ZrO₂-modified Al₂O₃-supported PdCu catalysts for the water denitrification reaction

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ABSTRACT

Monometallic Pd and bimetallic Pd–Cu catalysts supported on alumina, zirconia and ZrO₂–Al₂O₃ mixed oxides of different composition were prepared and evaluated in the catalytic denitrification of water. The supports were characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray (SEM/EDX), NH₃-adsorption thermogravimetry and specific surface areas measured by the BET method. XRD studies showed that the predominant phase in the ZrO₂-modified Al₂O₃ supports is the metastable tetragonal phase (57%) of zirconia. SEM/EDX results indicated that ZrO₂ crystals are distributed homogeneously on the supports. Temperature-programmed reduction (TPR) experiments carried out on bimetallic PdCu catalysts showed that Pd is well dispersed on the modified supports and that there is a strong interaction between both metals. The modification of Al₂O₃ by the addition of ZrO₂ not only improved the activity but also the selectivity to N₂ of the PdCu catalysts.

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1. Introduction

Nowadays, groundwater used for human consumption is contaminated with NO_3^- concentrations well above the maximum level allowed by the U.S. Environmental Protection Agency (10 ppm) [1]. Nitrate excess in water is mainly caused by fertilizers and waste effluents from certain industries.

The consumption of water with excess NO_3^- seriously affects human health mainly because it is reduced to NO_2^- in the human body. NO_2^- is combined with hemoglobin, which favors methemoglobinemia especially in children under six months who may suffer from the so-called "blue baby syndrome" that in many cases leads to death [2]. Moreover, NO_2^- could be converted into carcinogenic nitrosamine.

The reduction and elimination of NO_3^- from aqueous solutions using hydrogen over a solid catalyst is one of the most promising technologies. Most catalysts for nitrate reduction are composed of a noble metal and a promoter. The great majority of the bimetallic catalytic systems used in the denitrification of water are composed of noble metals such as Pd, Pt, Ru, Rh, or Ir and promoted by Cu, Sn, Ag, or In [3–5].

It is well-known that the performance of catalysts depends on the nature and structure of the active phase and the chemical and textural characteristics of the support. Different solids have been employed as supports in catalysts for the denitrification of water: alumina [6–8], zirconia, titania [9,10], activated carbon [11,12], SnO₂ [13], ceria [14], SiO₂ [15] and Mg/Al layered double hydroxide [16], and it has been demonstrated that different supports significantly affect the catalytic activity and selectivity of the process. Recently, Soares et al. reported a very complete study in which they used different materials as support, showing the remarkable effect they had on the performance of PdCu catalysts [17].

In the case of inert supports such as SiO₂ or Al₂O₃, one of the most widely accepted mechanisms for the reduction of NO_3^- involves its reduction to intermediate nitrite or directly to nitrogen gas or ammonium ion [6,18]. Since Vorlop et al. [19] published in 1989 the first study using solid catalysts for the removal of NO_3^- to date, bimetallic PdCu systems have been the most successful in terms of activity. According to the most accepted explanation, in these catalysts, bimetallic sites allow the reduction of NO_3^- to NO_2^-, which is then reduced to N₂ or over-reduced to NH_4^+ on monometallic Pd sites [20,21].

Zirconia has been used as support for catalysts and has received considerable attention due to a special combination of surface properties. It possesses chemical properties that may be of importance in the behavior of catalytic systems, namely acidity or basicity, as well as in their reducing and oxidizing ability [22,23].

Table 1
Nomenclature, textural properties and acidity of the prepared supports.

Nomenclature	Composition	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})[b]	D_p (nm)[a]	Acidity (μmol NH$_3$ m^{-2})
Z$_f$	ZrO$_2$ (as prepared)	309	0.18	2.4	n.d.
Z	ZrO$_2$ (calcined at 600 °C)	73	0.10	5.4	0.80
A	Al$_2$O$_3$ (calcined at 600 °C)	190	0.47	10.1	1.47
ZA-5	5 wt.%ZrO$_2$/Al$_2$O$_3$	184	0.47	10.2	1.47
ZA-10	10 wt.%ZrO$_2$/Al$_2$O$_3$	179	0.44	10.1	2.18
ZA-15	15 wt.%ZrO$_2$/Al$_2$O$_3$	175	0.46	9.9	3.40

[a] D_p (pore diameter) was estimated from BJH desorption determination.

[b] V_p (pore volume) was estimated from the pore volume determined using the adsorption branch of the nitrogen isotherm curve at $P/P_0 = 0.98$ single point.

With Pd as the active phase, ZrO$_2$ has been used in various oxidation reactions, such as the oxidation of CH$_4$ [24] and toluene [25]. In the case of a reduction reaction such as water denitrification, the use of zirconia as a slightly conventional support is interesting to study because of its capability to improve the performance of supported transition metals in hydrogenation reactions.

Despite its beneficial influence on the catalytic activity, the zirconia support has a low surface area. For that reason, this solid is often deposited on high surface area oxides, such as alumina or silica, in order to prepare ZrO$_2$ supports with greater area [26–28]. Zirconium oxide dispersed on alumina and silica is an attractive new class of supports, combining the unique chemical properties of ZrO$_2$ with the high surface area and the mechanical stability of alumina or silica supports [29]. It is possible to adjust the textural properties of ZrO$_2$–Al$_2$O$_3$ mixed oxides by changing the ratio of the two oxides during the preparation procedure to thereby design catalysts that are more selective [22].

The objectives of the present study were to develop monometallic Pd and bimetallic Pd–Cu catalysts supported on different oxides and to evaluate their activity and selectivity toward the catalytic denitrification of water. Alumina, zirconia and ZrO$_2$–Al$_2$O$_3$ mixed oxides of different composition were used as supports, employing a sol–gel procedure to prepare the ZrO$_2$-containing solids. These supports were characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray (SEM/EDX), NH$_3$-adsorption thermogravimetry and specific surface areas measured by the BET method. Besides, the reducibility of the mono- and bimetallic catalysts was studied by temperature-programmed reduction (TPR) experiments.

2. Experimental

2.1. Support preparation

2.1.1. ZrO$_2$ preparation

The precursor salt, ZrOCl$_2$·8H$_2$O (Fluka), was dissolved in distilled water. Aqueous ammonia was added until the pH of the solution reached a value of 10 and the formation of the gel was observed. The mixture was aged for 8 days at room temperature. The obtained precipitate was washed with distilled water until free from chloride ions (determined by AgNO$_3$), filtered and dried at 105 °C for 24 h. The hydrous zirconia was calcined at 600 °C for 2 h. The following equation represents the zirconia preparation:

$$ZrOCl_2 \cdot 6H_2O + OH^- \rightarrow ZrO_2 + 2Cl^- + H^+ + 6H_2O$$
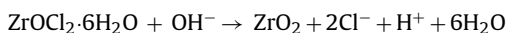
2.1.2. ZrO$_2$–Al$_2$O$_3$ preparation

Zirconia particles were grown onto the γ-Al$_2$O$_3$ support (Air Products, surface area 190 m^2 g^{-1}; pore volume 0.50 m^3 g^{-1}) by adding a ZrOCl$_2$·6H$_2$O solution onto γ-Al$_2$O$_3$ in an appropriate concentration so as to obtain 5, 10 and 15 wt.% ZrO$_2$ on Al$_2$O$_3$. In a typical procedure, the alumina support was suspended in deionized water under vigorous stirring. The appropriate amount of ZrOCl$_2$·6H$_2$O was dissolved into the resultant mixture and aqueous

ammonia was added dropwise until pH = 10. After aging the solids for 8 days, they were washed until no chloride ion could be detected with AgNO$_3$ solution in the filtrate. The materials obtained were dried at 105 °C and finally calcined at 600 °C for 2 h. These supports are designated ZA-*x*, where "*x*" indicates the ZrO$_2$ content.

Both the as-received commercial γ-Al$_2$O$_3$ and the γ-Al$_2$O$_3$ calcined at 600 °C (A) for 2 h were used for comparison purposes. The nomenclature of the supports is described in Table 1.

2.2. Catalyst preparation

The monometallic catalysts were prepared by impregnation using an aqueous solution of H$_2$PdCl$_4$ prepared from PdCl$_2$ (Sigma–Aldrich) in HCl (pH = 1) in order to obtain a catalyst containing 1 wt.% of palladium. The support was suspended in the aqueous solution containing the palladium salt for 24 h at room temperature. Then, the solids were dried at 105 °C and calcined at 400 °C for 2 h. To prepare the bimetallic catalysts, a certain amount of the monometallic catalyst was added to a solution of copper nitrate (Cu(NO$_3$)$_2$, Merck) of the appropriate concentration. This mixture was stirred for 2 h before drying at 105 °C and calcined at 400 °C (2 h). The catalysts are designated Pd/support or PdCu/support (see Table 2).

2.3. Characterization of supports and catalysts

The textural properties of the supports (specific surface area, S_{BET}, and pore volume) were measured by N$_2$ adsorption–desorption at −196 °C using a Micromeritics Accusorb 2100E apparatus. The S_{BET} was calculated by the BET equation and the pore volume (V_p) was estimated using the adsorption branch of the nitrogen isotherm curve at $P/P_0 = 0.98$ single point. The textural properties of the supports are listed in Table 1.

The structural characterization was completed by X-ray powder diffraction (XRD) performed on a Philips PW 1050/70 diffractometer using Cu Kα radiation (λ = 0.154 nm). XRD data were recorded in the range of 2θ = 5°–70° at a scanning speed of 2° min^{-1}. The

Table 2
Nomenclature and chemical composition of Pd and PdCu studied catalysts.

Nomenclature	Pd (wt.%)	Cu (wt.%)	Support
Pd/γ-Al$_2$O$_3$	1.0	–	Commercial γ-Al$_2$O$_3$
PdCu0.5/γ-Al$_2$O$_3$	1.0	0.3	Commercial γ-Al$_2$O$_3$
PdCu1/γ-Al$_2$O$_3$	1.0	0.6	Commercial γ-Al$_2$O$_3$
Pd/A	1.0	–	Al$_2$O$_3$ (calcined at 600 °C)
Pd/Z	1.0	–	ZrO$_2$ (calcined at 600 °C)
Pd/ZA-5	1.0	–	5 wt.% ZrO$_2$/Al$_2$O$_3$
Pd/ZA-10	1.0	–	10 wt.% ZrO$_2$/Al$_2$O$_3$
Pd/ZA-15	1.0	–	15 wt.% ZrO$_2$/Al$_2$O$_3$
PdCu/A	1.0	0.3	Al$_2$O$_3$ (calcined at 600 °C)
PdCu/Z	1.0	0.3	ZrO$_2$ (calcined at 600 °C)
PdCu/ZA-5	1.0	0.3	5 wt.% ZrO$_2$/Al$_2$O$_3$
PdCu/ZA-10	1.0	0.3	10 wt.% ZrO$_2$/Al$_2$O$_3$
PdCu/ZA-15	1.0	0.3	15 wt.% ZrO$_2$/Al$_2$O$_3$