ABSTRACT

The present research involves a detailed fundamental study of the selective catalytic reduction of nitrates (NO$_3^-$) in water mediums towards N$_2$ formation with H$_2$ in the presence of O$_2$ over Pd-Cu catalysts in a three-phase continuous flow stirred tank reactor. The current work reports, for the first time ever, that the selectivity of the reaction at hand can by adjusted by regulating the flow rate of the liquid medium (e.g., nitrates solution) in a CSTR process. Reaction selectivity towards N$_2$ as high as 96%, can be obtained under certain experimental conditions. Moreover, detailed mechanistic studies (SSTIKA-DRIFTS) have been performed on 1wt% Pd-0.5wt% Cu/γ-Al$_2$O$_3$ and 1wt% Pd-0.5wt% Cu/TiO$_2$-Al$_2$O$_3$ catalysts concerning the NO$_3^-$/H$_2$ and NO$_2$/$\text{H}_2$/O$_2$ reactions, in order to elucidate the promoting role of TiO$_2$ and O$_2$ in suppressing the unwanted NH$_4^+$ production. It is demonstrated, for the first time ever, that the mechanism of N$_2$ production strongly depends on the nature of the support and the presence of O$_2$ in the gas feed stream. Our present mechanistic results are consistent with findings in catalytic studies showing remarkable positive effect of the above parameters on the reaction’s selectivity towards nitrogen. In the case of oxygen, the reaction’s selectivity towards NH$_4^+$ was reduced by almost 60% after introducing 20 vol.% air in the reductive 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. Active adsorbed ionic nitrates were found to be on Cu, under any studied reaction conditions. Bidentate nitrates were proven to be active on Pd metal surface when oxygen is present in the gas feed stream. On the contrary, adsorbed bidentate nitrates on the support were determined to be active towards the NO$_3^-$/$\text{H}_2$ reaction. Based on the above results, it is therefore concluded that the reduction of bidentate nitrates is favoured on partially oxidized Pd, when the supply of oxygen is adequate for the reaction demands (<30 vol % air). One active intermediate species (linear NO) on Pd was identified to be involved in the reaction pathway towards N$_2$ formation on Pd-Cu/γ-Al$_2$O$_3$. The latter species were also observed in the case of Pd-Cu/TiO$_2$-Al$_2$O$_3$. In addition, adsorbed nitrosyls (NO$^+$) on the support were found to be active in the case of the NO$_3^-$/$\text{H}_2$/O$_2$ reaction over Pd-Cu/TiO$_2$-Al$_2$O$_3$. Moreover, adsorbed NOH species on Lewis acid sites of TiO$_2$ (Ti$^{4+}$-NO/NOH) have been considered as the active intermediates, subsequently leading to the formation of the undesired NH$_4^+$ in the case of Pd-Cu/TiO$_2$-Al$_2$O$_3$, while the same species appeared to be inactive on Pd-Cu/γ-Al$_2$O$_3$. Summarizing the above, the present work provides solid mechanistic evidence for the involvement of support in the overall reaction mechanism and the presence of a hydrogen spillover process towards the periphery of metal-support interface (location of active N-species).

Keywords: active species; catalytic denitrification; SSITKA-DRIFTS; supported Pd-Cu;
1. INTRODUCTION

Although a majority of techniques have been examined to prevent unwanted release of ammonium (NH$_4^+$) 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 to being able to determine the main factors controlling the reaction selectivity over bimetallic Pd-Cu supported catalysts. The mechanism of the catalytic reduction of nitrates over bimetallic Pd-Cu catalysts with H$_2$ has been proposed as a stepwise process consisting of two main steps: (i) hydrogenation of nitrate to nitrite 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 to nitrogen and ammonia on Pd ensembles via NO intermediates [1, 2, 3, 4, 5].

The present work aims to provide mechanistic data about the signalling pathways leading to NH$_4^+$ and N$_2$ production. In particular, a combined SSITKA-DRIFTS has been applied to study essential mechanistic aspects of the nitrate reduction sequence. SSITKA experiments, with the use of $^{15}$NO$_3^-$ stable isotope, coupled with in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were conducted on 1 wt % Pd–0.5 wt % Cu/γ-Al$_2$O$_3$ and 1 wt % Pd–0.5 wt % Cu/TiO$_2$-Al$_2$O$_3$ catalysts in order to determine (a) the chemical structure of adsorbed active and inactive (spectator) N-species formed during specific reaction conditions (NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$), (b) the location (Pd, Cu and support) of active N-species, and (c) the reactivity towards H$_2$ of N-species formed during the examined reactions.

2. EXPERIMENTAL

In the present work, two bimetallic catalysts, 1 wt % Pd–0.5 wt % Cu/γ-Al$_2$O$_3$ and 1 wt % Pd–0.5 wt % Cu/TiO$_2$-Al$_2$O$_3$ were prepared and examined towards the NO$_3^-$/H$_2$ and NO$_3^-$/H$_2$/O$_2$ reactions. The latter catalysts were prepared via modified wet impregnation method and catalytic experiments were conducted in a three-phase continuous flow stirred tank reactor (Autoclave Engineers, U.S.A., and PID Eng &Tech, Spain) equipped with a Mahoney-Robinson catalyst basket, in accordance to our previous work [6, 7, 8]. The physicochemical properties of the catalysts, the effectiveness of the alumina-coating procedure, the effect of several experimental parameters, and the surface composition of species it were thoroughly examined with a series of advanced techniques (BET, SEM-EDX, ICP-MS, SSITKA-DRIFTS).

The catalysts-reactants interactions and the potential reactive intermediates present during aqueous nitrate reduction (NO$_3^-$/H$_2$ or NO$_3^-$/H$_2$/O$_2$) were studied by infrared spectroscopy in a separate set of experiments. Steady state isotopic transient kinetic analysis (SSITKA) was used to establish the intrinsic reasons that lead to the remarkable catalytic behaviour of the Pd-Cu/TiO$_2$-Al$_2$O$_3$ in the presence of oxygen. The SSITKA (steady-state isotopic transient kinetic analysis) experiments involved the switch of the aqueous feed $^{14}$NO$_3^-$/$H_2$ or $^{14}$NO$_3^-$/$H_2$/O$_2$ to an equivalent in isotopic composition $^{15}$NO$_3^-$/$H_2$ or $^{15}$NO$_3^-$/$H_2$/O$_2$, respectively after steady state was achieved. Table 1 describes the necessary sequence of steps (SSITKA → A or B) performed for each kind of isotopic transient experiment conducted [7].
Table 1. Sequence of steps performed for SSITKA experiments

<table>
<thead>
<tr>
<th>experiment code</th>
<th>sequence of step changes of liquid flow over the catalyst sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSITKA</td>
<td>$^{14}$NO$_3$/H$_2$ or $^{14}$NO$_3$/H$_2$/O$_2$ (25 °C, 150 min) → $^{14}$NO$_3$/H$_2$/O$_2$ or $^{15}$NO$_3$/H$_2$/O$_2$ (25 °C, 150 min)</td>
</tr>
<tr>
<td>A</td>
<td>He (25 °C, 50 cc/min) → DRIFTS (5, 10, 15, 30, 45, 60 min) → He (50 °C, 15 min, 50 cc/min) → cool quickly to room temperature under He (25 °C, 50 cc/min) → background spectrum IR</td>
</tr>
<tr>
<td>B</td>
<td>background spectrum IR</td>
</tr>
</tbody>
</table>

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Perkin-Elmer Spectrum 100 spectrophotometer with the use of a high-temperature/high-pressure temperature control able DRIFTS cell (Praying Mantis™ Diffuse Reflectance Attachment, Harrick Scientific) equipped with ZnSe windows. About 40 mg (sample:Kbr = 1:1) of catalyst sample in fine powder form were used. After reaction (NO$_3$/H$_2$ or NO$_3$/H$_2$/O$_2$) or NO$_3$ adsorption from water at 25 °C, the catalyst samples were dried at room temperature in a desiccator. The total gas flow rate (He or H$_2$) in the DRIFTS cell was 50 NmL/min. For FTIR single-beam background subtraction, the spectrum of the catalyst solid in the absence of any adsorbed nitrates was taken in N$_2$ flow. FTIR spectra were collected under He or H$_2$ (gas phase) at the rate of 1 scan/s and at 2 cm$^{-1}$ resolution in the 800-2400 cm$^{-1}$ range under different temperatures (25, 100, 200, 400, 500°C) for various times (0, 5, 10, 15, 30, 45, 60 min). The averaged spectrum (40 spectra were collected) was then recorded. Spectra were analyzed by using the instrument’s Spectrum for Windows software (Perkin-Elmer).

3. RESULTS AND DISCUSSION

To gain more fundamental information concerning key aspects of the mechanism of the nitrate reduction and particularly to identify whether the active adsorbed N-species formed during the reactions at hand Steady State Isotopic Transient Kinetic Analysis (SSITKA) has been applied. This technique combined with DRIFTS can lead to the identification of the structure and the chemical composition of the active intermediate species that lead the reaction of nitrate reduction to the final products (N$_2$ and NH$_4^+$). In this SSITKA-DRIFTS study, an attempt was made to indentify various active N-species which are formed on the surface of 1 wt % Pd–0.5 wt % Cu/TiO$_2$–Al$_2$O$_3$ and 1 wt % Pd–0.5 wt % Cu/γ-Al$_2$O$_3$ catalysts during NO$_3$/H$_2$ or NO$_3$/H$_2$/O$_2$ reaction at 25°C. The adsorbed on catalytic surface N-species can either participate (active species) or not participate (inactive species or spectators) in the mechanism of the reaction. For the discrimination of the above species, as previously mentioned it is necessary to use the isotopic exchange technique called Steady State Isotopic Transient Kinetic Analysis. In the current research are presented the results of the identification of the active adsorbed intermediate N-species, which are formed in different positions on the surface of examined catalysts during various reaction conditions. More specifically, 120 minutes after the reaction ($^{14}$NO$_3$/H$_2$ or $^{14}$NO$_3$/H$_2$/O$_2$) started, at steady state isotopic exchange of the liquid feed current took place with the isotopic labelled $^{15}$NO$_3$. After a new equilibrium was established, DRIFTS spectra were taken, which were compared with the reference DRIFTS spectra taken after the reactions of $^{14}$NO$_3$/H$_2$ and $^{14}$NO$_3$/H$_2$/O$_2$. 


The observations illustrated in Figure 1 show the DRIFTS spectra that are taken under He after $^{14}\text{NO}_3$/H$_2$ or $^{14}\text{NO}_3$/H$_2$/O$_2$ reaction at 25°C. These latter spectra were used as reference for the identification of the active N-species against the spectra taken after $^{15}\text{NO}_3$/H$_2$ or $^{15}\text{NO}_3$/H$_2$/O$_2$ reaction, respectively.

As shown in Figure 1, six distinct peaks appear in the spectra under study, which were paired with the right N-species, according to literature [7]. The IR spectrum that was recorded with the Pd-Cu/Al$_2$O$_3$ catalyst after the NO$_3$/H$_2$/O$_2$ seems to be similar with the spectrum recorded after the NO$_3$/H$_2$ with the same catalyst, except for some quantitative differences. The surface coverage of the bidentate nitrates on the Pd (1642 cm$^{-1}$), bidentate nitrates on the support (1530 cm$^{-1}$) and ionic nitrates on the Cu cations (1395 cm$^{-1}$) appears to be relatively smaller in the case of NO$_3$/H$_2$/O$_2$ reaction. This result points out that the decrease of the surface coverage of Hydrogen (θ$_H$) at an Oxygen concentration of 4.2% per volume does not affect the degree of conversion of the nitrates. According to the catalytic experiments performed, the presence of oxygen in the reaction feed stream caused an increase of the conversion of the nitrates. It is also worth noting that the surface coverage of the nitrolys (NO$^+$) (2100 cm$^{-1}$) on the support decreased during the NO$_3$/H$_2$/O$_2$. As previously referred the nitrolys species are candidate precursor intermediate species of ammonia forms (eg. NOH). Oxygen seems to act as a suppressor of the NO$^+$ formation on the support, thus blocking the formation of ammonia ions. Another interesting observation made is the decrease of the surface coverage of the broad peak in the area of 1230-1000 cm$^{-1}$. This decrease is probably related to the low concentration levels of adsorbed NOH species (1165 cm$^{-1}$) on the support, which are possible precursor species of ammonia ions. These observations are directly related to the selectivity of the NO$_3$/H$_2$ reaction and further support the results from the catalytic experiments for the inhibitory action of Oxygen in the formation of NH$_4^+$. According to the catalytic studies made in the current study, the presence of Oxygen in the reaction causes significant decrease in the selectivity of the reaction towards the formation of NH$_4^+$. A further decrease in the intensity of the peaks at 1642, 1520 and 1395 cm$^{-1}$ was observed on the IR spectrum recorded for the Pd-Cu/Al$_2$O$_3$-TiO$_2$ after the NO$_3$/H$_2$. The peak at 1520 cm$^{-1}$, which corresponds to the bidentate nitrates adsorbed on the support had a significant decrease. According to the comparative results
of Figure 1, the effect of the support on the conversion factor of the nitrates is of high importance. On the contrary, the surface coverage of the intermediate nitrozyls (NO\(^\cdot\)) on the support (2100 cm\(^{-1}\)) for the Pd-Cu/γ-Al\(_2\)O\(_3\) catalyst does not seem to be affected from the presence of oxygen in the gas feed of the reaction. However, the presence of TiO\(_2\) on the support seems to have a negative effect on the surface concentration of nitrozyls (NO\(^\cdot\)) on the support. This is in accordance with the literature that Titatium dioxide has an inhibitory action in the formation of ammonium ions [7-9]. In the IR spectrum recorded with the Pd-Cu/TiO\(_2\)-Al\(_2\)O\(_3\) catalyst after the NO\(_3\)/H\(_2\)/O\(_2\) reaction, it was observed a further decrease of the coverage degree of nitrozyls (NO\(^\cdot\)) on the metal ion of the support (2100 cm\(^{-1}\)), of the bidentate nitrates on the support (1530 cm\(^{-1}\)) and of the NOH on the Lewis acid positions on the TiO\(_2\) (Ti\(^{4+}\)-NOH). Moreover, the peaks corresponding to bidentate nitrates on the Pd (1642 cm\(^{-1}\)) and to the nitrate ions on Cu (1395 cm\(^{-1}\)) showed the same degree of decrease with the Pd-Cu/γ-Al\(_2\)O\(_3\) catalyst after NO\(_3\)/H\(_2\)/O\(_2\) reaction and the Pd-Cu/TiO\(_2\)-Al\(_2\)O\(_3\) catalyst after NO\(_3\)/H\(_2\) reaction. It should also be noted that the apparent increase in the intensity of the peak at 1395 cm\(^{-1}\) is directly related to the decrease of the intensity of the peaks at 1520 and 1173 cm\(^{-1}\). These results are in total accordance with the results from the catalytic experiments that were performed for the same catalyst and for the same experimental conditions (NO\(_3\)/H\(_2\)/O\(_2\)). The use of bimetallic supported catalysts of Pd-Cu on a complex metal oxide of TiO\(_2\)-Al\(_2\)O\(_3\) in the reaction of reduction of nitrates with hydrogen in the presence of oxygen (NO\(_3\)/H\(_2\)/O\(_2\)) resulted in a increase in the conversion degree of the nitrates ions by 7% and a significant decrease in the selectivity towards NH\(_4\)^+ by 10%, compared with the Pd-Cu/γ-Al\(_2\)O\(_3\) catalyst [6, 7, 10].

The information that is extracted from the SSITKA-DRIFTS results of the current research, regarding the mechanisms of the reactions of NO\(_3\)/H\(_2\) (a) and NO\(_3\)/H\(_2\)/O\(_2\) (b) over the bimetallic Pd-Cu catalysts supported on Al\(_2\)O\(_3\) and TiO\(_2\)-Al\(_2\)O\(_3\) are illustrated in Figure 2.

In Figure 2a, the FTIR spectra recorded in the 2400-900 cm\(^{-1}\) area are compared for the Pd-Cu/γ-Al\(_2\)O\(_3\) catalytic after the reaction of NO\(_3\)/H\(_2\) at 25 °C under non-isotopic \(^{14}\)NO\(_3\) and isotopic feed (\(^{15}\)NO\(_3\)). Dencovolution (OriginPro 8.5) [9] and curve fitting for the spectra areas were performed. As shown in Figure 2a, the shape and the position of some IR peaks changes under the isotopic mixture of \(^{15}\)NO\(_3\)/H\(_2\). The peaks that present a swift after the isotopic exchange of the initial nitrate solution correspond to active intermediate species, which are formed on catalytic surface during the reaction at hand, and are highlighted with an arrow on the spectra. More specifically, three peaks of the IR spectra were shifted. In particular, the peaks that are shifted after the isotopic exchange of the NO\(_3\) solution are those which correspond to the linear NO on Pd (1702 cm\(^{-1}\) → 1669 cm\(^{-1}\)), the bidentate nitrates on the support (1529 cm\(^{-1}\) → 1507 cm\(^{-1}\)) and the nitrate ions on the Cu (1402 cm\(^{-1}\) → 1379 cm\(^{-1}\)). The latter active species lead the formation of final products towards the NO\(_3\)/H\(_2\) reaction.

Figures 2b shows the FTIR spectra that are obtained in the 2400-900 cm\(^{-1}\) range for the Pd-Cu/γ-Al\(_2\)O\(_3\) catalyst after the NO\(_3\)/H\(_2)/O\(_2\) reaction at 25°C under a non isotopic (\(^{14}\)NO\(_3\)\) and under isotopic (\(^{15}\)NO\(_3\)\) feed. As shown in Figure 2b, the shape and the position of some of the peaks of the IR spectrum have been moved under the isotopic mixture of \(^{15}\)NO\(_3\)/H\(_2)/O\(_2\). The peaks that shifted after the isotopic exchange of the initial solution of nitrates are represented in Figure 9b. More specifically, the peaks that correspond to linear NO on Pd (1699 cm\(^{-1}\) → 1670 cm\(^{-1}\)), bidentate nitrates on Pd (1642 cm\(^{-1}\) → 1604 cm\(^{-1}\)) and ionic nitrates on Cu cations (1403 cm\(^{-1}\) → 1365 cm\(^{-1}\)) are the only ones that are shifted after the liquid phase is exchanged. These species are the active intermediate species which are formed on the surface of the examined catalyst during the reaction at hand (NO\(_3\)/H\(_2)/O\(_2\)).
According to the above results, four different intermediate N-species actively participate in the mechanism of nitrate reduction over the Pd-Cu/γ-Al₂O₃ catalyst. These are the linear NO on the Pd, the bidentate nitrates on the support, the bidentate nitrates on the Pd and the ionic nitrate on the Cu cations. From the comparative analysis of the spectra that were recorded using the reaction conditions of NO₃⁻/H₂ (Figure 2a) and NO₃⁻/H₂/O₂ (Figure 2b), it can be safely said that the presence of oxygen in the gas feed of the reaction promotes the reduction of the adsorbed bidentate nitrates on the Pd. This could be related with the change of oxidative state (higher) of the metal due to the presence of the oxygen. The oxidized Pd atoms attract some of the electronic charge of the Pd-O bond, and as a result of the O-N and N=O bond, due to the dislocation of electrons. Adsorbed linear NO on the Pd is the intermediate N-species that seems to regulate the selectivity of the reaction. Since the NH₄⁺-selectivity significantly decreases in the reaction conditions of NO₃⁻/H₂/O₂, linear NO on the Pd in the presence of oxygen seems to selectively favour the formation of gaseous nitrogen instead of the ammonium ions. The identification of nitrate ions on the Cu cations as active N-species of the reaction, confirms the high reactivity of these species with hydrogen during the H₂-TPSR technique that will be the subject of a future publication. The latter is in full agreement with most of the literature where the reduction of NO₃⁻ to NO₂⁻ is almost solely attributed to the synergistic action of bimetallic crystallites of PdCu, whereas the reduction of NO₂⁻ towards NH₄⁺ and N₂, is due to Pd. It has been supported that hydrogen atoms that are adsorbed on the Pd reduce the nitrites (NO₂⁻), but they are inactive in the reduction of nitrates (NO₃⁻). In the case of Pd-Cu bimetallic supported catalysts, Pd contributes to the reduction of nitrates through the adsorption of H₂ and the diffusion of the atomic hydrogen via a spill-over to adjacent active Cu centers. However, the active contribution of the bidentate nitrates on the support during the NO₃⁻/H₂ reaction suggests the possible contribution of the support on the mechanism of the nitrate reduction depending on the conditions of the reaction. In the reaction at hand, the absence of oxygen in the feed gas stream resulted in a greater adsorptive breakage of hydrogen and diffusion of atomic hydrogen through spill-over towards the support. Based on the literature (4, 7, 10, 12-14), monometalic Pd supported catalysts show an acceptable activity towards the reduction of nitrates, confirming the active involvement of the support in the reaction at hand.

Figures 2c and 2d show the FTIR spectra that are obtained in the 2400-900 cm⁻¹ range for the Pd-Cu/TiO₂-Al₂O₃ catalyst after either the NO₃⁻/H₂ reaction (Figure 2c) or the NO₃⁻/H₂/O₂ (Figure 2d) reaction at 25°C under a non isotopic (¹⁴NO₃⁻) and isotopic (¹⁵NO₃⁻) aqueous feed. As shown in Figure 2c, three active N-species, more specifically adsorbed bidentate nitrates on the support, nitrozyls (NO) as an active intermediate species of both reactions (NO₃⁻/H₂ and NO₃⁻/H₂/O₂) indicate the participation of Titanium dioxide in the mechanism of nitrate reduction. Also, NOH may be an intermediate species of the reaction of the adsorbed NO with H₂, which leads selectively to ammonium ions (NH₄⁺). This view is supported in view of the active contribution of the adsorbed nitrozyls (NO⁺) on the support under NO₃⁻/H₂/O₂ reaction conditions. The above results seem to confirm the contribution of Titanium dioxide in the mechanism of the nitrate reduction with hydrogen. Moreover, it is noteworthy that the presence of oxygen in the reaction caused the same effect on the bidentate nitrates, as in the case of the Pd-Cu/γ-Al₂O₃ catalyst,
while the identification of active nitrate ions on the Cu confirms for once more, the importance that Cu is involved on the reduction of nitrates to nitrites.

As has been previously mentioned, several N-species that are adsorbed especially on the support show high reactivity with hydrogen. The results from the isotopic experiments are extremely useful since they reveal that only a small portion of the intermediate N-species that are formed on the catalytic surface during NO$_3$/H$_2$ or NO$_3$/H$_2$/O$_2$ reaction are active and react with H$_2$ to produce the final products that are mainly N$_2$ and NH$_4^+$. The adsorbed N-species that showed significantly high reactivity with hydrogen (DRIFTS) have been identified as active species (DRIFTS-SSITKA) for the Pd-Cu/y-Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalysts. More specifically, four out of the seven at least intermediate N-species that are formed on Pd-Cu/y-Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalysts are found to be active, depending on the chemical composition of the gas feed. The ionic nitrate on the Cu (1395 cm$^{-1}$) showed the greater reactivity with hydrogen. This is confirmed from the SSITKA results, according to which these species are active in the reaction, for both examined catalysts. In particular, the adsorbed bidentate nitrates on the Pd (1640 cm$^{-1}$) are found to be active only in the presence of oxygen (80 vol. % H$_2$/4.2 vol. % O$_2$) in the gas feed, whereas the adsorbed bidentate nitrates on the support (1531 cm$^{-1}$) are active only in the case of NO$_3$/H$_2$ reaction. Oxygen acts as a promoter of the reduction of the bidentate nitrates on the Pd rather than on the support. It could be suggested that main reasons that lead to the improvement of the N$_2$ selectivity of the NO$_3$/H$_2$ reaction in the presence of oxygen in the feed gas stream might be the ability of oxygen to regulate the hydrogen coverage on the metal surface (Pd and/or Cu and/or Pd-Cu), and also the oxidation state of the metallic phase/s towards an increase of N$_2$ selectivity. This is probably due to the higher oxidation state of the Pd due to the presence of the oxygen.

The fact that the solids Pd-Cu/y-Al$_2$O$_3$ and Pd-Cu/TiO$_2$-Al$_2$O$_3$ show greater conversion values for NO$_3^-$, as well as reduced selectivity values towards NH$_4^+$ in the presence of oxygen in the gas feed (80 vol. % H$_2$/4.2 vol. % O$_2$) suggests that the adsorbed bidentate nitrates on the support (1529 cm$^{-1}$) are reduced selectively to NH$_4^+$, whereas the adsorbed bidentate nitrates on the Pd (1640 cm$^{-1}$) are reduced selectively mainly to N$_2$. Linear NO on the Pd (1702 cm$^{-1}$) is active only in the case of the Pd-Cu/y-Al$_2$O$_3$ catalyst, whereas the NOH (1169 cm$^{-1}$) only on the Pd-Cu/TiO$_2$-Al$_2$O$_3$. The adsorbed nitroyls (NO$^+$) on the support (2094 cm$^{-1}$) appear as active species only in the case of Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalyst only under NO$_3^-$/H$_2$/O$_2$ reaction conditions. The increased selectivity towards N$_2$ that is observed in the case of the Pd-Cu/TiO$_2$-Al$_2$O$_3$ under NO$_3^-$/H$_2$/O$_2$ reaction conditions leads to the conclusion that the adsorbed NO$^+$ on the complex support of TiO$_2$-Al$_2$O$_3$ are probably lead to N$_2$, as well. Therefore, the excellent contact between the TiO$_2$ and Pd phases is expected to have a positive effect on the catalytic properties of the supported catalyst under question, since the right conditions for the formation of the intermediate adsorbed species of M-NO$_5^-$ (M=Metal of support). The NO on the Pd seems to be the rate determining species that is playing a key role in determining the selectivity of the reaction. It should be noted that hydrogen is chemisorbed only on metallic surfaces (e.g. Pd) and not on metaloxides surfaces (e.g. TiO$_2$-Al$_2$O$_3$) [14, 15]. The latter suggests that in order for the reduction of the NO to take place, the NO should be adsorbed on the Pd. However, the isotopic exchange with DRIFTS spectroscopy experiments showed that the active intermediate species of NO that are formed under NO$_3^-$/H$_2$/O$_2$ reaction conditions in the case of the Pd-Cu/TiO$_2$-Al$_2$O$_3$ catalyst are found on the M-NO$_5^-$ support. This result suggests that during the reaction, atomic hydrogen is diffused through spill over from the Pd to nearby support positions. The active contribution of Titanium Oxide to the aforementioned reaction is attributed to the significant increase of the contact surface between the metal and the support, which is a result of the interaction of the metal with the oxidized Titanium ions (Ti$^{3+}$). The interaction between the metal and the oxidized Titanium ions (Ti$^{3+}$) falls in the Interface Metal-Support Interactions (IMSI) category [16, 17].
Figure 2: DRIFTS spectra recorded over 1 wt % Pd-0.5 wt % Cu/γ-Al₂O₃ (a, b) and 1 wt % Pd-0.5 wt % Cu/TiO₂-Al₂O₃ (c, d) after 150 min of \( ^{14}\text{NO}_3/\text{H}_2 \) or \( ^{14}\text{NO}_3/\text{H}_2/\text{O}_2 \) reaction (\( \rightarrow \)) at 25 °C, and after 150 min following the isotopic switch \( ^{14}\text{NO}_3/\text{H}_2 \) or \( ^{14}\text{NO}_3/\text{H}_2/\text{O}_2 \rightarrow ^{15}\text{NO}_3/\text{H}_2 \) or \( ^{15}\text{NO}_3/\text{H}_2/\text{O}_2 \) (\( \leftarrow \)) at 25 °C. M: Metal cation on the support surface.

4. CONCLUSIONS

As previously mentioned, the present work provides fundamental mechanistic information for the fate of active N-species towards nitrate reduction pathway over supported Pd-Cu catalysts. Experiments revealed that the mechanism of \( \text{N}_2 \) production strongly depends on the nature of the support and the presence of \( \text{O}_2 \) (air) in the reaction. Latter parameters were found to significantly affect the formation of different adsorbed active intermediate N-species on the support or metal surface. Solid mechanistic evidence for the involvement of support and bimetallic crystallites (PdCu) in the overall reaction mechanism, as well as the presence of a hydrogen spillover process towards the periphery of metal (Pd) - support and metal (Pd) - metal (Cu) interface (location of active N-species) has emerged from this research. In particular, the presence of active N-species (e.g \( \text{NO}_3^- \), \( \text{NO}^{2+} \) and \( \text{NOH} \)) on the support surface, especially to Titanium dioxide, indicates that atomic hydrogen is diffused from Pd to support through spillover phenomenon, promoting the reduction of nitrates on the support. Moreover, this study provides incontrovertible evidences that Cu clusters appear as active sites for the nitrate reduction. In this case, hydrogen is dissociated on Pd, and migrated (spill over) onto the Cu sites of bimetallic PdCu clusters activating the reduction of nitrates, thus indicates a strong bimetal PdCu interaction. Furthermore, bidentate nitrates were found to be active on Pd only when oxygen was introduced in the feed gas stream. This is probably due to the higher oxidation state of Pd, which might favor the adsorption of \( \text{NO}_5^- \) (change of the Pd-\( \text{NO}_3^- \) bond/s strength), and the presence of Pd oxo-species which provide additional adsorption sites for \( \text{NO}_3^- \).
REFERENCES