Catalytic reduction of nitrates in water on Pt promoted Cu hydrotalcite-derived catalysts: Effect of the Pt–Cu alloy formation

A. Aristizábal [a], S. Contreras [a,*], N. Barrabés [b,1], J. Llorca [c], D. Tichit [b], F. Medina [a]

[a] Departament d'Enginyeria Química, Universitat Rovira i Virgili, Campus Sescelades, Av. Països Catalans 26, 43007, Tarragona, Spain
[b] Institut Charles Gerhardt UMR 5253 CNRS/UM2/ENSCM/UM1, Matériaux Avancés pour la Catalyse et la Santé, 8 rue Ecole Normale, 34296 Montpellier Cedex 5, France
[c] Institut de Tècniques Energètiques i Centre de Recerca en Nanoenginyeria, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

ARTICLE INFO

ABSTRACT

In this work, the role of the Pt–Cu interaction and the influence of the Pt metal loading in the catalytic reduction of nitrates in water have been studied, using Pt supported on CuMgAl mixed oxides catalysts in a continuous reactor. Following three Pt impregnation protocols different surface chemistries were obtained, as confirmed by BET, TPR, HRTEM, XRD and FTIR spectroscopy. In the first protocol, the presence of Cu and Pt–Cu alloy formation has been promoted, whereas the second protocol leads to separated Pt and Cu particles in close contact. The third protocol leads to the presence of Cu, Pt and Pt–Cu alloy particles. The different catalytic behaviors were related to the differences in the surface metal chemistry of the samples. Low ammonium formation was detected in all cases but nitrite concentrations need to be improved to fulfill the maximum admissible concentration of the EU legislation. It is concluded that: (i) the presence of Pt–Cu alloy particles leads to an increase in nitrogen selectivity, enhancing the nitrite reduction but showing lower nitrate conversion, and (ii) to maximize the nitrate conversion it is necessary to obtain mainly Pt particles interacting with Cu and Pt–Cu alloy particles.

1. Introduction

Groundwater pollution with high nitrate concentration represents an environmental problem worldwide [1]. Nitrate is a potential human health hazard, and drinking water standards were established by the governments to prevent health problems like clinical cyanosis [2,3]. Different techniques to remove nitrate from water had received attention [4–6] like catalytic reduction of nitrates [7,8], reverse osmosis [9], ion-exchange [10] and biological treatment [11,12]. The catalytic reduction of nitrates is one of the most eco-friendly technologies because it transforms nitrates into nitrogen and water [13]. This process using a bimetallic catalysts and hydrogen was firstly described by Vorlop and Tacke [14,15]. Different catalytic systems combining a noble metal (Pt or Pd) and a promoting metal (like Cu or Sn), supported on several materials, have been studied extensively for this reaction [16–22]. Their main drawback is the formation of ammonia and nitrite which are undesirable in drinking water and due to this recent studies in catalytic reduction of nitrates have been focused in the optimization of the activity and selectivity toward nitrogen formation ([23] and references herein). The incidence of several parameters of the process, such as reactor type [24,25], type of reducing agent [13,26], pH [27,28], and of the catalyst, such as synthesis method [19,29,30] and nature of the bimetallic pair [31], have been extensively studied. The surface chemistry of the metals [29] and the nature of the support [17,32,33] have shown to be key parameters in the optimization of the nitrogen formation.

The surface metal chemistry plays an important role in the catalytic reduction of nitrates, and the nature of the active sites (that can be tuned by the synthesis method) is crucial for the catalytic activity and selectivity. Due to this the clear identification of the optimal chemical state of the metals and the active sites nature is important to clarify the reaction mechanism involved, in order to optimize nitrogen selectivity and to determine the best synthesis method. Previous works have been focused in Pd–Cu or Pt–Cu bimetallic catalysts, and it is stated that this is a structure-sensitive process [34,35]. It has been clearly established that monometallic Pd or Pt particles are active sites to reduce nitrite selectively to nitrogen, and can reduce nitrate but at very low rate or are practically inactive [19,36]. Also, Yoshinaga et al. [35] suggested that edge and corner sites of Pd are active sites for ammonia formation while nitrogen is favorably formed on the terrace sites of the Pd crystallites. Due to these, to enhance the nitrogen selectivity it is necessary to avoid these active sites, for example, by

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* Corresponding author. Tel.: +34 977559680; fax: +34 977559621.
E-mail address: sandra.contreras@urv.cat (S. Contreras).
[1] Current address: Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria.

depositing atoms of another metal like copper in the edges and corners of the Pd particles. Furthermore, in order to increase the activity for nitrate reduction, a second non noble metal (like copper) is necessary, but its addition affects the nitrite reduction adversely in terms of selectivity to nitrogen [36]. To maintain the activity of the non noble metal (probably by spillover of hydrogen), a good contact with the noble metal is required [35]. Sá et al. [19] suggested that the promoter (non noble metal) is stabilized by the noble metal, and that this stabilization is due to the close contact between the metals that could be improved by an adequate synthesis method or by alloy formation. The alloy formation in the catalysts has been reported in several bimetallic systems [19,35–37] but in few cases is directly related to the catalytic behavior. Soares et al. [37] suggested that in order to obtain high activities the metals must be in close contact but not alloyed. Nevertheless, the influence of the metals interaction is still not clear and the changes in the catalytic behavior as a function of the alloy formation are still not fully understood.

On the other hand, the nature of the support, particularly its adsorptive capability, is of major importance to overcome diffusion limitations, which affect the kinetics and the selectivity of the reaction [24,25,33,38]. As it was demonstrated by Palomares et al. [33], calcined hydrotalcite-type materials could be an adequate catalyst support with high adsorption capacity for this reaction due to its peculiar reconstruction ability. Besides, different surface Pt states have been previously reported for Pt impregnated hydrotalcite-type catalysts [39] varying the Pt impregnation protocol. Hydrotalcites (HT) or layered double hydroxides compounds can be represented by the general formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[(A_{x/n}{}^{n-})]\cdot mH_2O$, where x is typically between 0.25 and 0.33, and A^{n-} is a n-valent interlayer anion. These compounds present positively charged brucite-like layers, $Mg(OH)_2$, with trivalent cations M(III) substituting divalent cations M(II) in octahedral sites. Upon calcination, they form homogeneous mixed metal oxides. Besides, reduction of the metal cation-containing ones generally leads to a high dispersion of the metallic crystallites. Depending on the nature of the cations, the mixed oxides can recover the initial lamellar structure when rehydrated in water. This property is generally called "memory effect" [40]. Catalysts obtained from Cu-containing HT precursors show high dispersion of copper [32,41]. Different types of HT have been used as catalyst supports for the reduction of nitrates in water [28,42,43]. Palomares et al. [32,33] found that Pd supported over CuMgAl calcined HT catalyst is more active and selective toward nitrogen in the reduction of nitrates than Pd–Cu/Al$_2$O$_3$ due to the higher copper dispersion and the reconstruction ability of the HT which reduces the diffusion limitations. Besides, Wan et al. [22] observed that the nitrite selectivity and the activity of the same type of catalysts is directly related to the adsorption capacity. The studies carried out with HTs as catalysts for nitrate removal have not been performed in a packed bed continuous reactor (PBR) and Pt was not used as noble metal until a recent study published by our group [44]. Pt instead of Pd has been chosen because Pt has been successfully used as noble metal for this reaction with other kinds of supports [16,45].

In order to contemplate how the surface metal chemistry affects the activity and selectivity in the nitrate reduction, catalysts obtained from CuMgAl HTs impregnated by different protocols with Pt have been synthesized and tested. Copper selected as the promoting metal was introduced during the formation of the HT phase by co-precipitation, obtaining after calcination small and highly dispersed CuO particles. The presence of Mg and Al cations in the HT structure will increase the reconstruction ability of the materials. Three different Pt impregnation protocols have been followed, looking for different Pt sites on the surface (as reported previously in [39]). The materials have been characterized by temperature programmed reduction (TPR), X-ray powder diffraction (XRD), infrared spectroscopy (IR), high resolution transmission electron microscopy (HRTEM) and nitrogen adsorption, in order to correlate physico-chemical properties with the catalytic activity in the nitrate reduction.

2. Experimental

2.1. Characterization techniques

Elemental chemical analysis of Cu, Mg and Al in the calcined hydrotalcite was determined by ICP spectroscopy. 0.5 g of sample was dissolved in 5 ml of HNO$_3$, and then it was diluted to 25 ml with distilled water. Also the Pt content of the different catalysts was determined.

Powder X-ray diffraction (XRD) patterns were measured using a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Gobel mirror) and vertical θ–θ goniometer, a 0.02° receiving slit and scintillation counter as detector. The angular 2θ diffraction range was between 5° and 70°. The data were collected with an angular step of 0.05° at 3 s per step. Cu-Kα radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA. X-ray patterns were compared to X-ray powder references to confirm phase identities using the Joint Committee on Powder Diffraction Standards (JCPDS, 2006) files.

The BET surface area of the catalysts and the calcined HT materials was determined in a Micromeritics ASAP 2010 apparatus, from the nitrogen adsorption isotherms at 77 K. Prior to the analysis the samples were degasified 5 h at 120 °C.

Temperature programmed reduction (TPR) analyses were performed in a TPD/R/O 1100 (ThermoFinnigan) equipped with a thermal conductivity detector (TCD). The reduction process was carried out between 30 °C and 900 °C, with a heating rate of 10 °C/min and with a flow rate of 20 ml/min of the reducing gas mixture (5% H$_2$ in argon).

High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL 2010F instrument equipped with a field emission source (point-to-point resolution 0.19 nm, resolution between lines 0.14 nm). Samples were dispersed on holey-carbon coated grids from ultrasonicated alcohol suspensions.

FT/IR analysis of the catalysts and the used catalysts were performed in a FT/IR-680 plus Jasco using an ATR-300/H Serie diamond detector with a measurement range of 4000–60 cm^{-1}. The analyses were performed with a resolution of 2 cm^{-1} and 32 scan times. Before the analysis the used catalysts were dried at 100 °C.

Chemical analysis of copper and platinum in the treated water was determined by atomic absorption spectroscopy (HITACHI Z-8200 Polarized Zeeman Atom Absorption Spectrophotometer). The samples were preserved with concentrated nitric acid.

2.2. Catalyst synthesis

A CuMgAl HT with molar ratios Mg/Cu = 1 and (Mg + Cu)/Al = 3 was prepared by co-precipitation at room temperature. An aqueous solution containing Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O in adequate amounts, and a second solution of sodium hydroxide (NaOH, 2 M) were slowly and simultaneously added to a beaker containing Milli-Q water under vigorous stirring. The pH value was maintained around 10 by NaOH (1 M) addition. The suspension was aged at room temperature under stirring overnight. The resulting solid, labelled as HT, was then filtered and washed several times with Milli-Q water. The solid was calcined at 450 °C overnight and labelled as HTcal.

Then, Pt was incorporated into the HTcalc support (0.5% or 1 %wt.) by three different protocols in order to obtain different interactions between Cu and the noble metal as previously