



Mechanistic aspects (SSITKA-DRIFTS) of the catalytic denitrification of water with hydrogen on Pd-Cu supported catalysts



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ABSTRACT

Detailed mechanistic studies (ex-situ SSITKA-DRIFTS) have been performed on 1 wt.% Pd-0.5 wt.% Cu/ γ -Al₂O₃ and 1 wt.% Pd-0.5 wt.% Cu/TiO₂-Al₂O₃ catalysts concerning the NO₃⁻/H₂ and NO₃⁻/H₂/O₂ reactions, in order to elucidate the promoting role of TiO₂ and O₂ in suppressing the unwanted NH₄⁺ production in water media. It is demonstrated, for the first time ever, that the mechanism of N₂ production strongly depends on the nature of the support and the presence of O₂ (air) in the gas feed stream. In particular, these parameters were found to significantly affect the formation of different adsorbed active intermediate N-species on the support or/and metal (Pd, Cu) surface, providing documentary information about the signalling pathways leading to the formation of NH₄⁺ and N₂. This study provides for the first time ever, an *alternative stepwise pathway* for the reduction of NO₂⁻(ads) to NO_(ads) and further to N₂ on the support or metal-support interface (metal cation sites), instead of Pd metal surface. Based on the results of the present work, it is concluded that the reduction of NO₂⁻(ads) species is favoured on partially oxidized Pd (when adequate supply of oxygen is available). In the case of Pd-Cu/TiO₂-Al₂O₃ (NO₃⁻/H₂), both adsorption and reduction of NO₂⁻(ads) take place on the support surface leading to the formation of NO_(ads) on TiO₂ (Ti⁴⁺-NO or Ti⁴⁺-NO⁺), which in turns leads to enhanced N₂ production. In addition, the latter system exhibits greatly enhanced selectivity towards N₂, under oxidizing conditions, possibly due to the interaction of NO_x species (e.g., Pd-NO/N, Ti⁴⁺-NO/NO⁺) at the metal-support interface. On the contrary, in the absence of both titanium dioxide in the support and oxygen in the feed, the sequential reduction of NO₃⁻(ads) takes place on different active sites of the catalyst surface, indicating that H₂ is easily dissociated on Pd particles and then spills over onto the Cu and the metal oxides (support), and secondly that NO_(ads) is possibly diffused from the support to adjusted Pd sites, for further reaction. These mechanistic findings are very important as they reveal, for the first time ever, the active involvement of the support in the reaction mechanism and its positive effect on N₂ production.

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1. Introduction

Although several strategies have been proposed and examined to prevent unwanted release of ammonium ions (NH₄⁺), as the main by-product of the hydrogenation of nitrates in aqueous media, none of them actually led to any great success. Therefore, a complete understanding of the key steps of the reaction mechanism regulating this process is critical in order to determine the main factors governing the reaction selectivity over Pd-Cu supported catalysts

on various metal oxides. The mechanism of the catalytic reduction of nitrates over bimetallic Pd-Cu catalysts with H₂ has been proposed as a stepwise process consisting of two main steps: (i) hydrogenation of nitrates to nitrites on Pd-Cu clusters, where the role of the noble metal is to dissociate molecular hydrogen, thus enabling copper-nitrate reduction, and (ii) the conversion of nitrite ions to nitrogen and ammonia on Pd sites via NO intermediates [1–8]. Based on literature data [6,7], adsorbed NO on Pd is considered as the key intermediate in the production of the desired (N₂) and undesired (NH₄⁺) products. Particularly, an in situ ATR-IR spectroscopic study on nitrites reduction over Pd/Al₂O₃ indicated the formation of NO on Pd surface [7]. The latter was also confirmed by Zhang et al. [1], based on ¹⁵N₂⁻ isotopic labelling

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experiments coupled with a GC–MS, over Pd–In/Al₂O₃ catalyst. Many studies have been conducted to verify the potential reaction pathway towards N₂ in the catalytic hydrogenation of nitrates [6–8]. The formation of nitrogen via NO as the main intermediate was found to occur through several paths. Recent advances showed that N₂ appears to be produced by desorption-mediated reaction of NO and atomic N [9–11]. The most compelling evidence to date for N formation has been obtained from Ultraviolet Photoelectron Spectroscopy (UPS); claiming that atomic N is generated via the surface catalytic reaction of NO with H₂, and not through the dissociation of NO on Pd [12]. Moreover, it was found that ammonium is formed through a series of sequential reactions involving the formation of intermediate atomic N as a first step (NO + H₂) [13], followed by subsequent reaction of N with H [14]. However, only a few related studies [8,15] were undertaken to provide information regarding the nature and the fate of the adsorbed surface N-species formed during nitrates reduction, due to the difficulty of using such technologies (e.g., DRIFTS) in aqueous media. In this respect, Sa and Anderson [8] studied the mechanism of nitrate reduction over Pd/TiO₂ catalyst using infrared spectroscopy (FTIR). The IR measurements were performed with a high concentration of pre-adsorbed species and with very low water flow rates (in the form of water vapour). The reactivity of adsorbed species towards H₂ as determined by FTIR increases in the following order, NO₃⁻ < NO₂⁻ < NO. Nitrate and nitrite were found to be selectively adsorbed at Lewis acid sites on titania following exchange with OH⁻, and reduction by Ti₄O₇ and Pd, respectively. On the contrary, NO was adsorbed on both the support and the metal, while it was reduced exclusively on Pd sites. In this case, hydrogen was dissociated on Pd, and migrated (spill over) onto the support activating the reduction of nitrates, thus indicating a strong metal-support interaction.

In previous preliminary studies it has been shown that the mechanistic pathway of nitrates reduction can be adequately traced using a modified *ex situ* DRIFTS experimental analysis [15–17]. DRIFTS studies indicated the formation of different active nitrogen containing species (in the term of reactivity) on catalyst surface (metal sites and metal-support interface) depending on the chemical composition of the support and the reaction conditions. Although DRIFTS studies were performed to assess the reactivity of intermediate N-species formed during catalytic reduction of NO₃⁻ with H₂ in aqueous media, this technique by itself, cannot provide experimental proof on the actual active species formed and the elementary steps of the reaction. Such a deep fundamental understanding of catalytic reactions is of prime importance for catalyst development. Steady State Isotopic Transient Kinetic Analysis (SSITKA) has been considered as the most powerful technique in performing mechanistic studies for heterogeneous gas-solid catalytic reactions. However, up to date, no studies concerning the catalytic mechanism of aqueous nitrate reduction has been reported by using the SSITKA–DRIFTS technique. The present work aims to provide documentary information about the signalling pathways leading to NH₄⁺ and N₂ production. Such information can ultimately result to better catalysts design to present high selectivity towards the desired product (N₂). In particular, a combined SSITKA–DRIFTS technique has been applied to study essential mechanistic aspects of the reaction at hand. SSITKA experiments, with the use of ¹⁵NO₃⁻ stable isotope, coupled with *ex situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were conducted on 1 wt.% Pd–0.5 wt.% Cu/γ–Al₂O₃ and 1 wt.% Pd–0.5 wt.% Cu/TiO₂–Al₂O₃ catalysts after specific reactions conditions (100 vol.% H₂ or 80 vol.% H₂/20 vol.% air) in order to determine: (a) the chemical structure of adsorbed active and inactive (spectator) N-species, (b) the location of active N-species (metal phase or support) and (c) the fate of intermediate N-species in nitrate reduction.

It is demonstrated that essential aspects of the mechanism of N₂ and NH₄⁺ formation strongly depend on the nature of the *catalyst support* and the *feed composition* as well. It was proven, for the first time, that the chemical composition of the support has a great impact on the fate of intermediate $M_{Pd}^{dormetalcationofthesupport} - NO_x$ species (e.g., linear NO, NO⁺), leading to the production of N₂ versus NH₄⁺.

2. Experimental section

2.1. Catalysts preparation and characterization

In the present work, two bimetallic catalysts i.e., 1 wt.% Pd–0.5 wt.% Cu/γ–Al₂O₃ and 1 wt.% Pd–0.5 wt.% Cu/TiO₂–Al₂O₃, were prepared and examined towards the NO₃⁻/H₂ and NO₃⁻/H₂/O₂ reactions. Coated γ–alumina spheres with 5 wt.% metal oxide (TiO₂) loading were prepared by immersing commercial γ–alumina spheres (d = 1.8 mm, Sasol, 604130) in a 2-propanol solution containing the desired amount of metal oxide precursor Ti[OCH(CH₃)₂]₄ (Aldrich). The spheres were left in solution for 24 h under mild stirring at room temperature. The impregnated alumina spheres were first dried at 120 °C and then calcined at 500 °C for 4 h prior metal (Pd and Cu) deposition. The effectiveness of the alumina-coating procedure described above and the effect of several experimental parameters on it were examined by Scanning Electron Microscopy–Dispersive X-ray (SEM–EDX) and Inductively Coupled Plasma – Mass Spectrometry (ICP–MS).

The supported bimetallic catalysts were prepared by a standard impregnation method using aqueous precursor solutions in order to obtain a palladium loading of 1 wt% and a copper loading of 0.5 wt.% Pd was initially deposited on the coated γ–alumina spheres by the incipient wetness impregnation method using Pd(NO₃)₂ (Aldrich) as precursor of palladium metal. After impregnation and drying at 120 °C, the solid samples were calcined in air at 500 °C for 4 h. The resulting monometallic solid was then impregnated with an aqueous solution of Cu(NO₃)₂ (Aldrich). After impregnation of Cu and drying at 120 °C, the resulting solid catalyst was calcined in air at 500 °C for 4 h prior use.

Scanning Electron Microscopy (SEM) studies were performed on the fresh solid catalyst after calcination. SEM analyses revealed that the above mentioned experimental procedure led to a uniform metal (Pd and Cu) distribution on alumina spheres. Pd and Cu dispersion and mean particle size were also determined by selective chemisorption of H₂ at 25 °C according to the following procedure: After calcination in a 20%O₂/He gas mixture at 500 °C for 2 h, the catalyst was reduced in H₂ (1 bar) at 300 °C for 2 h. The feed was then changed to He and the temperature was increased to 500 °C in He flow until no hydrogen desorption was observed. A possible H-spillover that might have taken place at 300 °C was eliminated by the latter procedure. The reactor was then quickly cooled in He flow to 25 or 200 °C and the feed was changed to a 1%H₂/He gas mixture for 30 min. The feed was then changed back to He and kept at 25 or 200 °C for 5 min before the temperature of the catalyst was gradually increased to 600 °C (30 deg/min) to carry out a TPD (Temperature Programmed Desorption) experiment. From the amount of hydrogen desorbed, the amount of metal (m: Pd or Cu) in the sample, and assuming H/m_s = 1:1, the dispersion of metal was estimated. The actual Pd and Cu loadings (wt%) were measured by Atomic Absorption Spectroscopy (AAS) using a PG – 90 AA Spectrophotometer or Inductively Coupled Plasma – Mass Spectrometry (ICP–MS).

The specific surface area of the commercial metal oxide supports used was examined by N₂ adsorption at 77 K (BET method) using a multi-point Micromeritics Gemini V System.

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