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Catalytic wet air oxidation of ammonia over supported noble metals

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ABSTRACT

Highly active and selective supported noble metal catalysts were studied in the catalytic wet air oxidation of ammonia. Under the applied reaction conditions (200 °C, 50 bar total pressure) only nitrites and molecular nitrogen were detected as primary products. Nitrates formed upon oxidation of nitrites. Platinum-based catalysts were shown to be the most active and among the most selective toward molecular nitrogen. The control of the oxygen coverage at the catalyst surface (metal–oxygen bond energy) was evidenced to have a key impact on both the activity and the selectivity. The retro-disproportionation and nitrous acid decomposition reactions appeared to impact the selectivity upon the conversion of nitrites to nitrates.

1. Introduction

Ammonia in water is a top environmental issue. It is increasingly used in major industrial production plants (fertilizers, urea...) [1] and often produced as an intermediate upon decomposition of higher nitrogen-containing organic compounds [2]. Conventionally, ammonia can be removed from water via nitrification/denitrification biological processes [2–6]. Such technology is certainly cheap and quite easy to implement but limited to low ammonia concentrations ($\leq$100 mg L^{-1}). Furthermore, it requires quite long treatment times (>1 week) and large volumes of sewage sludge are produced.

One possible alternative is the catalytic wet air oxidation process (CWAO) [7,8]. It consists in oxidizing pollutants in water under high pressure (1–50 bar oxygen partial pressure) and at high temperature (140–230 °C) in presence of a catalyst. It has several advantages such as the possibility to treat highly concentrated effluents in only hours and without producing any harmful gases and sludge.

The efficiency of the CWAO process for the treatment of ammonia has already been demonstrated. The first patent was filed by Okada et al. [9], claiming that noble and transition metals were active in the ammonia CWAO at 265 °C under 70 bar total pressure (14 bar of oxygen partial pressure). Later on, Qin et al. [10] showed that alumina-supported noble metal catalysts are more active and selective toward molecular nitrogen in the CWAO of ammonia at 230 °C under 15 bar total pressure (3 bar of oxygen partial pressure) compared to transition metals. Similar results were reported by Taguchi et al. [11] over titanium dioxide supported catalysts at 160 °C under 6 bar of oxygen partial pressure. However, little comparison is possible considering the very different reaction conditions used in these studies. Looking specifically at noble metals, most studies focused on platinum, palladium and ruthenium. Oliviero et al. [12] reported about the evaluation of ceria-supported catalysts at 200 °C under 20 bar oxygen partial pressure. Platinum turned out to be the most active while palladium was the most selective toward molecular nitrogen. Ukropec et al. [13] used carbon-supported catalysts at 151 °C under 15 bar total pressure (0.6 bar oxygen partial pressure). Similarly, platinum turned out to be the most active. However, no comparison between the different metals in terms of selectivity is possible due to the lack of data at a given ammonia conversion.

Accordingly, in this study, five different noble metals (platinum, palladium, ruthenium, iridium, rhodium) supported on either titania or zirconia have been systematically evaluated and compared in the CWAO of ammonia. Furthermore, a somehow better understanding of the reaction mechanism was achieved by evaluating the influence of the metal and the support on both the activity and the selectivity toward nitrites, nitrates and dinitrogen.

2. Materials and methods

2.1. Catalysts

2.1.1. Preparation

The platinum, iridium, ruthenium and rhodium precursors (H_2PtCl_6, $Ru(NO)(NO_3)_3$, $IrCl_3$, $RhCl_3$) were purchased from Alfa

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Table 1
Characteristics of the catalysts.

Catalyst	Metal precursor	Metal loading (wt.%)	Average metal crystallite size (nm)	pH_{PZC}
Pt/TiO_2	H_2PtCl_6	2.9	6	3
Pd/TiO_2	$Pd(NH_3)_4(NO_3)_2$	2.8	5	7
Ru/TiO_2	$Ru(NO)(NO_3)_3$	3.0	2	3
Ir/TiO_2	$IrCl_3$	2.5	2	3
Rh/TiO_2	$RhCl_3$	2.8	2	3
Pt/ZrO_2	H_2PtCl_6	2.5	5	3
Pd/ZrO_2	$Pd(NH_3)_4(NO_3)_2$	2.8	2	7
Ru/ZrO_2	$Ru(NO)(NO_3)_3$	3.0	2	4
Ir/ZrO_2	$IrCl_3$	2.5	2	3
Rh/ZrO_2	$RhCl_3$	2.9	2	3

Aesar, while the palladium salt ($Pd(NH_3)_4(NO_3)_2$) was purchased from Aldrich. Two different commercial oxides were used as supports: titanium dioxide (DT-51, Millennium) and zirconium dioxide (XZO 632/18, MEL Chemicals). The platinum, iridium, ruthenium and rhodium catalysts were prepared via wet impregnation while ruthenium was introduced on the support via incipient wetness impregnation. The metal loading was fixed at ca. 3 wt.% in all cases.

After impregnation, the solid was (i) dried overnight at 100 °C under static air, (ii) reduced under flowing H_2 ($30\,mL\,min^{-1}$) at 300 °C for 2 h and (iii) finally passivated at room temperature under 1 vol.% O_2 in N_2 ($30\,mL\,min^{-1}$) for 30 min.

2.1.2. Characterization

The specific surface area of the supports was determined by nitrogen adsorption–desorption at 77 K using a Micromeritics ASAP 2020 instrument.

X-ray diffraction (XRD) was used to identify the crystalline phases of the samples and estimate the metal particle size after Rietveld refinement (Fullprof). Diffractograms were acquired with a Bruker D8 Advance A25 (Cu $K_{\alpha 1+2}$: 0.154184 nm, $2\theta = 4–70°$, step = 0.02°).

The pH at the point of zero charge was measured using two different methods [14,15] with the pHmeter cell M240 from Radiometer equipped with a silver/silver chloride electrode.

The metal loading on the catalysts was measured by ICP-OES (Inductively Coupled Plasma—Optical Emission Spectroscopy) using an ACTIVA spectrophotometer from Horiba JOBIN-YVON.

The specific surface area of the titanium dioxide (TiO_2 DT-51) and zirconium dioxide (ZrO_2 XZO 632/18) supports was measured to be 96 and 74 $m^2\,g^{-1}$, respectively. The titanium oxide support consisted in a pure anatase phase while ZrO_2 contained traces of the tetragonal phase in addition to the monoclinic phase. However, after impregnation of the metal and pretreatment under hydrogen, only the monoclinic phase was detected in the case of zirconia.

In addition, the pH_{PZC} of titania was measured to be ca. 3 and 5 in the case of TiO_2 and ZrO_2, respectively, indicating that ZrO_2 was slightly less acidic than TiO_2.

After impregnation of the metal, the biggest crystallites were detected on the platinum catalysts (5–6 nm). In the case of palladium, the average crystallite size was 5 and 2 nm for the catalysts supported on titania and zirconia, respectively. A more homogeneous crystallite size ca. 2 nm was measured for the other metals. The actual metal loading varied between 2.5 and 3 wt.% for the different catalysts. The pH_{PZC} was acidic for all catalysts, except for the palladium catalysts. These results are summarized in Table 1.

Table 2
Characteristics of the mobile phases and the columns for the ion chromatography analysis.

Analysis	Mobile phase	Column
Anion	Na_2CO_3 ($3.2\,mmol\,L^{-1}$) $NaHCO_3$ ($1\,mmol\,L^{-1}$) Flow rate: $0.7\,mL\,min^{-1}$	Metrosep A Supp 5 150/4.0
Cation	Nitric acid ($1.7\,mmol\,L^{-1}$) Dipicholinic acid ($0.7\,mmol\,L^{-1}$) Flow rate: $0.9\,mL\,min^{-1}$	Metrosep C 4 150/4.0

2.2. Catalytic wet air oxidation

Ammonia oxidation was performed in a 280 mL batch reactor made of Hastelloy C22 equipped with a magnetically driven stirrer. In a typical run, 150 mL of a $60\,mmol\,L^{-1}$ ammonia solution (Sigma Aldrich, 28–30 vol.% NH_3) and 0.6 g catalyst were introduced in the reactor. After purging the reactor with argon several times, to eliminate any trace of oxygen in the solution, a 4 bar residual pressure of argon was maintained in the reactor to avoid any boiling phenomenon. The reactor was subsequently heated to 200 °C. The time when air was introduced in the reactor to reach 50 bar total pressure was considered as zero time for the reaction. Upon reaction, liquid samples were periodically withdrawn from the reactor and analyzed to measure the total nitrogen content in solution (TN), the pH and the ammonia, nitrites and nitrates concentrations (see Section 2.3). After 6 h reaction, the reactor was cooled down to 25 °C and the catalyst was recovered by filtration for further analysis.

2.3. Analysis

The liquid samples were analyzed by ion chromatography (Metrohm 881 IC Pro) equipped with an automated sampler (863 Compact Autosampler) and two distinct detectors for the anions and the cations. The characteristics for the mobile phases and columns used for the analysis of both the anions (NO_2^-, NO_3^-) and the cations (NH_4^+) are presented in Table 2. Calibration curves in the range below $10\,mg\,L^{-1}$ were established using $NaNH_4$ (Normapur 99.5%), $NaNO_3$ (Sigma-Aldrich >99%) and $NaNO_2$ (Sigma-Aldrich >97%).

The total nitrogen content (TN) in the liquid samples was measured using a TOC-V_{CSH} analyzer coupled with a TN unit (TNM-1) from Shimadzu. In our study, TN corresponds to the total nitrogen content in ammonium, nitrites and nitrates. The nitrogen balance could be assessed from the comparison of the TN values with the ion chromatography results.

3. Results and discussions

3.1. Blank experiments

Blank experiments, in the absence of any catalyst, were carried out under argon or air at 200 °C under 50 bar total pressure (34 bar argon or air partial pressure). The results are presented on Fig. 1.

The data point at −60 min corresponds to the ammonia concentration in solution just before heating. Upon heating from room temperature to 200 °C, the ammonia concentration in solution decreased from 60 down to $50\,mmol\,L^{-1}$ due to the ammonia vaporization into the gas phase. Upon reaction under either argon or air at 200 °C, the ammonia concentration profiles were very similar and no ammonia oxidation was evidenced. After cooling the reactor down to ca. 25 °C, the ammonia concentration in solution returned to $60\,mmol\,L^{-1}$, further indicating that ammonia did not get oxidized in the gas phase as well.

Additional tests were also performed in the presence of the bare TiO_2 and ZrO_2 supports in order to evaluate their potential catalytic