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Short Communication

Synthesis of Pd/Al₂O₃ coating onto a cordierite monolith and its application to nitrite reduction in water





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ABSTRACT

The catalytic properties of Pd/Al₂O₃ coating onto cordierite monolith channels for the nitrite reduction in water were studied. This coating was synthesized producing an alumina layer via washcoat and adding the palladium species to this layer by immersion into a PdCl₂ solution. Different characterization techniques, XRD, XPS, SEM and EDX were used to study the physicochemical and morphological properties of the catalytic coatings. The comparison of these results along with the catalytic behaviors allowed comprehension of Pd active sites and their way of acting. The structured catalyst so obtained was active and stable in the nitrite reduction.

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1. Introduction

The excess of nitrates in water as a consequence of the use of fertilizers or effluent outfalls from urban residuals or from certain industries [1] is harmful for human health due to their reduction to nitrites (NO_2^-), which combine with hemoglobin in the human blood to form a toxic compound of methahemoglobin [2].

The catalytic reduction of nitrates/nitrites in water, has received considerable attention [3] since it is an economically profitable process. It is one of the most widely studied hydrogenation reactions for the treatment of underground water [4]. Nevertheless, the control of the selectivity to nitrogen (lower formation of NH_4^+ and NO_2^-) is a key problem in the development of future catalytic technologies for the abatement of nitrates.

Even though important efforts have been carried out in the development of effective catalysts for the nitrate reduction, the practical use of such materials is still limited due to the generation of ammonia, which is the principal by-product of this catalytic system [5]. Investigations have focused on obtaining catalysts through the use of metals, different metal mixtures and metallic oxides as supports [6,7]. It is of interest to adhere these catalysts to the walls of a structured substrate, such as ceramic monoliths [8]. Thus, the pressure drop decreases and the separation of the catalyst at the end of the process is feasible.

The aim of this work was to generate a stable layer of Pd/Al_2O_3 on the walls of a cordierite monolith, analyze its activity and selectivity in nitrite reduction in water and understand Pd active sites and their way of acting.

2. Experimental

2.1. Cordierite monolith pieces

Commercial monoliths of cordierite $(2MgO:2Al_2O_3:5SiO_2)$ were cut in portions of 8×8 cells and 2 cm of length. Then, these pieces were washed with acetone in ultrasonic bath for 30 min and then in water. Finally the pieces were dried in stove at 120 °C for 30 min.

2.2. Al₂O₃ coating onto monolith walls

The pieces were immersed into a commercial suspension containing 20% of Al_2O_3 colloidal (Nyacol AL20) for 1 min. The suspension excess was blown for 20 s. Then, the pieces were dried at 120 °C for 6 h. Finally, they were calcined at 700 °C for 4 h. The entire cycle was repeated until the total gain in weight percentage was around 30%. The structured support so obtained was identified as Al_2O_3 -COR.

2.3. Incorporation of Pd to the Al₂O₃ coating

Al₂O₃-COR samples were immersed into a PdCl₂ (8000 mg/L) solution for 1 min. The solution excess was blown for 10 s and then, the pieces were dried in stove for 6 h. The process was repeated five times and 1% w/w referred to the Al₂O₃-COR weight was reached. The structured catalyst so obtained was identified as Pd/Al₂O₃-COR.

2.4. Catalytic coating characterization

XRD patterns of the structured catalysts and the cordierite monolith were acquired with an XD-D1 Shimadzu instrument, using $CuK\alpha$

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A. Devard et al. / Catalysis Communications 34 (2013) 26-29

radiation at 30 kV and 40 mA. The scan rate was 1° min⁻¹ in the $2\theta = 10-90^{\circ}$ range.

The samples were examined in a scanning electronic microscope (SEM), JEOL, JSM 35C, equipped with an X-ray energy dispersive spectrometer (EDS).

The surface species were analyzed by XPS using a SPECS instrument, Phoibos 150, with an X-ray source (AlK α) at 100 W and 10 kV. The C1s peak with BE of 284.6 eV was taken as reference.

2.5. Reaction experiments

Prior to the reaction test, the structured catalysts were reduced in H_2 flow at 250 °C for 1 h. The reaction test was performed in batch condition in a three-necked round bottom flask (250 mL) equipped with a magnetic stirrer (700–800 rpm). A gas bubbling device, having a flow rate of 400 mL min⁻¹, was used to bubble either N₂ or H₂. Experiments were carried out at room temperature, and atmospheric pressure.

A volume of 80.0 mL of distilled water was loaded into the flask and purged with N_2 flow for 20 min. Then, two structured catalysts were held in the middle of the flask and the N_2 purge was repeated. Subsequently, a hydrogen flow was fed to the reactor. The reaction started when a concentrated nitrite solution was added to the vessel in order to achieve 25, 50, 100 and 200 NppmNO₂⁻ (concentration of nitrogen in the form of nitrite). A pH of ca. 5 was maintained during the reaction time by the addition of small amounts of HCI [9].

Two catalytic reactions can take place:

$$2NO_2^- + H_2 \rightarrow N_2 + 2OH^-$$

 $NO_2^- + 3H_2 \rightarrow NH_4^+ + 2OH^-$

Small samples were taken from the vessel for the determination of nitrite and ammonium using the colorimetric technique [10].

The pH was kept constant during reaction since the reduction of nitrite led to the formation of hydroxide ions. Previous studies indicated that the pH of 5 is appropriate to perform these reaction experiments [11].

3. Results and discussion

3.1. Catalytic coating characterization

3.1.1. Al₂O₃ coating (Al₂O₃-COR)

Fig. 1 shows the weight gain percentage of the Al₂O₃ coating after each cycle of immersion–blowing–drying–calcination for four samples. Six cycles were necessary to achieve an average weight gain of 30%.

3.1.2. Crystalline phases of structured catalyst (Pd/Al₂O₃-COR)

The diffractograms of the structured catalyst (Pd/Al_2O_3 -COR) and the structured support (Al_2O_3 -COR) are presented in Fig. 2 along with those of the original cordierite monolith (COR) and γ -Al₂O₃ powder.

The characteristic XRD diffractions of COR are clearly identified in both XRD patterns of structured systems, Pd/Al₂O₃-COR and Al₂O₃-COR. Likewise, comparing the latter two patterns with that corresponding to γ -Al₂O₃, the existence of an overlap between the signals attributed to the cordierite and those of the alumina is observed. However, some modifications in the signals around 20:45.6 and 65.7° of the structured system patterns compared with those of cordierite are evident (Fig. 2, dash lines). These changes could be attributed to the Al₂O₃ layer developed on both structured systems.

The PdO₂ pattern (JCPDS34-1101) indicates that the most intense signal is at $2\theta = 54.6^{\circ}$. The PdO diffractogram (JCPDS41-1107) has a strong signal at $2\theta = 33.9^{\circ}$. On the other hand, the Pd° pattern (JCPDS46-1043) shows a signal at $2\theta = 40.2^{\circ}$, which is the most intense. Thus, no signals that may be attributable to Pd compounds are observed in the Pd/Al₂O₃-COR pattern, suggesting a good distribution of Pd species in the γ -Al₂O₃



Fig. 1. Weight gain percentages after each alumina washcoating cycle.

coating. This analysis is in agreement with that reported by Persson et al. [12].

3.1.3. Morphology of Pd/Al₂O₃ coating

In order to analyze the Pd/Al_2O_3 coating morphology and its homogeneity, SEM micrographs of different structured catalyst portions were obtained. The micrograph of the channel wall (Fig. 3a) shows that the catalytic layer is homogeneously distributed and the original monolith wall macroporosity remains fairly unchanged, indicating that the layer thickness is thin. The surface region near to the channel wall intersection shows some areas with the formation of interconnected cracks (Fig. 3b). Besides, an increase of the layer thickness at the channel corner (Fig. 3c) occurred because of the washcoating fluid-dynamic process.

The micrograph of the channel wall of structured catalyst after being used in the reaction is shown in Fig. 3d. No significant differences were observed regarding the micrograph of the fresh structured catalyst (Fig. 3a), indicating the good stability of the Pd/Al₂O₃ coating so obtained, although it was immersed in a water flow for several hours.



Fig. 2. X-ray patterns of: Al₂O₃, original cordierite monolith (COR), structured support (Al₂O₃-COR) and structured catalyst (Pd/Al₂O₃-COR).

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A. Devard et al. / Catalysis Communications 34 (2013) 26-29



Fig. 3. SEM micrographs of the structured catalyst (Pd/Al₂O₃-COR). View of (a) channel wall, (b) channel edge, (c) channel corner, and (d) channel surface after being tested in reaction.

3.1.4. Element distribution on Pd/Al₂O₃-COR

28

The results obtained via the EDS allow analysis of Al, Si, Mg and Pd in the structured catalyst (Table 1). The Mg and Si elements, which belong to the cordierite compound, are found in certain amounts together with Al in the central region of the channel walls but are absent in the regions near the corners. This is due to the differences in the layer thickness of both regions. In this sense, the identification of Si and Mg in the center confirms that the thickness in that region is noticeably thinner. The thin layer would be a consequence of the high porosity of the cordierite monolith walls that facilitates the diffusion of the colloidal solution inside the walls during washcoating.

The Pd was well distributed on the entire catalytic coating, having an average Pd/Al ratio of 0.11. This ratio in the channel corners was 0.14 because its higher layer thickness avoided the cordierite interference in the EDS analysis. Therefore, the latter value may be taken as the genuine Pd/Al ratio.

3.1.5. Pd species on the surface of the Pd/Al₂O₃ coating

The XPS spectrum of fresh Pd/Al_2O_3 -COR and those of the structured catalyst after reduction in H_2 at 250 °C and after the reaction test are presented in Fig. 4. The binding energy (BE) range shown corresponds to the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ doublet.

The XPS signals at 343.5 and 338.5 eV, which are related to the palladium doublet in its oxidized state, are shown in the XPS profile of the fresh sample (Fig. 4a). The doublet is shifted to lower BE values, 341.0 and 336.0 eV (Fig. 4b), when the catalyst was reduced, indicating the complete reduction to Pd°. These results are in agreement with those reported by Ivanova et al. [13] in relation to the Pd/Al₂O₃. Even though the BE of the Pd3d_{5/2} for Pd° is in the narrow range of 335.1–335.4 eV, these authors established that the shift to a larger BE value (336.1 eV) is due to the small sizes of the Pd clusters.

The photoelectronic profile of the Pd3d core level of the structured catalyst after being tested in the nitrite reduction reaction (Fig. 4c) contains two doublets, one at 344.0 and 338.6 eV, while the other is at 341.0 and 336.4 eV. The latter is associated with Pd° species, whereas the former is a consequence of the presence of PdOx on the coating. This observation is also consistent with that reported for powder Pd

Table 1

EDX analysis in different regions of the structured catalyst.

Pd/Al ₂ O ₃ - COR	Channel region	% w/w Mg	% w/w Al	% w/w Si	% w/w Pd	Si/Al	Pd/Al
Fresh	Channel center	3.03	65.84	25.84	5.75	0.39	0.09
	Channel corner	nd ^a	87.59	nd	12.41	0.00	0.14
Reduced	Channel center	1.61	73.98	16.93	7.49	0.23	0.10
	Channel corner	nd	88.16	nd	11.84	0.00	0.13

^a Not detectable.

catalysts [11,14]. Therefore, the partial re-oxidation from Pd° to PdOx during the reaction substantiates the participation of the catalytic coating Pd as an active site.

3.2. Catalytic activity

The nitrite conversions under reaction conditions are shown in Fig. 5a, reaching 100% in all cases with reaction times between 120 and 200 min.

Fig. 5b shows NH_4^+ concentration, which is an undesirable product. Thus, a catalyst with a low selectivity to this product and a high selectivity to nitrogen is required. The structured catalyst, Pd/Al_3O_2 -COR, is always able to achieve NH_4^+ concentrations lower than 10 NppmNH₄⁺. Hence, the combination of reduced and oxidized palladium particles obtained in the catalytic coating favored the nitrite reduction to nitrogen against the over-reduction to ammonia. Barrabés et al. [15] claim



Fig. 4. XPS signals of Pd/Al_2O_3 -COR: (a) fresh, (b) reduced, and (c) after being tested in reaction. $Pd3d_{3/2}$ (---), $Pd3d_{5/2}$ (---).

A. Devard et al. / Catalysis Communications 34 (2013) 26-29



Fig. 5. (a) Concentration of nitrites (NppmNO₂⁻) and (b) ammonia (NppmNH₄) during the reduction reaction of 25 NppmNO₂⁻ (\blacktriangle), 50 NppmNO₂⁻ (\blacklozenge), 100 NppmNO₂⁻ (\blacksquare), and 200 NppmNO₂⁻ (\bigstar).

that Pd° is able to reduce the nitrite ions via the H_2 dissociation on its metal surface. Besides, and based on the XPS analysis, these authors report that the Pd surface after the reaction contains the surface pair Pd°/PdOx, thus suggesting the redox reaction between nitrite ions and Pd particles. In this case, during the N_2 formation, the metal surface would be oxidized and then the hydrogen would restore the metal surface.

4. Conclusions

It was possible to obtain a structured catalyst, Pd/Al_2O_3 -COR, which is active in the reduction of nitrites and has the advantage of generating low amounts of ammonium, indicating a greater selectivity to nitrogen.

A thin catalytic layer was produced while most of the original monolith wall macroporosity remained. Nevertheless, an increase of the layer thickness at the channel corner occurred because of the washcoating fluid-dynamic process. The coating so obtained presented a good adherence even after the reaction in a batch system under stirring and under a pH around 5. The Pd particles were well distributed on the entire catalytic coating, having an average Pd/Al ratio of 0.14. Palladium was in its oxidized state on the fresh structured catalyst and a strong metal-support interaction took place during the calcination due to a shift in the binding energies of Pd $3d_{5/2}$ for the oxidized component. After a treatment in H₂, the PdOx particles were reduced to Pd°. Finally, the reduced and oxidized states of palladium were present on the catalytic coating after the reaction, as expected.

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