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Sol-gel palladium catalysts for nitrate and nitrite removal from drinking water

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Abstract

Alumina-copper oxide supports can be obtained by cogelation yielding uniformly sized spheres with high surface areas and unimodal mesoporosity, that can be employed as supports for Pd catalysts obtained by impregnation. These are characterized by SEM, XRD, BET, H_2 chemisorption and TPR, and can be successfully used in the hydrogenation of nitrate (nitrite) in water with minor ammonia formation.

Keywords: Sol-gel palladium catalysts; Nitrate; Nitrite; Drinking water

1. Introduction

The removal of nitrate and nitrite from drinking waters is becoming a problem of major concern, since the ever increasing use of natural or synthetic fertilizers in agricultural areas results in an increase of the level of these salts both in surface waters as an effect of weathering and in underground waters as a consequence of incomplete fixation in the soil.

Current methods to address this problem involve either biological digestion with microorganisms [1] or the use of ion exchange resins [2], both with their own disadvantages. More recently, catalytic hydrogenation according to the following equations has been suggested [3] as a potential decontamination method:

$$2NO_3^- + 5H_2 \rightarrow N_2 + 2OH^- + 4H_2O \qquad (1)$$

$$2NO_2^- + 3H_2 \rightarrow N_2 + 2OH^- + 2H_2O \qquad (2)$$

The best catalysts for this purpose have proven to be some Pd-Cu/Al_2O_3 catalysts that carry out the above reactions very efficiently. However, major problems arise from the difficulty to modulate the activity of the catalysts to avoid further hydrogenation to ammonia (Eq. (3)). Furthermore, the small grain size employed allows their use only in reactors equipped with a stirring apparatus.

$$NO_3^- \xrightarrow{H_2/cat} NO_2^- \xrightarrow{H_2/cat} NH_4^+ \qquad (3)$$

We have developed a sol-gel procedure [4] that is suitable also for obtaining spherical monosized mixed oxides of diameter variable in the range 0.1–2 mm, where the metal component can be well distributed within the support by cogelation. In

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this work we wish to report our attempts to prepare bimetallic catalysts by subsequent impregnation of these materials with palladium salts and some preliminary data on their catalytic activity in reactions (1)–(3). The catalysts can be close-packed into columns without significant pressure drop in the water to be purified.

2. Experimental

Supports were prepared according to the following procedure. A commercial dispersible alumina was mixed with copper acetate, additioned with polyvinyl alcohol (1–5%) and a surface active agent isooctyl-phenoxy-polyethoxyethanol (0.2%). The sol was dropped into a solution of tetramethylammonium hydroxide. The gel spheres were aged for 1 h and washed with water to pH 7. They were dried by azeotropic dehydration with toluene and finally calcined at 550°C for 3 h. The final spheres had all the same diameter (1.7 ± 0.1 mm).

All catalysts (5% Pd content) were prepared by wet impregnation of the supports with H_2PdCl_6 solution. After drying at 110°C for 18 h, they were calcined in air at 500°C for 1 h and finally reduced in 5% H_2 in N_2 at 350°C for 6 h. The presence of chlorides was eliminated by Soxhlet extraction with water for 18 h, followed by final drying at 110°C for 18 h. Traditional bimetallic Pd-Cu catalysts were prepared identically using γ-Al_2O_3 (AKZO). Cu was introduced as a $CuCl_2$ solution by wet impregnation prior to the calcination step.

The morphology was studied both by scanning electron microscopy (SEM) on a Philips 505 instrument and on an optical Reichert Polyvar 2 microscope.

X-ray diffraction (XRD) patterns were obtained by a Siemens D 500 powder diffractometer equipped with a graphite crystal monochromator using a Copper Kα X-ray radiation source. Experiments were run in step-scan mode with a step interval of 0.02° 2Θ and a count rate of 1 s per step over the range of 5 to 90° 2Θ.

The Pd dispersion from the average particle size was calculated according to Ref. [5].

Nitrogen adsorption and desorption were measured at −198°C with an automatic Carlo Erba Sorptomatic 1800 adsorptiometer. The samples were pretreated at 300°C under vacuum (1.33 Pa).

In the temperature programmed reduction (TPR) experiment the sample was calcined at 500°C for 1 h in an oxidizing flow (5% O_2 in Ar), cooled to 25°C, treated with pure Ar and then reduced by heating (10°C/min) to 800°C in a 5% H_2 in Ar mixture, according to a previously described technique [6].

Catalytic activity was tested at 25°C in a batch reactor. In a typical experiment, the catalyst was suspended in water, hydrogen was flowed for 15 min and the reaction was started by adding an appropriate amount of concentrated KNO_3 or $NaNO_2$ solution in order to make a 100 mg/l final solution. The course of the reaction was monitored by addition of HCl to neutralize OH^- formed according to Eqs. (1)–(3), in order to maintain the initial pH (3.9–4.5) constant. The reaction mixture was periodically sampled and the concentrations of NO_3^- and NO_2^- were determined by ion chromatography. Ammonia was analyzed with a gas sensitive electrode.

3. Results and discussion

Two support samples with different copper loads (2 and 4%) were prepared along with a third sample of pure alumina, having the same shape and size distribution, that was prepared for comparison with the same synthetic method. A summary of their physical properties is shown in Table 1.

Table 1
Physical properties of the supports

Sample	Cu (weight %)	BET ($m^2 g^{-1}$)	V_p (ml g^{-1})	r_p^{max} (nm)
Al_2O_3	0	317	0.67	3.5
2 Cu-Al_2O_3	2	311	0.65	3.3
4 Cu-Al_2O_3	4	300	0.50	2.6

XRD patterns of these materials did not show either copper oxide crystallinity or spinel formation ($Al_2O_3 \cdot CuO$), as was detected for higher copper loads (e.g., 20%) [7] and the copper was found uniformly distributed within the Al_2O_3 matrix. The alumina is present as γ-alumina.

Energy Dispersive System (EDS) mapping of Cu, made on sections of several spheres, revealed a uniform distribution of this element within the alumina matrix.

All samples have similar textural characteristics (Table 1), i.e., BET surface areas around 300 m^2/g, pore volumes around 0.6 ml/g and an unimodal mesoporosity distribution with average pore radius r_p^{max} ca. 3 nm with absence of microporosity. Nitrogen adsorption and desorption were measured at 77K showing Type H2 hysteresis loop following IUPAC and the total pore volume V_p can be deduced from the adsorption branch at $P/P_0 = 0.99$. Pore size distribution, following the BJH method and deduced from the desorption branch, shows an unimodal mesoporosity distribution. As a typical example the adsorption isotherm and pore distribution of sample 2 Cu-Al_2O_3 is shown in Fig. 1. For the same sample the t-plot analysis shows capillary condensation above 0.6 nm, the y-intercept shows absence of microporosity. From the slope of the linear part, the surface area S_t was found to be 351 m^2/g. The cumulative pore volume V_{cum}, deduced from the desorption branch, was 0.62 ml/g.

The Pd catalysts dispersed on the above supports were prepared by impregnation method. Again, a series of traditional Pd-Cu bimetallic catalysts dispersed on γ-Al_2O_3 was prepared for comparison.

Table 2
Physical properties of the 5% Pd hydrogenation catalysts

Sample	Shape	Cu (weight %)	Pd part. size (Å)	% Exposed
Pd/Al_2O_3	spheres	0	70	16
$Pd/2\,Cu$-Al_2O_3	spheres	2	70	16
$Pd/4\,Cu$-Al_2O_3	spheres	4	50	22
Pd/γ-Al_2O_3	powder	0	70	16
Pd-$1\,Cu/\gamma$-Al_2O_3	powder	1	100	11
Pd-$2\,Cu/\gamma$-Al_2O_3	powder	2	140	8

X-ray analysis of the catalysts shows the presence of well dispersed metal with particles of average diameter 50–70 Å (Table 2) in the case of the samples dispersed on the Cu-Al_2O_3 spheres. However, a shift in the Pd peak position seems to indicate the possible formation of an alloy. This cannot be safely evidenced because of the partial overlapping with the peaks of the matrix. The metal particle size increases to 100–140 Å for the bimetallic samples prepared on commercial γ-Al_2O_3. No evidence for the presence of metallic Cu was ever found.

EDS mapping of Pd, determined on sections of several spheres, revealed a uniform distribution of this metal within the support particle.

A summary of TPR experiments carried out on 2% Cu containing samples is shown in Fig. 2 and are typical. The profile of the Cu/γ-Al_2O_3 sample (curve A) is indicative of Cu reduction in the region 200–400°C, while Pd/γ-Al_2O_3 shows a band with a maximum at ca. 70°C (curve B) typical of the reduction of residual Pd oxychlorides [8]. In the bimetallic sample (curve C), only one strong band is present with two maxima at 90 and 130°C, that combines the reduction of both Pd and

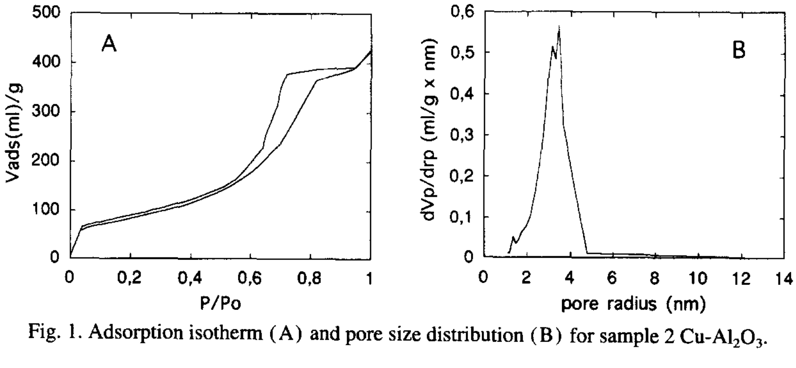

Fig. 1. Adsorption isotherm (A) and pore size distribution (B) for sample 2 Cu-Al_2O_3.

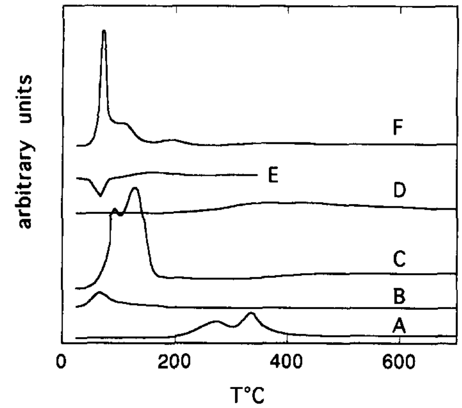

Fig. 2. Summary of TPR results on different samples: A 2 Cu/γ-Al_2O_3; B Pd/γ-Al_2O_3; C Pd-2 Cu/γ-Al_2O_3; D 2 Cu-Al_2O_3; E Pd/Al_2O_3; F Pd/2 Cu-Al_2O_3.

Cu precursors and is strongly indicative for the formation of a Pd-Cu intermetallic compound [9].

A similar behaviour is displayed by the 2 Cu-Al_2O_3 spheres albeit with some modifications. The reduction of Cu (curve D) is spread over a very broad interval (250–650°C) in agreement with the intimate dispersion of CuO inside the Al_2O_3 matrix indicated also by the EDS mapping reported above. Pd/Al_2O_3 spheres unexpectedly shows the presence of Pd β-hydride [10,11] (curve E), which indicates that the reduction of PdO on the Al_2O_3 spheres occurs already at room temperature. Finally, the Pd/2 Cu-Al_2O_3 sample (curve F) shows one maximum at 70°C with a large shoulder at 180°C. Again, this observation seems to support the idea of the formation of an intermetallic species (or an alloy) upon reduction, in agreement with the previous X-ray findings (see above). The different intensities between curve A and curve D and between curve C and curve F, referring to similar phenomena, seem to indicate a lower reducibility of CuO in the spheres compared to the traditional samples in agreement with the different physical state of CuO in the two cases: bulk oxide in the former and surface oxide in the latter.

All catalysts were tested in the hydrogenation of water solutions containing 100 ppm KNO_3 (or $NaNO_2$) using a slurry reactor operating at atmospheric pressure under hydrogen flow. The reaction can be monitored by continuous titration of the OH^- produced (Eqs. (1)–(2)) that allows to determine the reaction rate. A typical reaction profile for the hydrogenation of nitrate is shown in Fig. 3. As can be seen, only a very small amount of nitrite is formed as intermediate, while at the end of the reaction, complete consumption of nitrate (nitrite) is observed. Ammonia formation occurs rapidly. A short summary of the catalytic activity of these catalysts is reported in Table 3. As can be seen the activity is good even when the catalysts are used as spheres. Grinding (170–200 mesh) increases greatly the activity that may be higher than that of traditional bimetallic Pd-Cu catalysts. As was already known, Pd alone is a poor catalyst for the hydrogenation of nitrate, but excellent for the hydrogenation of nitrite.

Compared to previous catalysts [3] prepared in the same fashion, they appear to be significantly more active under similar conditions. Moreover, at variance with previous examples [3], nitrite build-up during the course of the reaction is virtually negligible, thus making unnecessary the use of a Pd-only catalyst for the hydrogenation of the in-situ formed nitrite. In general, a comparison of the data obtained with the sphere and the ground catalysts seems to indicate that the reaction is diffusion controlled. As can be seen from Table 3, ammonia formation generally remains in the 4–9 ppm range, indicating a moderate selectivity (60–80%) for the catalysts. Reducing the hydrogen flow, a factor that was reported [3] to decrease

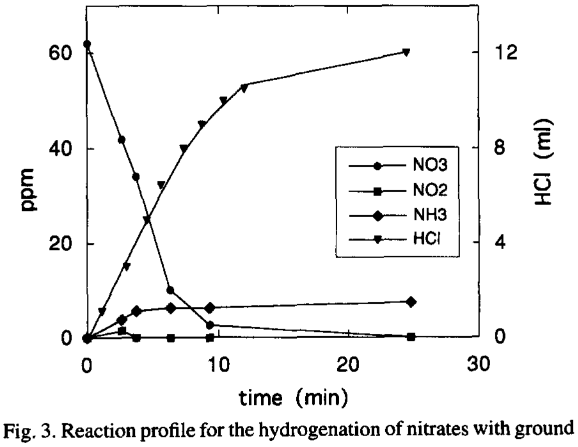

Fig. 3. Reaction profile for the hydrogenation of nitrates with ground Pd/2 Cu-Al_2O_3.

Table 3
Hydrogenation of nitrates and nitrites at 25°C

Catalyst	Nitrate		Nitrite	
	Activity (mg/min g Pd)	NH_3 form. (ppm)	Activity (mg/min g Pd)	NH_3 form. (ppm)
Pd/2 Cu-Al_2O_3 spheres	16.6	4.6	15.2	4.3
Ground	98.8	5.9	356	7.1
Pd/4 Cu-Al_2O_3 spheres	15.6	5.9	9.95	13.8
Ground	231	7.1	220	9.5
Pd/Al_2O_3 spheres	0.85	13.4	8.1	5.5
Pd/γ-Al_2O_3	6.9	18	161	4.8
Pd-1 Cu/γ-Al_2O_3	144	8.8		
Pd-2 Cu/γ-Al_2O_3	126	7.8		

Reaction conditions: 0.24 g cat. 5% Pd in 150 ml H_2O containing 100 ppm KNO_3 ($NaNO_2$); hydrogen flow 150 ml/min.

the ammonia formation below 0.5 ppm, does not appear to influence significantly the present catalysts (Table 4). Decreasing the H_2 flow from 150 to 2.5 ml/min determined only a slight decrease in ammonia formation and the observed specific activity (Table 4) is strongly indicative of mass transfer limitation. This point was definitely confirmed by a conversion vs. catalyst weight plot (Fig. 4), that indicated mass transfer limitations, even with ground catalysts, under the conditions of Table 3 and Table 4.

In order to slow down the activity and test the actual properties of the catalysts in a chemical regime, the pressure of hydrogen was lowered maintaining constant its flow. The effect is reported in Table 5 and indicates that even under these conditions diffusion limitation can be suspected.

In conclusion, in this preliminary work the synthesis of pre-shaped catalysts suitable for continuous flow applications in the purification of drinking water from nitrate and nitrite contamination has been accomplished. However, the catalytic activity seems even too high for a successful

Table 4
Effect of H_2 flow on the performance of ground Pd/2 Cu-Al_2O_3 in the hydrogenation of KNO_3 at 25°C

H_2 flow (ml/min)	Activity (mg/min g Pd)	NH_3 form. (ppm)
150	98.8	6.6
30	74.5	6.6
5	39.3	5.5
2.5	61.1	4.6

Reaction conditions: 0.24 g cat, H_2 1 bar, 150 ml H_2O, 100 ppm KNO_3.

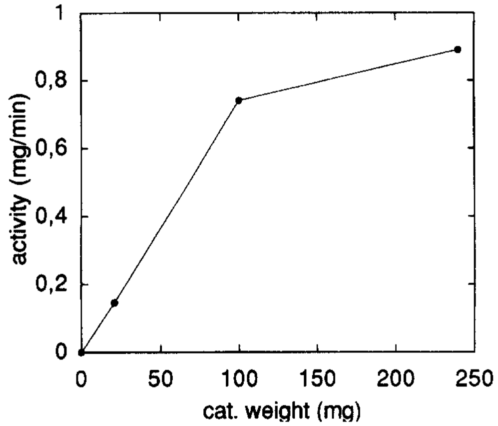

Fig. 4. Effect of the catalyst weight (Pd/2 Cu-Al_2O_3 ground) on the catalytic activity. Reaction conditions as in Table 3.

Table 5
Effect of H_2 pressure on the performance of Pd/2 Cu-Al_2O_3 in the hydrogenation of KNO_3 at 25°C

Catalyst shape	H_2 press. (atm)	Activity (mg/min g Pd)	NH_3 form. (ppm)
ground	1.0	146	9.8
	0.33	101	7.6
	0.11	46.8	7.1
spheres	1.0	23.3	9.2
	0.092	3.6	6.2

Reaction conditions: 0.10 g cat, H_2 30 ml/min, 150 ml H_2O, 100 ppm KNO_3.

modulation of the selectivity aimed to avoiding appreciable hydrogenation of nitrate and nitrite to ammonia. Indeed, at least in one case, Hörold et al. [3] could comply with the European acceptable level of NH_3 (<0.5 ppm) in drinking waters, but this was obtained only by reducing strongly the reaction rate. Under similar conditions the catalysts here described are still very active and a chemical regime in substrate conversion is never attained. Future work on the effects of the metal loading, the particle size, the nature of the Pd-Cu interaction and its exploitation to modulate the selectivity is certainly called for to unveil the actual properties of these catalysts and exploit their potential practical utility.

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