ELSEVIER

Catalysts based in cerium oxide for wet oxidation of acrylic acid in the prevention of environmental risks

Adrián M.T. Silva, Rita R.N. Marques, Rosa M. Quinta-Ferreira*

Department of Chemical Engineering, University of Coimbra, Polo II-Pinhal de Marrocos, 3030-290 Coimbra, Portugal

Abstract

Acrylic acid is a refractory compound for the non-catalytic wet oxidation (WO) process and can seriously damage the environment when released in industrial effluents. Oxidation of acrylic acid by catalytic wet oxidation (CWO) was studied in slurry conditions in a high-pressure batch reactor at 200 °C and 15 bar of oxygen partial pressure. Several solid cerium-based catalysts prepared in our laboratory were used (Ag/Ce, Co/Ce, Mn/Ce, CeO, MnO) and evaluated in terms of activity, selectivity and stability. Mn/Ce shows the higher activity in 2 h with 97.7% reduction of total organic carbon (TOC) followed by: MnO(95.5%) > Ag/Ce(85.0%) > Co/Ce(65.1%) > CeO(61.2%). Attempts were also carried out to analyze the influence of different Mn/Ce molar ratios. High percentages of Mn lead to practically total organic carbon concentration (TOC) abatements while low ratios lead to the formation of non-oxidizable compounds. Acrylic acid was readily degraded by all the catalysts pointing out the high importance of using a catalytic process. pH was an indicator of the reaction pathway and acetic acid was found as the major reaction intermediate compound; however it is completely oxidized after 2 h with exception for Co/Ce, CeO and MnO. Carbon adsorption and leaching of metals were poorly found for Mn/Ce indicating high stability. The catalyst microstructure after the reaction was analyzed and formation of whiskers of β-MnO₂ (or less probably MnOOH) were observed at the catalyst surface. Therefore, Mn/Ce revealed to be a promising catalyst for the treatment of effluents containing acrylic acid; nevertheless, its commercialization depends on further research.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Environment; Pollution; Acrylic acid effluents; Wet oxidation; Catalysts; Manganese; Cerium

1. Introduction

The wet oxidation (WO) process has been earning an important industrial role nowadays in different chemical companies for the treatment of toxic effluents [1,2]. However, short chains carboxylic acids have been found as refractory compounds for this technology [3]. In particular, acrylic acid ($C_3H_4O_2$) is thermally stable up to high temperatures (280 °C) and in terms of total organic carbon concentration (TOC) is poorly oxidized below 250 °C [4]. For this reason, the oxidation of this compound is a rate controlling step in the complete TOC degradation of different pollutant solutions [3]. Acrylic acid is widely used in several industries (painting, chemical fibers, adhesives, paper, oil additives, detergents) and when released in effluents serious damage

to the environment can be caused due to its high toxicity for aquatic organisms [5].

Catalysis research is a key factor in the development of the WO environmental technology, aiming pollutant abatements under milder operating conditions. However, few attempts have been carried out in literature for the catalytic oxidation of acrylic acid. The catalysts used in WO can be generally divided into three categories: (1) oxides of the transition metals, (2) supported noble metals and (3) metal salts and their complexes. The homogeneous catalysts are normally avoided since due to their toxic contamination they should be removed from the solution in a second treatment step. Heterogeneous catalysts applications based in noble metals (Pt, Ru, Pd, Rh, Ir, Ag) and oxides metals (Mn, Co, Cu, Zn, V, Ni, Fe, Bi, Ti) using different supports (Al₂O₃, CeO₂, TiO₂, ZrO₂, NaY zeolite) are summarized in different review papers [1,3,6,7]. Regarding the heterogeneous catalysts, both categories present advantages and drawbacks. Noble metals are expensive components increasing considerably the process cost. On the other hand, oxides of the transition metals

* Corresponding author. Tel.: +351-239-798-723;
fax: +351-239-798-703.
E-mail addresses: adrian3@eq.uc.pt (A.M.T. Silva), rosa@eq.up.pt
(R.M. Quinta-Ferreira).

have been found in some cases as unstable due to deactivation by leaching of the metals to the liquid phase, fouling of surface and adsorption of carbonyl compounds by the catalyst [6]. In this context, it is quite important to develop economical, active and stable catalysts that can be effective for degradation of organic compounds by WO.

Olivero et al. [8] studied the oxidation of acrylic acid under Ru noble metal catalysts based in carbon, cerium and carbon-cerium. They concluded that both supports containing carbon do not provide a high activity to the catalyst (less than 40% of acrylic acid conversion), while a total oxidation is obtained using Ru/Ce. However Ru is an expensive material and it is our goal to find out more economic catalysts. Since cerium is considered as a promoter active support, different cerium-based catalysts were selected in the present work (Mn/Ce, Ag/Ce, Co/Ce). These catalysts were selected taking into account their activity in the oxidation of other compounds such as acetic acid [3], formaldehyde [9], phenol [10] and ammonia [11]. In the oxidation of polyethylene glycol (PEG-200) Ru/Ce showed higher activity than Mn/Ce using the same reaction conditions; however, it is also reported that acetic acid was not degraded totally with Ru/Ce while complete removal was obtained with Mn/Ce [7]. Therefore, as referred, the Ru/Ce catalyst presented selectivity toward specific substances. Since Mn/Ce is an economical catalyst with high activity in the oxidation of a wide range of compounds [3,6,9] and it is most active than Ru/CeO_2 in the oxidation of acetic acid, which is expected as intermediary compound of the reaction, Mn/Ce was selected for this work and its activity was compared with Ag/Ce and Co/Ce. The most effective catalyst (Mn/Ce) was evaluated under different molar ratios of the respective metal. Experiments were also carried out with both pure oxide metals (MnO and CeO) in order to understand the effect of these metals in the Mn/Ce composite oxide.

2. Experimental

2.1. Material, catalysts and equipment

Acrylic acid (2-Propenoic acid-$C_3H_4O_2$) 99.5% stabilized with 180 to 220 ppm of hydroquinone monomethyl ether (4-methoxyphenol-MEHQ-$C_7H_8O_2$) was obtained from Acros organics. Mn/Ce, Co/Ce, Ag/Ce, MnO and CeO catalysts were prepared in our laboratory by precipitation according the procedures described elsewhere [9] and using the corresponding metal nitrates as precursors (Riedel-de-Häen and Labsolve). The molar composition ratios for Co/Ce and Ag/Ce was 70/30 and for Mn/Ce 70/30 and 22/78. Mn/Ce, Co/Ce, MnO and CeO were prepared with a mixed aqueous solution of metal salts (15 g of metal salt/100 ml), poured into 200 ml of a 3 M NaOH solution. The precipitate was filtrated, washed five times with 500 ml of ultra pure water and dried at 100 °C over night, followed

by calcination at 350 °C for Co/Ce and 300 °C for Mn/Ce, Co/Ce, MnO and CeO catalysts. An aqueous solution of silver nitrate and cerium nitrate was used to prepare the Ag/Ce catalyst. An NaOH 3 M solution, prepared from a sodium hydroxide salt (Merck), was added until a pH equal to 10 was achieved. The precipitate was filtrated, washed three times with ultra pure water and dried over night at 100 °C, followed by calcination at 300 °C. The catalysts were crushed in order to obtain a fine power with particle sizes mainly in the range 125–841 μm; this range was previously tested as appropriate to ensure the elimination of internal diffusion resistances.

The oxidation process was studied in a laboratorial unit with a high-pressure 1 l autoclave of 316 stainless steel (Parr-model 4531M) described elsewhere [9]. The autoclave was initially charged with 450 ml of deionized water and preheated up to 200 ± 1 °C. As soon as this temperature was attained, 50 ml of a pre-calculated acrylic acid solution was injected in order to attain a concentration of 1000 ppm (500 ppm in terms of TOC) in the reactor. High purity oxygen (99.999%) was then introduced and this was taken as the "zero" time for reaction. All catalytic experiments were carried out in slurry conditions with 3 g of powder catalyst (6.0 g/l), oxygen partial pressure of 15.0 ± 0.3 bar and 350 ± 3 rpm agitation velocity.

2.2. Analytical techniques

The samples withdrawn periodically from the reactor were analyzed for pH and TOC concentration in a Shimadzu 5000 TOC Analyzer, which operates based on the combustion/non-dispersive infrared gas analysis method. The carboxylic acids concentrations were determined by high performance liquid chromatography (HPLC-Knauer system), equipped with an UV detector (set at 209 nm) and a SS-Column of 300 × 8 mm internal diameter and 10 μm particle size, which consists of a sulfonated cross-linked styrene-divinylbenzene copolymer as a stationary phase (Eurokat H). The column was set at 25 °C and a mobile phase of 0.01 N H_2SO_4 with a flow rate of 1 ml/min was used. Leaching of manganese was determined by atomic absorption (Spectrometer Perkin Elmer-3300). In the end of the experiment the catalyst was recovered in order to evaluate the carbon concentration on the solid by means of elemental analysis (Finsons Instruments EA 1108 CHNS-O). Catalyst texture and morphology were examined at different scales/magnifications by scanning electron microscopy (SEM) on a JEOL JSM-5310 scanning microspore and by transmission electron microscopy (TEM). For the TEM analysis the samples were prepared by suspending the powder in ethanol and pouring the solution into holy carbon coated copper grids. Analysis were carried out at an operating voltage of 200 kV in a Jeol 2000 FX transmission electron microspore equipped with a Link AN 10000 EDXS (energy-dispersive X-ray spectroscopy) system with a UTW Si (Li) detector.

3. Results and discussion

3.1. Catalytic activity of different cerium-based catalysts

The results of our study are shown in Fig. 1(a–f) where TOC reduction, pH profiles and intermediate compounds are represented. The catalyst efficiency was measured taking into account the TOC concentration of the solution as principal parameter, since besides acrylic acid degradation it is important to guarantee the conversion of the overall organic carbon in solution to carbon dioxide and water. Fig. 1(a) represents the TOC reduction for the non-catalytic wet oxidation as well as for the catalytic process when using different cerium-based catalysts at constant molar ratio of 70/30. While acrylic acid solutions can not be oxidized in terms of TOC without the use of a catalyst, cerium-based catalysts showed significant activities and high conversions. The cerium support (CeO) also revealed catalytic properties leading to a final reduction of 61.2%. Activity of CeO was also reported by Imamura et al. [12] in the oxidation of a model wastewater referring that such activity can be due to the mobility of the surface oxygen. Combining cerium oxide with Co, Ag or Mn, the efficiency of the oxidation process in 2 h increased by the following order: Co/Ce 70/30(65.1%) < Ag/Ce 70/30(85.0%) < Mn/Ce 70/30(97.7%). Therefore, Mn showed to be the best metal to be combined with Ce in terms of catalytic activity. The catalyst Mn/Ce 70/30 showed high efficiency and high reaction rate that made possible to obtain 94.1% of TOC reduction in the first 30 min and 97.7% after 1 h. Using Ag/Ce 70/30 the TOC reduction increased also significantly until 80.9% in the first 30 min; however, the subsequent plateau in 85.0% revealed the possible formation of refractory compounds which were not able to be decomposed. The Co metal does not improve significantly the activity of CeO. This can also be observed in Fig. 1(b) where the increment in TOC removal by adding a transition metal (Mn, Ag or Co) to CeO is represented. After 75 min the influence of the Co content is negligible and the maximum effect is observed at 15 min where the efficiency of Co/Ce 70/30 is 25% higher than the one related to CeO. For all the catalysts the maximum value of the efficiency increment was obtained in the range of 15–30 min, namely 50.0% for Ag/Ce 70/30 and 62.4% for Mn/Ce 70/30. Therefore, the improvement on the activity of Ce by Co, Ag and Mn is more important in the initial reaction times with better results to Mn. In a recent paper [9] dedicated to the oxidation of formaldehyde solutions stabilized in methanol, our results also revealed that Mn/Ce showed higher activity than Ag/Ce and Co/Ce, being possible to obtain practically the complete oxidation in terms of TOC for Mn/Ce. Therefore, these potential results obtained for aldehyde and alcohol oxidation are emphasized with the present study regarding the effectiveness of the Mn/Ce catalyst extended to unsaturated carboxylic acids.

3.2. Effect of Ce and Mn on the catalytic activity of Mn/Ce

Fig. 1(c) shows that higher TOC reductions were obtained in 2 h with Mn/Ce 70/30 (97.7%) than with Mn/Ce 22/78 (87.0%); however the initial rates (first 20 min) are not significantly affected by the molar ratio of manganese and cerium. In both cases an asymptotic value in TOC reduction was observed approximately after 30 min of reaction. However, for the Mn/Ce 70/30 such plateau corresponds to a practically total reduction while for Mn/Ce 22/78 a high content of TOC is still not oxidized. In fact, a significant fraction of refractory compounds representing 13% of the initial TOC concentration was not suitable to be oxidized by the low-manganese catalyst. The effect of the Mn content in TOC reduction for different reaction times is also highlighted in Fig. 2 where it is shown that even if the combination of Mn with Ce revealed a higher effect in the initial times of the oxidation process, for longer periods the effect of Mn is also beneficial. The interaction between the two components of the Mn/Ce catalyst was carefully characterized by Chen et al. [13]. According to these authors the active sites should be considered as two groups: one related to the higher oxidation state of manganese oxide species and another based on the lower oxidation state of manganese with catalytic properties fomented by the effect of Ce^{4+}. In pure manganese oxide three possible high oxidation states are found $+2$, $+3$ and $+4$, which confers high activity to MnO. When cerium is added, the surface of manganese seemed to be different with lower oxidation states. However, it is known that if manganese is added to cerium, the concentration of Ce^{4+} increases in detriment of Ce^{3+} and the electrons of the higher state of cerium seem to be transferred to Mn [13]. Therefore, the high activity of Mn/Ce 70/30 can be explained by an efficient equilibrium of the electrons transfer, while in the Mn/Ce 22/78 the low content in manganese do not promote the increase of Ce^{4+} species, decreasing then the catalytic activity.

Using the catalyst based only in the transition metal (MnO) a final TOC reduction of 95.5% is reached which is similar with the one related to Mn/Ce 70/30 (97.7%) and higher than for Mn/Ce 22/78 (87.0%). Therefore, the final high TOC abatement with Mn/Ce seems to be due to the effect of the manganese oxide. However, the reaction for MnO is significantly slower than when a Mn/Ce composite is used; in fact, one can observe in Fig. 1(c) that in 30 min a reduction of 94.1% is obtained for Mn/Ce 70/30 against the lower value (45.2%) related to MnO. Cerium can then improve the catalytic activity of the manganese transition metal oxide in a significant way. This is in accordance with the results of Chen et al. [13], since although the higher oxidation states of manganese are related to MnO, the global efficiency is due to two different groups of activation sites which are believed to exist in Mn/Ce 70/30. The results obtained for oxidation of acrylic acid are in agreement with the literature since Imamura et al. [11] in studies with Mn/Ce for
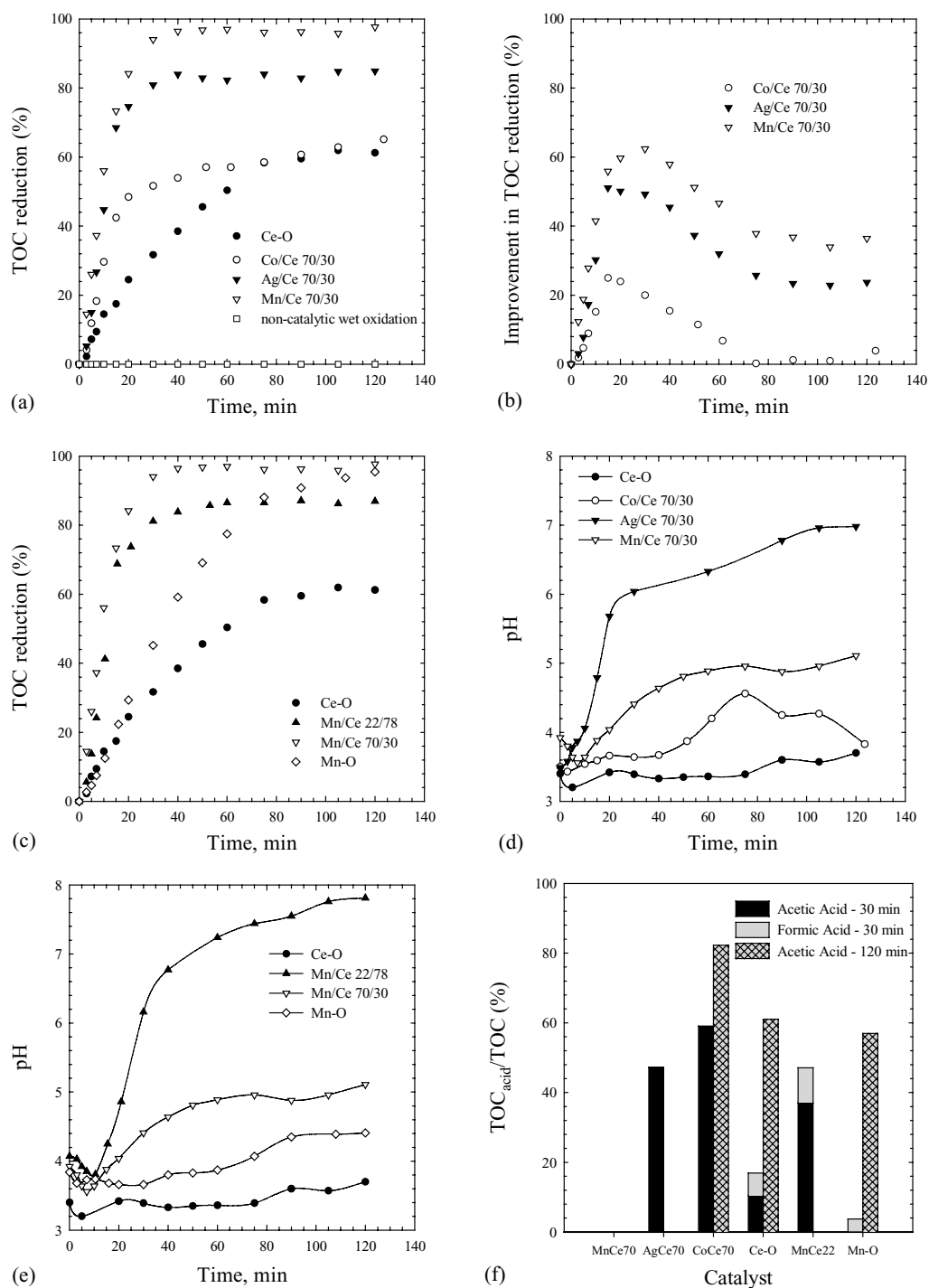
Fig. 1. (a) TOC reduction as a function of time for non-catalytic wet oxidation and different cerium-based catalysts; (b) Increment in TOC reduction of cerium-based catalysts in relation to pure cerium oxide (CeO); (c) TOC reduction as a function of time for different Ce and Mn catalysts; (d) pH profiles of the solution for different cerium-based catalysts; (e) pH profiles of the solution for different Ce and Mn catalysts; (f) Acetic and formic acid percentages in terms of TOC for different catalysts after 30 min and 120 min of reaction; (200 °C, 15 bar oxygen partial pressure and 6 g/l catalyst concentration).

oxidation of ammonia concluded that Mn/Ce with a mol.% of 70/30 was more active than using other ratios. Imamura et al. [14] found for polyethylene glycol the maximum in a mol.% of 40/60. Chen et al. [13] for the oxidation of phenol found as the most active catalyst Mn/Ce 60/40. Silva

et al. [9] in the oxidation of formaldehyde point an optimal range of Mn content of 70–80%. The optimal ratio for all the compounds seems to occur in the 40/60–80/20 window.

Therefore, manganese has a crucial role in the high TOC abatement and the combination with cerium will increase
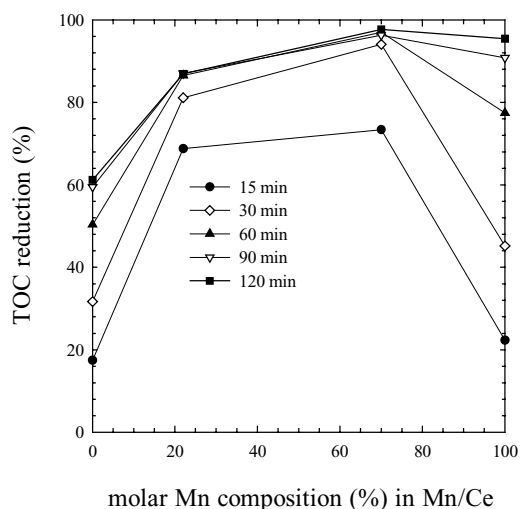
Fig. 2. TOC reduction as a function of the molar Mn composition in the Mn/Ce catalysts for different reaction times (200 °C, 15 bar oxygen partial pressure and 6 g/l catalyst concentration).

significantly the initial reaction rate. However, high percentages of cerium can also have some undesired influence in the final TOC reduction after 2 h when Mn/Ce 22/78 is less active than MnO. Finally with Mn/Ce 70/30 it is possible to combine both wanted effects: high TOC reduction as well as high initial reaction rates.

3.3. pH evaluation

The change in the pH of solutions submitted to the oxidation treatment is an indicator of how the reaction proceeds [15]; the evolution of pH was then investigated and the results are shown in Fig. 1(d) and (e), which are related to the experiments represented in Fig. 1(a) and (c) respectively. In general these pH values show the same trends that have been typically found in CWO [15,16]: a slight decrease in the first minutes followed by a subsequent increase. These trends were only different for Ag/Ce and Co/Ce (Fig. 1(d)); in the first case the initial decrease was not observed and in the second one a final decrease after 75 min was detected. For Co/Ce this decrease seems to be related with the slight increase in the TOC reduction observed in Fig. 1(a) for the same reaction time. For Ag/Ce the initial high increase in TOC reduction was followed by a high increase in pH (which may be due to the formation of carbon dioxide and water) and after 30 min, when the TOC reduction reached a plateau, the pH increased slowly. Moreover, the formation of a precipitate with time was observed in the samples that were withdrawn from the reactor. Therefore, this catalyst is not recommended for the process since the formation of this precipitate will originate another contamination source.

For the Mn/Ce catalysts (Fig. 1(e)) a rapid decrease seems to indicate the formation of low weight carboxylic acids that may be potential intermediates products of the reac-

tion. However, the further increase observed mainly for the Mn/Ce 22/78 catalyst should be due to the formation of carbon dioxide and water. For both monometallic catalysts (MnO and CeO) the pH does not change drastically probably due to its slower reaction rate.

3.4. Pathway mechanistic interpretation

In order to draft a mechanistic pathway of the reaction, the conversion from acrylic acid into intermediates compounds in the liquid phase was evaluated during the course of the oxidation reaction. Regarding acrylic acid it was found that this compound is rapidly oxidized by all the catalysts while its degradation was not possible when submitted to the non-catalytic wet oxidation at 200 °C. Therefore, the use of a catalyst is strongly necessary in the oxidation of acrylic acid. It is our objective to obtain a catalyst able to reduce the TOC concentrations as much as possible with the aim to purify at the maximum level the effluents containing acrylic acid. In this context the contribution for the total TOC of remaining chemical compounds was evaluated. After 30 min of reaction the ratio between the TOC associated to acetic and formic acids (TOC_{acid}) and the global TOC are represented in Fig. 1(f). These results show that acetic acid is an important reaction intermediate. It was not detected for Mn/Ce 70/30, probably due to the fact that at 30 min it had already been oxidized since at this time only 5.9% of the initial TOC is found in solution. For MnO acetic acid was also not detected being formed only formic acid. For CeO and Mn/Ce 22/78 formic acid was detected with considerably lower percentages than those of acetic acid. After 120 min these catalysts are able to oxidize totally the formic acid. Also acetic acid was completely degraded for Mn/Ce and Ag/Ce catalysts, while significant contents were found for CeO (61.1% of TOC), Co/Ce (82.3% of TOC) and MnO (57.0% of TOC).

Therefore, these results point out that: (1) Mn/Ce 70/30 is able to reduce readily all the carbonyl compounds; (2) the reaction of Mn/Ce 22/78 and CeO seems to have initially the same mechanistic pathway, with formation of acetic and formic acid; however the presence of manganese makes possible the subsequent total degradation of both acids. Also Ag/Ce 70/30 is able to decompose the acetic acid initially formed; (3) the non-oxidizable TOC concentration observed for Mn/Ce 22/78 in Fig. 1(c) and for Ag/Ce 70/30 in Fig. 1(a) is not due to acetic and formic acids but probably to other carbonyl species resulting from the acetic acid oxidation which were not identified. In fact, acetic acid is detected at 30 min of the reaction time and not observed at 120 min (Fig. 1(f)), whereas the global TOC remains approximately constant during this time period; (4) Co/Ce and CeO are catalysts with low activity since an increase in the percentage of acetic acid was observed in the final times of the oxidation reactions; (5) in the case of MnO a low percentage of TOC was in the solution after 2 h (Fig. 1(c)), mainly due to acetic acid (Fig. 1(f)), which strengthens the con-

clusion that the combination of cerium with manganese is preferable for oxidation of acetic acid than the use of the isolated metals.

Comparing the activity of the Ru/Ce catalyst used by Olivero et al. [8] with the results obtained in this work with Mn/Ce, it is important to highlight that in both cases acetic acid is a reaction intermediate compound. Those authors concluded that acetic acid was not oxidizable in their experiments. Imamura et al. [17] refer that at 200 °C acetic

acid is 44.5% removed with Ru/Ce while complete degradation is obtained with a Mn/Ce catalyst under the same reaction conditions, pointing out Mn/Ce as more selective for acetic acid degradation than Ru/Ce. Therefore, these results in addition to the ones achieved in our work reveal the high activity of Mn/Ce and reinforce that Mn/Ce is preferable to Ru/Ce in the treatment of wastewaters containing acrylic acid having also in mind the high cost of noble metals.
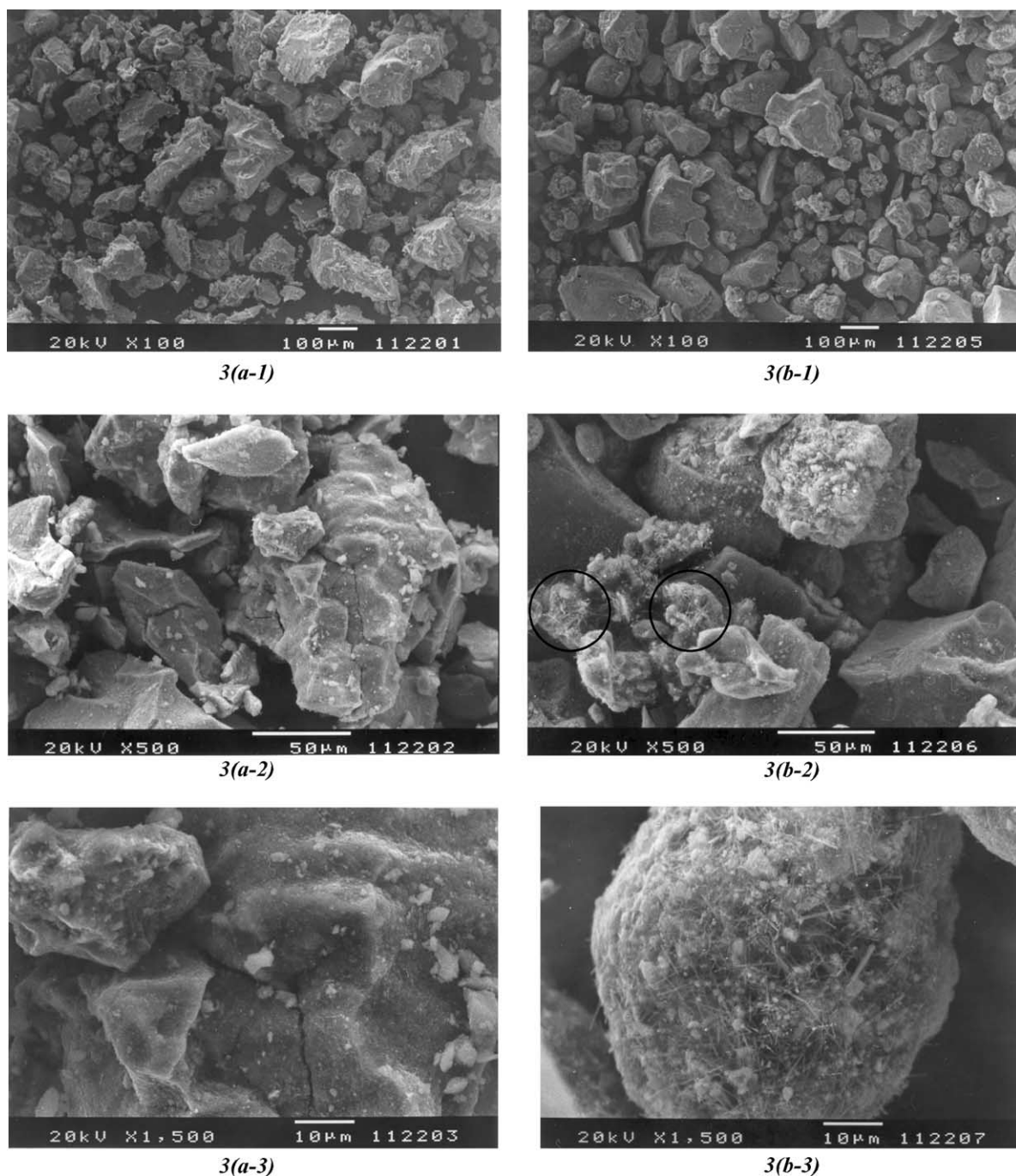

Fig. 3. SEM photographs showing different scales/magnifications: (a) fresh Mn/Ce 70/30; (b) used Mn/Ce 70/30 catalyst: (1) 100×; (2) 500×; (3) 1500×; (4) 3500×; (5) 20,000×.
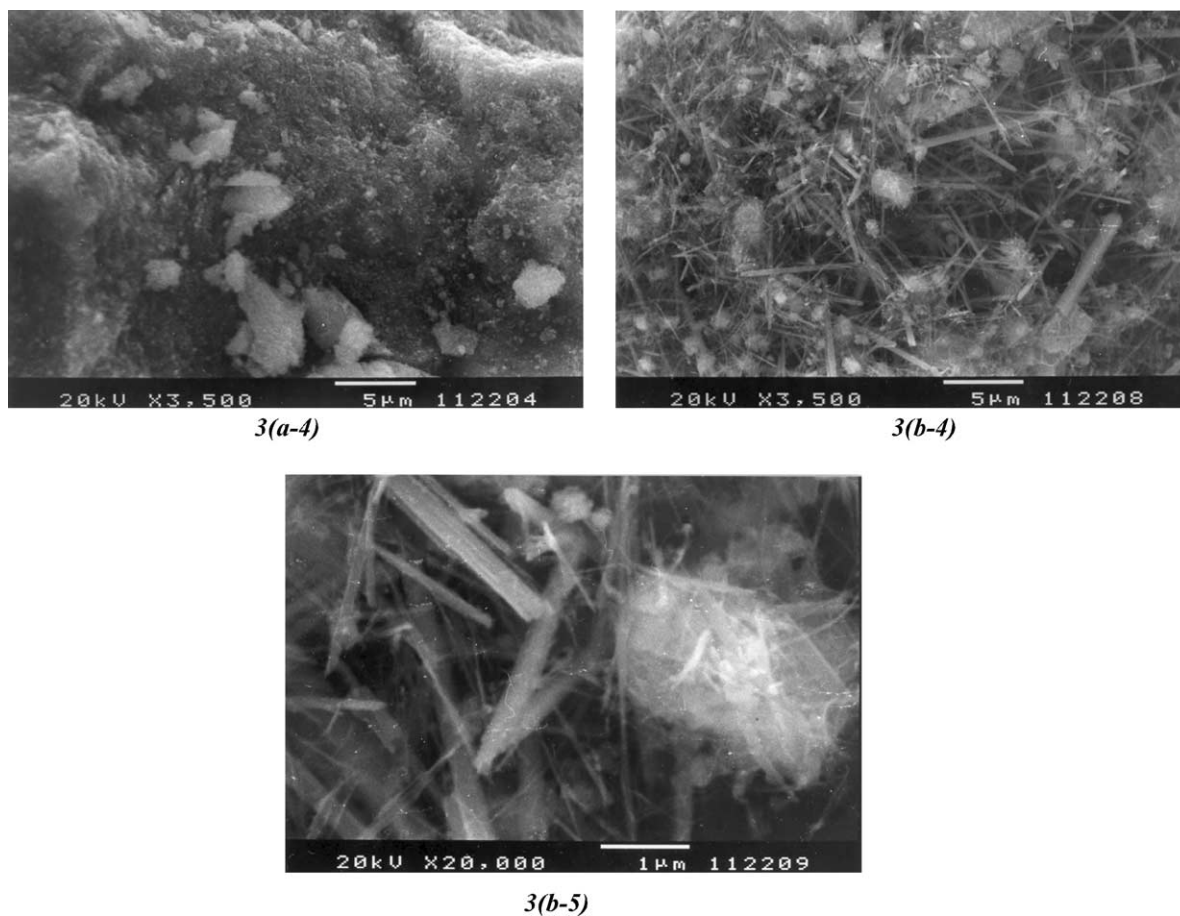
3(a-4)

3(b-4)

3(b-5)

Fig. 3. (*Continued*).

3.5. Mn/Ce catalyst stability

The stability of the solid catalysts has been found as dependent on the pollutant matrix contained in the effluents; for instance, high metal leaching was observed for Mn/Ce when applied in the oxidation of polyvinyl alcohol [18] contrarily to the high stability of this catalyst found in the treatment of formaldehyde effluents [9]. Therefore, it is important to evaluate the Mn/Ce catalyst stability for acrylic acid.

3.5.1. Carbon adsorption

The carbon adsorption by the Mn/Ce 70/30 catalyst was evaluated after the recovery of the catalyst at the end of the experiment. A low content of 0.095% (w/w) C was found, which corresponds to 2.85 ppm of carbon in the 3 g of catalyst charged in the reactor; therefore, from the initial solution with 500 ppm of TOC, approximately 0.57% (w/w) C was adsorbed. Chen et al. [13] reported that a Mn/Ce 60/40 catalyst (similar to the one used in our study) is the most effective in terms of resistance to carbon deposition, since high manganese content, high surface area and high oxidation state are related with this catalyst. Hussain et al. [19] developed a new potassium-doped Mn–Ce–O with the aim to improve the catalyst in the phenol oxidation and to

reduce the carbon adsorption found in previous studies as responsible for catalyst deactivation [10]. In fact, the results obtained under the present study (C: 0.095%, w/w) are significantly lower (seven times) than the ones obtained by those authors with the K-promoted catalyst (C: 0.7%, w/w). Platinum was also used as promoter for the Mn/Ce stability [20], but higher values of deposited carbon (near 200 ppm) were found when compared with the ones obtained in this work. We believe that phenol reactions make propitious the formation of polymeric compounds at the catalyst surface blocking the active sites. For the acrylic acid oxidation this shortcoming was not detected by elemental analysis and the Mn/Ce revealed to be stable in terms of carbon adsorption.

3.5.2. Leaching of Mn to the liquid phase

The stability of the Mn/Ce catalysts was also analyzed in terms of the Mn metal leached to the liquid phase. Concerning Mn/Ce 70/30, 1.697×10^{-3} g/l of leached Mn was detected after 120 min, which corresponds to 0.06% of the initial Mn concentration (2.87 g/l), while a non-detectable content for Mn/Ce 22/78 was found ($<0.002 \times 10^{-3}$ g/l). These results indicate that the Mn/Ce catalyst presents high stability. Since the elution of Mn from the composite oxide catalyst practically did not occur, the effluent after the

wet oxidation process is free from contamination by metal ions and can be securely released to the environment without a secondary treatment for metal separation. Therefore, the good activity of the Mn/Ce catalyst referred above is strengthened by its high stability in terms of leaching as well as of low carbon adsorption.

3.6. Mn/Ce micromorphology analysis

3.6.1. Scanning electron microscopy (SEM)

SEM photographs of Mn/Ce 70/30 are presented in Fig. 3(a) for fresh catalyst and 3(b) for used catalyst after reaction. Different scales/magnifications were examined (100×; 500×; 1500×; 3500×; 20,000×) and interesting textures and morphologies can be visualized. For magnification 100× the differences observed between the fresh and used catalysts (Fig. 3(a-1) and (b-1)) seem to be not very significant. However, a higher magnification (Fig. 3(a-2) and (b-2)) shows polished surfaces for the used catalyst while the fresh one seems to have more rough surface with small irregularly bulges. Moreover, it is interesting to note that in Fig. 3(b-2) small filaments are already observed in some particles of the used catalyst (inside circles). The magnification to 1500× in Fig. 3(b-3) clearly reveals the formation of a filament mesh that covers entire particles,

not observed in the fresh catalyst (Fig. 3(a-3)). Fig. 3(b-4) (3500×) shows that these filaments seem to be present in high quantity as well as various bright points are observed. Fig. 3(b-5) (20,000×) clearly shows one of these points which is constituted by embroiled agglomerated filaments. Taking into account the scales referred in the figures, it can be concluded that such whiskers have different lengths up to approximately 10 μm. These whiskers that were formed under the CWO process with the Mn/Ce catalyst were not yet referred in the literature at our knowledge. It is then our belief that these observations can be quite important for the commercial development of this catalyst. In this context it is important to know the constitution of these filaments.

Moulijn et al. [21] refer the formation of filaments due to carbon in catalysed reactions of hydrocarbons, which are decomposed at the metal surface of small crystallites. Afterwards the carbon diffuses through the metal forming a carbon nanotube between the support and the crystallite. However, taking into account the elemental analysis presented above, which revealed a low carbon quantity in the catalyst, it is not likely that in our case those filaments can be constituted by carbon. Therefore, transmission electron microscopy, energy-dispersive X-ray spectroscopy (EDXS) and selected-area electron-diffraction patterns (SAED) analyses were carried out in order to identify such filaments.
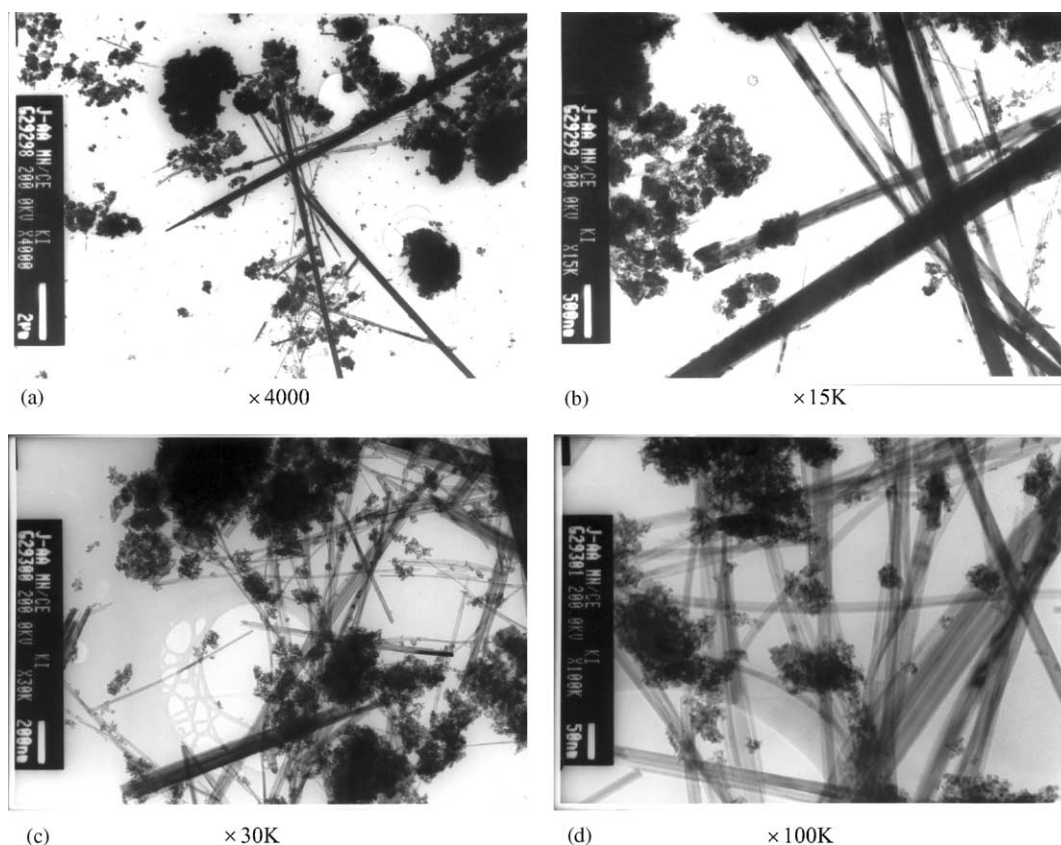

Fig. 4. TEM micrograph of the Mn/Ce 70/30 catalyst after reaction at 200 °C and 15 bar oxygen partial pressure, for different scales/magnifications: (a) 4000×; (b) 15,000×; (c) 30,000×; (d) 100,000×.
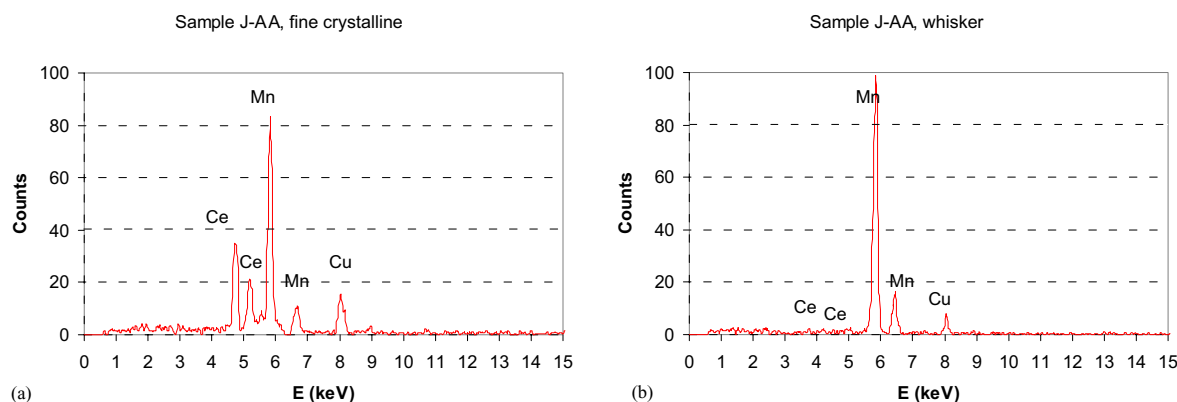
Fig. 5. EDXS analysis of the Mn/Ce 70/30 catalyst after reaction at 200 °C and 15 bar oxygen partial pressure: (a) polycrystalline material; (b) whiskers.

3.6.2. Transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDXS) and selected-area electron-diffraction patterns (SAED)

Fig. 4(a–d) correspond to the TEM photographs obtained at magnification of 4000×, 15,000×, 30,000× and 100,000×, respectively. The same whiskers observed by SEM are now clearly showed with the TEM analysis. Moreover, particles of polycrystalline material can also be observed. In Fig. 4(a) the long whiskers present a shape similar with a needle: larger in the middle and narrow in the end. In Fig. 4(b) different whiskers with width up to 0.5 μm can be observed. For high magnification photographs (Fig. 4(c) and (d)) the whiskers look flattened and very thin.

In order to analyze the metal constitution of the polycrystalline material as well as the one of the whiskers formed after the reaction, EDXS analysis were carried out and the results of Fig. 5 were obtained. In the polycrystalline material manganese and cerium were detected (Fig. 5(a)) while in the whiskers only Mn was found in EDXS spectra (Fig. 5(b)).

The analysis of the phases of Mn and Ce was performed by the interpretation of the SAED patterns that are shown in Fig. 6(a) for the polycrystalline material and in Fig. 6(b–d) for the whiskers. In the diffraction pattern of fine polycrystalline material, containing Ce (as seen in EDXS spectra), few diffuse rings can be observed. Normally, measuring only the d-values of these diffuse rings is not enough to determine which phase is present. However, in Fig. 7(a) the calculated (simulated) pattern for cubic CeO_2 is compared with the experimental SAED pattern observed in Fig. 6(a). One can see that they agree very well, so we can conclude that the polycrystalline material is composed of cubic cerium.

On the other hand, SAED patterns of the whiskers can be indexed (Fig. 7(b)) as β-MnO_2 (Pyrolusite) by comparing with the correspondent simulated pattern represented in Fig. 8(a). The same pattern could be also indexed as MnOOH (the simulated pattern in Fig. 8(b)) but in this case there should be also visible spots with larger d-values.
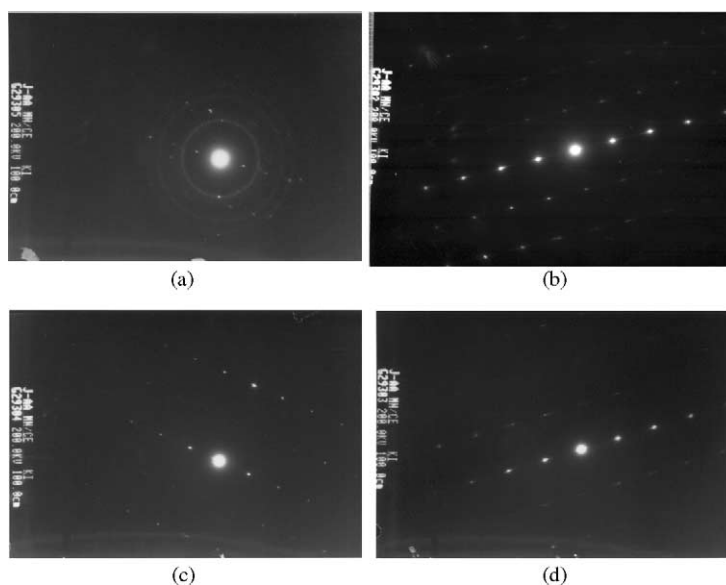

Fig. 6. Selected-area electron-diffraction (SAED) patterns: (a) polycrystalline material; (b)–(d) whiskers.
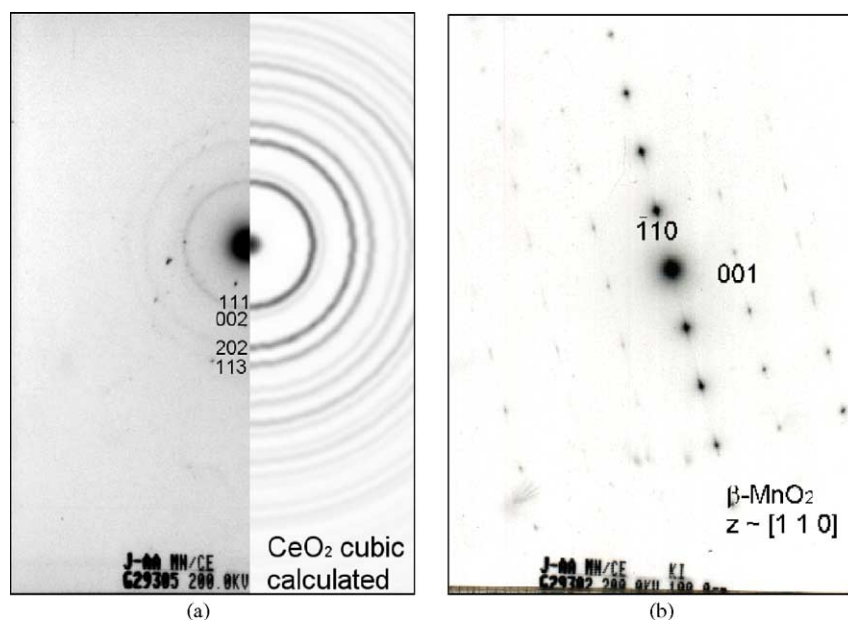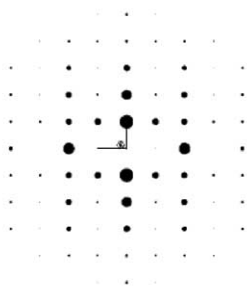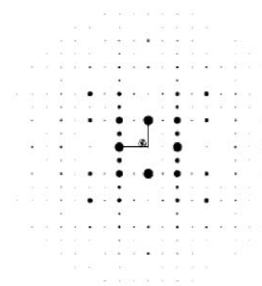
Fig. 7. Interpretation of the SAED patterns for (a) the polycrystalline material; (b) whiskers.

Crystal : mno₂   / Acc. voltage [kv] : 200 / Camera length [mm] : 1022   Crystal : mnooh / Acc. voltage [kv] : 200 / Camera length [mm] : 863

(a)   g1 : (-1, 1, 0) / g2 : (0, 0, 1) / zone axis : [1, 1, 0]   (b)   g1 : (0, -2, 0) / g2 : (0, 0, -2) / zone axis : [1, 0, 0]

Fig. 8. Simulated electron diffraction pattern (SAED) for (a) β-MnO$_2$; (b) MnOOH.

Therefore, it is more probable that these whiskers are of β-MnO$_2$.

In the literature several authors [22–24] have been developing methods for preparation of MnOOH and β-MnO$_2$ whiskers because they gained a considerable importance in many technological applications. These preparation methods are based in a hydrothermal procedure by mixing distilled deionized water, a Mn precursor and other compound as CTAB-cetyltrimethylammonium bromide [22] or TAH-tetraethylammonium hydroxide [23]. The CWO reaction process occurs in similar operating conditions and this fact can be the cause of the formation of such whiskers. In fact, Sun et al. [22], who obtained MnOOH and β-MnO$_2$, showed in their paper very similar TEM images with the ones presented in Fig. 4(a–d). On the other hand Sharma and Whittingham [23] as well as Kanasaku et al. [25] showed a SEM image similar with Fig. 3(b-5) where several

whiskers were observed. Thus, the analysis performed in this work and the results found in the literature seem to be consistent, indicating that after the reaction with the catalyst Mn/Ce 70/30 the whiskers formed are of β-MnO$_2$ and/or MnOOH.

Therefore, in the present work a step forward in the research of an active, stable and economic catalyst for the CWO process was carried out and we believe that more studies can lead to the Mn/Ce catalyst commercialization since the efficiency of this catalyst for effluents containing acrylic acid was strongly highlighted with our results.

4. Conclusions

Our catalytic results point out Mn/Ce 70/30 to be an important catalyst for reduction of the environmental impact

concerning effluents containing acrylic acid. This catalyst presents high selectivity for oxidation of acrylic acid as well as for all the reaction intermediates compounds, since 94.1% in TOC reduction was obtained in 30 min and 97.7% in 120 min. The combination of high molar percentages of manganese with cerium is an important key factor in the high activity of the Mn/Ce composite catalyst, since for MnO low initial reaction rates were found and poor manganese contents in Mn/Ce catalysts leads to the formation of non-oxidizable compounds (13% of the initial TOC). CeO alone and Co/Ce did not show high activity for TOC oxidation probably due to the formation of acetic acid, the major reaction intermediate compound that was identified in this case, which was not able to be further decomposed by these catalysts. Ag/Ce shows high activity for the initial reaction; however a not oxidizable fraction of TOC (15%) was detected.

The Mn/Ce catalyst showed high stability regarding carbon adsorption and leaching of the metals to the liquid phase. Formation of whiskers was observed in the used catalyst by both SEM photographs and TEM micrograph. The EDXS leads to conclude that these whiskers are constituted by manganese, in the form of β-MnO_2 and/or MnOOH, being however the last one less probable. Therefore, our experiments revealed that the Mn/Ce 70/30 catalyst is a crucial driver to improve the carbon removal of acrylic acid in contaminated wastewaters, being then able to preserve environmental quality.

Acknowledgements

References

[1] F. Luck, Catal. Today 53 (1999) 81.
[2] S.T. Kolaczkowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh, Chem. Eng. J. 73 (1999) 143.
[3] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2.
[4] R.V. Shende, J. Levec, Ind. Eng. Chem. Res. 39 (2000) 40.
[5] Fluka Chemie GmbH and Riedel-deHaën, Scientific Research, Madrid, 2003, p. 46.
[6] Y.I. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 37 (1998) 309.
[7] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743.
[8] L. Olivero, J. Barbier, D. Duprez, A. Guerrero-Ruiz, B. Bachiller-Baeza, I. Rodríguez-Ramos, Appl. Catal. B 25 (2000) 267.
[9] A.M.T. Silva, I. Castelo-Branco, R.M. Quinta-Ferreira, J. Levec, Chem. Eng. Sci. 58 (2003) 963.
[10] S. Hamoudi, K. Belkacemi, F. Larachi, Chem. Eng. Sci. 54 (1999) 3569.
[11] S. Imamura, A. Doi, S. Ishida, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 75.
[12] S. Imamura, I. Fukuda, S. Ishida, Ind. Eng. Chem. Res. 27 (1988) 718.
[13] H. Chen, A. Sayari, A. Adnot, F. Larachi, Appl. Catal. B 32 (2001) 195.
[14] S. Imamura, M. Nakamura, N. Kawabata, J. Yoshida, S. Ishida, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 34.
[15] W. Zhu, Y. Bin, Z. Li, Z. Jiang, T. Yin, Wat. Res. 36 (2002) 1947.
[16] S.H. Lin, S.J. Ho, Appl. Catal. B 9 (1996) 133.
[17] S. Imamura, Y. Okumura, T. Nishio, K. Utani, Y. Matsumura, Ind. Eng. Chem. Res. 37 (1998) 1136.
[18] A.M.T. Silva, R.N.P. Vaz, R.M. Quinta-Ferreira, J. Levec, Can. J. Chem. Eng. 81 (2003) 566.
[19] S.T. Hussain, A. Sayari, F. Larachi, Appl. Catal. B 34 (2001) 1.
[20] S. Hamoudi, F. Larachi, G. Cerrella, M. Cassanello, Ind. Eng. Chem. Res. 37 (1998) 3561.
[21] J.A. Moulijn, A.E. van Diepen, F. Kapteijn, Appl. Catal. A 212 (2001) 3.
[22] X. Sun, C. Ma, Y. Wang, H. Li, Inorg. Chem. Commun. 5 (2002) 747.
[23] P.K. Sharma, M.S. Whittingham, Mater. Lett. 48 (2001) 319.
[24] S. Ardizzone, C.L. Bianchi, D. Tirelli, Coll. Surf. A 134 (1998) 305.
[25] T. Kanasaku, K. Amezawa, N. Yamamoto, Solid State Ionics 133 (2000) 51.