Wet Oxidation of Formaldehyde with Heterogeneous Catalytic Materials

Mirella Gutiérrez-Arzaluz, Miguel Torres-Rodríguez, Violeta Mugica-Alvarez, Julia Aguilar-Pliego, and Mario A. Romero-Romo

***Abstract*—This work addresses the activity of the catalytic performance of Pt and Ce-Mn-based materials, during the catalytic wet formaldehyde oxidation reaction at ppm concentrations. The comparison of Pt supported in alumina vs. Ce-Mn-based catalysts is presented. The total conversion was 80% with Pt/Al_2O_3 at 80°C, which turned out to be more effective in removing the organic pollutant compared with the mixed oxide. By-products formation such as acetic and oxalic acids was determined along with carbonaceous deposits.**

***Index Terms*—Catalytic wet oxidation, formaldehyde removal, oxidation, Pt and Ce-Mn catalysts, batch reactor.**

I. INTRODUCTION

Catalytic wet oxidation processes are three-phase reactions that are somewhat difficult to operate: therefore, they are not technologically ready for commercial application. Presently, it is widely recognized that catalytic wet air oxidation (CWAO) needs further development to become a commercial option, economically viable and environmentally responsible, capable of removing the organic waste generated elsewhere and increasing the possibility to face emerging problems in treating toxic wastewater.

The wet air oxidation (WAO) processes degrade organic pollutants dissolved in water, either partially through an oxidizing agent in biodegradable products, or fully mineralizing them into harmless inorganic compounds, such as CO_2, H_2O and inorganic salts, which remain in the liquid phase [1].

Compared to wet air oxidation (WAO) technology, the catalyst present in the catalytic wet air oxidation (CWAO) brings in smaller energy requirements [1]; also, there are advantages coupled, since greater oxidation conversion is attained. Consequently, less severe conditions can be used to reduce the chemical oxygen demand, as in this process the organic compounds are oxidized to inorganic usable by-products such as CO_2 and H_2O.

Formaldehyde (HCHO) is an important environmental pollutant, widely known for its adverse health effects [2]. It has been chosen as model (molecule) pollutant in the wet catalytic oxidation reaction. This work proposes the use of two catalyst types: one based on a noble metal supported on α-Al_2O_3 that is active to the oxidation of refractory compounds and another based on metal oxides, which is more resistant to fouling, despite its lower activity.

II. EXPERIMENTAL METHODS

The Ce-Mn mixed oxides-based catalysts were prepared through co-precipitation, under controlled additions of the precursor solution containing an excess basic agent (NH_4OH 30% weight), followed by calcination at 350℃, as reported in previous works [3]. Also, samples of commercial alumina impregnated with Pt by means of the incipient wetness impregnation with Pt precursor dissolution to obtain a 1% weight metal load, were prepared here. The actual support used to prepare this catalyst was a commercial sample (α-Al_2O_3 powder, Sigma-Aldrich). The hexachloroplatinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$, Sigma-Aldrich 99.9%, with a platinum content of 38-41%) was used as Pt precursor. After drying the powder for about 24 hours at room temperature, the reduction to metal was effected at 350℃ in H_2 atmosphere for two hours before the sample was heat treated with N_2 gas, also at 350℃ for two hours.

The samples were characterized using different techniques, like powder XRD on a Phillips diffractometer X-expert using Cu Kα radiation, scanning 2θ from 5 to 80°. Surface topography and elemental composition were established by means of SEM/EDS in a LEO 440 microscope with secondary electrons and EDS detectors. Also, FTIR was carried out in a VARIAN spectrophotometer model 3600 in the IR region with wavelengths in the mid-infrared (between 500 and 4000 cm^{-1}), finely grinding the samples in an agate mortar. Texture measurements like the specific surface area, pore diameter and volume, were performed with a Micromeritics ASAP 2020 equipment, using N_2 physisorption to obtain highly detailed information on textural properties of the solids manufactured.

The activity of the catalytic systems was studied during catalytic wet formaldehyde oxidation (CWO) reaction at ppm concentrations. The tests were conducted in a conventional stainless steel *batch* reactor (commercial autoclave Parr Reactor), for the liquid phase, using pure oxygen (PRAXAIR, 99.6% purity) as an oxidizing agent at 80℃ reaction temperature; the initial formaldehyde concentration was 200 or 1000 ppm. The ratio: catalyst mass to reaction volume was 2.38 g l^{-1}; testing was carried out at two different oxygen pressures, namely, 40 and 100 psi (2.76 or 6.89 bar). The

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catalytic HCHO oxidation test was studied during four hours. The reaction progress was monitored by gas chromatography using an HP 5890 series II Plus chromatograph with flame ionization detector (FID) and GC Chem Station software ((© Agilent Technologies), along with a capillary column HP PLOT Q 30m long and 0.32mm in diameter, suitable for separating organic acids and formaldehyde of low molecular weight. The CO_2 was determined through the classical NaOH 0.1 M method.

III. RESULTS

A. Characterization

1) Specific surface area measurements (BET)

The specific surface area, pore diameter and pore volume measured, are reported in Table I. The values obtained for surface area of the Ce-Mn mixed oxides were 85-130 $m^2 g^{-1}$, which are within the order of magnitude reported in the literature [4]-[6]. However, for the system Pt/Al_2O_3, low surface area (28.55 $m^2 g^{-1}$) values were obtained due to the low surface area of the commercial support (α-alumina) [7]-[9].

TABLE I: RESULTS OF N2 ADSORPTION-DESORPTION ANALYSIS

Sample	BET (m^2g^{-1})	Pore Diameter (Å)	Pore Volume (cm^3g^{-1})
Ce-Mn	129.93	27.65	0.088
Pt/Al_2O_3	28.55	241.62	0.184

2) X-ray diffraction (XRD)

Fig. 1 shows the XRD patterns recorded from the Ce-Mn sample calcined at 350℃. The diffractograms were compared with the ICDD data base to identify the phases (i.e. CeO_2 (JCDS 34-0394)). The samples exhibited fluorite-type face centered cubic structure; the fact that the diffraction pattern is slightly shifted respect to the ceria pattern, is because the Ce-Mn mixed oxide lattice parameters are different with respect to pure oxides, thus suggesting that the manganese ions are likely to be incorporated within the cerium oxide lattice, probably leading to formation of solid solutions between the manganese and cerium oxides; the Mn^{4+} ionic radius (0.053nm) is smaller than that of the Ce^{4+} ion (0.094nm), which is in agreement with the data reported in the literature [10]-[12].

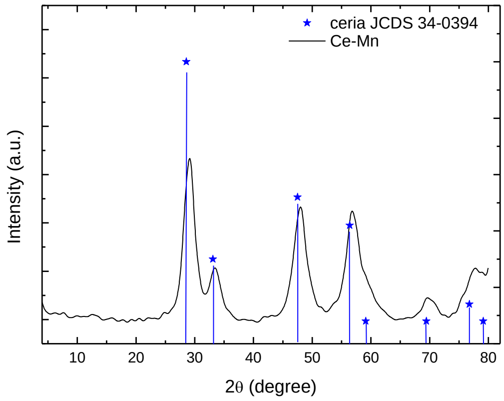


Fig. 1. XRD pattern of the Ce-Mn oxides sample.

Fig. 2 shows the Pt/Al_2O_3 XRD diffractogram and that of the α-Al_2O_3 commercial support. After the Pt addition, the overall appearance of the characteristic peaks suggests that the crystallinity is not affected. The presence of Pt can be corroborated with the peaks that appeared at 40° and 46° 2θ, which show that the platinum has been poorly dispersed on the support and distributed in crystallites of considerable size.

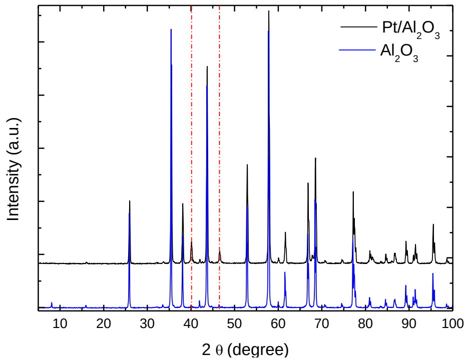
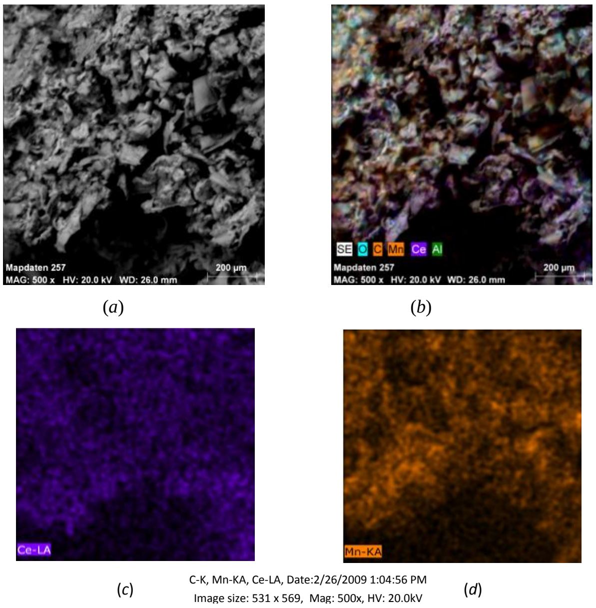


Fig. 2. XRD patterns of the samples Pt/Al_2O_3 and Al_2O_3.

3) Scanning electron microscopy (SEM/EDS)

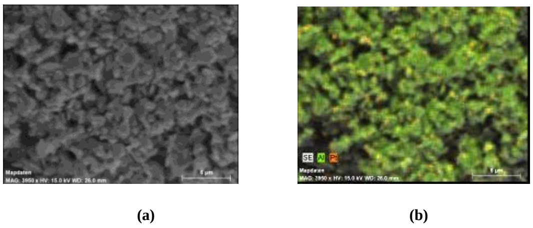
Fig. 3(a) shows the morphological features of the Ce-Mn sample as determined through secondary electron imaging, that reveals an aggregation of irregular shapeless particles. Fig. 3(b) presents a SEM/EDS image that confirms the presence of Ce and Mn in the samples. The images presented in Fig. 3(c) and d are elemental mappings of the metals distributed over the sample: Ce can be identified by the purple color (Fig. 3(c)) and Mn by orange (Fig. 3(d)), respectively.



(a) (b)

(c) C-K, Mn-KA, Ce-LA, Date:2/26/2009 1:04:56 PM
Image size: 531 x 569, Mag: 500x, HV: 20.0kV (d)

Fig. 3. Micrographs of the sample Ce-Mn. (a) SEM Ce-Mn. (b) Ce-Mn mapping. (c) Ce mapping. (d) Mn mapping.



(a) (b)

Fig. 4. (a) SEM micrographs of the sample Al_2O_3. (b) SEM/EDS of the Pt/Al_2O_3.

Fig. 4(a) is also a SEM secondary electron image revealing aggregation of alumina particles, although they are shapeless. The mapping in Fig. 4(b) reveals that the Pt is distributed homogeneously over the surface of the alumina.

B. *Catalytic Wet Formaldehyde Oxidation*

1) *Pt/Al_2O_3 catalytic test*

For the elimination of formaldehyde with an initial 200 ppm concentration, tested at two different oxygen pressures, namely 40 and 100 psi. After four reaction hours at 80°C, the HCOH conversion was in both cases about 80%. From Fig. 5, it can be inferred that the greater the oxidizing agent pressure, the more stimulated is the pollutant oxidation initial velocity, as indicated by the greater slope of the curve corresponding to 100 psi pressure. Fig. 5 shows a comparison of the plots indicating that for 50% formaldehyde conversion, it required twice as much time when using 40 psi pressure compared to 100 psi. The increase in the initial reaction rate is associated with a greater amount of dissolved oxygen in the aqueous phase, at 100 psi, which actually means an increased oxidation rate of the organic matter [8].

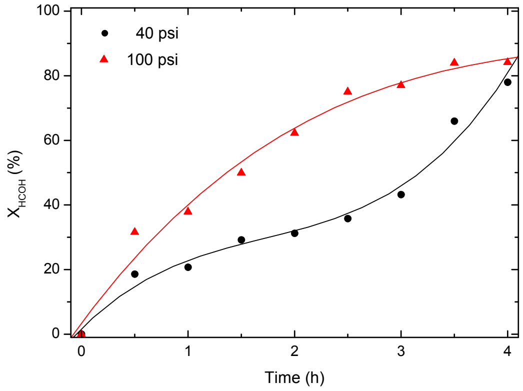


Fig. 5. HCOH conversion with Pt/Al_2O_3 catalyst a 40 and 100 psi of O_2.

Fig. 6 shows that platinum incorporation on the commercial alumina had a favorable effect, because the formaldehyde conversion was twice that observed in the test reaction performed without Pt, also on a commercial alumina powder.

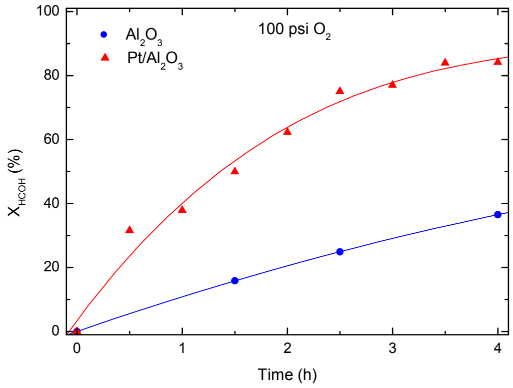


Fig. 6. HCOH conversion with Pt/Al_2O_3 catalyst and Al_2O_3.

During formaldehyde removal it was observed the presence of secondary reaction products such as oxalic acid and acetic acid, though their concentrations were different in both tests, namely at 40 and 100 psi O_2, over 80 ppm for oxalic acid, and slightly more than 60 ppm for acetic acid, see Fig. 7. Thus, formation of these products through formaldehyde oxidation is not dependent on the amount of oxygen present in the reaction. Therefore, it is important to study the dependence on temperature of the formation of these products, since according to Silva *et al.* [8], the temperature is a key factor in the formaldehyde CWO. It should be noted that in addition to these products in the liquid phase, there were other solid products present, like carbonaceous deposits that were not quantified. Also in the gas phase there was unwanted CO_2, among others. The concentration of these other products is modified by the amount of oxygen present: hence, it would be important to elucidate whether this would correspond to HCOH mineralization.

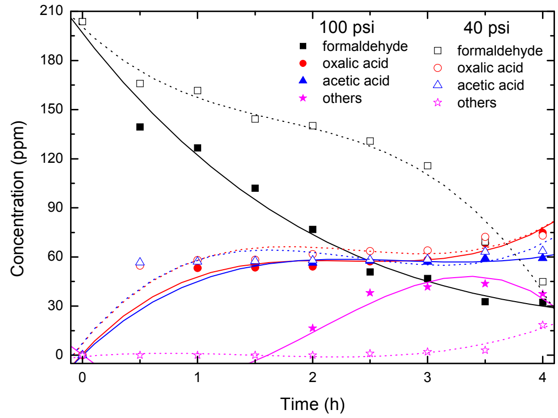


Fig. 7. Concentration of different species as a function of oxidizing agent pressure: 40 and 100 psi O_2.

Besides the effect of oxygen pressure, the effect of initial concentration of formaldehyde, 200 to 1000 ppm, was also studied. Fig. 8, clearly shows that most of the pollutant is eliminated when there is less of it in the middle of the reaction, since according to other authors, when working with high concentrations of pollutant and mild reaction conditions (around 90°C and 5 bar O_2), the catalyst exhibited loss of activity after the first minutes of reaction [13]-[16], because the active surface is mostly covered by adsorbed formaldehyde.

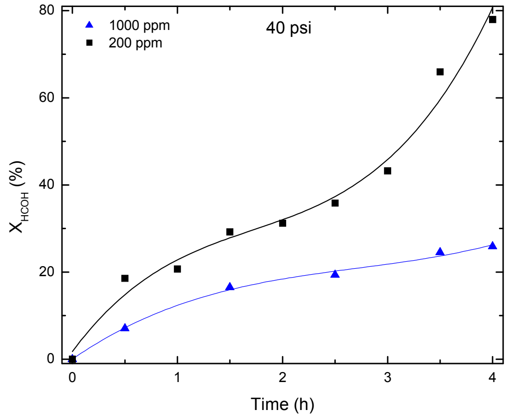


Fig. 8. Conversion rate at two different initial concentrations, 200 and1000 ppm as a function of formaldehyde oxidation time.

Some authors [14]-[16], reported this behavior and explained it on consideration of the large sensitivity that the contaminant's conversion displays as a function of the relationship between its concentration and the catalyst's mass, which is typical of competitive reactant adsorption in heterogeneous catalytic processes. In addition, it is proposed that the catalyst may undergo a rapid and strong deactivation by formation of carbonaceous deposits, which are irreversibly adsorbed on the surface of the catalyst and, as expected, on its active centers.

In this work, the formation of carbonaceous deposits was identified by FTIR analysis that ratified a considerable increase in the intensities of some characteristic bands in the region 1700-1000 cm^{-1}. The bands are difficult to allocate to they occurred in the region of the water fingerprint as a result of moisture in the atmosphere, refer to Fig. 9. These bands overlap considerably with those of some hydrocarbon or carbon compounds. Reduction of the catalyst at 350°C leads to high values of dispersed platinum which induces a significant formation of carbonate species, as Mikulov *et al.* (2007) [17] reported.

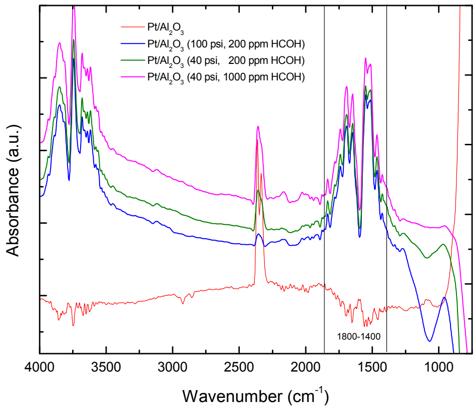


Fig. 9. FTIR spectra of samples of the series Pt/Al$_2$O$_3$ tests before and after CWO reaction.

2) *Catalytic test for Ce-Mn*

Catalytic activity tests for the Ce-Mn catalyst were performed with an initial 200 ppm formaldehyde concentration, at 40 psi oxygen pressure and 80°C; only 60% HCOH conversion was obtained after four hours.

Fig. 10 shows the performance of the Ce-Mn during four hours; it can be seen that during the first minutes formaldehyde elimination produces only the formation of oxalic acid, but after two hours it begins to form acetic acid (less than 20 ppm) and other reaction products, such as carbonaceous deposits and/or CO$_2$.

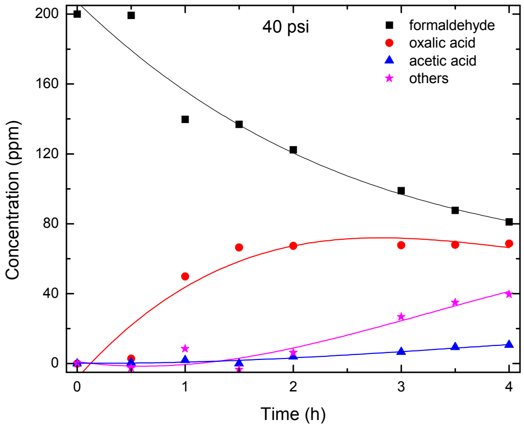


Fig. 10. Concentration of formaldehyde reaction with Mn-Ce catalyst.

The fact that greater oxalic acid content was observed may be due to an initial formaldehyde polymerization. The formation of low molecular weight carboxylic acids; this is a common step during the oxidation process, comprising refractory compounds difficult to oxidize, such as oxalic, acetic acid and formic acid, mainly [2].

The formation of carbonaceous deposits could only be corroborated by FTIR that also shows a considerable increase in the intensities of some bands coincident with the water vapor bands, but which may also be due to hydrogenated carbonate compounds formation or CO$_3^{2-}$ species (1440, 1530 and 1600 cm^{-1}) [17] (see Fig. 11).

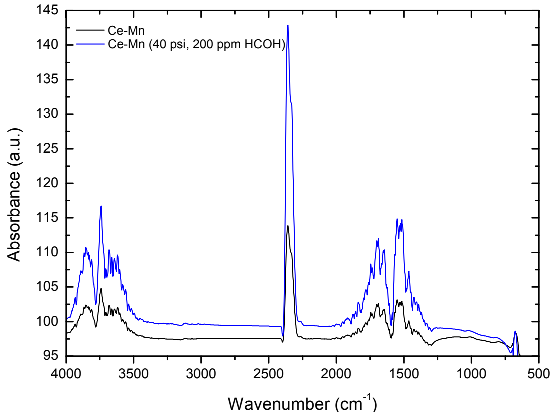


Fig. 11. IR spectra of samples of the Ce-Mn series before and after testing the CWO reaction.

Fig. 12 compares the reaction concentrations for both types of catalysts; it is clear that formaldehyde elimination occurs at faster and greater proportion when testing the Pt-based catalyst, due to the increased activity exhibited by the noble metal, which is in agreement with the results reported here and those reported by other authors [7], [9]. For both reaction tests, the oxalic acid concentration is similar, but that of the acetic acid changes significantly, having a lower formation percentage with the Ce-Mn system. In both cases it appears that during the first 90 minutes reaction, there is practically no formation of other products (CO$_2$ and carbonaceous deposits, among others).

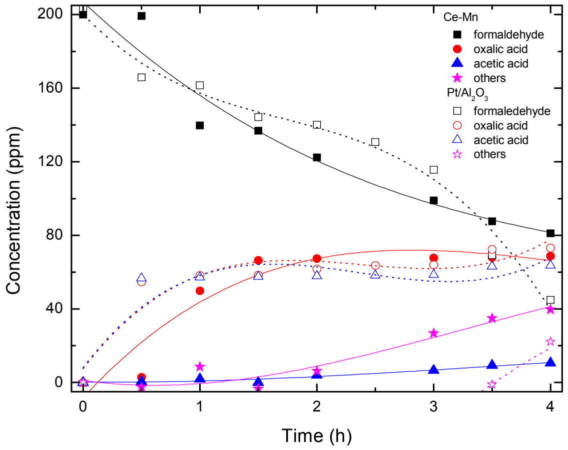


Fig. 12. CWO formaldehyde concentration profile vs time for catalyst Pt/Al$_2$O$_3$ and Ce-Mn.

IV. CONCLUSIONS

The Ce-Mn catalyst displayed crystallographic structure characteristic of fluorite as revealed by the XRD results. The specific area value is in the range of like materials compared to those reported in the literature. The incipient wet impregnation method permitted the deposition of platinum on alumina according to the results XRD and SEM-EDS, which imparted the catalysts good activity for formaldehyde elimination.

The catalytic activity tests at 80°C temperature produced 80% elimination of formaldehyde with Pt-based catalyst for the CWO, which turned out to be more effective in removing the pollutant compared with the mixed oxide. Increasing the oxidizing agent pressure permitted greater formaldehyde elimination. Byproducts formation such as acetic and oxalic acids was determined along with carbonaceous deposits.

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REFERENCES

[1] J. Levec and A. Pintar, "Catalytic wet-air oxidation processes: A review," *Catal. Today*, vol. 124, pp. 172-184, June 2007.

[2] A. Silva, I. Castelo-Branco, R. Quinta-Ferreira, and J. Levec, "Catalytic studies in wet oxidation of effluents from formaldehyde industry," *Chem. Eng. Sci*., vol. 58, pp. 963-970, February 2003.

[3] M. Gutiérrez, "Development of catalytic membranes for phenol elimination in aqueous streams," Ph.D. dissertation, Dept. Chemical & Environmental Engineering, University of Zaragoza, Zaragoza, Spain, 2007.

[4] C. Bozo, N. Guilhaume, and J. M. Herrmann, "Role of the ceria–zirconia support in the reactivity of platinum and palladium catalysts for methane total oxidation under lean conditions," *J. Catal*., vol. 203, pp. 393-406, October 2001.

[5] J. J. Delgado, "Preparation and characterization of Ce-Mn and Ce-Zr oxides. Application in the wet oxidation of phenol," Ph.D. dissertation, Dept. Materials Science and Metallurgical Engineering and Inorganic Chemistry, Faculty of Science, University of Cádiz, Puerto Real (Cádiz), Spain, 2003.

[6] S. Hamoudi, F. Larachi, G. Cerrella, and M. Cassanello, "Wet oxidation of phenol catalyzed by unprompted and platinum-promoted manganese/cerium oxide," *Ind. Eng. Chem. Res*., vol. 37, pp. 3561-3566, August 1998.

[7] D. Lee and D. Kim, "Catalytic wet air oxidation of carboxylic acids at atmospheric pressure," *Catal. Today*, vol. 63, pp. 249-255, December 2000.

[8] A. Silva, R. Quinta-Ferreira, and J. Levec, "Catalytic and noncatalytic wet oxidation of formaldehyde. A novel kinetic model," *Ind. Eng. Chem. Res*., vol. 42, pp. 5099-5108, September 2003.

[9] J. Qin, Q. Zhang, and K. T. Chuang, "Catalytic wet oxidation of *p*-chlorophenol over supported noble metal catalysts," *Appl. Catal. B: Environ*., vol. 29, pp. 115-123, January 2001.

[10] X. Tang, J. Chen, X. Huang, Y. Xu, and W. Shen, "Pt/MnO_x–CeO_2 catalysts for the complete oxidation of formaldehyde at ambient temperature," *Appl. Catal. B: Environ*., vol. 81, pp. 115-121, May 2008.

[11] M. Machida, M. Uto, D. Kurogi, and T. Kijima, "MnO_x–CeO_2 binary oxides for catalytic NO_x sorption at low temperatures. Sorptive removal of NO_x," *Chem. Mater*., vol. 12, pp. 3158-3164, September 2000.

[12] S. Hamoudi, F. Larachi, A. Adnot, and A. Sayari, "Characterization of spent MnO_2/CeO_2 wet oxidation catalyst by TPO–MS, XPS, and S-SIMS," *J. Catal*., vol. 185, pp. 333-344, July 1999.

[13] S. Hamoudi, A. Sayari, K. Belkacemi, L. Bonneviot, and F. Larachi, "Catalytic wet oxidation of phenol over $Pt_xAg_{1-x}MnO_2/CeO_2$ catalysts," *Catal. Today*, vol. 62, pp. 379-388, December 2000.

[14] H. Chen, A. Sayari, A. Adnot, and F. Larachi, "Composition–activity effects of Mn–Ce–O composites on phenol catalytic wet oxidation," *Appl. Catal. B: Environ*., vol. 32, pp. 195-204, August 2001.

[15] J. J. Delgado, J. A. Pérez-Omil, J. M. Rodríguez-Izquierdo, and M. A. Cauqui, "The role of the carbonaceous deposits in the catalytic wet oxidation (CWO) of phenol," *Catal. Com*., vol. 7, pp. 639-643, September 2006.

[16] M. Abecassis-Wolfovich, R. Jothiramalingam, M. V. Landau, M. Herskowitz, B. Viswsanathan, and T. K. Varadarajan, "Cerium incorporated ordered manganese oxide OMS-2 materials: Improved catalysts for wet oxidation of phenol compounds," *Appl. Catal. B: Environ*., vol. 59, pp. 91-98, March 2005.

[17] J. Miculová, J. Barbier, S. Rossignol, D. Mesnard, D. Duprez, and C. Kappenstein, "Wet air oxidation of acetic acid over platinum catalysts supported on cerium-based materials: Influence of metal and oxide crystallite size," *J. Catal*., vol. 251, pp. 172-181, October 2007.

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