



# Catalytic wet air oxidation of N,N-dimethylformamide aqueous solutions: Deactivation of TiO<sub>2</sub> and ZrO<sub>2</sub>-supported noble metal catalysts

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## ABSTRACT

N,N-dimethylformamide (DMF) is largely used as versatile solvent in various processes. It is thus present in large quantities in many industrial effluents. Oxidation of aqueous solutions of DMF with air was conducted at 180–230 °C under 50–70 bar total pressure in a batch reactor, in the absence or in the presence of heterogeneous noble metal catalysts (platinum, palladium, and ruthenium) supported on TiO<sub>2</sub> or ZrO<sub>2</sub>. Under the examined reaction conditions, DMF decomposition and oxidation produced dimethylamine (DMA), methylamine (MA), and ammonium as the major N-containing products. Formic acid was also intermediately formed from the scission of the C–N bond. Nitrites and nitrates were only present in very low amounts. The addition of a catalyst accelerated the initial rates of DMF and TOC (total organic carbon) conversions, but the selectivity to N<sub>2</sub> was low. The production of DMA and MA was demonstrated to be very much detrimental to the chemical stability of these catalysts. A dramatic leaching of the noble metals occurred because of the complexation with the free lone pair electrons on the nitrogen atom of these amines.

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## 1. Introduction

Wet air oxidation is a process that might be used for the mineralization of organic pollutants in water. It consists in an oxidation at elevated temperature (150–320 °C) under high air or pure oxygen pressure (5–200 bar) and it is suitable for the treatment of aqueous effluents which cannot be treated biologically or which are too diluted for incineration [1–4].

N,N-dimethylformamide (DMF) is a powerful polar aprotic solvent which has the ability to dissolve a wide variety of organics, inorganics and resins and it has a relatively low vapour pressure [5]. Therefore, DMF is commonly used in the production of a wide range of organic chemicals and polymers, including polyurethane synthetic leather, dyes, pharmaceuticals, pesticides, polyimide resins, synthetic fibres, and polymeric membranes. It is also used as an extraction agent in the petrochemical industry. The global production of DMF was estimated at ca. 270,000 tonnes per year in 1994 [5] and there has been since an increasing demand in the production. Since it is miscible in all proportions with water and because it is extensively used in the industry, DMF is commonly found in high concentrations in many industrial wastewaters [6]. DMF is also known to have adverse impacts on the environment and the health [7,8]. Once rejected to the environment, it is found

to be highly stable and resistant to photochemical decompositions [9]. It only undergoes a slow biodegradation, even though specific DMF-degrading bacterial strains could be isolated and characterized [10–13] and it rapidly reaches inhibitory concentrations for conventional wastewater treatment plants.

In the view of its frequent occurrence in industrial wastewaters and because it is toxic and hardly biodegradable, the development of new technologies to eliminate DMF is gaining more and more attention. In many cases, when its concentration is high, DMF can be partially or totally recovered from the wastewater by distillation. However, in such a process large volumes of water must be evaporated, since DMF has the highest boiling point and the energy consumption is high [14]. In other cases, DMF-containing wastes are treated via incineration.

Hydrothermal oxidation technologies might be implemented to convert a maximum of the nitrogen in DMF to harmless N<sub>2</sub> (minimization of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>) and simultaneously convert carbon to CO<sub>2</sub>. The destruction of DMF (ca. 8.4 mM) to benign compounds has been investigated under supercritical conditions ( $T > 374$  °C and  $P > 220$  bar) using hydrogen peroxide as the oxidant in a continuous plug flow reactor [15]. The intermediates identified by GC–MS were trimethylamine (TMA), dimethylamine (DMA), methylamine (MA) and methanol. The oxidation of such amines was also studied under supercritical conditions by Benjamin and Savage [16,17] and Li and Oshima [18,19], using air as the oxidant.

Such wastewaters should also be effectively treated under subcritical conditions in the 150–280 °C temperature range under

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10–30 bar via wet air oxidation (WAO). To reduce the severity of the operating conditions and to achieve a higher mineralization, homogeneous as well as solid catalysts can be used [1–4]. The most active heterogeneous catalysts in catalytic WAO are mixtures of metal oxides (Cu, Zn, Mn, Co, Bi) or noble metal supported catalysts. The latter catalysts have been shown to be active and leaching-resistant in the oxidation of many model pollutants [20–22] and real industrial wastewaters [23,24].

Over the past decades, considerable efforts have been made to eliminate C-containing pollutants from waters. Regarding the nitrogen-containing contaminants, the studies are less numerous and most of them concentrated on the N-containing aromatic compounds (aniline, nitrophenol, and nitrobenzene) or ammonia as model compounds [25–29]. Azo-dyes were also investigated [4]. On the opposite, little information is available on catalytic studies conducted on aliphatic amines or amides. The oxidation of methyl- and dimethylamine was studied in the presence of active carbons at 195 °C under 16 bar oxygen [30]. According to the authors, the conversion of amines ranged between 25 and 45% after 2 h reaction. Noble metal-based catalysts seemed efficient in the degradation of such compounds. A Ru/Ce catalyst has been shown to catalyse the oxidation of acetamide [32]. A complex mixture of acetonitrile, DMF and carbamide was oxidised at 160–260 °C under 20–40 bar O<sub>2</sub> in the presence of several solid catalysts [33]. Total conversion of carbamide was achieved after 1 h using a Ru/graphite-like carbon at 120–240 °C under 10 bar oxygen partial pressure with selectivity to N<sub>2</sub> of 70%. A 3 wt.% Ru catalyst supported on high-surface area zirconia was tested in the oxidation of 2.61 g L<sup>-1</sup> DMF solutions [34]. Nearly complete DMF conversion was claimed, with 88% selectivity to N<sub>2</sub>.

We have evaluated the possibility to depollute an effluent from a manufacture of polymeric membranes, containing both glycerol and DMF, using CWAO in the presence of noble metal supported catalysts. In this study, we describe the experiments performed on DMF aqueous solutions.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

For the preparation of the catalysts, commercial TiO<sub>2</sub> (DT51 from Millenium, anatase, 92 m<sup>2</sup> g<sup>-1</sup>) and ZrO<sub>2</sub> supports (Mel Chemicals, monoclinic, 90 m<sup>2</sup> g<sup>-1</sup>) were used. Both supports are mesoporous, with a mean pore size of 9 nm. They are known to be leaching-resistant materials under the applied reaction conditions. Catalysts containing 3 wt.% of metal (Pt, Ru, Pd) were prepared by incipient-wetness impregnation using aqueous solutions of H<sub>2</sub>PtCl<sub>6</sub>, Ru(NO)(NO<sub>3</sub>)<sub>3</sub> or Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>. After drying overnight at 110 °C, the reduction was carried out under flowing H<sub>2</sub> (30 mL min<sup>-1</sup>) at 300 °C for 2 h. Finally, the catalyst was flushed with Ar, passivated under 1% O<sub>2</sub>/N<sub>2</sub> at room temperature and finally stored under argon.

The specific surface area of the samples was obtained from nitrogen adsorption measurements performed in a static volumetric apparatus (Micromeritics ASAP 2010). XRD characterizations were performed using a Siemens D5005 diffractometer with Cu K $\alpha$  radiation at 0.154184 nm. Transmission electron microscopy (TEM) direct observations were carried out on a JEOL 2010 microscope (200 kV, resolution 0.19 nm). The metal leaching was evidenced via ICP-OES analysis (inductively coupled plasma-optical emission spectroscopy) on the final mixtures (Activa, Horiba JOBIN YVON).

### 2.2. Catalytic oxidation experiments

All chemicals were commercial ones and analytical grade. DMF (>99.9%) was purchased from Aldrich. Dimethylamine (DMA) and

methylamine (MA) feed solutions were prepared by dilution of 40 wt% aqueous solutions purchased from Fluka. Deionised water was used to prepare all solutions.

Catalytic wet air oxidation experiments were performed in a 300 mL batch reactor made of Hastelloy, described elsewhere [23,24]. It is equipped with a magnetically driven stirrer set at 1200 rpm to avoid any mass transfer limitations of air in the aqueous phase. Temperature was maintained constant with an electronic controller. 150 mL of an aqueous solution containing 68.4 mmol L<sup>-1</sup> DMF (5 g L<sup>-1</sup>) or DMA or MA, and 0.5 g catalyst were introduced into the reactor. After purging under argon to remove any trace of air, the reactor was heated to the desired reaction temperature. Air was injected in the reactor up to the predefined pressure. This time was considered to be zero time for the reaction. The liquid samples, withdrawn at different time intervals, were centrifuged at 1100 g and filtered through a 0.45  $\mu$ m membrane filter. The last liquid sample was withdrawn after the reactor was rapidly cooled down. Since no difference was observed between the last two samples at the reaction temperature and after cooling, we could conclude that no volatile compound was present in the gas phase in significant amount. This point will not be further discussed. Furthermore, after the sampling, some air was introduced again to maintain the pressure constant.

### 2.3. Analysis

Under our experimental conditions, dimethylamine (DMA), methylamine (MA), formic acid and ammonium ions were the dominant products. Nitrites and nitrates were produced as relatively minor products.

DMF and carboxylic acids concentrations were determined by HPLC on a ICsep Coregel 107H column with a 0.005N H<sub>2</sub>SO<sub>4</sub> solution as the mobile phase (0.5 mL min<sup>-1</sup>) using a refractive index detector. All products were identified based on their retention times compared to commercial compounds. DMA, MA, ammonium, nitrite and nitrate ions were analysed, after dilution by a factor of 10, using high performance ionic chromatography (HPIC, Dionex) equipped with cationic (CS16) and anionic (AS14A) columns. The eluents (1.1 mL min<sup>-1</sup>) were H<sub>2</sub>SO<sub>4</sub> 11 mM for cations and (Na<sub>2</sub>CO<sub>3</sub> 8 mM + NaHCO<sub>3</sub> 1 mM) for anions.

The total organic carbon (TOC) and total nitrogen (TN) analysis were carried out on a TOC-VCSH analyser coupled with a TN unit (TNM-1) from Shimadzu. The inorganic carbon is converted to CO<sub>2</sub> by addition of HCl and purged using air. The non-purgeable TOC is then burnt in a catalytic oven at 680 °C and the CO<sub>2</sub> which is produced is quantified via an IR detector. The TN which represents the total amount of nitrogen in the liquid phase includes DMF, DMA, MA, ammonium, nitrate and nitrite. It was measured using a NO<sub>2</sub>-specific chemiluminescence detector. The amount of CO<sub>2</sub> and N<sub>2</sub> produced may be calculated from the difference between the amount of C and N introduced as DMF and the TOC and TN measured in the liquid phase at any time, respectively. Furthermore, the carbon and nitrogen mass balances could be verified from the comparison between the HPLC, HPIC and TOC–TN analysis in order to ascertain that all intermediate and final products were correctly identified and quantified.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the TiO<sub>2</sub> and ZrO<sub>2</sub>-supported Pt, Pd and Ru catalysts. The support ZrO<sub>2</sub> appeared to be essentially monoclinic, with a very little cubic phase. In turn, TiO<sub>2</sub> was pure anatase. No diffraction peak characteristic of the Ru and Pt

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