



Catalytic studies in wet oxidation of effluents from formaldehyde industry

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Abstract

Development and design of active catalysts for the oxidation of formaldehyde present in wastewaters is of great importance. In this context, catalytic performance studies for oxidation of high formaldehyde containing solutions (1500 ppm) were carried out in a semibatch high-pressure reactor at 190–220°C and 15–35 bar of oxygen partial pressure. The removal efficiency of total organic carbon (TOC) was evaluated experimentally under different solid catalysts, using several heterogeneous composite oxides prepared in our laboratory (Mn/Ce, Co/Ce and Ag/Ce), as well as a commercial catalyst (CuO–ZnO/Al₂O₃). The Mn/Ce catalyst was the more active leading to high TOC conversions (99.4%). The TOC reductions were lower using Co/Ce, Ag/Ce and CuO–ZnO/Al₂O₃, respectively, 71.3%, 54.2% and 78.7%. Attempts were made to identify the influence of different Mn/Ce ratios. A high molar fraction of Mn leads to high TOC abatements. During the preparation procedure of catalysts the drying temperature does not affect significantly the catalytic area while increasing calcination temperature leads to lower surface areas. Carbon capacity adsorption was not observed for the Mn/Ce and CuO–ZnO/Al₂O₃ catalyst and leaching of the correspondent metals, Mn, Cu and Zn, was not significant. The catalytic wet oxidation (CWO) process was studied with an industrial high formaldehyde concentration effluent (800 ppm). Using an Mn/Ce catalyst the formaldehyde concentration decreased from 800 to 0.1 ppm and ammoniacal nitrogen from 420 to 155 ppm while 91.7% in TOC reduction was observed. These conversions were higher than those obtained with the commercial CuO–ZnO/Al₂O₃ catalyst. Therefore, Mn/Ce catalysts seem to be interesting options for the treatment of effluents from formaldehyde industry by CWO process.

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1. Introduction

Water is an essential resource to maintain life in the planet and unfortunately has not been adequately preserved. Environmental protection is one of the major worldwide concerns of our days and it is our duty to prevent pollution through studies directed towards existing and future remedial solutions for industrial effluents treatment. Formaldehyde (HCHO) is an important environmental pollutant, with evidence of adverse effects on health. Recently this concern has been increased by studies suggesting that formaldehyde may be a carcinogen compound for humans. In fact, formaldehyde causes squamous cell carcinomas in the nasal cavities of laboratory rats and can exert its mutagenic and carcinogenic effects by damaging DNA and inhibiting its

repair (Andersen & Dennison, 2001; Tomkins, McMahon, & Caldwell, 1989). This compound enters in the environment water system mainly as a result of human activities, being the major sources the discharge of industrial wastewaters (Cotsaris & Nicholson, 1993). It is widely used in chemical industry, wood processing, paper industry, textile processing and so many other industries.

Due to their toxicity, liquid effluents containing high formaldehyde concentrations (800–1500 ppm) are difficult to treat by conventional processes, such as biological systems, since formaldehyde can react with DNA, RNA and protein and damage the cells which may cause death of microorganisms (Lu & Hegemann, 1998). It will be then required the use of advanced technologies that can operate isolated or in combination with the conventional systems to make possible a significant improvement in the effluent water quality. In this domain, chemical oxidation treatments emerge as promising solutions. In particular, catalytic wet oxidation (CWO) is an interesting upgraded alternative to

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non-catalytic wet oxidation (WO), since milder operating conditions can be used due to the presence of solid catalysts involving consequently lower costs in pollutants removal. Hence, catalytic studies have nowadays a great importance in industrial effluents treatment by wet oxidation.

Information in literature concerning catalytic liquid formaldehyde oxidation is scarce. It is therefore greatly important to develop an active, cheap and stable catalyst for formaldehyde degradation purposes by CWO. The present work is mainly related with experimental tests using different catalysts in order to evaluate their performance in the CWO of formaldehyde. The main goal addresses an oxidation treatment able to get lower levels of final pollutants in the wastewaters, which may be suitable for a post-biological treatment or even for direct discharge in the environment, if the process reaches high levels of pollutants removal. The costs involved in the CWO process are crucially important for industrial application, and therefore in our work the catalysts to be tested were selected taking into account the economical aspects and the performances referred in the literature for the CWO treatment of others compounds.

Matatov-Meytal and Sheintuch (1998) in their paper review referred different metal oxides and noble metal catalysts that have been used in various CWO studies, such as CuO, ZnO, MnO, AgO, CoO, NiO, Ru, Pt, supported typically in CeO₂, Al₂O₃, ZrO₂ and TiO₂. Normally the active catalysts used for aromatic compounds oxidation lead to similar behaviour in what concerns the TOC reduction trends for aliphatic compounds. In the temperature range 160–250°C, copper oxide is the most active catalyst for phenol oxidation and its activity can be increased with mixtures of Co, Zn and Ti. In our work was selected a commercial copper-zinc catalysts from the *Süd-Chemie Group*, Munich, that have been used by several authors in the CWO of aqueous phenol solutions (Pintar & Levec, 1992, 1994; Pintar, Bercic, & Levec, 1997), *p*-coumaric acid (Mantzavinos, Hellenbrand, Livingston, & Metcalfe, 1997), azo dyes (Donlagic & Levec, 1998) and in industrial effluents (Quinta-Ferreira, Silva, & Redondo, 2001).

Imamura, Fukuda, and Ishida (1988) studied the CWO of poly(ethylene glycol) over a ruthenium catalyst and concluded that formaldehyde and formic acid are formed during the reaction being further oxidised. They also concluded that the use of cerium oxide as support of ruthenium improves its catalytic activity, more than other materials, such as, Al₂O₃, NaY zeolite, ZrO₂ and TiO₂. For this reason, cerium oxide was selected as support for the catalysts prepared in our laboratories. However, due to the high cost of ruthenium, more economical metal oxides were used in our work, having in mind their industrial applications. Moreover, the noble metals revealed to be more sensitive to poisoning than metal oxides when used in water phase oxidation (Matatov-Meytal & Sheintuch, 1998). Mn/Ce and Co/Ce composite oxides were selected for our studies, since previous works showed their high activity in the oxidation of different model compounds, such as refractory low weight carboxylic acids (Imamura,

Nakamura, Kawabata, & Yoshida, 1986). Nowadays, the Mn/Ce oxide seems to be one of the more promissory active catalysts. It will be however required more studies about the effective performance of such catalyst when applied to an industrial wastewater (Matatov-Meytal & Sheintuch, 1998). Moreover, since Ag/Ce catalyst was pointed out as quite active in the gaseous formaldehyde oxidation (Imamura, Uchi-hori, & Utani, 1994), we decided to analyse its performance in the oxidation of liquid formaldehyde.

Therefore, our research work was carried out using different laboratorial catalysts supported on cerium oxide, namely composites oxides of manganese (Mn), silver (Ag) and cobalt (Co). A comparison of these results with a commercial catalyst of copper and zinc oxides supported on aluminium oxide (CuO–ZnO/Al₂O₃) was also achieved.

2. Experimental

2.1. Material and catalysts

The catalysts of Mn/Ce, Co/Ce and Ag/Ce were prepared according to two different procedures described in the literature (Imamura & Doi, 1985; Imamura et al., 1986, 1994), by using the corresponding metal nitrates as precursors, namely manganese nitrate (Riedel-de-Häen), cobalt nitrate (Riedel-de-Häen), silver nitrate (Labsolve) and cerium nitrate (Riedel-de-Häen).

Procedure 1: Ag/Ce catalyst was prepared by co-precipitation of a mixed aqueous solution of silver nitrate and cerium nitrate containing known molar ratios (Imamura et al., 1994). An NaOH 3 M solution, prepared from a sodium hydroxide salt (Merck), was added until a pH equal to 10 was reached. The precipitate was filtrated and washed several times with ultra pure water and was then dried over night at 100°C, followed by calcination at 300°C. A catalyst with a molar composition of 7% Ag and 93% CeO₂ was obtained, being designed as Ag/Ce 7/93.

Procedure 2: Mn/Ce and Co/Ce catalysts were prepared by co-precipitation of a mixed aqueous solution of metal salts (15 g of metal salt/100 ml) (Imamura & Doi, 1985; Imamura et al., 1986). The solution was poured into 200 ml of a 3 M NaOH solution. The precipitate was filtrated and washed five times with 500 ml of ultra pure water. It was dried at 100°C over night, followed by calcination at 300°C and 350°C, respectively, for Mn/Ce and Co/Ce catalysts. The molar composition ratios of the catalysts we prepared were for Mn/Ce 60/40, 70/30, 75/25, 80/20 and for Co/Ce 50/50. Before calcinations all catalyst were crushed to fine powder in order to provide maximum specific surface area for reaction.

In order to analyse the influence on the BET areas of the drying and calcination temperatures, various Mn/Ce 70/30 samples were prepared by using different drying/calcinations temperatures: 100°C/300°C; 80°C/500°C; 100°C/500°C. The BET results, obtained through gaseous adsorption analysis, indicate that the increase on the drying temperature,

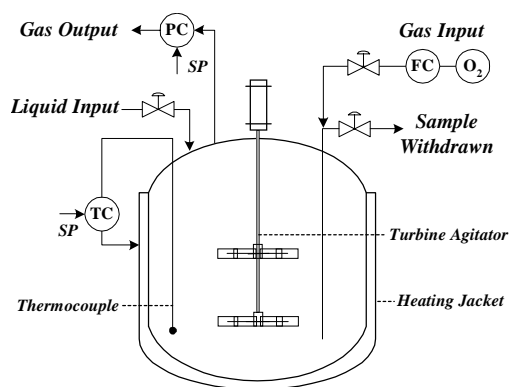


Fig. 1. Experimental equipment: TC—temperature controller; PC—back pressure controller; FC—flow controller.

from 80°C to 100°C, had no effect on the surface area (93.88 to 93.89 m²/g). However, when different calcination temperatures were used, namely 300°C and 500°C, a significant variation in the BET area was observed, from 102.48 to 93.89 m²/g, pointing out the importance of this parameter on catalyst preparation, which will have lower surface areas when higher temperatures are used.

The commercial catalyst was obtained in cylindrical pellets from *Süd-Chemie Group*, Munich and is a mixture of copper oxide (CuO—41% weight) and zinc oxide (ZnO—47% weight) supported on aluminium oxide (Al₂O₃—10% weight), with a surface area of 60 m²/g and a particle diameter of 5 mm. This catalyst was crushed in order to obtain particles of 250 μm.

2.2. Oxidation equipment

The oxidation was carried out in a 316 stainless steel high-pressure 1 l autoclave (*Parr Instrument Company*, model 4531M) equipped with two six-bladed mechanically driven turbine agitator. The thermocouple and liquid sample line are well immersed in the solution. This system allows operating conditions up to 130 bar and 350°C and is equipped with a PID temperature controller (*Parr*, model 4842). The oxygen flow was controlled by an electronic mass flow controller (*Hastings*) and a 316 stainless steel filter with 0.5 μm pore sizes (*Swagelok*) was used to avoid catalyst particles in the samples withdrawn from the reactor. The experimental set-up is schematised in Fig. 1.

2.3. Procedure for formaldehyde oxidation

For simulated formaldehyde effluents, the autoclave was initially charged with 450 ml of deionised water and pre-heated up to a pre-selected temperature to be maintained along the experiment. As soon as this temperature was attained, 50 ml of formaldehyde solution of known concentration was injected into the autoclave in order to attain the desired level of formaldehyde concentration inside the reactor (1500 ppm; pH = 4). This injection was followed by

the injection of oxygen into the autoclave and this time was taken as the “zero” time for the reaction. When industrial wastewater was used, the reactor was charged with the overall effluent to be oxidised (500 ml). All catalytic experiments were carried out in slurry conditions with 3.0 g of powder catalyst (6 g/l). The oxygen partial pressure (15.0–35.0 ± 0.3 bar), agitation velocity (350 rpm ± 3 rpm) and reaction temperature (190–220°C ± 1°C) were maintained during the course of the reaction. Samples were withdrawn periodically and analysed for *total organic carbon* (TOC). At the end of experiments the liquid sample was analysed by *atomic absorption* in order to detect the presence of leached Mn (when Mn/Ce was used) and Cu, Zn or Al (for CuO–ZnO/Al₂O₃). For these catalysts carbon adsorption was evaluated by *elemental analysis*.

2.4. Analytical techniques

TOC was determined with a Shimadzu 5000 TOC Analyser, which operates based on the combustion/non-dispersive infrared gas analysis method. Total carbon (TC) was first measured and then the inorganic carbon (IC) was evaluated. Total organic carbon (TOC) was determined by the difference between these two values of TC and IC. The uncertainty in this parameter, quoted as the deviation of three separate measurements, was never larger than 2% for the range of the TOC concentrations measured. *BET surface area* of the catalysts were determined with an accelerated surface area and porosimetry analyser ASAP 2000 from Micromeritics. *Elemental analysis* was performed to detect the carbon adsorption in catalyst, using a Finsons Instruments EA 1108 CHNS-O, equipped with a pre-packed ox/red quartz reactor. The catalyst was previously filtered and dried. Standards solutions of phenanthrene, sulphanilamide and BBOT were obtained from Fisons Instruments. *Atomic absorption* spectrometer Perkin Elmer-3300, with hollow cathode lamps (Cathodeon) and standard solutions from BSB-Spectrol, was used to measure the leaching of copper, zinc, aluminium and manganese in liquid phase.

3. Results and discussion

3.1. Catalytic wet oxidation of formaldehyde solutions

The present work emerges from the need to find out a catalyst able to oxidise the organic matter of industrial effluents containing high formaldehyde concentrations. In this context, different cerium-based catalysts that showed high activity in the degradation of other pollutants by the CWO process (*Imamura et al., 1986, 1994*) were prepared in our laboratory to be used on the formaldehyde oxidation. A simulated wastewater prepared according the levels of this compound on industrial effluents was firstly analysed. Various Mn, Co and Ag supported catalysts were tested and the results were mainly expressed in terms of TOC content of

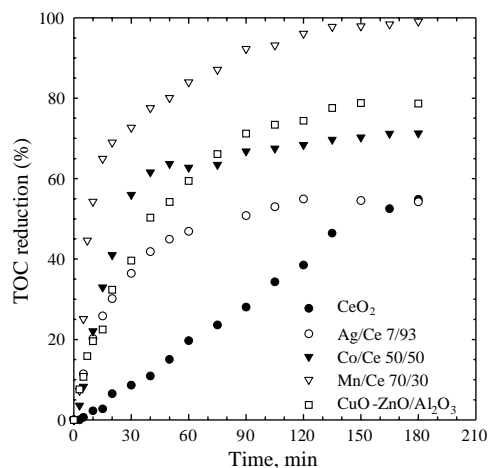


Fig. 2. TOC reduction as a function of time for different cerium supported and CuO–ZnO/Al₂O₃ catalysts (6 g/l catalyst concentration; 200°C; 15 bar oxygen partial pressure).

the reactional mixture along the time (Fig. 2). The operating conditions used in these studies (200°C; 15 bar oxygen partial pressure; 6 g/l catalyst) were based on preliminary studies and are in agreement with the usual conditions referred in literature. The material support (CeO₂) also showed catalytic properties with a linear evolution of the TOC abatement during reaction leading to 54.8% reduction. Combining this material with Ag, Co or Mn a substantial increase in the initial reaction rate is observed. The Mn/Ce 70/30 is the most effective catalyst allowing a nearly complete TOC reduction after 3 h (99.1%). Ag/Ce 7/93 seems to be the less appropriate catalyst for this process leading only to 54.2% oxidation, which must be also due to the low content on the active metal (7%). Thus, the catalytic properties of the cerium support are strongly improved using complementary metal oxides with the following order of activity: Mn/Ce 70/30 > Co/Ce 50/50 > Ag/Ce 7/93.

These results were also compared with those obtained with a commercial catalyst based on Cu–Zn oxides supported on aluminium oxide. A quite good performance of this catalyst was also detected and comparing with the Co/Ce results a crossover of both curves is observed: the higher initial rate velocity for Co/Ce is overpassed by the commercial catalyst on the final times of reaction. In fact, 39.6% reduction is obtained with Cu–Zn after 30 min, while 56% oxidation is observed with Co/Ce 50/50. However, after 2 h, 68.4% reduction was achieved with Co/Ce, against 74.4% for the Cu–Zn oxide catalyst.

CWO using the Mn/Ce 70/30 catalyst was compared with two different treatments: thermolysis (non-oxygen and non-catalyst) and non-catalytic WO (Fig. 3). Even at elevated temperatures formaldehyde solutions show high thermodynamic stability when catalyst is not used, since no significant oxidation is obtained and an accentuated induction period is observed in both cases. After 1 h, 5.3% TOC conversion is achieved with these non-catalytic processes

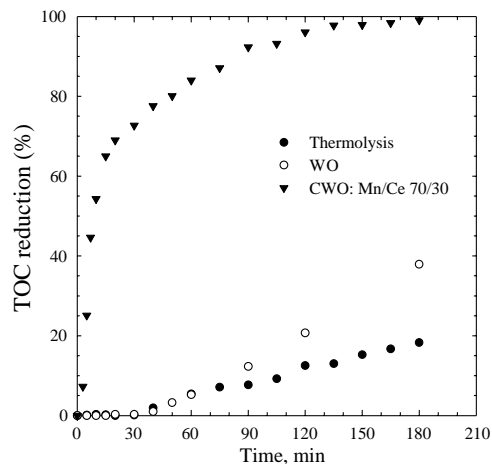


Fig. 3. TOC reduction as a function of time in Thermolysis (200°C); WO—non-catalytic wet oxidation (200°C and 15 bar oxygen partial pressure); CWO—catalytic wet oxidation (200°C and 15 bar oxygen partial pressure; 6 g/l of Mn/Ce 70/30).

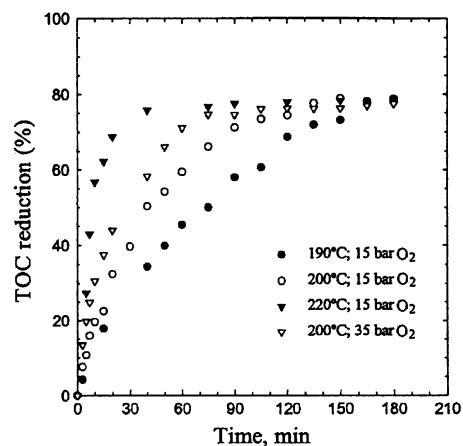


Fig. 4. TOC reduction as a function of time for different temperatures (190–220°C), different oxygen partial pressures (15–35 bar) and 6 g/l of CuO–ZnO/Al₂O₃.

and even in 3 h only 18.3% reduction for thermolysis and 38.1% for WO was observed. However, the presence of catalyst originates a rapid destruction of the organic compounds. Therefore, formaldehyde solutions are not suitable to be treated by thermolysis or WO processes without the use of an active catalyst. In fact, all the catalysts (Fig. 2) led to TOC reductions higher than those obtained in the experiments without catalyst (Fig. 3), which points out that the presence of a catalyst is essential for formaldehyde solutions oxidation.

The above studies showed that contrary to Mn/Ce catalyst, the total TOC degradation is not achieved when using the commercial catalyst. The same results were obtained with different temperatures (190–220°C) and different pressures (15–35 bar) (Fig. 4).

A temperature increment of 30°C resulted in an evident acceleration of the reaction rate in the initial times: in 15 min

62.2% of TOC reduction is achieved for 220°C while 17.8% for 190°C was observed. TOC decrease was scarcely affected by increasing oxygen partial pressure; thus, temperature is a key factor controlling the reaction rate in the catalytic oxidation. However, for long reactions periods, both operating variables do not affect the final TOC reduction, since a final value around 20% is always obtained even when such parameters are increased quite considerably. This fact points out that a certain amount of organic matter in the reactional system is non-oxidisable with this catalyst while for the Mn/Ce catalyst the pollutant degradation was almost complete (Fig. 2). The existence of non-oxidisable compounds was also referred by Hu, Lei, Chen, and Yue (2001) on the treatment of a printing and dyeing wastewater.

The formation of low weight carboxylic acids in solution is a common step in the wet oxidation processes, since they are refractory compounds difficult to oxidise. In the formaldehyde solution oxidation, it is mainly expected the formation of formic acid due to its higher oxidised state when compared with formaldehyde. In this work the presence of formic, acetic and oxalic acids were evaluated using *high performance liquid chromatography* (HPLC) analysis as referred by Shende and Levec (1999). Only formic acid was detected as an intermediary compound; however, it was also observed its further complete oxidation. Other typical stable intermediates have been found in WO studies such as methanol and ethanol. The activation energies associated to their oxidation reaction are high, even greater than those corresponding to acetic acid, a typical end-product in wet oxidation process (Li, Chen, & Gloyna, 1991). Since the commercial formaldehyde solution used in our work is stabilised with methanol, its concentration was evaluated along the reaction and it was observed a constant value when the commercial catalyst was used (around 20% in TOC concentration), which corresponds to the final non-oxidisable organic matter observed in Fig. 4, even at severe operating conditions. Contrarily, methanol is completely oxidised with the Mn/Ce catalyst. It may oxidise to formaldehyde, which will be degraded directly into final products or into formic acid, which, in turn, will oxidise to carbon dioxide. The effectiveness of the Mn/Ce catalysts can be then explained by the high selectivity to the oxidation of methanol, which is not oxidised by the commercial catalyst. Using the CuO–ZnO/Al₂O₃ catalyst, the CWO process can be eventually used as a complementary process simultaneously with a post-biological treatment, since the significant TOC reduction achieved are suitable for further microorganisms digestion. If the Mn/Ce catalyst is used, the CWO process can fulfil the required TOC removal for the direct discharge of wastewaters in environment.

3.1.1. Catalysts stability

After 3 h of oxidation reaction, adsorbed carbon was evaluated by elemental analysis for the Mn/Ce 70/30 and for

the commercial catalysts. No capacity for carbon adsorption was identified pointing out that TOC removal was caused by oxidation and not by adsorption. Another important issue that has to be taken into account in what concerns the chemical stability of these ceramic catalysts involves the analysis of the leaching behaviour of the active metals to the liquid phase during reaction. The occurrence of this phenomenon may lead to the deactivation of the catalyst due to the irreversible loss of catalytic species. Moreover, diffusion of metals from the solid matrix may contaminate the liquid effluent being then required a post-treatment for separation of metals from the final effluent. In our studies, eluted metals were detected by atomic absorption analysis performed on the experiments carried out with the operating conditions referred in Fig. 2 for Mn/Ce 70/30 and CuO–ZnO/Al₂O₃. After 3 h for Mn/Ce 70/30 at a pH of 4.6, the leaching of Mn was 9×10^{-6} g/l and for CuO–ZnO/Al₂O₃ the eluted component in the liquid phase was 1.1×10^{-5} g/l for Cu, 3.0×10^{-3} g/l for Zn and Al was not detected. The values obtained for Cu, Zn and Al metals in this work are significantly lower than the values reported by Mantzavinos, Hellenbrand, Livingston, and Metcalfe (1996) using the commercial catalyst on the CWO of *p*-coumaric acid at different operating conditions. For example, in experiments with 4.4 g/l of catalyst, 130°C, initial pH of 3.5, 60 min of reaction time, 1.8×10^{-2} g/l of Cu, 4.2×10^{-2} g/l of Zn and 1.0×10^{-3} g/l of Al were reported. Thus, both catalysts in our study showed relatively good stability for our system, since in spite of the severe operating conditions the leaching of metals was not significant.

3.1.2. Mn/Ce catalysts

The previous results clearly indicate that among the catalysts under study, those based on Mn and Ce oxides are the most active for an oxidation process where formaldehyde is the main pollutant. In order to evaluate the effect of the Mn composition, different Mn/Ce ratios were analysed (60/40, 70/30, 75/25, 80/20). TOC reduction for formaldehyde simulated effluent is represented in Fig. 5(a) as a function of the reaction time for various Mn/Ce ratios and in Fig. 5(b) as a function of the catalyst composition for various reaction times. Fig. 5(a) shows that all the Mn/Ce catalysts under study provoke a rapid attack to TOC destruction in the initial times of the CWO process. Nevertheless, Fig. 5(b) highlights in a more clear way the effect of Mn content for the different reaction times, showing a more pronounced influence of this active metal in the initial times than for long reaction times. In fact, while in 15 min 25.9% reduction is gained when 80% Mn is used instead 60%, after 3 h only a slight difference of 2.5% was detected. Fig. 5(b) emphasises that Mn is an important component to improve the catalytic activity, since its absence reveals a very slow reduction in TOC concentrations: in 3 h only 54.8% is achieved with CeO₂, while for all the other Mn catalysts total oxidation is nearly obtained.

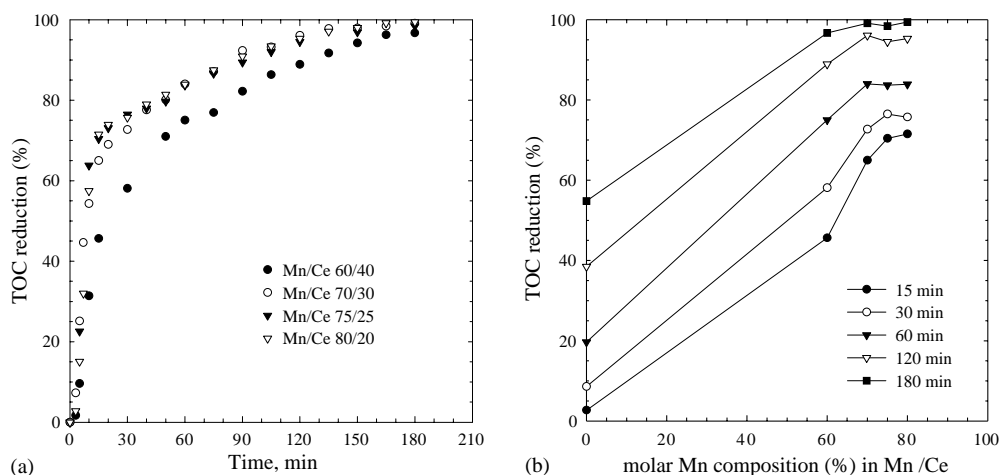


Fig. 5. (a) TOC reduction as a function of time for different Mn/Ce catalysts (6 g/l catalyst concentration; 200°C; 15 bar oxygen partial pressure). (b) TOC reduction as a function of molar Mn compositions in the Mn/Ce catalyst different reaction times (6 g/l catalyst concentration; 200°C; 15 bar oxygen partial pressure).

The Mn/Ce 80/20 is the most active catalyst, showing 71.5% TOC decrease in 15 min and almost complete destruction of organic compounds in 3 h (99.4%). On the range of Mn composition we tested, 60–80%, the improvement on TOC reduction was not significant for long reaction times, though higher TOC abatements were observed on the initial reaction times for higher Mn contents.

3.2. Catalytic wet oxidation of industrial effluents

Aiming industrial applications, the CWO process was tested with an industrial high formaldehyde concentration effluent (800 ppm) obtained from a formalin synthesis industry and wood processing for urea–formaldehyde–resin production. The two more active catalysts found in the previous studies for formaldehyde laboratorial solutions were used in these experiments, namely a laboratorial Mn/Ce and a commercial catalyst CuO–ZnO/Al₂O₃.

The results presented in Fig. 6 show that when the Mn/Ce catalyst was used the TOC degradation in the effluent (IE—industrial effluent) is much more important than the one obtained with CuO–ZnO/Al₂O₃ catalyst. In fact, after 3 h the final conversion for Mn/Ce was 91.6% and even in 1 h the conversion rate was already high (68.5%). The difference between TOC reduction in the simulated (LS—laboratorial solution) and industrial effluent may be due to the presence of compounds that are more difficult to oxidise in industrial wastewaters. Such differences are higher when the commercial catalyst is used, pointing out that this catalyst is less active for other compounds that exist in the industrial effluent but are not present in the formaldehyde solutions prepared in laboratory. It is therefore worthwhile to strengthen that using Mn/Ce catalysts on the CWO process at industrial level a significant TOC reduction can be achieved.

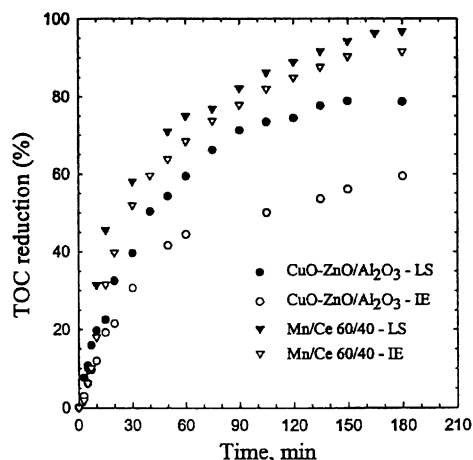


Fig. 6. TOC reduction as a function of time for application of the Mn/Ce 60/40 and CuO–ZnO/Al₂O₃ catalysts to a laboratorial solution (LS) and an industrial effluent (IE) (6 g/l catalyst concentration; 200°C; 15 bar oxygen partial pressure).

The formaldehyde concentrations along the reaction process were also analysed, and almost a total disappearance of formaldehyde was detected (Table 1). For the Mn/Ce catalyst, practically 100% of formaldehyde degradation is obtained in 180 min (from 800 to 0.1 ppm) and with the commercial catalyst slightly lower conversions were observed, namely 99.8% (from 800 to 1.5 ppm). Therefore, both catalysts seem to be highly active for the formaldehyde degradation, suggesting that TOC concentrations are due to the presence of refractory compounds, such as formic acid and methanol. pH values for different reaction times are referred in Table 1. Leaching of Mn for the industrial effluent was not significant, namely 3×10^{-6} g/l (at a pH of 7.7), which was even lower than for the simulated wastewater (9×10^{-6} g/l at a pH of 4.6). For the commercial catalyst, the leaching of

Table 1
Formaldehyde and ammoniacal nitrogen concentrations and pH values along time for Mn/Ce 60/40 and CuO–ZnO/Al₂O₃ catalysts

| <i>t</i> (min) | Formaldehyde (ppm) | | | Ammoniacal nitrogen (ppm) | | | pH | | |
|----------------------------------------|--------------------|-----|-----|---------------------------|-----|-----|-----|-----|-----|
| | 0 | 30 | 180 | 0 | 30 | 180 | 0 | 30 | 180 |
| Mn/Ce 60/40 | 800 | 0.4 | 0.1 | 420 | 248 | 155 | 7.2 | 9.2 | 7.7 |
| CuO–ZnO/Al ₂ O ₃ | 800 | 85 | 1.5 | 420 | 240 | 230 | 7.2 | 8.2 | 9.0 |

Cu and Zn were, respectively, 2.5×10^{-4} and 2.6×10^{-4} g/l (at a pH of 9.0) for the industrial effluent and 1.1×10^{-5} and 3×10^{-3} g/l (at a pH of 5.9) for the simulated wastewater. These results point out a high stability of these catalysts for different pH values, in particular for the Mn/Ce catalyst. Ammoniacal nitrogen is another typical pollutant compound present in this type of wastewaters and therefore its concentration was also followed. With the Mn/Ce catalyst a reduction from 420 to 155 ppm in 3 h was observed (Table 1), leading to 63.1% conversion, higher than when the commercial catalyst was used (45.2%). In fact, [Imamura and Doi \(1985\)](#) refers a high activity of the Mn/Ce catalysts in ammonia treatment by CWO. Therefore, this process is potentially promising for wastewaters containing formaldehyde in what concerns TOC abatements, total formaldehyde degradation, as well as ammoniacal nitrogen reduction.

4. Conclusions

The main goal of our work addressed the search of catalysts suitable to be used on the CWO process of effluents containing high formaldehyde concentrations (800–1500 ppm). An active and stable catalyst based in economical metals was obtained for formaldehyde containing solutions, namely the Mn/Ce catalyst. It was observed that higher calcination temperatures lead to lower BET surface area while drying temperatures have no effect. Using such catalyst high TOC conversions were achieved (99.4%). These conversions were higher than those attained with a commercial CuO–ZnO/Al₂O₃ catalyst (78.7%). Using other metal composites based on cerium, Co/Ce and Ag/Ce, the conversions were lower (71.3% and 54.2%). The cerium support used in the preparation oxide metals catalysts showed catalytic properties. In any case, the use of catalyst is highly recommended for improving the oxidation process, since in non-catalytic processes such as thermolysis and non-catalytic wet oxidation, only 18.3% and 38.1% of TOC reduction was, respectively, achieved. Stability of Mn/Ce and CuO–ZnO/Al₂O₃ catalysts was studied and no carbon adsorption capacity or significant leaching of metals was observed. While Mn/Ce catalysts revealed the possibility to achieve total TOC reduction, a non-oxidisable organic matter in the reactional system was observed under the process using the commercial catalyst, even increasing pressure and temperature. Studies with different molar compositions of

Mn/Ce revealed that increasing the Mn metal composition in the range of 60–80% leads to more active catalysts for initial reaction times; meanwhile for long time periods no significant improvement in activity is observed.

The CWO process using an Mn/Ce catalysts on the treatment of an industrial high formaldehyde concentration effluent from a formalin synthesis industry and wood processing for urea–formaldehyde–resin production, showed high TOC reduction (91.7%); total formaldehyde oxidation; and a quite significant ammoniacal nitrogen abatement (63.1%). Therefore, the Mn/Ce catalysts seem to be quite interesting for the catalytic wet oxidation technology. Several studies have to be carried out in the future to make possible its commercialisation.

Notation

| | |
|----------|---------------------------|
| <i>t</i> | time, min |
| <i>T</i> | temperature, °C |
| TOC | total organic carbon, ppm |
| CWO | catalytic wet oxidation |
| WO | wet oxidation |

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