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Activated carbon cloth-supported Pd–Cu catalyst: Application for continuous water denitrification

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Abstract

Pd–Cu catalysts supported on woven fibrous cloths have been tested for continuous nitrate hydrogenation in water. The results demonstrate that activated carbon cloth (ACC) is an adequate support for the Pd–Cu bimetallic catalysts giving better activity and selectivity than that of supports like glass fibers cloth (GFC) and GFCs coated with Al_2O_3 or SnO_2, which were also studied.

A series of 2% Pd–Cu/ACC catalysts were prepared by selective deposition of Cu on Pd/ACC and examined at steady state in a continuous three-phase radial flow reactor. The activity and selectivity of the bimetallic catalysts depend on the Cu:Pd ratio and the metal loading. The beneficial effect of copper on nitrate hydrogenation activity with a Pd–Cu/ACC catalyst is probably related to the formation of an active Pd–Cu ensembles working as active sites for nitrate-to-nitrite reduction. The maximal nitrate conversion was achieved with 0.6 wt.% Cu–2 wt.% Pd/ACC catalyst showing a 92% selectivity towards gaseous products.

Keywords: Pd–Cu catalyst; Activated carbon cloth; Liquid-phase hydrogenation; Nitrate

1. Introduction

Among reductive catalytic processes proposed for water purification [1], the catalytic hydrogenation of nitrates [2] is viewed as a promising emerging technology for removal of nitrates from polluted water; high concentrations of nitrate usually result from over-fertilization [3]. The hydrogenation process can approximately be described by consecutive and parallel reactions:

$$NO_3^- + H_2 \rightarrow NO_2^- + H_2O \quad (1a)$$

$$2NO_2^- + 3H_2 \rightarrow (NO, N_2O) \rightarrow N_2 + 2H_2O + 2OH^- \quad (1b)$$

$$NO_2^- + 3H_2 \rightarrow NH_4^+ + 2OH^- \quad (1c)$$

showing that the nitrates undergo hydrogenation to nitrites and then to gaseous nitrogen (target product) and dissolved ammonia (undesired by product) [4].

Significant effort has been devoted in the past decade for preparation and optimization of catalysts for this process. It has been shown that while single noble metals (Pd, Pt) are active only with respect to nitrite hydrogenation, many supported noble metals with a metal promoter (Cu, Sn, In), show satisfactory performance for conversion of dissolved nitrate ions [4]. The Pd–Cu catalyst, suggested a decade ago by Horold and Vorlop [2] is still considered to be the best catalyst for the process.

The activity and selectivity of the bimetallic catalyst in nitrate hydrogenation is highly dependent on the preparation method, mode of noble metal promoting, metal-promoter ratio as well as operation conditions. Support selecting is also of importance for this process: various materials such as metal oxides (silica, alumina [5,6], zirconia [7], titania [8]), polymers [9], granular active carbon [10,11] and other materials [12] have been investigated as support for Pd–Cu catalysts and it was shown that the support had greatly affected the catalyst's activity and selectivity towards reaction products.

Currently, there is a growing interest in using novel structured supports like monoliths, foams, membranes as well as fibrous cloths [13]. Cloths woven from thin μm-sized fibers reduce the diffusion distance and produce a low-pressure drop in fixed beds and in multi-phase reactors in which one or more dissolved species have to react with gaseous compounds of limited solubility. Moreover, cloth-

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type catalysts are preferable to monoliths when rapid fluctuations in the flow regime occur, as often-encountered in applications for environmental protection. Catalytic cloths combine an open macrostructure with mechanical flexibility, allowing new options for the design of catalytic reactors.

Recently, we have studied some novel Pd-based catalytic cloths for hydrodechlorination [14] and for nitrite and nitrate hydrogenation [15–17] and obtained promising results. In this aspect it is interesting to support Pd–Cu on the activated carbon cloths (ACC), that have been proven to have a great potential as a catalytic support, especially for the expensive noble metals, since a high metal loading and dispersion can be achieved. In addition to their high apparent surface area (about of 1500 m^2/g), ACCs have many other advantageous characteristics when compared with traditional activated carbons, like a morphological network formed by short micro-pores with narrow size distribution, ensuring fast adsorption and desorption, low resistance to the passage of fluid and high fluid permeability.

In this work, following a previously reports on use Pd–Cu/glass fiber cloth (GFC) as a catalyst for nitrate hydrogenation [16] and Pd/ACC for nitrite hydrogenation [17], we extend the study of a Pd–Cu catalytic cloths for nitrate removal in a radial-flow reactor operated in steady state with pre-dissolved hydrogen in the water. Most previous studies used batch reactor. Pd–Cu catalysts used in this work were prepared by the controlled reduction of copper salt on Pd/ACC, in order to obtain optimal contact of the two metals. We examined systematically the effect of the support material, and for the best Pd–Cu/ACC catalyst we optimized the metal content and the Pd/Cu ratio required for good catalytic activity and selectivity. Results of catalytic experiments are discussed along with catalyst characterization by HRSEM and CO chemisorption.

2. Experimental

2.1. Preparation of catalytic cloths

As a support, activated carbon cloth (ACC 523-15) employed in this study was purchased from Nippon Kynol™. The ACC was pre-treated in aqueous solution (4.5 wt.%) of HNO_3 and then rinsed in distilled water. For comparative purposes woven cloth made from glass fibers (GFC YO212 from Fothergil Engineered Fabrics, UK) was also used. In order to increase the specific surface area, GFC YO212 was pre-treated first with hot aqueous HCl solution (3–4 wt.%) to leaching non-silica components (support GFC). Then, the surface of fibrous glass was modified by aluminum oxide (support AlO–FC) or by tin oxide (support SnO–FC) using impregnation with aqueous solutions of $Al(NO_3)_3$ or $SnCl_2$, followed by calcination in air at 200 °C for 12 h.

Bimetallic catalytic cloths were prepared in two stages. First, Pd/cloth was obtained by incipient wetness impregnation method using H_2PdCl_4 (dihydrogen tetrachloropalladate(II)) from solution of $PdCl_2$ (pure, Fluka) in hydrochloric acid). In this impregnation technique the volume of the metal precursor solution does not exceed the water adsorption capacity that was determined for each support during exposure to water for overnight at room temperature. After impregnation, cloth was heat first at 90 °C overnight to eliminate of solvent and calcined at 300 °C for 5 h in flowing argon, and then was washed to remove chloride ions, which become both from decomposition of H_2PdCl_4 during calcination. Final concentration of chloride ions in rising waters was detected using $AgNO_3/HNO_3$. After drying at 120 °C for 2 h, the samples were reduced at 200 °C for 1 h under flowing hydrogen.

In the second step, a given amount of Pd/cloth was placed on a rotating drum and immersed into a solution of copper formate ($Cu(HCO_2)_2$, reagent grade Aldrich) required concentration under flowed argon. The copper formate catalytically decomposes only at the surface of Pd particles even at room temperature, according reaction scheme [18]:

$$Cu(HCO_2)_2 \rightarrow Cu + 2CO_2 + H_2 \tag{2}$$

which thereby is generating the metallic Cu selective only at the Pd surface. This preparation technique can be regarded as a controlled surface reaction. The solution regularly checked spectrometrically at $\lambda_{max} = 778$ nm for presence of copper ions in solution. Then cloth was separated from the liquid and dried overnight under argon stream at 90 °C. The metal composition of fresh and used cloths (after dissolution in concentrated HNO_3/HCl) was verified by elementary analysis performed with inductively coupled plasma emission spectrometry (ICP-ES Perkin-Elmer Optima 3000 DV instrument).

2.2. Catalytic hydrogenation

Catalytic cloths were tested for nitrate hydrogenation in flow reactor system operated with pre-dissolved hydrogen in the water [19]. In a typical run, a solution of nitrate (1.82 mmol/l from $NaNO_3$, reagent grade, Aldrich) in distilled water saturated with gaseous H_2 (>99.99%, Orgim, Israel) was fed into radial flow tubular reactor with rolled catalytic cloth at 25 °C.

In order to avoid hydrogen limitations in the reactor, saturation of hydrogen in nitrate solution was performed under pressure before reactor. The equilibrium concentration of the dissolved concentration of hydrogen (C_{H_2}) in water follows Henri's law:

$$C_{H_2} = P_{H_2}\alpha$$

where P_{H_2} is the hydrogen pressure and α is the hydrogen solubility constant (for water at 25 °C $\alpha = 0.89$ mmol $H_2/(l_{H_2O})$ bar). According to the reaction stoichiometry the concentration of dissolved hydrogen at the reactor inlet should be $C_{H_2} > 2.5C^0_{NO_3}$, (taking into account that some of the hydrogen can be spent on by-reactions). The pressure of hydrogen was adjusted to 6 bar (to achieve a molar H_2/NO_3^- ratio of about 3). Since maximal conversion is about NO_3^- 90%, it suggests that dissolved hydrogen is not exhausted. The amount of catalyst placed in the reactor was 2.2 g; pH of nitrate solution was 5.5 and the liquid feed flow rate was 5 ml/min (0.3 l/h).

The steady state nitrate disappearance rate r (mmol NO_3^-/h g catalyst), used as a characteristic of catalytic activity, was calculated according to:

$$r = \frac{(C^0_{NO_3} - C_{NO_3})F}{W_{cat}} = \frac{(C^0_{NO_3} \times X_{NO_3})F}{W_{cat}} \tag{3}$$

where $C^0_{NO_3}$ and C_{NO_3} are the measured nitrate ions concentrations (mmol/l) in the reactor influent and effluent, respectively, X_{NO_3} is the nitrate conversion, W is the weight of catalytic cloth (g) and F is the flow rate of nitrate solution (l/h).

The yields (Y_i) of nitrite and ammonium ions ($i = NO_3^-$ or NH_4^-) were calculated as:

$$Y_i = \frac{C_i}{C^0_{NO_3}} \tag{4}$$

The yield of total gaseous products (i.e., N_2 and, possibly, N_2O and NO) is denoted as total nitrogen removal (TNR) and is calculated as:

$$\mathrm{TNR} = \frac{C^0_{NO_3^-} - (C_{NO_3^-} + C_{NO_2^-} + C_{NH_4^+})}{C^0_{NO_3^-}} \tag{4a}$$

assuming that nitrite and ammonium ions are the only dissolved side products formed. The selectivity (fractional yield) towards each reaction product (S_i), was calculated as follows:

$$S_i = \frac{C_i}{(C^0_{NO_3^-} - C_{NO_3^-})} \tag{5}$$

Nitrate and nitrite concentrations were measured by ion chromatography (761 Compact IC, Methrom) using conductivity detection. Separation and elution of the anions were carried out on anion analytical column METROSEP A SUPP 4 (4 mm × 250 mm); the mobile phase was carbonate/bicarbonate effluent and sulfuric acid regenerant. Ammonium ions concentrations were measured spectrophotometrically with Nessler reagent at $\lambda_{max} = 500$ nm. The filtered through 0.2 μm membrane filter (Millipore HAWP) effluent samples were also analyzed by ICP-ES to quantity any leaching of the Pd and Cu species.

2.3. Characterization of Pd–Cu/ACC catalysts

Specific surface areas of supports and catalysts were measured by BET method using N_2 adsorption-desorption at −196 °C via a ASAP 2010 (Micromeritics). The samples were set in the ampoule in woven form. The values of pH at the point of zero charge (pzc, i.e. the pH value at which the total surface of the support is electroneutral) were determined by the so-called batch equilibrium pH drift method [20].

Metallic particles on the prepared samples (mounted on specimen holders with carbon conductive tape) were characterized with a field emission gun high-resolution digital scanning electron microscope HRSEM (LEO 982 cooperation Zeiss–Leica). The dispersion of palladium was determined by CO-chemisorption via volumetric sorption analyzer ''ASAP 2010 Chemi'' instrument (Micromeritics). Before the measurements, the samples after evacuation were reduced in a stream of H_2 at 100 °C to avoid the formation of β-PdH. Under these conditions the adsorption of CO on Cu was reported to be very weak and largely physical in nature [21].

3. Results and discussion

3.1. Support selection and catalyst stability

First, Cu-Pd bimetallic catalysts supported on four cloth supports with the same total metal content (2.6 wt.%) and the same Cu/Pd atomic ratio (0.5), were tested for nitrate hydrogenation (Fig. 1). Pd–Cu/ACC catalyst showed higher nitrate removal activity and TNR than Pd–Cu/GFC, Pd–Cu/AlO–GF and Pd–Cu/SnO–GF under the reaction conditions used (Table 1). This suggested that the higher specific surface area of Pd–Cu/ACC might play a very important role in catalytic performance. Surface complexes of the amphoteric surface of the fibrous cloth used may contribute to the interaction with water-dissolved ionic species [17] and the obtained results could be also explained by the expected ability of ACC to concentrate NO_3^- anions in the water–solid interface by ionic forces. Because the pH of nitrate solution is lower that the pzc of Pd–Cu/ACC catalyst (8.3), the Pd–Cu/ACC catalyst surface is becoming positively charged and the attraction of nitrate anions on Pd–Cu/ACC is favored, in

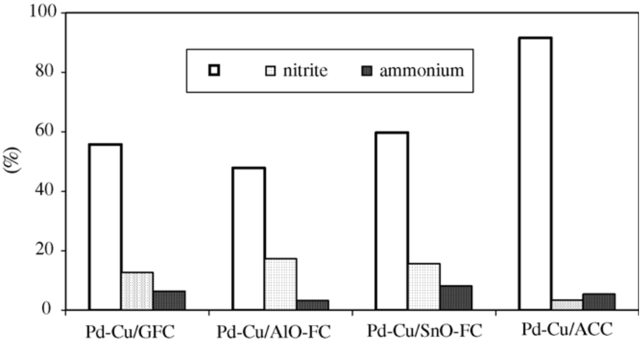

Fig. 1. Nitrate conversion (open column) and selectivity towards nitrite and ammonium ions during nitrate hydrogenation over Pd–Cu catalysts supported on various fibrous cloths. The 2.2 g catalyst with Pd = 2.0 wt.% and Cu = 0.6 wt.%; reaction time 3 h.

Table 1
Characteristics, denitrification activity and stability of Pd–Cu catalytic cloths

Catalyst[a]	BET-ssa (m^2/g catalyst)	pzc	Steady state rate (mmol NO_3^-/(h g catalyst))[b]	pH out	Metal loss (%)[c]	
					Pd	Cu
Pd–Cu/ACC	1510	8.3	0.23	7.2	0.04	0.1
Pd–Cu/GFC	1.7	3.2	0.14	6.5	2.2	5.6
Pd–Cu/SnO–FC	4.9	3.5	0.15	6.5	0.5	1.3
Pd–Cu/A–FC	3.5	4.4	0.12	6.4	0.4	8.5

[a] Pd = 2 wt.%, Cu = 0.6 wt.% (Cu:Pd atomic ratio = 0.49).
[b] Reaction time 3 h.
[c] Percentage of the amount of metal vs. that in the fresh catalyst.

contrast to the situation of oxide supports, which have a pzc that is lower than the pH of nitrate solution.

Table 1 lists also the leached amounts of Pd and Cu during 6 h of reaction. With Pd–Cu/ACC catalyst the loss of metals were negligibly small. However, in the case of three other glass-based supported catalysts, Pd and Cu dissolution was considerably larger. Our results are consistent with that of Yoshinaga et al. [10] who found granular activated carbon to be a better and stable support for Pd–Cu catalyst than silica, alumina or zirconia for nitrate hydrogenation in flow tubular reactor.

Therefore, the ACC was selected as suitable support for the further study. As shown in Fig. 2, ACC is woven from long threads of ca. 0.5 mm in diameter; these threads consist of a bundle of elementary fibers of 10 μm in diameter.

3.2. Effects of Cu on properties of Pd–Cu/ACC catalysts

In principle, promoting of noble metal can be performed: (a) by common loading of support with noble and second promoter metal precursor (via impregnation, deposition-precipitation, etc.) and/or (b) by modification of a parent noble metal catalyst [22]. Thus, it was demonstrated that nitrates are more rapidly and selectively reduced on bimetallic catalyst, when both metals (Pt–Cu [23] or Pd–Sn [24]) are in close contact, i.e., when they are prepared in a way that creates bimetallic active sites. Pd–Cu catalysts used in this work were prepared by the controlled reduction of copper salt on parent Pd/cloth, in order to obtain optimal contact of the two metals.

In order to gain information on the metallic particles supported on ACC, studies of the metal particle size and dispersion of supported metal particles that are two important characteristic of a catalyst, related to metal interaction with the support, were performed by means of HRSEM and CO-chemisorption.

3.2.1. Characterization of Pd–Cu/ACC catalysts

Fig. 3 presents typical HRSEM micrographs of the monometallic Pd/ACC and two bimetallic Cu–Pd/ACC catalysts at different Cu:Pd atomic ratio. Image (A) with 2 wt.% Pd/ACC do not show evidence of particle populations with highly different sizes, while the selective deposition of Cu to Pd/ACC (micrographs B, C) leads to broader distribution of large together with small particles. Similar results have been reported addition of Sn to Pt supported on carbon [26]: as the tin loading increases a broader particle size distribution, with the average particle diameter shifted towards larger values, was noted. The mean particle size d for each sample was calculated as follows:

$$d = \frac{\sum n_i d_i}{\sum n_i} \tag{6}$$

where n_i is number of particle with diameter d_i. The sizes of individual particles were measured manually on HRSEM micrographs; the large metal particles, of more than 30 nm in size, were not taken into account. From the metal particle size d, the specific surface area of supported metal particles (S_M, m^2/g_{cat}) was calculated assuming semi-spherical morphology for the crystallites:

$$S_M = \frac{3 \times 10^3 (f_{Pd}/\rho_{Pd} + f_{Cu}/\rho_{Cu})}{d} \tag{7}$$

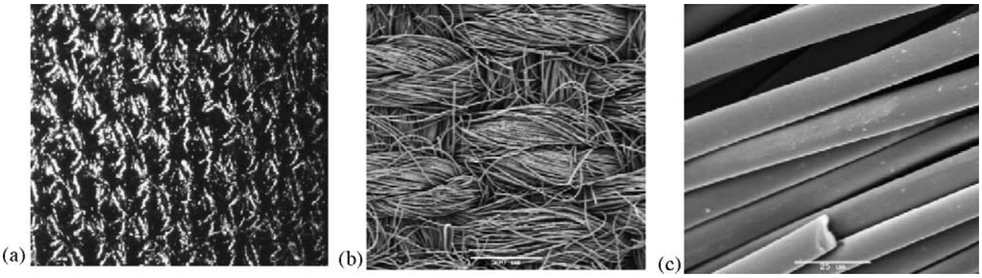

Fig. 2. Macrostructure of ACC (a and b) and a magnified view of fibers in ACC (c).

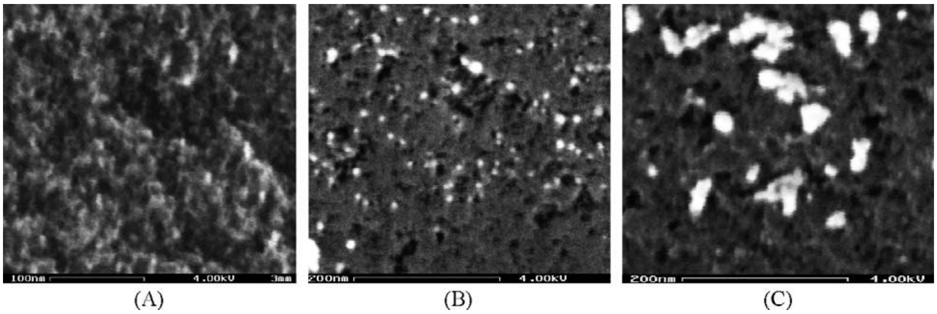

Fig. 3. Typical HR SEM pictures of 2 wt.% Pd/ACC (A) and 2 wt.% Pd–Cu/ACC samples with Cu:Pd atomic ratio of 0.49 (B) and 1.5 (C).

Table 2
Characteristics of supported metal particles and the denitrification activity of 2% Pd–Cu/ACC catalysts with different Cu to Pd ratio

Cu/Pd (atomic ratio)	d (nm)[a]	S_M (m^2/g catalyst)[a]	D_{Pd} (%)[b]	S_{Pd} (m^2/g catalyst)[b]	Conversion ($X_{NO_3^-}$,%)[c]	Steady state rate, mmol NO_3^-/h g catalyst (mmol NO_3^-/h g Pd)
0	2.5 ± 0.4	2.0	21.0	1.9	0	0
0.23	3.1 ± 0.7	1.9	10.8	1.0	52.2	0.13 (6.5)
0.49	5.7 ± 1.1	1.2	4.1	0.4	91.6	0.23 (11.5)
1.00	10.2 ± 1.4	0.9	2.0	0.2	77.8	0.19 (9.5)
1.51	18.9 ± 2.4	0.6	0.9	0.1	60.4	0.15 (7.5)

[a] From HRSEM.
[b] From CO-chemosorption data.
[c] Reaction time 3 h.

where ρ_{Pd} (12.02 g/cm^3) and ρ_{Cu} (8.9 g/cm^3) are the bulk density; $f_{Pd} = m_{Pd}/m_{cat}$ and $f_{Cu} = m_{Cu}/m_{cat}$ are weight fraction of Pd and Cu metals, respectively.

CO-chemisorption on Pd is widely used to measure the Pd dispersion, while adsorption of CO on Cu atoms is largely physical in nature [21,25]. Therefore, CO-chemisorption allows us to selectively determine the concentration of Pd atoms exposed to the metal particle surface providing differentiation between the Pd and Cu atoms on the surface of bimetallic particles. The palladium dispersion for each sample was calculated assuming that the chemisorption mean stoichiometry X_{Pd-CO} is 1 [25]:

$$D_{Pd} = \frac{V_{CO} M_{Pd} X_{Pd-CO}}{22414\, f_{Pd}} \tag{8}$$

here, V_{CO} is CO chemisorbed gas STP volume; M_{Pd} is the atomic weight of Pd (106.4 g/mol), and the constant 22414 refers to molar density (cm^3/mol).

The values of specific surface area of Pd atoms exposed to the metallic particle surface (S_{Pd} m^2/g cat.) were determined from CO-chemisorption, using Eq. (9)[25]:

$$S_{Pd} = \frac{2.7 \times 10^{15} V_{CO} X_{Pd-CO}}{P_{Pd}} \tag{9}$$

where P_{Pd} is the surface density of palladium atoms (1.27×10^{15} atom/cm^2).

By interpreting the obtained data one should bear in mind that lateral resolution of HRSEM used (≈1 nm) resulted in some loss of information for the smallest metallic particles and the accuracy of our approach to determine the metal particle size and, in turn, the values of S_M and D was checked by independent CO-chemisorption method. As can seen from Table 2, the value S_M for monometallic 2 wt.% Pd/ACC sample calculated using Eq. (7) from HRSEM micrograph (2.0 m^2/g catalyst) is close to the value derived from CO-chemisorption measurement and calculated using Eq. (9) (1.9 m^2/g catalyst). Negligible discrepancy between these two values (≈1%) indicates clearly that mode used for determination of average particles sizes, is accurate and correct.

Table 2 shows the mean particle diameter, the dispersion and the surface of metallic particles for different Cu loading

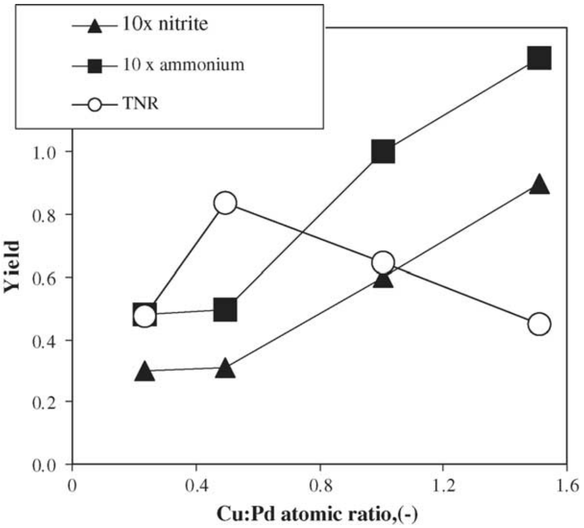

Fig. 4. Effect of Pd:Cu atomic ratio in 2 wt.% Pd–Cu/ACC on the yield of products formed during nitrate hydrogenation. Reaction time 3 h.

Table 3
Denitrification efficiency of Pd–Cu/ACC catalysts with different metal content

Catalyst	Nitrate conversion (%)[a]	Rate (mmol NO_3^-/(h g Pd))	Selectivity (%)	
			NO_2^-	NH_4^+
1 wt.% Pd–0.3 wt.% 5Cu/ACC	67.7	17.0	1.9	3.2
2 wt.% Pd–0.6 wt.% Cu/ACC	91.6	11.5	3.4	5.4
4 wt.% Pd–1.2 wt.% Cu/ACC	83.6	5.3	3.6	5.5

[a] Reaction time 3 h.

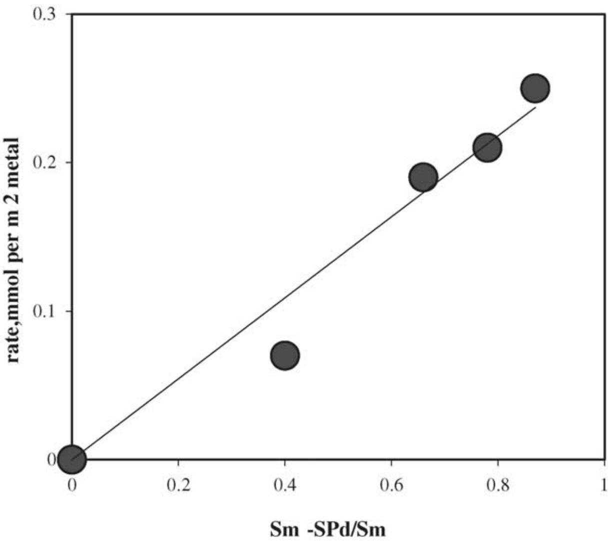

Fig. 5. Denitrification rate referred to metal surface area versus the relative surface fraction covered by Cu atoms.

of supported 2 wt.% Pd /ACC catalysts. The selective deposition of Cu on Pd/ACC led to a significant increase of mean particle size *d* that, in turn, led to decline in dispersion (D_{Pd}) from 21 to 0.9% (by increasing of Cu:Pd atomic ratio from 0.23 to 1.5), indicating the presence of surface Pd atoms even at high Cu coverage. Furthermore, increasing in Cu:Pd atomic ratio is accompanied by declining the specific surface area of supported metal particles (S_M) and the surface of Pd atoms ($S_{Pd} < S_M$) that reflected the partial blocking of Pd atoms by Cu atoms. This cannot be simply explained on the basis of the increase of metal particle size observed on these samples. It is instead most likely that copper species decorate the surface of palladium particles blocking the palladium sites required for the chemisorption.

3.2.2. *Interpretation of catalytic activity/selectivity of Pd–Cu/ACC*

The denitrification efficiencies for Pd–Cu/ACC catalysts with different Cu-loading are compared on Table 2 and Fig. 4. It has been found that the catalytic activity and the selectivity to reaction products are quite different depending on Cu: Pd atomic ratio. The denitrification rate (mmol h^{-1}/g catalyst) and TNR were observed to pass through a local maximum at Cu:Pd atomic ratio of about 0.5. For higher Cu:Pd atomic ratios the yields of nitrite and ammonium ions sharply increased.

Pd/ACC monometallic catalyst was found to hardly have any activity for nitrate reduction; thus, coexistence of Pd and Cu is indispensable for hydrogenation of nitrates. If each surface Cu atom formed one Pd–Cu bimetallic active site and if these Pd–Cu ensembles are responsible for nitrate-to-nitrite conversion then nitrate disappearance rate referred to metal surface area must be proportional to the relative surface fraction covered by Cu atoms. As can one see from Fig. 5, this proposition is well supported by the experiments and can be regarded as an indication for the existence of Cu–Pd ensembles working as active sites for nitrate-to-nitrite reduction.

By fixing the Cu:Pd atomic ratio to be 0.5, the effect of total metal content on ACC support has been investigated. As shown in Table 3, low metal content (1.3 wt.%) or high metal content (5.2 wt.%) is not beneficial for nitrate conversion (and for the corresponding rate based on g catalyst weight), and optimal content is 2.6 wt.%. However, the nitrate hydrogenation rates, based on Pd metal weight (mmol nitrate h^{-1} $g_{Pd}{}^{-1}$) were observed to diminish with increase of metal loading. This observation suggests that atomic arrangement of active particles on the surface of catalyst rather than the metal loading has a great influence on nitrate removal activity or that the metal-support interaction should be accounted for. To draw more fundamental conclusions about the active sites involved in process, detailed and extended studies of surface characteristics of supported metal particles are required; results of that effects using quantum chemical calculations will be reported in further contributions.

4. Summary

The results presented here show that of the four supports studied for the Pd–Cu bimetallic catalysts for the liquid-phase hydrogenation of nitrates Pd–Cu/ACC is more active and selective than Pd–Cu supported on glass fibers cloth (GFC) and on GFCs coated with Al_2O_3 or SnO_2. The main results and conclusions obtained in a study of series of 2% Pd–Cu/ACC catalysts prepared by selective deposition of Cu on Pd/ACC, and characterized by CO-chemisorption and HRSEM data for nitrate hydrogenation in a radial-flow reactor at steady state are the following:

- Increasing the Cu:Pd atomic ratio led to larger supported metal particles and, in turn, to smaller specific surface area of supported metal particles (S_M) accompanied by a declining fraction of Pd surface atoms.
- With varying the Cu:Pd atomic ratio the nitrate disappearance rate and yield of nitrogen pass through a maximum at the atomic ratio of Cu:Pd of about 0.5. The atomic arrangement of active particles on the surface of catalyst rather than the metal loading has a great influence on nitrate removal activity.

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