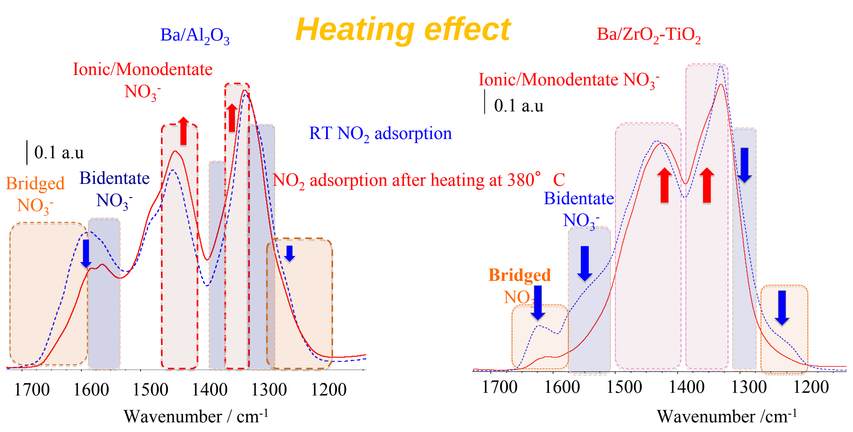
Support **directly involved** or **distinct diffusion rate** into Ba particles?

In situ characterization : NO_2 adsorption

	Al_2O_3	Ba/Al_2O_3	ZrO_2-TiO_2	Ba/ZrO_2-TiO_2
Specific Area (BET) $m^2.g^{-1}$	200	200	100	100
NO_2 adsorbed	n/mmol.g^{-1} (saturation)	n/mmol.g^{-1} (saturation)	n/mmol.g^{-1} (saturation)	n/mmol.g^{-1} (saturation)
RT	/	1.48	/	1.41
Heated @ 380° C	1.35	1.07	1.81	1.68



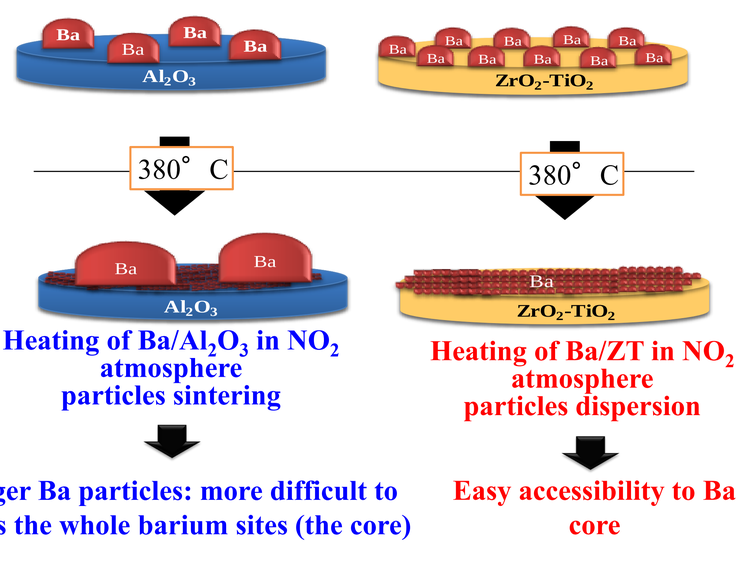
After Ba loading the contribution of the ZT support for NOx adsorption sites is negligible



Formation of ionic NO_3^- species onto Ba phase are favored upon heating

The 'model'

Al_2O_3: 6.75 10^{-3} mmol.m^{-2} and ZrO_2-TiO_2: 1.81 10^{-2} mmol.m^{-2}



Heating of Ba/Al_2O_3 in NO_2 atmosphere particles sintering

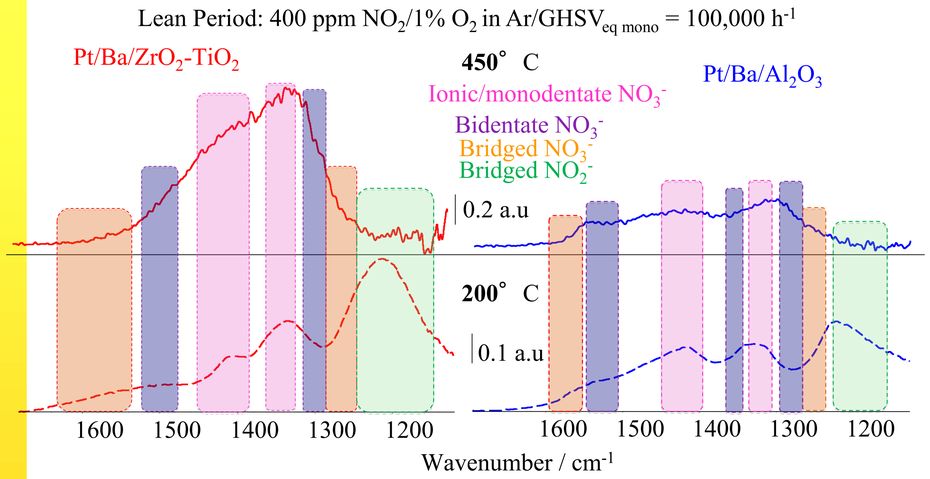
Larger Ba particles: more difficult to access the whole barium sites (the core)

Heating of Ba/ZT in NO_2 atmosphere particles dispersion

Easy accessibility to Ba core

Operando catalyst 'surface' study: adsorption sites

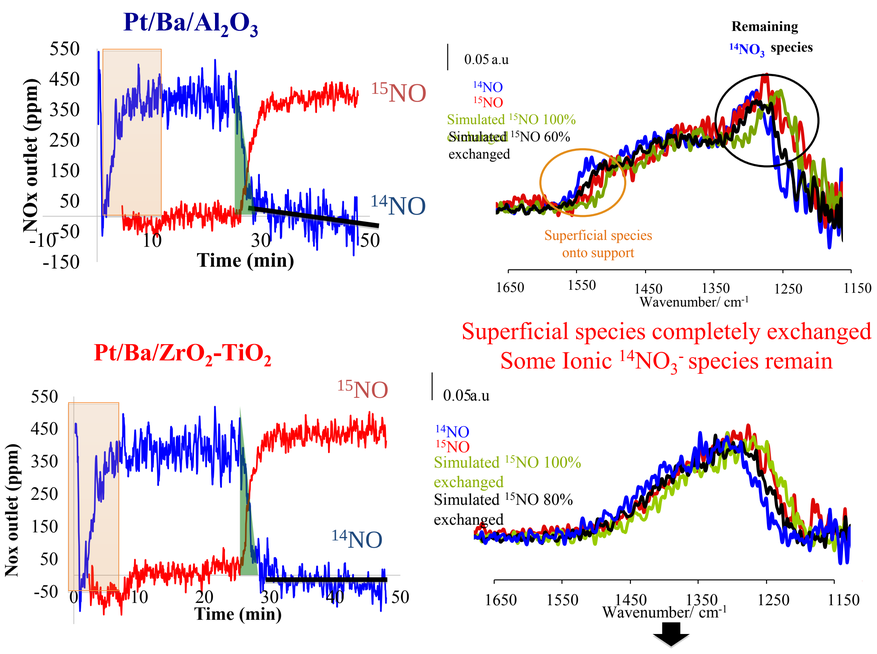
Lean Period: 400 ppm NO_2/1% O_2 in Ar/$GHSV_{eq\ mono}$ = 100,000 h^{-1}



@ 300 sec: higher amount of Ba(NO_2^-) @ 200° C and Ba(NO_3^-) @ 450° C over ZT => faster diffusion into smaller Ba particles.

Diffusion 'time' into Ba particles core depends on the Ba particles size ➡ Support effect

Application: SSITKA of NO storage at 450° C



Quasi - complete exchange $^{14}NO_3^-$ ➔ $^{15}NO_3^-$ species