

# $H_2$ -SCR over 0.3%Pt/5%SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst: investigations in the reaction pathways.

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## Significance and Relevance

The pathways and mechanistic aspects of the H<sub>2</sub>-SCR on platinum-based catalysts remain a topic of debate. In this study, we investigated the reaction pathways over a low-loaded supported platinum catalyst depending on the temperature. Our results indicate that NO decomposition occurs mainly below 100 °C, predominantly yielding N<sub>2</sub>O. The formation of NH<sub>3</sub> is observed from 70 °C and the NH<sub>3</sub>-SCR reaction can occur, but only in the 70-120 °C temperature range, leading mainly to N<sub>2</sub>O. Importantly, at temperatures exceeding 120 °C, catalytic activity is mainly driven by the NH<sub>3</sub> oxidation by O<sub>2</sub>. To our knowledge ammonia oxidation has not previously been recognized as the main reaction in H<sub>2</sub>-SCR reaction pathways.

## Preferred topic: Automotive and stationary emission control.

2<sup>nd</sup> choice for the topic: Air cleaning and combustion. Preferred presentation: **Oral preferred** or Short Oral.

## **Introduction and Motivations**

 $H_2$  internal combustion engine ( $H_2$ -ICE) could serves as a viable clean solution for heavy vehicles and could significantly contribute to decarbonizing the transport sector. However, a deNO<sub>x</sub> treatment may be necessary. One attractive approach is to implement a  $H_2$ -SCR after-treatment system. According to the literature, the  $H_2$ -SCR mechanism can be divided into two distinct routes, namely (i) the NO adsorption/dissociation based on a Langmuir-Hinshelwood mechanism and (ii) the oxidation– reduction pathways.<sup>1</sup>Regardless of the mechanism considered, a typical volcano shaped curve in  $NO_x$ conversion is obtained. This phenomenon occurs because the competitive  $H_2$  combustion reaction is intensifies as the temperature rises, particularly above 150 °C on precious metals.

The oxidation–reduction mechanism the NO reduction process involves complex reactions between gaseous NO or weakly adsorbed oxidized species (NO<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>) and adsorbed reduced N-compounds (NH<sub>x</sub>).<sup>2</sup> In this study, we investigate the reaction pathways of the H<sub>2</sub>-SCR over a low-loaded platinum-based catalyst, with a special focus on (i) the role of NH<sub>3</sub> as possible intermediate species and (ii) the origin of undesired N<sub>2</sub>O emission.

## **Materials and Methods**

The 0.3%Pt/5%SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared using a silica-alumina support provided by Sasol and previously hydrotreated under synthetic air with 10 % H<sub>2</sub>O at 700 °C, 4 h (296 m<sup>2</sup> g<sup>-1</sup>). Platinum was introduced *via* wet impregnation using Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> salt. After drying, the resulting powder was treated under N<sub>2</sub> at 700 °C, 4 h and finally hydrotreated at 600 °C, 4 h (Pt dispersion: 35 %).

The catalytic behaviour of the sample (30 mg) was investigated using various reaction mixtures, as depicted in Table 1. The feed gas and effluent compositions were monitored using online MKS 2030 Multigas infrared analyser for NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>. Additionally, a Pfeiffer Vacuum mass spectrometer was used to record the H<sub>2</sub> signal. The N<sub>2</sub> formation was calculated based on the assumption that only NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> were formed as N-compounds.

Table 1. Reactional mixtures depending on the type of catalytic test (total flow: 150 mL min<sup>-1</sup>).

Catalytic test	NO (ppm)	NH₃(ppm)	H <sub>2</sub> (%)	O <sub>2</sub> (%)	N <sub>2</sub>
H <sub>2</sub> -SCR	400	-	1	2	balance
NO+H <sub>2</sub> reaction	400	-	1	-	balance
NH₃-SCR	400	400	-	2	balance
NH <sub>3</sub> oxidation	-	400	-	2	balance



### **Results and Discussion**

As expected, the NO<sub>X</sub> conversion in H<sub>2</sub>-SCR conditions (Fig. 1A) showed a volcano-shaped curve. The conversion started below 50 °C, with N<sub>2</sub>O as main product. Interestingly, despite a high WHSV of 300 L h<sup>-1</sup>/g<sub>cata</sub> (30 mg catalyst, total flow rate of 150 mL min<sup>-1</sup>), some ammonia was detected from 70 °C, with a maximum yield recorded near 100 °C. At this temperature complete NO<sub>X</sub> conversion was achieved, with N<sub>2</sub> emerging as the main reduction product. At higher temperatures, a secondary N<sub>2</sub>O emission was observed. To explain these complex profiles, especially the role of NH<sub>3</sub> as possible intermediate and the origin(s) of the undesired N<sub>2</sub>O emission, various reaction mixtures were used to study the NH<sub>3</sub> formation and its reactivity.

Removing oxygen (NO+H<sub>2</sub> reaction, Fig. 1B) had no influence in the 50-100 °C temperature range, indicating that the actives sites were mainly covered by NO<sub>x</sub> species, with N<sub>2</sub>O as the main reaction product (accordingly, H<sub>2</sub> conversion was shifted to lower temperature when NO was removed from the reaction mixture, results not shown). The NH<sub>3</sub> emission started near 70 °C, consistent with the H<sub>2</sub>-SCR conditions (Fig. 1A). Considering the ammonia reactivity, the NH<sub>3</sub>-SCR (Fig. 1C) can occur from 70 °C, exhibiting significant activity from 100 °C. However, this reaction within the H<sub>2</sub>-SCR process can only proceed when both NH<sub>3</sub> and NO<sub>x</sub> are available simultaneously, which is possible only in a very narrow range (Fig 1A, also confirmed varying the involved catalytic mass from 5 to 200 mg). Moreover, the distribution of N<sub>2</sub> and N<sub>2</sub>O in the 100-350 °C temperature range in NH<sub>3</sub>-SCR did not match with the results observed in H<sub>2</sub>-SCR (Fig. 1A). On the contrary, the second N<sub>2</sub>O emission wave observed in H<sub>2</sub>-SCR (Fig. 1D). An overview of the H<sub>2</sub>-SCR reaction pathways depending on the temperature is proposed in Fig. 1E, highlighting the NH<sub>3</sub> reaction routes.



**Figure 1:** 0.3% Pt/5%SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalytic behavior (C: conversion; Y: yield) depending on the reaction mixture reported in Table 1 and proposed H<sub>2</sub>-SCR reaction scheme depending on the temperature.

## References

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