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Catalytic wet air oxidation of ammonia over M/CeO_2 catalysts in the treatment of nitrogen-containing pollutants

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Abstract

Ammonia, a well-known by-product of chemical, fertiliser and metallurgy industries, is also the most refractory product of nitrogen-containing compound oxidation. Consequently, NH_4^+ is a key component of waste disposal of conventional processes like anaerobic digestion or nitrification/denitrification. Catalytic wet air oxidation (CWAO) process, able to eliminate organic matter with non toxic by-product formation, was investigated for ammonium ions removal from wastewater. Oxidation of aniline and of ammonia were carried out on mono- and bimetallic noble metal catalysts (Pt, Ru, Pd, etc.) prepared by impregnation and supported on cerium oxides. In liquid phase, at high temperature (150–250 °C) and high pressure of oxygen (20 bar), a Ru/CeO_2 catalyst is able to achieve the elimination of refractory nitrogenous organic products like aniline. The greatest interest of CWAO compared to the classical biological one, is that the selectivity towards molecular nitrogen is much higher (>90%). Indeed, in this process, ammonium ions give essentially N_2, via hydroxylamine and below 200 °C. At higher temperatures the rate of conversion is extremely high but nitrite and nitrate ions appear in the effluent. On a RuPd/CeO_2 catalyst, the optimal temperature for ammonia conversion is then 200 °C. In these conditions, the N_2 selectivity is up to 90%.

Keywords: Catalytic wet air oxidation; Aniline; Ammonia; Ammonium ion; Oxidation of nitrogen compounds; Noble metal catalysts; Cerium oxide

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1. Introduction

Large amounts of ammonia are generated and released from industrial processes such as chemical fertiliser production [1], agriculture [2], oil refining and petrochemistry [3], metallurgy [4], and wastewater treatments [5,6]. Ammonium ions have environmental negative effects such as eutrophication of the rivers [7] and are toxic for the aquatic life even in very low concentrations [4].

Nowadays, ammonia can be removed from waste by nitrification/denitrification biological process [8,9]. Ammonium ions are oxidised to nitrate ions which are then reduced to molecular nitrogen. This relatively cheap treatment has, however, a low yield especially for continuous treatment and produces high amounts of sludge [5].

Among the wastewater treatments, catalytic wet air oxidation (CWAO) appears as one of the most promising [10]. The process consists in oxidising the pollutants under oxygen pressure (5–200 bar) at elevated temperatures (125–320 °C) and in the presence of a catalyst (oxides, supported noble metals, etc.) [11]. It concerns typically effluents with medium chemical oxygen demand from 10 to 150 $g\,l^{-1}$ and finds its greater application for treating toxic pollutants. Indeed, in the last decades, numerous authors

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have demonstrated CWAO efficiency in a large range of compounds such as carboxylic acids [12], aromatics [13], polymers [14], and N-, O-containing organic compounds [8]. While oxidising organic compounds, acetic acid appears as the most refractory intermediate [15,16] and its oxidation has been extensively studied. Concerning catalytic wet air treatment of N-containing compounds, ammonia, in this turn, is pointed out as refractory to further oxidation [8,9]. As it is a key intermediate in oxidation of larger N-containing molecules like aniline or dye, this study has been focused on ammonia wet air oxidation.

2. Materials and methods

2.1. Catalysts

The supports were two commercial Rhodia Rare Earth ceria HSA5 ($A_{\mathrm{BET}} = 160\,\mathrm{m}^2\,\mathrm{g}^{-1}$) and HSA5M ($A_{\mathrm{BET}} = 40\,\mathrm{m}^2\,\mathrm{g}^{-1}$) used without any treatment. Mono- and bimetallic catalysts were obtained by impregnation or co-impregnation of the desired support with aqueous solution of metallic precursor salts ($Ru(NH_3)_6Cl_3$, $Pt(NH_3)_4(OH)_2$, $Pd(NO_3)$, $Rh(NO_3)_3$). In all the cases, the metal loading was adjusted to $0.5\,\mathrm{mmol\,g}^{-1}$. For bimetallic catalysts, the number after the metal symbol corresponds to the molecular percentage of each metal (i.e. Pd25Ru75/CeO_2(40) is the Pd–Ru bimetallic catalyst supported on the low area ceria containing 25 mol% of palladium and 75 mol% of ruthenium). The catalysts were reduced in H_2 at 350 °C before each run.

2.2. Oxidation reaction conditions

Oxidation reactions were carried out in a 0.44 l Hastelloy C22 autoclave. The temperature reaction was in the range 120–230 °C. 160 ml of aqueous solution, containing the pollutant ($20\,\mathrm{mmol\,l}^{-1}$ of aniline or $50\,\mathrm{mmol\,l}^{-1}$ of ammonia) and $4\,\mathrm{g\,l}^{-1}$ of catalyst, were introduced in the reactor. For ammonia oxidation, a phosphate buffered solution (0.1 M, pH = 6.8) was used in order to stabilise the acidic form ($\mathrm{p}K_\mathrm{a} = 9.25$). After an initial purge of the autoclave under helium, the autoclave is heating up to the reaction temperature. The reaction starts after addition of 20 bar of O_2 (maintained constant during the experiment).

2.3. Analysis

Liquid phase was regularly sampled and analysed by HPLC. Nitrogen-containing compounds, NO_3^-, NO_2^- and NH_2OH were quantified on a UV detector at 210 nm after separation on a C18 Inertsil ODS2 column (5 μm, $L = 15$ cm, ϕ4.6 mm). The mobile phase composition was for 1 l: 150 ml of acetonitrile, 1.65 ml of octylamine and 0.4 g of $(NH_4)_2HPO_4$ (pH = 6) in ultra-pure water (18 MΩ). Ammonium ion analysis was performed on an ionic chromatograph equipped with a conductimeter. The column was a Universal cations supplied by Alltech ($L =$ 10 cm, ϕ4.6 mm) and the mobile phase, an oxalic acid solution (0.002 M). The TOC values were obtained on a DC-190 Dohrmann carbon analyser.

The gas samples were analysed on a GC equipped with a catharometer. A Porapak Q packed column (1/4 in., 1 m) was inserted in the reference line while the working line combined two packed columns: Pt/Al_2O_3 (1/4 in., 0.5 m) followed by a 5A molecular sieve (1/4 in., 1.5 m). Hydrogen was chosen as carrier gas. Even with the use of the 5A molecular sieve column, the Pt pre-column was used to reduce more than 98 mol% of oxygen by H_2 in order to obtain a higher sensibility for nitrogen measurements. Concentration of N_2 in the gas phase was determined by standardisation with the He gas peak as reference. The use of Porapak Q column allowed CO_2 and N_2O analyses.

3. Results and discussion

3.1. Evolution of nitrogen-containing by-products during aniline CWAO

CWAO of aniline was carried out on a Ru/CeO_2 (160) catalyst at various temperatures under 20 bar of oxygen. The organic and mineral forms of nitrogen were determined after 3 h of reaction. Selectivities for each form and aniline conversion are reported in Fig. 1. The conversion obtained without any catalyst, respectively, at 160 and 200 °C is of 20 and 80%. In the presence of the support alone the conversion reaches 25% at 160 °C. These results show that the aniline conversion starts at relatively low temperature (<120 °C). The N-organic initial by-products are essentially nitrophenol, aminophenol, nitrobenzene and

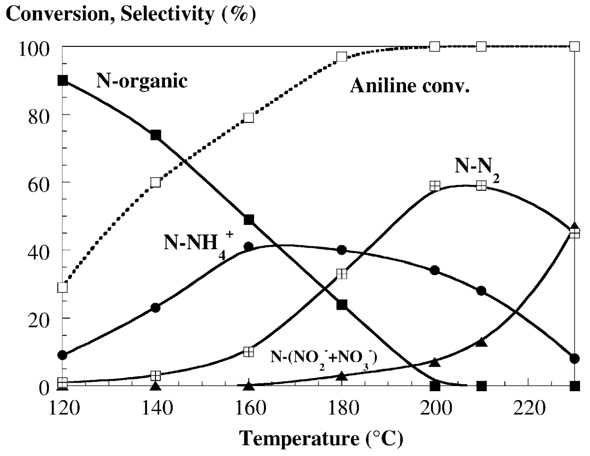

Fig. 1. CWAO of aniline on Ru/CeO$_2$ (160) versus temperature. Selectivity for each N-form and aniline conversion after 3 h of reaction ($P(O_2) = 20$ bar, $[\text{aniline}]_0 = 20\,\text{mmol}\,\text{l}^{-1}$, $[\text{catalyst}] = 4\,\text{g}\,\text{l}^{-1}$).

condensed oligomers like azo-, azoxy-benzene and hydrazo-benzene [17]. N in organic compounds is analysed both in the liquid phase and on the catalyst. The maximal deposit occurs at 160 °C where 20% of the initial N is on the catalyst after 3 h. At temperature above 150 °C, the N–C bond cleavage leads to large amounts of ammonium ions. This fact was clearly demonstrated by Chakchouk et al. [8] in the case of the conventional wet air oxidation of various N-containing compounds with H_2O_2 as oxidant and Fe^{2+} as catalyst at 200 °C. It can be noticed that at this temperature range, the carbon balance is completed by the formation of carboxylic acids which are the main by-products [18]. At higher temperatures, between 180 and 200 °C, in the presence of the Ru/CeO$_2$ (160) catalyst, NH_4^+ ions are oxidised quite selectively into molecular nitrogen. The same result was observed, but above 260 °C, when heterogeneous Mn/Ce [8,19] or Co/Bi [20] catalysts were used in the presence of oxygen. As shown in Fig. 1, above 200 °C, the reaction pathway is also significantly oriented towards the undesirable nitrite and nitrate ions. A temperature of 200 °C is then optimal to perform the CWAO reaction of ammonium ions.

3.2. CWAO of ammonia on Ru/CeO$_2$ (160) catalyst

In all experiments carried out on ammonia, the following products have been identified: hydroxylamine, dinitrogen, nitrites, nitrates. Minute amounts of hydroxylamine were detected at the very beginning of reaction. The product concentration curves are given in Fig. 2 for the standard reaction at 200 °C on Ru/CeO$_2$ (160) in mmol of N. No adsorption

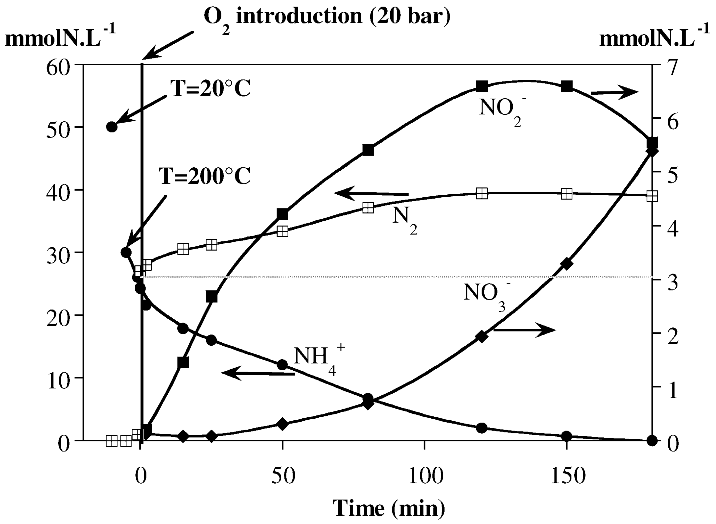

Fig. 2. CWAO of ammonia. Product concentration evolutions on Ru/CeO$_2$ (160) (200 °C, $P(O_2) = 20$ bar, $[NH_4^+]_0 = 50\,\text{mmol}\,\text{l}^{-1}$, $[\text{catalyst}] = 4\,\text{g}\,\text{l}^{-1}$).

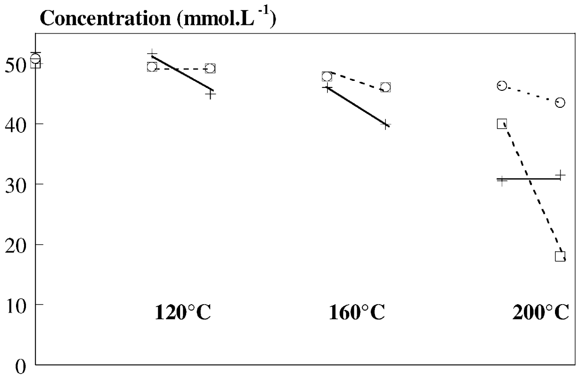

Fig. 3. Ammonia disparition in the liquid phase due to liquid–gas equilibrium. (+) without oxygen nor catalyst, (○) with oxygen and without catalyst, (□) with oxygen and catalyst.

phenomena was pointed out as the nitrogen balance was around 100% in any case. The bare support has no activity for this reaction.

In order to explain the shape of these curves, the gas–liquid equilibrium of ammonia has to be taken into account. Indeed, in the experimental conditions, even using an acidic buffer, an important part of ammonia is present in the gaseous phase [21]. In Fig. 3, the evaporation process is first followed during the heating period with plateau of 1 h at three temperatures without oxygen nor catalyst. The evaporation occurs gradually. If the equivalent of 20 bar of oxygen at 200 °C is added at room temperature, then the evaporation is somehow limited. Same result is obtained with the same pressure of helium. With oxygen and catalyst, the experiment points out that ammonia conversion only starts at 200 °C. In this case, the desperation of ammonia leads to the formation of by-products.

Ammonia equilibrium corresponds to Eqs. (1) and (2) of the scheme of ammonia oxidation given below where $*$ denotes an active site. This equilibrium occurs only during the heating period. Then, when oxygen is added, the equilibrium is limited and the reaction happens only in the liquid phase. Tests carried out on gaseous ammonia, with or without the ruthenium catalyst, have shown that the oxidation is rapid and totally selective into nitrogen (Eq. (3)). This explains the fast formation of nitrogen when oxygen is added. Then, the oxidation takes place essentially in the liquid phase on the catalyst surface (Eqs. (4)–(13)). Specific studies show that in the presence of 20 bar of oxygen, the equilibrium 2 is shifted to the left. The scheme is proposed in accordance with the intermediate identification as well as with the scheme proposed by Qin and Aika [22] for ammonia oxidation in the liquid phase. The scheme is also close to the ones given for ammonia oxidation in the gas phase [23].

$$\mathrm{NH_4}^+ + \mathrm{H_2O} \rightleftarrows \mathrm{NH_{3(aq)}} + \mathrm{H_3O}^+ \tag{1}$$

$$\mathrm{NH_{3(aq)}} \rightleftarrows \mathrm{NH_{3(gas)}} \tag{2}$$

$$2\mathrm{NH_{3(gas)}} + 1.5\mathrm{O_{2(gas)}} \rightarrow \mathrm{N_{2(gas)}} + 3\mathrm{H_2O} \tag{3}$$

$$\mathrm{O_{2(gas)}} \rightleftarrows \mathrm{O_{2(aq)}} \tag{4}$$

$$\mathrm{O_{2(aq)}} + 2* \rightleftarrows 2\mathrm{O}* \tag{5}$$

$$\mathrm{NH_4}^+ + \mathrm{O}* \rightarrow \mathrm{NH_3OH}^+ + * \tag{6}$$

$$\mathrm{NH_3OH}^+ + \mathrm{H_2O} \rightleftarrows \mathrm{NH_2OH} + \mathrm{H_3O}^+ \tag{7}$$

$$\mathrm{NH_2OH} + * \rightarrow \mathrm{NH}* + \mathrm{H_2O} \tag{8}$$

$$\mathrm{NH}* + \mathrm{O}* \rightarrow \mathrm{HNO}* + * \tag{9}$$

$$\mathrm{HNO}* + \mathrm{NH}* \rightarrow \mathrm{N_2} + \mathrm{H_2O} + 2* \tag{10}$$

$$\mathrm{HNO}* + \mathrm{O}* \rightarrow \mathrm{HNO_2} + 2* \tag{11}$$

$$\mathrm{HNO_2} + \mathrm{H_2O} \rightleftarrows \mathrm{NO_2}^- + \mathrm{H_3O}^+ \tag{12}$$

$$\mathrm{NO_2}^- + \mathrm{O}* \rightarrow \mathrm{NO_3}^- + * \tag{13}$$

The catalyst is required for the oxidation in the liquid phase and it plays an essential role in the selectivity towards nitrogen. Too active a catalyst orientates the oxidation towards undesired nitrites and nitrates (Eqs. (11)–(13)). Same results are obtained when hydroxylamine is used as the starting reactant and indicated that $\mathrm{NH_2OH}$ is the key intermediate in the ammonia oxidation. Its oxidation (Eqs. (8)–(10)) is not a limiting step but a determining one for nitrogen selectivity. A high selectivity to nitrogen is achieved when N-recombination reaction 10 is faster than a secondary oxidation of the HNO species (Eq. (11)). It can be noticed that under oxidative conditions and without catalyst, $\mathrm{NH_2OH}$ gives preferentially nitrogen. The proposed scheme is in accordance with the decreasing pH noted while no buffer is used.

3.3. CWAO of ammonia on monometallic catalysts

Three noble monometallic catalysts were prepared on the high area ceria support and compared in

Table 1
CWAO of ammonia on monometallic catalysts[a]

Catalyst	Initial rate (mmol h^{-1} g^{-1})	N_2 (%)	NO_2^- (%)	NO_3^- (%)
Pd/CeO_2 (160)	7.5	91	8	1
Ru/CeO_2 (160)	2.5	50	47	3
Pt/CeO_2 (160)	16	69	28	3

[a] Initial rates of conversion and N-N_2 selectivities at 50% of conversion (200 °C, $P(O_2) = 20$ bar, $[NH_4^+]_0 = 50$ mmol l^{-1}, [catalyst] = 4 g l^{-1}).

CWAO of NH_4^+. The initial rates of conversion (IR in mmol h^{-1} g^{-1} of catalyst) and the selectivities (in %) towards N-nitrogen, N-nitrite and N-nitrate ions determined at 50% of conversion are reported in Table 1. In any case, nitrogen is the major by-product. At pH 6.8, nitrite ions are still present at the end of the reaction. At lower pH values the nitrate form is favoured. In the gas phase, N_2O or NO are under detection limits (50 ppm). It appears clearly that the platinum catalyst showed a higher activity compared with Pd and Ru. Ukropec et al. [24] have observed the same result on TiO_2. Even if the initial rate on Pd is lower than on Pt, Pd presents the highest selectivity for molecular nitrogen (>90%). Similar results were reported by Taguchi and Okuhara [25] who have obtained 100% of selectivity to N_2 on a 0.25 wt.% Pd/TiO_2 catalyst. In our reaction conditions, compared to the other noble metals, ruthenium gives clearly the less impressive results for the CWAO of ammonia.

3.4. CWAO of ammonia on bimetallic catalysts

Contrary to what was mentioned earlier for ammonia, ruthenium is the most active metal for CWAO of various organic pollutants [12,18]. Consequently, in order to perform the complete oxidation of nitrogen-containing organic compounds, bimetallic catalysts were prepared by co-impregnation of palladium and ruthenium salts. Whatever the catalyst the metal loading was maintained constant. The two cerium oxides (CeO_2 (40) and CeO_2 (160)) were used as supports. The initial rates of conversion and the selectivities for nitrogen at 50% of conversion are given in Fig. 4 versus the palladium percentage in

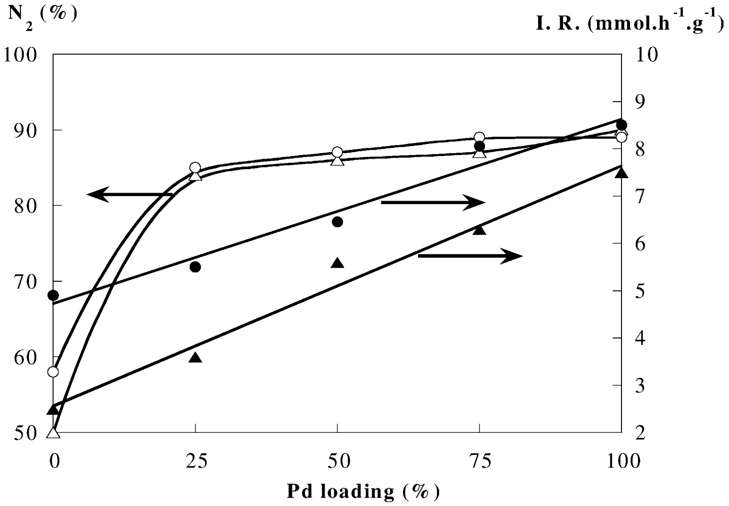

Fig. 4. CWAO of ammonia on bimetallic Pd–Ru catalysts. Influence of the Pd loading and the support area on the initial rates of conversion (▲, ●) and N-N_2 selectivity (△, ○). (●, ○) for CeO_2 (40); (▲, △) for CeO_2 (160) (200 °C, $P(O_2) = 20$ bar, $[NH_4^+]_0 = 50$ mmol l^{-1}, [catalyst] = 4 g l^{-1}).

the bimetallic $(100 \times \mu\mathrm{mol\,Pd\,g^{-1}}/(\mu\mathrm{mol\,Pd\,g^{-1}} + \mu\mathrm{mol\,Ru\,g^{-1}}))$. In any case, it appears clearly that the initial rate of ammonia conversion is linked to the palladium loading. Concerning the conversion, no synergetic effect is observed. Nevertheless, the combination of palladium and ruthenium induces a significant improvement in nitrogen selectivity whatever the Pd loading. The most important result is that, contrary to what is obtained for C-compounds elimination, the initial rates of ammonia conversion are higher on the low area ceria support. In a previous study, we have showed that the total mineralisation (CO_2 formation) of the carbonaceous compounds is favoured by the presence of a large area ceria support [26]. The initial rate of carbon mineralisation is proportional to the metal/support interface length. In this case, the limiting step of the mechanism is the oxygen activation by the metal. As carboxylic acids are more strongly adsorbed than oxygen over noble metals [12], the better distribution of Ru–Ce pairs at the surface of Ru/CeO_2 accelerates the oxygen transfer from liquid phase to the metal sites. In the case of ammonia oxidation, the reaction have to be oriented towards the nitrogen recombination (Eq. (11)). As this was shown by Qin and Aika [22], an excess of oxygen species at the catalyst surface orientates the reaction towards the formation of nitrates. The supported CeO_2 (40) catalysts appears as a good alternative in order to perform with high activity and selectivity the CWAO of ammonia. Further studies are in progress in order to determine the oxygen partial pressure effect.

4. Conclusion

In CWAO of N-containing pollutants a very active ruthenium-containing catalyst is required. Large amounts of ammonium ion are produced during the elimination of N-organic compounds. Nitrite and nitrate ions are undesirable by-products of ammonia oxidation. Even if platinum is a very active metal for this reaction, Pd is added as second metal to the Ru/CeO_2 monometallic catalyst in order to control ammonia oxidation and favour nitrogen formation. A synergy effect between Ru and Pd is observed and enhances the catalyst selectivity towards nitrogen. Oxygen transfer at the catalyst surface is linked to the surface area of the ceria support. Ammonia oxidation and nitrogen selectivity increase when the oxygen transfer is quite limited. Oxygen becomes in this case a poisonous species for N recombination on the catalyst surface.

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