Partially hydrophobized catalyst particles for aqueous nitrite hydrogenation

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ABSTRACT

The aim of this work is to synthesize catalysts support particles that are partly hydrophobic and partly hydrophilic, with the ultimate goal to manipulate the performance of Pd supported catalysts on these supports for hydrogenation of nitrite in water. Partly hydrophobic alumina supports were successfully prepared *via* physically mixing of hydrophobic α-alumina and hydrophilic γ-alumina, and *via* varying the amount of perfluorinated-octyltrichlorosilane (FOTS) on pure γ-alumina. The results from elemental analysis, SEM-EDX, XRD and contact angle measurements confirmed that the materials indeed contained hydrophobic and hydrophilic domains. Pd catalysts on supports produced *via* the mixing method resulted in a slightly increased turnover frequency as compared to the original supported Pd catalyst. Remarkably, Pd supported on partially hydrophobic alumina exhibited increased selectivity to ammonia instead of N_2, which is attributed to enhanced transfer of H_2 to the active sites, *via* interaction of the catalyst particles with gas bubbles.

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1. Introduction

Nitrate (NO_3^-) excess in water is caused by fertilizers and water effluents from certain industries. Nitrate can reduce to nitrite (NO_2^-) and its removal from water has been widely studied during the last 20 years [1–10]. The most important reason to study the removal of nitrites is its high contaminant property potentially causing cancer or blue baby syndrome [11,12]. Because of that, the European Environmental Agency (EEA) has established a legal nitrite limit in water, 0.1 mg/L for drinking water.

The nitrate and nitrite removal from water has been attempted using different techniques, including catalytic hydrogenation [13,14]. This procedure uses hydrogen as reducing agent to catalytically transform nitrite to nitrogen. Several materials have been used as catalysts supports like alumina, titania and active carbon. The catalytic active site for nitrite hydrogenation is a noble metal, either Pd or Pt, whereas nitrate hydrogenation needs addition of a less noble metal, i.e. Cu [3–10].

A disadvantage of this method is the formation of ammonia [15], which has a legal limit in water of 0.5 mg/L, as established by the EEA. The catalytic denitrification involves three phases: gas (hydrogen), liquid (water containing nitrites) and solid (catalyst).

To achieve both high activity and selectivity, proper contact between the three phases is essential. Studies related to reactor design, reaction conditions and catalyst have been presented. Most notably, membrane reactors were studied for nitrate reduction, enabling controlled hydrogen diffusion [16–18]. Optimizing hydrogen transfer to the active sites as well as increasing the hydrogen concentration will enhance the reaction rate. Unfortunately, it also results in enhanced formation of ammonia as the selectivity depends on the ratio of H-species to N-species (H/N ratio) on the active sites [4,6,8,9,19]. This ratio is determined by the local concentration of nitrite as well as hydrogen at the active sites. The challenge is to find the optimal hydrogen concentration, balancing between activity and selectivity. When reducing the hydrogen concentration to prevent ammonia formation, mass transfer limitations of hydrogen will become more dominant. Therefore, it is very important to develop catalysts and reactors that can operate efficiently at very low hydrogen concentration without significant diffusion limitation.

In this paper the synthesis of partially hydrophobized materials is presented. Such materials improve contact between the three phases, inspired on previous work by Aran et al. [20]. In that study, the authors modified a porous α-alumina tube that was used as a mesoreactor. The outer part of the α-alumina tube, which is in direct contact with the gas, is hydrophobized while the inner part, contacting the liquid and supporting the active Pd nanoparticles, remained hydrophilic. In this way an optimized contact is achieved

between the gas and the liquid, minimizing diffusional distance. Although the performance of this device was not yet optimal, the achievement to manipulate the gas–liquid interface very close to the supported active sites was demonstrated at (meso-) reactor scale. Constant conversions were obtained even at very low hydrogen concentrations.

The goal of the current study is to explore a similar approach for slurry catalyst reactors, by synthesizing catalyst particles that contain hydrophobic as well as hydrophilic domains. The idea is that hydrophobic domains adhere to gas bubbles, enhancing transfer of hydrogen from the bubbles to the active sites, whereas hydrophilic domains allow efficient transport of dissolved nitrite ions. We demonstrate that manipulation of interfacial characteristics within single support particles influences conversion and selectivity in nitrite reduction.

2. Experimental

2.1. Materials

Commercial α-Al_2O_3 (Sumitomo Chemicals, $5\,m^2/g$) and γ-Al_2O_3 powder (BASF, $179\,m^2/g$) were used as catalyst supports in this study. Palladium(II) 2,4-pentanedione ($Pd(acac)_2$, Aldrich, 99%) in toluene (Merck, ACS) was used as catalyst precursor solution. For the surface modification steps a perfluorinated-octyltrichlorosilane (FOTS, Aldrich, 97%) and n-hexane as solvent (Sigma–Aldrich, ACS) were used as received. Sodium nitrite ($NaNO_2$, Sigma–Aldrich, ACS) was used as source for nitrite ions (NO_2^-) dissolved in MilliQ water.

The synthesis of particles with both hydrophilic as well as hydrophobic domains was attempted in two ways, either by mixing hydrophilic and hydrophobic particles or by partial hydrophobization of a hydrophilic sample. The first method comprises hydrophobization of α-alumina, followed by mixing this material with hydrophilic γ-alumina; finally the mixture was pelletized and then crushed to obtain particles containing both phases. The second method was to partially hydrophobize γ-alumina using silanes, in one single step and using different amounts of FOTS.

2.2. Physical mixture of hydrophobic α-alumina and γ-alumina

1.5 gram of α-alumina was immersed to a 2.5 mM solution of FOTS in hexane (40 mL) for 5 min, removed from the liquid and placed in an oven at $100\,°C$ for 1 h. After that, the sample was rinsed with hexane and dried at room temperature (adapted from [21]). FOTS is adsorbed on the surface in the first step and heating at $100\,°C$ is aimed at improving the bonding of FOTS. The final rinsing removes the excess of FOTS which is not chemically bonded.

Pd was deposited on the γ-alumina surface following the subsequent recipe: the desired amount of $Pd(acac)_2$ (1 wt%) was dissolved in 40 mL of toluene. The γ-alumina was added and the solvent was evaporated at $50\,°C$. Once the sample was dried, it was placed in an oven and calcined at $250\,°C$ during 1 h in air and then reduced at the same temperature during 2 h using a mixture of H_2 and N_2 (1:1).

0.5 g of hydrophobized α-alumina was mixed in a mortar with 0.5 g of Pd/γ-alumina. The mixture was pressurized at 4000 bar during 1.5 min in a cold isostatic press. The pellet was broken and sieved to obtain particle sizes between 0.1 and 0.04 mm.

2.3. Partial hydrophobization of γ-alumina

The Pd was first deposited on the γ-alumina surface following the same procedure as described in the previous section. The adsorption of FOTS was performed using 40 mL of hexane solution with different amounts of FOTS and different times for adsorption
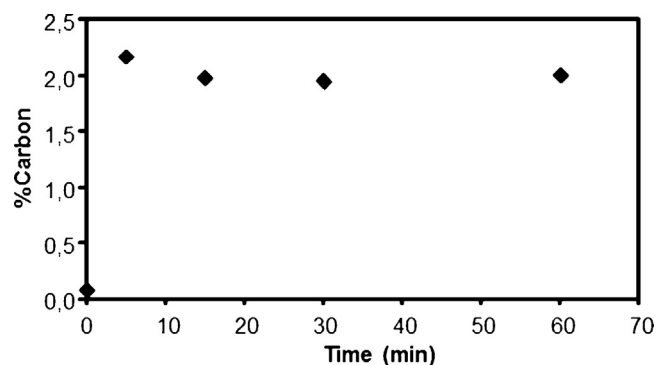

Fig. 1. Carbon weight percentage as a function of time surface modification of alumina immersed in 0.4 mmol of FOTS solution.

(0.1 mmol, 0.4 mmol, 1.6 mmol and 2 mmol of FOTS, for times varying between 5 and 180 min). As an example, for 0.1 mmol of FOTS and 5 min of adsorption: 1.5 gram of γ-alumina was immersed to a solution containing 0.1 mmol of FOTS in hexane (40 mL). They were kept in the solution for 5 min, taken out and placed in an oven at $100\,°C$ for 1 h as described in the previous section. Finally, the sample was rinsed with hexane to remove any excess of silanes, and dried at room temperature.

2.4. Characterization

To determine qualitatively the hydrophobicity of the materials, contact angle measurements were performed on a pellet of the sample. Surface roughness of the pellet will significantly influence the contact angles, but the method allows comparison of samples and to determine the trends in the macroscopic hydrophobicity. The water contact angle was measured using an OCA 15 Dataphysics. The surface area and the pore volume were obtained from the N_2 adsorption isotherm obtained at 77 K (Micromeritics Tristar). X-ray fluorescence spectroscopy (XRF) was used to determine the palladium loading on the samples. CO chemisorption (Micromeritics, ChemiSorb 2750) at room temperature was used to determine the dispersion of palladium on the samples. XRD was performed using a PANalytical X'Pert-APD powder diffractometer equipped with a position sensitive detector analyzed over the 2θ-range 5–90°. Scanning Electron Microscopy (LEO 1550 FEG-SEM) equipped with energy dispersive X-ray analysis (EDX, Thermo Noran Vantage system) was used to qualitatively study the distributions of Pd and FOTS through the material surface. Weight loss of the samples after adding FOTS was determined using thermogravimetrical analysis (TGA/SDTA851e, Mettler Toledo). Elemental analysis (CHNS-O Analyzer, Interscience, Thermo Scientific) was used to determine the amount of FOTS on the surface by calculating the surface coverage of FOTS (SC) using the following equation:

$$SC\left(\frac{mol\,FOTS}{m^2}\right) = \%C\,\frac{1}{100}\,\frac{g\,C}{g\,total}\,\frac{1\,mol\,C}{12\,g\,C}\,\frac{1\,mol\,FOTS}{8\,mol\,C}\,\frac{1\,g\,total}{BET\,m^2} \quad (1)$$

where %C is the carbon-weight-concentration as obtained from the elemental analysis and BET is the surface area of the material according to N_2 physisorption.

The value of %C is determined by elemental analysis as a function of immersion time for the different amounts of FOTS (see Fig. 1 for an example). Experimental values for %C are obtained from the equilibrium value, which is rapidly achieved.

2.5. Catalytic performance

Catalytic tests were done in a stirred batch reactor at room temperature and atmospheric pressure. The reactor was glass made