

## On the unexpected promoting effect of the Cl-containing Pd precursor on the CH<sub>4</sub>-SCR of NO<sub>x</sub> of Cl-free Pd/WO<sub>x</sub>-ZrO<sub>2</sub> catalysts

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### Introduction

The selective catalytic reduction of NO<sub>x</sub> assisted by CH<sub>4</sub> (CH<sub>4</sub>-SCR) has received great attention as it may offer an attractive alternative to the SCR by ammonia (NH<sub>3</sub>-SCR). Despite numerous studies performed on the CH<sub>4</sub>-SCR, the development of more efficient and durable catalytic formulations is still of the utmost interest to meet the ever more drastic regulations on the emissions from stationary sources. Transition metals supported on zeolites have been extensively studied for such a reaction [1-3]. These catalysts, however, are severely affected by water vapor [4] and SO<sub>x</sub> which are present in the real exhausts at ppm levels. To overcome these drawbacks, alternative supports such as acidic sulfated- or tungstated-zirconia have been studied and have shown interesting capabilities for the CH<sub>4</sub>-SCR [5-9]. Among transition metals, Pd is one of the most active [5]. To avoid deactivation of sulfated-zirconia supports at high temperature due to sulfate loss, tungstated-zirconias are privileged [7-9]. In these studies, however, various Pd precursors were used which made it difficult to draw definite conclusions about the influence of the nature of the Pd precursor on the CH<sub>4</sub>-SCR for Pd/WO<sub>x</sub>-ZrO<sub>2</sub> (Pd/WZ) catalysts.

This work aims at shedding light on the influence of the nature the Pd precursor on the CH<sub>4</sub>-SCR for WZ-supported catalysts.

### Materials and Methods

Two Pd(0.25 wt%)/W(12 wt%)Z catalysts were synthesized by impregnation of the corresponding Pd precursor (PdCl<sub>2</sub> or Pd(NO<sub>3</sub>)<sub>2</sub>, Johnson Matthey) on a WZ support prepared by refluxing a commercial zirconium oxyhydroxide (MEL Chemicals, XZO880/01) and ammonium metatungstate (Fluka) in H<sub>2</sub>O at 110 °C for 20 h. For comparison purpose, impregnation of PdCl<sub>2</sub> was also carried out on ZrO<sub>2</sub> (Pd/Z). After drying, the samples were calcined at 650 °C for 3 h in static air. The catalysts were characterized by N<sub>2</sub> physisorption, XRD, XPS, Raman spectroscopy and CO adsorption followed by FTIR. Steady-state CH<sub>4</sub>-SCR (1500 ppm CH<sub>4</sub>, 7 % O<sub>2</sub> and 500 ppm NO<sub>x</sub> in N<sub>2</sub>) was carried out in a quartz micro-reactor coupled to a set of specific detectors under a GHSV of about 40,000 h<sup>-1</sup> [10].

### Results and Discussion

For both catalysts (PdCl<sub>2</sub>/WZ and Pd(NO<sub>3</sub>)<sub>2</sub>/WZ), a maximum in the NO<sub>x</sub> conversions is observed at 500 °C (Fig. 1a) with CH<sub>4</sub> conversions close to 40 % (Fig. 1b). Yet, PdCl<sub>2</sub>/WZ exhibits a much greater (+ 63 %) yield in N<sub>2</sub> than that found for Pd(NO<sub>3</sub>)<sub>2</sub>/WZ (Fig. 1a). It can be noted that despite the fact that Pd/Z oxidizes CH<sub>4</sub> at slightly lower temperatures than the W-promoted samples (Fig. 1b), it does not catalyze the removal of NO<sub>x</sub>, as no activity could be observed (Fig. 1a). This clearly shows the importance of acidity for CH<sub>4</sub>-SCR.

XRD patterns do not show any significant difference between both W-promoted catalysts, in which the tetragonal zirconia phase is mainly (~ 90 %) stabilized. In contrast, Raman measurements clearly reveal that the use of PdCl<sub>2</sub> limits the sintering of W, since only polytungstate species (WO<sub>4</sub>) are observed with W=O and W-O-W contributions at 1021 and 825 cm<sup>-1</sup>, respectively, whereas that of Pd(NO<sub>3</sub>)<sub>2</sub> shows the additional presence of WO<sub>3</sub> (ν<sub>W-O-W</sub> at 809 cm<sup>-1</sup>). In agreement with the greater dispersion of W on PdCl<sub>2</sub>/WZ, the adsorption of CO at 77 K followed by FTIR reveals a greater Brønsted acidity for this material, both in terms of number (contributions ν<sub>CO</sub> at 2177 cm<sup>-1</sup> and ν<sub>OH</sub> at 3480 cm<sup>-1</sup>) and strength (Δν<sub>OH</sub>) of acid sites, than that of Pd(NO<sub>3</sub>)<sub>2</sub>/WZ. Yet, elemental analysis and XPS of PdCl<sub>2</sub>/WZ show that Cl<sup>-</sup> is fully removed after calcination. Hence, the use of a Cl-containing Pd precursor plays a crucial role during the catalyst preparation without poisoning the final catalyst.

### Significance

In most cases, the use of chlorinated precursors is avoided, as the deposition of Cl<sup>-</sup> on the support may negatively influence the catalytic properties of the as-prepared materials. This study shows that overcoming such a preconceive idea may lead to the preparation of materials with improved efficiency for environmental concern.

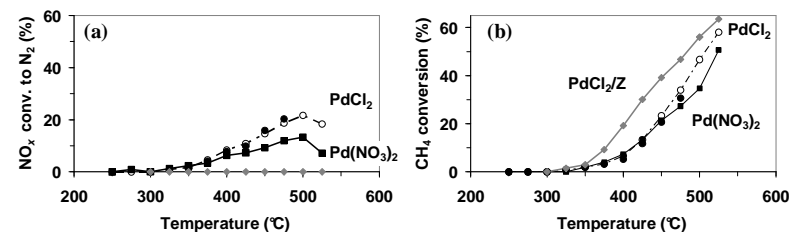


Figure 1: (a) NO<sub>x</sub> and (b) CH<sub>4</sub> conversions for: PdCl<sub>2</sub>/WZ (1<sup>st</sup> exp. ●, 2<sup>nd</sup> exp. ○), Pd(NO<sub>3</sub>)<sub>2</sub>/WZ (■) and PdCl<sub>2</sub>/Z (◆)

### References

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