



# A comparative study of the H<sub>2</sub>-assisted selective catalytic reduction of nitric oxide by propene over noble metal (Pt, Pd, Ir)/γ-Al<sub>2</sub>O<sub>3</sub> catalysts



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## ABSTRACT

The impact of H<sub>2</sub> as additional reducing agent on the SCR of NO with C<sub>3</sub>H<sub>6</sub> in excess oxygen, was comparatively explored over low noble metal loading (0.5 wt%), Pt/γ-Al<sub>2</sub>O<sub>3</sub>, Pd/γ-Al<sub>2</sub>O<sub>3</sub>, Ir/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. To gain insight into the role of H<sub>2</sub>, the reactions NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> (R#1), NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> + H<sub>2</sub> (R#2), NO + H<sub>2</sub> + O<sub>2</sub> (R#3) were employed. In respect to propene oxidation, the Pd > Pt > Ir sequence was obtained under R#1, since they exhibit complete conversion at 220, 250, 325 °C, respectively; all metals exhibit moderate deNO<sub>x</sub> performances (X<sub>NO</sub>, <40%). H<sub>2</sub> co-presence (R#2) promotes both the NO and C<sub>3</sub>H<sub>6</sub> conversions, which is valid in the whole temperature interval investigated (50–400 °C), being more substantial for Pt/γ-Al<sub>2</sub>O<sub>3</sub> and Ir/γ-Al<sub>2</sub>O<sub>3</sub>, less beneficial for Pd/γ-Al<sub>2</sub>O<sub>3</sub>. A two-maxima feature is obtained on X<sub>NO</sub> pattern (at ~100 and ~230 °C) of Pt and Pd during R#2. The low temperature maximum—attributed to NO reduction by H<sub>2</sub>—is substantially more pronounced on Pt than Pd, offering X<sub>NO</sub> ~90% and S<sub>N<sub>2</sub></sub> ~85%; the high temperature maximum—attributed to NO reduction by C<sub>3</sub>H<sub>6</sub>—is higher by ~15% on both Pt and Pd, in respect to the values obtained during R#1, while S<sub>N<sub>2</sub></sub> remained unaffected. Different X<sub>NO</sub> pattern with one maximum is obtained over Ir, implying a synergistic interaction between H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>. This synergy is accompanied by a substantial widening of the NO reduction window toward lower temperatures and a considerable increase on both X<sub>NO,max</sub> and S<sub>N<sub>2</sub></sub> (from X<sub>NO</sub> ~30% with S<sub>N<sub>2</sub></sub> ~55% during R#1 to X<sub>NO</sub> ~70% with S<sub>N<sub>2</sub></sub> ~95% during R#2). The specific features of all reactions and metals employed are comparatively discussed.

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## 1. Introduction

Non-stoichiometric lean-burn engines have recently gained considerable attention, due to their advantages in relation to fuel efficiency and CO<sub>2</sub> emissions. Consequently, significant research efforts have been devoted to the SCR of NO<sub>x</sub> by hydrocarbons under lean-burn conditions [e.g. 1–4]. However, the three-way converters (TWCs), which are highly efficient in controlling NO, CO and hydrocarbon emissions from conventional gasoline-fueled vehicles that operate close to stoichiometric conditions, have been found to be insufficient under conditions of excess oxygen [e.g. 1–8].

Supported noble metal catalysts—typically bimetallic Pt/Rh and Pd/Rh constitutions supported on (BaO, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, etc)-enriched Al<sub>2</sub>O<sub>3</sub> carrier—remained till today the best active phases among many other alternatives in TWC technology. This situation is attributed to their adequate three-way activity (simultaneous removal of CO, NO and HCs), good steam-thermal stability and high tolerance to sulfur poisoning [7,8]. Supported noble metal catalysts are also for many years at the center of focus in the field of SCR of NO<sub>x</sub> under lean-burn conditions, in the view of their application in lean-burn gasoline or diesel engines as well as in stationary fuel combustion processes [1–8]. The NH<sub>3</sub>-SCR process, which is currently the best choice for de-NO<sub>x</sub> processes in stationary power applications and chemical plants [4–6], experiences drawbacks related to the storage and slip of ammonia, although it may be pointed out that urea (as an NH<sub>3</sub> carrier)-SCR process is now commercially available for use on diesel truck and some lighter vehicles. This reality motivates significant

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efforts for the development of novel catalytic systems, capable for the efficient lean NO<sub>x</sub> reduction using in principle the gases which already exist in the effluents as reducing agents, e.g., unburned hydrocarbons, H<sub>2</sub> or CO [1–25]. Most of these studies are once again concentrated on the use of supported Pt-group metal catalysts (in particular Pt), due to their typically high thermal/chemical stability and good de-NO<sub>x</sub> activity.

To this end, the lean propene-SCR of NO<sub>x</sub> on Pt-group metals supported on alumina, appeared to be efficient only in a very narrow temperature window ( $\Delta T \sim 100^\circ\text{C}$ ) with NO conversion values typically being below than 60%, and N<sub>2</sub>-selectivity values at the maximum NO conversion less than  $\sim 40\%$ . These achievements are far away from those required for practical applications. More specifically, the active deNO<sub>x</sub> windows of both Pt and Pd appear at similar temperatures (typically close to 250–300 °C) and suffer by low N<sub>2</sub>-selectivities, whereas, the lean deNO<sub>x</sub> activity of Ir-based catalysts is taking place at higher temperatures (ca. 400–600 °C), accompanied, however, by better N<sub>2</sub>-selectivity values [e.g., 2,20–22]. In addition, Pt and Pd forms N<sub>2</sub> only in the presence of a reductant, in contrast to Ir where N<sub>2</sub> is formed under conditions where the reducing agent is completely consumed [2,20–26]. The Pt- and Pd-catalysed NO + C<sub>3</sub>H<sub>6</sub> (+ excess O<sub>2</sub>) reactions have been found to be subjected to promotional effects (by alkalis), that substantially improve the de-NO<sub>x</sub> performance [9,10,12]. The same promoter species, however, were found to inhibit the Ir-catalyzed reaction [11,25].

Another interesting trend of the Pt-group metals catalyzing lean NO<sub>x</sub> reduction, that gained considerable interest in the last years, is the use of H<sub>2</sub> or more importantly, the employment of both H<sub>2</sub> + CO as reducing agents [27–42]. Most of the studies were once again concentrated on Pt, until the pioneering work of Lambert and coworkers [37–41], who turned the interest on Pd-based catalysts as well; they revealed that Pd is very efficient for the lean NO<sub>x</sub> reduction by H<sub>2</sub> + CO, overcoming some of the intrinsic catalytic weaknesses of Pt, as for example the poisoning influence of CO at high CO:H<sub>2</sub> ratios. Support-mediated promotional effects induced by TiO<sub>2</sub> incorporation onto the  $\gamma\text{-Al}_2\text{O}_3$  support of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was the key point for this effective catalysis [40,41]. Later on, Konsolakis et al. [42] further improved the performance of Pd on this process, by developing a doubly-promoted Pd(K)/Al<sub>2</sub>O<sub>3</sub>-(TiO<sub>2</sub>) catalyst, which successfully combines, in a synergistic manner, support-mediated promotion (by TiO<sub>2</sub>) with surface induced promotion (by K). The resulted benefits with this novel doubly-promoted catalyst were the high NO<sub>x</sub> conversion (ca. 85%) accompanied by promising N<sub>2</sub>-selectivities (ca. 85%) in a wide temperature window (ca. 150–350 °C) [42].

Apart from the aforementioned efforts on the lean NO<sub>x</sub> reduction by H<sub>2</sub> + CO, and to the best of our knowledge, the study of the Pt-group metals catalyzed SCR of NO<sub>x</sub> with hydrocarbons + H<sub>2</sub> as the reducing agent mixture is absent. Only few studies concerning the H<sub>2</sub>-assisted, lean SCR of NO<sub>x</sub> with hydrocarbons (mainly propene, propane or octane), focused on Ag catalysts, can be found in the relevant literature [e.g. 43–47].

The purpose of the present communication is to investigate for the first time, and in a comparative manner, the lean NO<sub>x</sub> reduction by propene, H<sub>2</sub> as well as by propene + H<sub>2</sub> over supported (on  $\gamma\text{-Al}_2\text{O}_3$ ), low loading (0.5 wt%), Pt, Pd and Ir catalysts. Catalyst performance evaluation was carried out in a wide temperature range (50–400 °C), under the following reaction conditions: NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> (R#1), NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> + H<sub>2</sub> (R#2) and NO + H<sub>2</sub> + O<sub>2</sub> (R#3). Moreover, complementary characterization studies involving N<sub>2</sub> physisorption (BET method), hydrogen temperature programmed reduction (H<sub>2</sub>-TPR), X-ray diffraction (XRD) and electron microscopy techniques [transmission (TEM) and scanning transmission (STEM)] were carried out to gain insight into the H<sub>2</sub>-induced enhancement on C<sub>3</sub>H<sub>6</sub>-SCR of NO<sub>x</sub> over Pt-group metals.

## 2. Experimental

### 2.1. Catalysts preparation, characterization and performance evaluation

Low metal loading (0.5 wt%) Pt-, Pd- and Ir-catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$  were prepared. The  $\gamma\text{-Al}_2\text{O}_3$  carrier used in this study was prepared by precipitation, employing an aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. The pH value was raised up to 10 by adding an aqueous solution of 25 v/v% NH<sub>3</sub> and kept at this value for 3 h while stirring the solution. After filtration the derived material was dried at 110 °C for 12 h and calcined at 600 °C for 2 h, under air flow. Incorporation of the Pt, Pd and Ir active phases into the  $\gamma\text{-Al}_2\text{O}_3$  support was employed by the incipient wetness impregnation method using aqueous solutions of the Pd(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, IrCl<sub>3</sub>·H<sub>2</sub>O and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O noble metals' precursors. The derived samples were dried at 100 °C overnight and finally calcined under air flow at 600 °C for 3 h.

The as prepared catalysts were characterized by means of their textural (BET), structural and morphological (XRD, TEM, STEM) and redox (H<sub>2</sub>-TPR) characteristics. Catalyst performance evaluation, in terms of conversion and selectivity, was performed in a continuous flow, tubular, fixed-bed, quartz reactor under the desired reaction conditions (i.e., R#1: NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>, R#2: NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> + H<sub>2</sub> and R#3: NO + H<sub>2</sub> + O<sub>2</sub>).

BET surface areas ( $S_{\text{BET}}$ ) of the catalytic samples were determined by the N<sub>2</sub> adsorption-desorption isotherms at  $-196^\circ\text{C}$  using the Nova 2200e (Quantachrome) flow apparatus, according to Brunauer-Emmett-Teller (BET) method at the relative pressure in the range of 0.05–0.30. The total pore volume calculation was based on nitrogen volume at the highest relative pressure, whereas the average pore size diameter was determined by the BJH method. Prior to measurements the samples were degassed at 350 °C for 5 h under vacuum.

X-ray powder diffraction (XRD) on a Siemens D 500 diffractometer at 40 kV and 30 mA with Cu K $\alpha$  radiation ( $\lambda = 0.154\text{ nm}$ ) was employed to determine the catalysts crystalline structure. Diffractograms were recorded in the  $2\theta = 2\text{--}80^\circ$  range at a scanning rate of 0.02° over 2 s. The Scherrer equation, if applicable, was employed to determine the particle size of different phases based on their most intense diffraction peaks.

High resolution transmission electron microscopy (HRTEM), carried out in a JEOL 2011HRTEM, operating at 200 kV, with a point resolution of 0.23 nm was used for the structural characterization of the catalysts. Elemental analysis was performed by means of the energy-dispersive X-ray spectroscopy (EDS), using an Oxford Instruments INCAx-sight liquid nitrogen cooled detector with an ultrathin window. Samples for microscopy observations were prepared by gently grinding the catalyst powders in high-purity ethanol using an agate pestle and mortar. A drop of the solution was subsequently deposited onto a lacey C-film supported on a Cu grid and allowed to evaporate under ambient conditions. In addition, high resolution scanning transmission electron microscopy (HRSTEM) was performed using a JEOL 2100F 200 kV FEG-STEM/TEM equipped with a CEOS Cs corrector on the illumination system. The geometrical aberrations were measured and controlled to provide less than a  $\pi/4$  phase shift of the incoming electron wave over the probe-defining aperture of 17.5 mrad. High angle annular dark-field (HAADF) HRSTEM images were acquired on a Fischione Model 3000HAADF detector with a camera length such that the inner cut-off angle of the detector was 50 mrad. The scanning acquisition was synchronized to the 60 Hz AC electrical power to minimize 60 Hz noise in the images and a pixel dwell time of 15.8  $\mu\text{s}$  was used.

H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) measurements were performed by loading 100 mg of catalyst in a quartz fixed bed

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