

# Low-Temperature Catalytic Oxidation of High Concentration Nitrogenous organic compounds over MnO<sub>2</sub>-CeO<sub>2</sub>/MWCNTs

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## Abstract:

Low-temperature catalytic oxidation of high concentration nitrogenous organic compounds was carried out in a batch reactor over MnO<sub>2</sub>-CeO<sub>2</sub>/MWCNTs. It is indicated that MnO<sub>2</sub>-CeO<sub>2</sub>/MWCNTs is a high-efficiency catalyst for aniline wastewater treatment. Under the optimum reaction conditions, the COD removal of aniline amounted to 93% at 393K. The catalyst in the oxidation of other nitrogenous organic compounds also exhibited relatively excellent catalytic activity. The order of degradation degree of nitrogenous organic compounds is as following: p-nitrophenol > p-phenylenediamine > p-toluidine > aniline, it showed that diamine was more difficult to oxidize than monoamine.

## Introduction:

Catalytic oxidation of nitrogenous compounds in the wastewater treatments process is a challenge. Most of the nitrogenous compounds come from industrial activity and in particular from chemical, petrochemical and food industries [1]. These substances present a very high toxicity in wastewater and the removal efficiencies of some metal catalysts on nitrogenous compound are not high, except in the high temperature and pressure conditions [2-4]. The purpose of this paper is developing a highly active transition metal catalyst for catalytic oxidation of N-containing pollutants under mild reaction conditions.

## Experimental

The preparation method of the catalysts adopted co-precipitation and ultrasonic impregnation techniques. The Mn loading was fixed at 4 wt.%, n(Mn) : n(Ce) = 7 : 3 (mol ratio). The oxidation reactions were performed in a 60 mL stainless steel autoclave equipped with a magnetically driven stirrer. Typically, in an oxidation process, 20 mL nitrogenous compounds aqueous solution (COD =5000 mg/L), hydrogen peroxide and catalyst were placed in the reactor. After reaction for 120 min, the liquid samples were taken from the reactor for COD analysis.

## Results and discussion

Fig 1. shows the TEM image of MnO<sub>2</sub>-CeO<sub>2</sub>/MWCNTs and MnO<sub>2</sub>/MWCNTs. The image reveals that the active components are homogeneously dispersed and adhered on the external surface of MWCNTs. Aggregation is not observed because ultrasonic and the addition of CeO<sub>2</sub> can effectively disperse the manganese on the support. No peaks of MnO<sub>2</sub> and CeO<sub>2</sub> were observed in the XRD patterns (Fig 2). This indicated the high dispersion of MnO<sub>2</sub> and CeO<sub>2</sub> particles on the surface of MWCNTs consistent with the previous TEM results.

The results indicated that the catalytic activities were quite different with different sizes of MWCNTs carrier preparation for catalytic oxidation of aniline. This is the reason of

increasing surface area of the catalyst support in favor dispersion of the catalytic active component. But when the diameter of the carbon nanotubes is less than 8 nm, the COD removal of aniline was only 73.6%(Table 1.). May be the surface of the catalyst pore size is small, not conducive to the diffusion of reactant and products to the bulk phase [5].

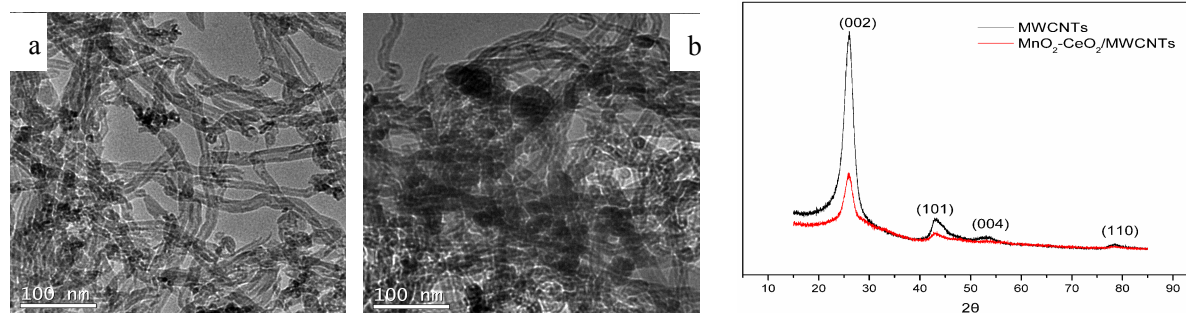


Fig 1. TEM of Mn-Ce/MWCNTs (a) and Mn/MWCNTs (b). Fig 2. XRD of catalysts

Table 1. COD removal of aniline with catalysts supported on different MWCNTs

specifications	MWCNTs-1	MWCNTs-2	MWCNTs-3	MWCNTs-4
OD (nm)	<8	10-20	20-30	>50
Length ( $\mu\text{m}$ )	10-30	10-30	10-30	10-20
BET ( $\text{m}^2/\text{g}$ )	>500	>200	>110	>40
<b>COD removals (%)</b>	<b>73.6</b>	<b>92.0</b>	<b>92.6</b>	<b>58</b>

The prepared  $\text{MnO}_2\text{-CeO}_2/\text{MWCNTs}$  catalysts were tested in the CWAO of highly concentrated nitrogenous organic compounds such as p-toluidine, p-phenylenediamine and p-nitrophenol. The COD removals of p-toluidine and p-phenylenediamine were 89.6% and 77.2% respectively. For the p-nitrophenol, the COD removal was only 47.9% (low electronic density was not in favour of oxidation) under mild reaction conditions (Table 2.).

Table 2. Catalysis oxidation of various wastewaters over  $\text{MnO}_2\text{-CeO}_2/\text{MWCNTs}$

Nitrogenous compounds	Reaction Temperature(K)	$\text{H}_2\text{O}_2$ (ml)	COD removals (%)
p-toluidine	393	0.77	89.54
p-phenylenediamine	393	0.77	77.15
p-nitrophenol	393	0.77	47.98

## Conclusions

The prepared  $\text{MnO}_2\text{-CeO}_2/\text{MWCNTs}$  catalyst is a high-efficiency catalyst for nitrogenous organic compounds wastewater treatment under the mild reaction conditions. At 393 K,  $\text{H}_2\text{O}_2$  as oxidant, the COD removal of aniline amounted to 93%. The order of degradation degree of other nitrogenous organic compounds is as following: p-nitrophenol > p-phenylenediamine > p-toluidine > aniline, it showed that diamine was more difficult to oxidise than monoamine. As a rule, functionalized molecules are generally more easily oxidized, increased nitrogen atoms are not conducive to the complete degradation of organic matter.

## References

- [1] S.V. Mishra, V.M. Mahajani, J.B. Joshi, *Ind. Eng. Chem. Res.* 1995, 34, 2.
- [2] L. Oliviero, J. Barbier, Jr., D. Duprez, *Appl. Catal. B*, 2003, 40, 163–184
- [3] Morales-Torres, S., A. M. T. Silva, et al. *Appl. Catal. B*, 2011, **105**(1-2): 86-94.
- [4] Ersöz, G. and S. Atalay, *J. Environ. Manage.* 2012, **113**: 244-250.
- [5] H. Vu, F. Goncalves, R. Philippe, E. Lamouroux, et al. *J. Catal.*, 2006, 240(1): 18-22