



Selective catalytic reduction of NO by H₂/C₃H₆ over Pt/Ce_{1-x}Zr_xO_{2-δ}: The synergy effect studied by transient techniques



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ABSTRACT

A series of Pt/Ce_xZr_{1-x}O_{2-δ} (x = 0.4–0.6) solids were synthesized and evaluated for the SCR of NO under lean burn conditions (2.5 vol% O₂) using C₃H₆ and H₂ as reducing agents. SSITKA-Mass Spectrometry, SSITKA-DRIFTS and other *in situ* DRIFTS experiments were conducted for the first time to gather fundamental information in explaining the remarkable H₂/C₃H₆ synergy effect towards steady-state selective reduction of NO into N₂ at T > 400 °C. In particular, the chemical structure of adsorbed *active* and *inactive* (spectator) NO_x species formed under C₃H₆-SCR, H₂-SCR and H₂/C₃H₆-SCR of NO and the surface coverage and site formation of *active* NO_x were probed. The Pt/Ce_{1-x}Zr_xO_{2-δ} catalysts present significant differences in their H₂-SCR performance (NO conversion and N₂-selectivity) in the low-temperature range of 120–180 °C but practically the same catalytic behavior at higher temperatures. It was proved that the *active* NO_x of the H₂-SCR path reside within a reactive zone around each Pt nanoparticle which extends to *less than one lattice constant* within the support surface. The chemical structure of the *active* intermediate was proved to be the *chelating nitrite*, whereas nitrosyl, monodentate and bidentate nitrates were considered as inactive species (spectators). It was illustrated for the first time that the presence of 15 vol% H₂O in the H₂-SCR feed stream applied over the 0.1 wt% Pt/Ce_{0.5}Zr_{0.5}O₂ catalyst results in a 25% decrease in the concentration of *active* NO_x, thus partly explaining the drop in activity observed when compared to the H₂-SCR in the absence of H₂O. A remarkable activity and N₂-selectivity enhancement was observed at T > 400 °C when both H₂ and C₃H₆ reducing agents were used compared to H₂-SCR or C₃H₆-SCR alone. This *synergy effect* was explained to arise mainly because of the increase of θ_H by the presence of -CH_x species derived from adsorbed propylene decomposition on Pt, which block sites of oxygen chemisorption, and of the increase of surface oxygen vacant sites that promote the formation of a more active chelating nitrite (NO₂⁻) species compared to the case of H₂-SCR.

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1. Introduction

In spite of the fact that considerable research has been devoted to the selective catalytic reduction of NO_x by hydrocarbons under lean-burn conditions for mobile applications (HC-SCR) [1–6], this technology has not yet found application. Instead, the development of lean NO_x trap (LNT) for gasoline and of the urea-SCR for diesel vehicles (especially heavy-duty trucks) to meet current NO_x emissions standards are the current de-NO_x technologies, which are subjected to further improvements [4,7].

The beneficial role of H₂ in HC-SCR has first been reported on Ag-based catalysts [8–14] and recently only in C₃H₆-SCR over alumina-supported Pt, Pd and Ir catalytic systems [15]. Further investigations in HC/H₂-SCR with novel catalyst formulations for lean-burn applications, where H₂/HC reducing agents are found in the exhaust gas stream or can be produced on-board (e.g. diesel or gasoline lean burn engines) should therefore be considered. Low-temperature (120–200 °C) H₂-SCR on a 0.1 wt% Pt/CeO₂ catalytic system with a wide temperature window of operation (e.g. NO-conversion >50%) and N₂-selectivities in the 40–80%-range has been reported [16]. Furthermore, platinum-free WO_x-promoted Ce_{1-x}Zr_xO₂ solids were investigated for the first time towards H₂-SCR [17], where NO-conversions in the 30–50% range and N₂-selectivities larger than 80% were reported in the temperature range of 200–450 °C. These catalytic systems might be considered to

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serve as reference for future catalyst developments (based on low-loading Pt or Pd) towards lean-burn applications, if modified ceria supports and the use of gas mixtures with an appropriate ratio of H_2/HC reducing agents of NO_x are used.

The role of C_3H_6 , CO and H_2 on the efficiency and selectivity of NO_x storage reduction (NSR) process over a 2.1 wt% Pt/ CeO_2 -Zr O_2 catalyst has been investigated [18]. It was concluded that the presence of such reducing agents in the lean gas mixture can lead to the competition between NO_x storage and reduction steps. Also, the N_2O selectivity is a strong function of reaction temperature and reductant species [18]. In a recent work [6], temporal analysis of products (TAP) was used to study the NO reduction to N_2 over H_2 - and C_3H_6 -reduced (La, Zr)-doped CeO_2 at 560 °C with the goal to understand the lean de- NO_x catalytic chemistry by hydrocarbons. It was found [6] that a C_3H_6 -reduced solid outperformed that of H_2 -reduced owing to the deeper degree of reduction and the presence of carbonaceous deposits. No evidence was found that these carbonaceous residues play a direct role in the NO conversion. Their role was to extend the effectiveness of the catalyst in the conversion of NO under lean burn conditions by creating new oxygen vacancies responsible for the decomposition of NO into N_2 gas. The carbonaceous deposits are preferentially oxidized to CO_2 by lattice oxygen species of the (La, Zr)-doped CeO_2 solid [6].

In the present work we report the effect of the use of a mixture of H_2 and C_3H_6 reducing agents of NO in the presence of 2.5 vol% O_2 and in the 150–600 °C range over 0.1 wt% Pt supported on $Ce_{1-x}Zr_xO_{2-\delta}$ carriers. A strong remarkable synergy effect was found in the 450–600 °C range, which resulted practically in the complete conversion of NO into N_2 gas (N_2 -selectivities >97%). At temperatures lower than 450 °C, the H_2 -SCR appears as the most effective de- NO_x process over this catalytic system. In order to promote the fundamental knowledge on the intrinsic reasons that lead to the observed remarkable synergy effect between H_2 and C_3H_6 towards NO_x reduction, SSITKA (use of ^{15}NO isotope gas) coupled with *in situ* Mass Spectrometry and DRIFTS and other transient experiments were conducted for the first time. In particular, the focus of the present investigation was to obtain information on important kinetic parameters, such as: (a) the chemical structure of adsorbed *active* and *inactive* (spectator) NO_x species under C_3H_6 -SCR, H_2 -SCR and H_2/C_3H_6 -SCR and (b) the surface coverage and location (Pt or support) of *active* NO_x .

2. Experimental

2.1. Catalyst preparation

The synthesis of $Ce_{1-x}Zr_xO_{2-\delta}$ supports ($x=0.4-0.6$ or $Ce/Zr=0.67-1.5$) was carried out using the citrate sol-gel method. Appropriate amounts of $Ce(NO_3)_3$ (Fluka) and $ZrO(NO_3)_2$ (Across) were dissolved in water and citric acid ($C_6H_8O_7 \cdot H_2O$, Merck) was then added under continuous stirring. The resulting solution was stirred under vacuum for gradual evaporation of water at 60 °C. The final gel was dried under CO_2 supercritical conditions (180 atm and 80 °C) and the solid product obtained was then calcined in air from room T to 500 °C at the heating rate of 0.5 °C min^{-1} . The supported Pt catalysts were prepared by impregnating the $Ce_{1-x}Zr_xO_{2-\delta}$ supports with a given amount of aqueous solution of $H_2Pt^{IV}Cl_6$ (Aldrich) so as to obtain the desired 0.1 wt% Pt loading. After gradual evaporation of water at 70 °C for 4 h, the resulting slurry was dried at 120 °C overnight and then calcined in a furnace (ELF 11/6, Carbolite, static air) at 500 °C for 2 h (heating rate of 50 °C min^{-1} from 25 to 500 °C). Prior to any catalytic measurements, the fresh catalyst sample was pretreated with 20 vol% O_2/He (50 $NmL \cdot min^{-1}$) at 500 °C for 2 h followed by reduction in 25 vol% H_2/He (50 $NmL \cdot min^{-1}$) at 220 °C for 2 h.

2.2. Catalyst characterization

2.2.1. Textural and X-ray diffraction studies

The $Ce_{1-x}Zr_xO_{2-\delta}$ supports were characterized for their texture by the physical adsorption method (adsorption of N_2 at 77 K) using a Micromeritics Gemini III surface area and pore size analyzer. The specific surface area (SSA, $m^2 \cdot g^{-1}$, BET method) of the solid supports was measured after the sample was degassed in N_2 gas at 350 °C for 2 h. The primary mean crystallite size of the $Ce_{1-x}Zr_xO_{2-\delta}$ solids was estimated from powder XRD studies (particles in powder form with less than 100 μm in size; Shimadzu 6000 diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$)) and after using the Scherrer formula. X-ray diffractograms were recorded in the 10–80° 2θ range with a step scan of 2° min^{-1} . *In situ* XRD studies were performed over the fresh catalyst samples after treatment with a 20 vol% O_2/He (50 $NmL \cdot min^{-1}/2 h$) gas mixture in the 200–600 °C range followed by 25 vol% H_2/He (50 $NmL \cdot min^{-1}/2 h$) gas treatment in the 200–600 °C range.

2.2.2. X-ray photoelectron spectroscopy (XPS) and Raman studies

The surface oxidation state and composition (atom-%) of cerium in the three $Ce_{1-x}Zr_xO_{2-\delta}$ - supported Pt ($x=0.4-0.6$ or $Ce/Zr=0.67-1.5$) solids was investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis). The excitation was performed by using a conventional dual anode X-ray source (Specs XR 50, Mg $K\alpha$ line (1253.6 eV)). Fitting and integration of X-ray photoelectron peaks were performed by using the commercial software CASAXPS (CASA software Ltd). Raman spectroscopy was used to characterize the oxygen sub-lattice of $Ce_{1-x}Zr_xO_{2-\delta}$ solids before and after reaction conditions (*ex situ*). Raman spectra were recorded using a Horiba Jobin Yvon-Labram HR UV-vis-NIR (200–1600 nm) Raman Microscope Spectrometer and a laser with a wavelength of 632 nm. The spectra recorded were the average of 10 scans at the resolution of 2 cm^{-1} .

2.2.3. H_2 temperature-programmed desorption (TPD) studies

The dispersion of Pt metal in the 0.1 wt% Pt/ $Ce_{1-x}Zr_xO_{2-\delta}$ solids was determined by selective H_2 chemisorption at 25 °C followed by temperature-programmed desorption (TPD) in He flow (30 $NmL \cdot min^{-1}$) previously described [19,20]. A 0.5-g fresh catalyst sample was first calcined in a 20 vol% O_2/He gas mixture (50 $NmL \cdot min^{-1}$) at 500 °C for 2 h and then reduced in pure H_2 (50 $NmL \cdot min^{-1}$) at 220 °C for 2 h. Quantitative analysis of the effluent gas stream from the microreactor was performed using an *on line* quadrupole mass spectrometer (Omnistar, Balzers) equipped with a fast response inlet capillary/leak valve (SVI050, Balzers) and data acquisition systems. A $H/Pt_s = 1$ for hydrogen chemisorption stoichiometry was considered.

2.3. Catalytic performance studies

The gas flow-system used for performing catalytic studies consisted of a flow measuring and control system (mass flow controllers, MKS Instruments, Model 47C), mixing chambers and a quartz fixed-bed microreactor (~ 2 mL nominal volume) [19,21]. Analysis of the dry effluent gas stream from the reactor was performed using mass spectrometer (Balzers, model Omnistar, $amu = 1-300$) for H_2 ($m/z=2$) and O_2 ($m/z=32$) and NO_x chemiluminescence analyzer (Thermo Electron Corporation, model 42C) for NO and NO_2 . An *on line* infrared gas analyzer (Teledyne Analytical Instruments, model IR 7000) was used for the measurement of N_2O [22]. A mass of 0.3 g of catalyst (powder, $0.1 < d_p < 0.2 \text{ mm}$) and a total volume flow rate of 200 $NmL \cdot min^{-1}$, resulting in a GHSV of 33,000 h^{-1} ($L/L_{cat,bed}/h$) were used. The feed concentrations regarding NO and O_2 were kept constant at the level of 150 ppm and 2.5 vol%, respectively, whereas those of H_2 and C_3H_6

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