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Using the “memory effect” of hydrotalcites for improving the catalytic reduction of nitrates in water

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Abstract

The role of the support in the catalytic hydrogenation of nitrates in the liquid phase using a Pd–Cu/Mg/Al hydrotalcite is studied. The material has been characterized by X-ray diffraction, infrared spectroscopy, elemental analysis, and surface area. It is shown that the use of calcined hydrotalcites as support reduces the problems associated with mass transfer limitations observed on Pd–Cu/Al_2O_3, by introducing a new concept of active supports. In this case by taking advantage of the “memory effect” of calcined hydrotalcites, the nitrates are forced to be located between the positively charged layers of the hydrotalcite and therefore close to the reductive active sites. The nitrates are reduced to nitrites that remain in the same position, and these are further reduced to nitrogen or in a much lower extent to ammonia. These final compounds due to their inadequate charge are released to the solution, reducing the problems related with diffusion limitations that strongly affect the selectivity of the reaction. This has been proved by studying separately the adsorption and reaction steps with different characterization techniques.

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1. Introduction

Nitrate concentration in water supplies in many agricultural areas has experienced an important increase in the last 10 years, mainly caused by the use of fertilizers necessary for an intensive agricultural production. The increasing rigorousity of the drinking water quality standards, 50 mg/L in the European Union or 25 mg/L in USA (guide level), generates the urgent need to develop a new technology for nitrate removal from aqueous solutions.

Conventional techniques for groundwater denitrification are relatively costly and they need in some cases a secondary posttreatment of the effluent and the sludge generated. In addition, these techniques cannot be easily suited to variable nitrate contents, flow of water, temperature, and other uncontrolled factors [1]. Recently, it has been shown that the most adequate way from an environmental point of view to remove nitrates is to convert them into gaseous nitrogen by liquid-phase nitrate hydrogenation on noble metal catalysts [2–6]. This process allows the removal of the pollutants in a sustainable manner. However it should be taken into account that the catalyst to be used in this reaction must be very active since the reaction should be carried out at low temperature. Moreover, the catalyst must be selective to avoid the production of nitrite and ammonia ions, which are more toxic than the nitrates. Typically, metal-oxide supported bimetallic catalysts, combining a noble metal, usually Pd or Pt, and another metal, such as Cu, Sn, or In, supported on alumina have been applied for this reaction [6–9].

Some studies have focused on the composition and preparation of the catalysts [10–15] and their application on various reactor types [15–17], studying the influence of different reductants [12,18,19] or the presence of different ions [5,7]. It has been shown that the kinetics and the selectivity of the process are severely limited by diffusion [15,16,20], and it becomes of paramount importance, to design catalysts that can overcome this problem.

In the present work, we will show that it is possible to diminish the problems associated with diffusion limitations by using Pd–Cu/Mg/Al hydrotalcites as catalysts, since in this case the reactant ions and the reaction products are captured

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or released, by ionic interactions at the hydrotalcite interlayer space. By combining X-ray diffraction, infrared spectroscopy, elemental analysis, and surface area techniques, we have studied each one of the elementary steps of the reaction.

2. Experimental

2.1. Catalyst preparation

Cu/Mg/Al hydrotalcites were prepared by a standard coprecipitating procedure using two solutions. The first solution contained $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $Cu(NO_3)_2 \cdot 5H_2O$, having a (Al + Mg + Cu) molar concentration of 1.5. The second solution contained NaOH and Na_2CO_3 in adequate concentrations to obtain the total precipitation of aluminum, magnesium, and copper in the former solution and to fix the pH at a value of 13. Both solutions were added, while vigorously stirring, at a total flow rate of 30 cc/h, for 4 h. The gel was aged under autogenous pressure conditions at 333 K for 14 h, filtered, and then washed with distilled water until the pH was 7 and carbonate was not detected in the filtrate. The hydrotalcite was calcined at 823 K in air for 9 h before reaction, obtaining a Cu/Mg/Al mixed oxide. Over this material palladium was wet impregnated using a solution of palladium nitrate that was dried at 423 K. Finally, the resulting solid was calcined for 1 h at 773 K and then reduced in hydrogen for 4 h at the same temperature.

In order to compare the activity and the selectivity of this material, a catalyst with the same palladium and copper content, but supported on alumina (supplied from Merck), was prepared by a standard impregnation method. The powder catalyst was activated in a flow of hydrogen at 773 K for 90 min.

The chemical composition of both catalysts was determined by atomic absorption spectroscopy and the results are shown in Table 1.

2.2. Catalyst characterization

The surface areas of the catalysts were obtained in an ASAP 2010 apparatus, using the BET method from the nitrogen adsorption isotherms at 77 K.

Table 1
Chemical composition and textural characteristics of the catalysts

Sample	Cu (wt%)	Pd (wt%)	Mg/Al ratio (mol)	Surface area (m^2/g)
$Pd/Cu–Al_2O_3$	1.5	5.1	0	195[a] 155[b]
Pd–Cu/Mg/Al	1.5	4.9	4	190[a] 1[b]

[a] Calcined sample (prior to reaction).

[b] Rehydrated sample (during the reaction).

X-ray diffraction patterns (XRD) were collected using a Philips X'Pert diffractometer (Cu-K_α radiation and curved copper monochromator), provided with a variable divergence slit and working in the fixed irradiated area mode.

Fourier transform infrared spectra were recorded in transmission mode, with potassium bromide-pressed disks, by accumulating 32 scans at 4 cm^{-1} resolution between 400 and 4000 cm^{-1} using a Nicolet 710 Fourier transform infrared spectrometer.

A Fissons EA-1108CHNS-O elemental analyzer was employed to determine the N content of the samples.

2.3. Catalytic test

The catalysts were tested in a 1-L glass reactor equipped with a Teflon stirrer. The N_2 and H_2 were fluxed into the vessel below the impeller and their flow was controlled by electronic mass flow controllers. In a typical run, 0.85 g of the powder catalyst previously reduced with hydrogen at 773 K was charged into the reactor and the content of the reactor was purged with hydrogen for 1 h. The reaction starts with the addition of a concentrated KNO_3 solution, in order to achieve a total concentration of 90 mg/L in the liquid. During the reaction a hydrogen flow of 500 cc/min was introduced in the reactor. The experiments were carried out at 293 K, and the reactor was stirred at 500 rpm. The reaction progress was followed by taking, at defined periods, small aliquots for the determination of nitrate, nitrite, and ammonia concentration by UV/vis spectroscopy (Shimadzu double-beam spectrophotometer, Model UV-2101 PC) combined with reagent kits for photometric analysis (Merck, Spectroquant®).

3. Results and discussion

3.1. Characterization of the catalysts previous to reaction

The X-ray pattern of the Cu/Mg/Al sample prior to calcination (Fig. 1A) shows the presence of a well-crystallized hydrotalcite phase. After Pd impregnation and subsequent calcination, the XRD pattern (Fig. 1B) is evidence of the presence of a mixed oxide phase, which possesses a typical ill-crystalline MgO-like structure, previously described for calcined hydrotalcite [21], with peaks at 37.0, 43.1, and 62.9°. In addition to this phase the presence of diffraction peaks at 34.0 and 54.9° indicates that a PdO phase was also formed. After the reduction of the Pd–Cu/Mg/Al sample with hydrogen at 773 K, the characteristic reflections of palladium oxide disappear, while new peaks at 40.0, 46.5, and 68.0° assigned to Pd^0 appears (Fig. 1C), indicating that relatively large Pd^0 crystallites (> 5.0 nm) have been formed. In contrast, there are no characteristic XRD peaks associated with copper species, suggesting a good dispersion of the copper. Moreover, it was observed that there is a shift of approx. 0.3° toward higher 2θ, i.e., lower d spaces, as

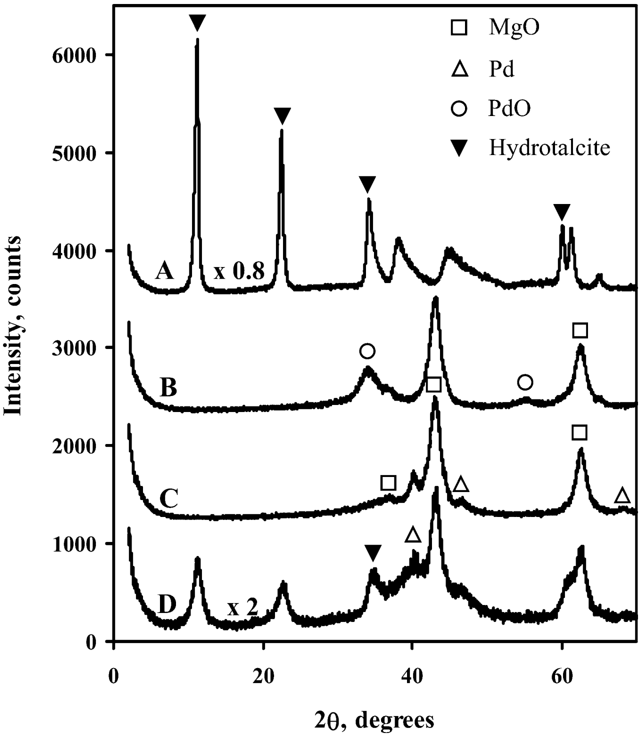


Fig. 1. XRD powder pattern of the catalyst. (A) Cu/Mg/Al hydrotalcite before calcination, (B) Pd–Cu/Mg/Al hydrotalcite catalyst after calcination, (C) Pd–Cu/Mg/Al catalyst after reduction, (D) Pd–Cu/Mg/Al hydrotalcite catalyst contacted with the nitrate solution.

well as a broadening of the Pd metal diffraction peaks of the Cu–Pd-containing samples with respect to those containing only Pd. These observations could suggest that Cu and Pd are forming an alloy on the catalyst [22] as it occurs for Cu–Pd catalysts supported on alumina [12,23], as well as a reduction of the crystal size of the metal particles. The observed broadening of the X-ray diffraction peaks is larger on hydrotalcite than on alumina, suggesting that smaller metal particles are obtained on the former support than on alumina. A more detailed study of the Cu–Pd active species is still in progress.

The resulting material has a high surface area of 190 m^2/g (Table 1), that drops to values as low as 1 m^2/g when the material is in contact with the aqueous solution of nitrates. Meanwhile, the ill-MgO-like structure of the calcined hydrotalcite starts to collapse, turning into an hydrotalcite phase, as evidenced by the XRD peaks appearing at 11.2, 22.5, 34.4, and 60.2° (Fig. 1D), that will be the active catalyst during the denitrification process.

The regeneration of the hydrotalcite phase in the material is attributed to the presence of nitrates compensating the positively charged layers, as was supported by measuring the nitrogen content of the regenerated sample by elemental analysis (see Table 2, time of reaction = 0 min). In addition, the presence of nitrates in the hydrotalcite was confirmed by the intense band observed at 1384 cm^{-1} in the infrared spectrum of the material (Fig. 2), that is typically assigned [24] to the presence of NO_3^- groups and that is not observed when the calcined hydrotalcite was regenerated with water without nitrates. These results can be explained by considering the memory effect [25,26] of calcined hydrotalcite structures, that when rehydrated recovers its positively charged layered structure forcing the nitrate anions present in the media to be located in the interlayer space compensating the positive charge.

Table 2
N-elemental analysis of the Pd–Cu/Mg/Al hydrotalcite catalyst at different reaction times

Time of reaction (min)	0	10	40	50	100	200
Content of N (%)	0.50	0.50	0.44	0.27	0.19	0.03

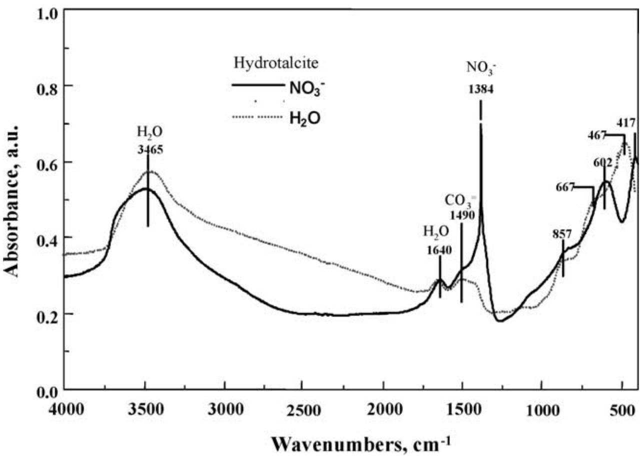


Fig. 2. Infrared spectra of the Pd–Cu/Mg/Al calcined hydrotalcite catalyst, (—) contacted with the nitrate solution and (...) contacted with water.

3.2. *Characterization and activity of the catalysts during the denitrification reaction*

The activity and selectivity of the Pd–Cu/Mg/Al hydrotalcite catalyst for the hydrogenation of nitrates is shown in Fig. 3, where they are compared with those of a Cu–Pd catalyst supported on alumina with the same active metal content. On both catalysts, the concentration of nitrates diminishes in the course of the reaction to give N_2 as the main product, although nitrites and ammonia are formed. Nitrite appears as a primary and unstable product, that presents a maximum concentration at 85–90% of nitrate conversion. After this, it decreases and completely disappears after 120 min of reaction when using Pd–Cu/Mg/Al hydrotalcite as catalyst. On the other hand, with Pd/Cu–Al_2O_3, the nitrite concentration does not go to zero. Moreover, the amount of ammonia formed as a secondary product (Fig. 3B) is about three times larger on the alumina than with the Pd–Cu/Mg/Al hydrotalcite catalyst. These results indicate that there is a clear benefit of using the hydrotalcite-supported catalyst if compared with the normally used alumina-supported catalyst.

The results obtained here could be explained by considering the capacity of hydrotalcites to concentrate anions in

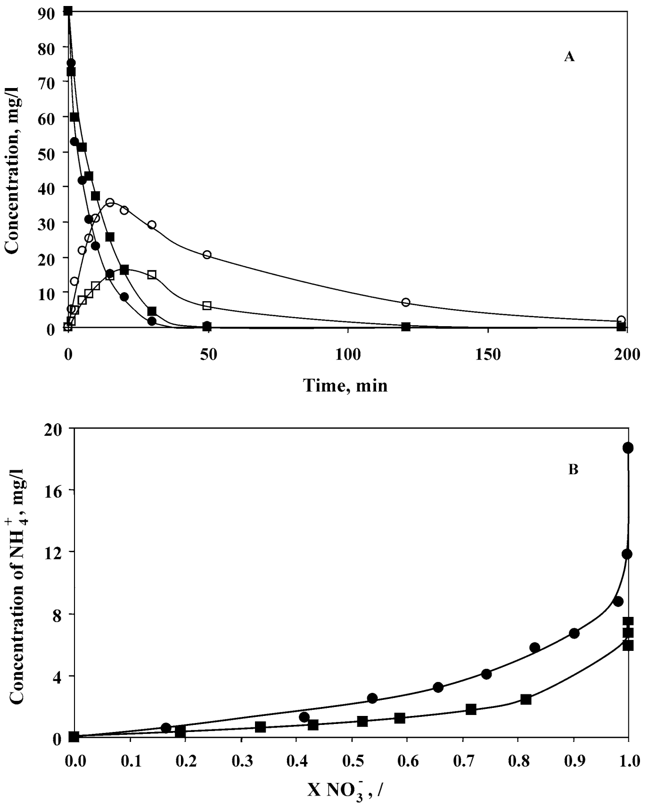


Fig. 3. (A) NO_3^- (●,■) and NO_2^- (○,□) concentration profiles as a function of time for: (●,○) Pd/Cu–Al_2O_3 and (■,□) Pd–Cu/Mg/Al hydrotalcite catalysts. (B) Ammonium ion concentration as a function of nitrate conversion for (●) Pd/Cu–Al_2O_3 and (■) Pd–Cu/Mg/Al hydrotalcite.

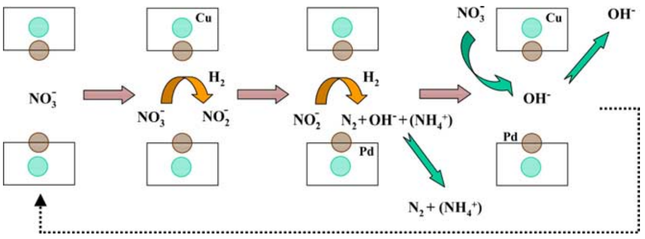
the interlayer space. Although the surface area of the regenerated hydrotalcite is very low, the nitrates are concentrated by ionic forces between the layers, as described in the first part of this work. Therefore, the nitrates are reduced by the neighboring Pd/Cu active sites to nitrites:

$$NO_3^- + H_2 \rightarrow NO_2^- + H_2O.$$

Since this first reduction step does not involve any modification in the charge of the anions located in the interlayer space, the nitrites formed should remain in the interlayer space to compensate the positively charged hydrotalcite structure, and this will facilitate the reduction of nitrites to nitrogen:

$$2NO_2^- + 3H_2 \rightarrow N_2 + 2OH^- + 2H_2O.$$

During the above reaction step, the electroneutrality of the system is maintained by the OH^- anions produced during NO_2^- reduction. These will balance the hydrotalcite charge while the nitrogen (or in less extension ammonia) formed will be easily released to the solution. This proposal is supported by the observed increment of the pH during the course of the reaction (from 10.6 to 11.2). The above catalytic behavior will diminish the problems related with diffusion limitations that affect the selectivity of the reaction [15,16,20].



Scheme 1.

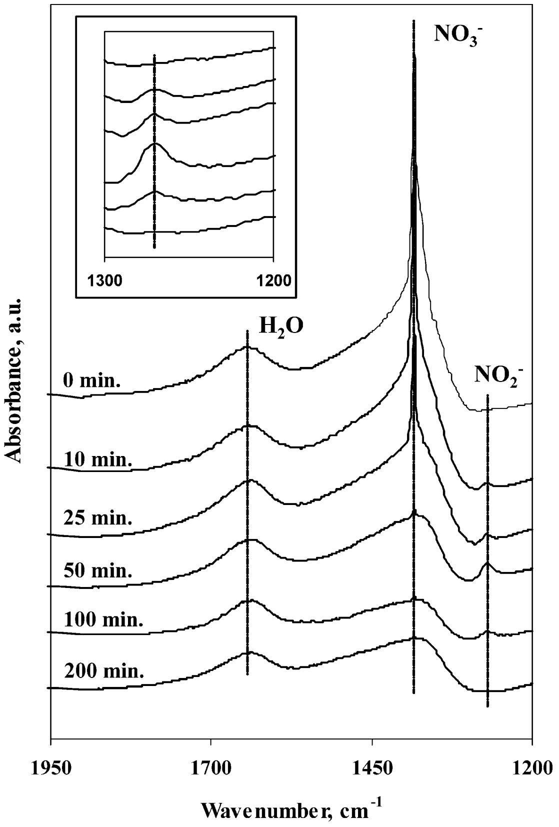


Fig. 4. Infrared spectra of the Pd–Cu/Mg/Al hydrotalcite catalysts withdrawn at different reaction times (infrared spectra between 1300 and 1200 cm^{-1} is enlarged in the top of the figure).

The OH^- ions located in between the hydrotalcite layers can be exchanged in the presence of more NO_3^- anions [25], and a new reaction cycle will start.

Taking into account all the above, a reaction scheme for the reduction of NO_3^- on Cu–Pd hydrotalcite catalysts is proposed in Scheme 1 (note that in this scheme, the position of the Pd and Cu species is only indicative that these centers are randomly distributed in the catalyst). In order to check the reliability of the proposed mechanism, experiments at different reaction times were carried out withdrawing the catalyst from the reaction media. The samples were characterized by infrared and elemental analysis of nitrogen, and Fig. 4 shows the infrared spectra of the withdrawn catalysts. The sample at zero time presents two infrared bands at 1633 and 1384 cm^{-1} assigned to the bending O–H vibration of the water molecules and to the asymmetric stretching N–O vibration of the nitrate anions, respectively. During the course of the reaction, the intensity of the band at 1384 cm^{-1}, assigned to nitrates, decreases and another band at 1268 cm^{-1}, assigned to nitrites, appears. The band assigned to nitrates disappears after 50 min of reaction, time that corresponds with 100% of nitrate conversion. Meanwhile the band assigned to nitrites (1268 cm^{-1}) grows to a maximum at 50 min, and then decreases until it disappears after 100 min of reaction.

These results match very well with the evolution of nitrogen content on the catalyst at different reaction times (see Table 2) as measured by elemental analysis. It can be seen that since the first moment, the hydrotalcite is adsorbing the nitrates until reaching the electroneutrality of the layered material. The nitrogen content in the catalyst is stable until the concentration of nitrates in the solution is almost zero (after 40 min), then the percentage of N in the samples starts to decrease because the negative charged nitrogen compounds in the solution starts to be too few to compensate the partial positive charge in the hydrotalcite interlayer space. Nevertheless as nitrites are still present in the solution, the percentage of N does not go to zero until the end of the reaction when all the nitrates and nitrites have been reduced to nitrogen.

These experiments provide evidence that when a Pd–Cu/Mg/Al hydrotalcite is used as a catalyst for the reduction of nitrates, the reaction is occurring in the interlayer space of the hydrotalcite (see Scheme 1). The infrared spectra of the samples at different reaction times show the bands assigned to nitrate and nitrite, indicating that the nitrates located in the hydrotalcite are being reduced to nitrites. When all the nitrates in the solution have been reduced, only a band assigned to nitrite is observed and finally both infrared bands disappear due to the further reduction into nitrogen or ammonia. As the presence of cations or uncharged species in the interlayer space of the hydrotalcites is unfavored, nitrogen or ammonia are released to the solution by ionic forces, yielding to the OH^--compensated hydrotalcite. This was evidenced by the N elemental analysis of the sample at the end of the reaction that shows the absence of any N compound in the catalyst. Then, the use of the hydrotalcite-based catalysts for the nitrate reduction reduces the diffusion limitations problems that strongly affect the reaction selectivity in other materials as Pd–Cu catalysts supported on alumina. This is afforded by taking advantage of the “memory effect” of the hydrotalcite layered materials, but it does not apply for alumina that produces larger amounts of ammonia and nitrites.

4. Conclusions

The results clearly show that hydrotalcites are very adequate supports for the metals used for the catalytic reduction of nitrates with hydrogen. When this material is used for the reaction, nitrates tend to be placed in the interlayer space, where they are closer to the neighboring metallic active sites, reacting fast with the hydrogen present in the media. This occurs until neutral or positive charged reaction products are formed. These species are released from the catalyst to the media avoiding the problems related with mass transfer limitations, which have been described to severely affect the selectivity of the reaction for other catalysts. The proposed mechanism is well supported by catalytic experiments, infrared spectroscopy, X-ray diffraction, and N-elemental analysis.

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