

Challenges in Oily Sludge from Petroleum Industry and Bilge Waters treatment by Catalytic Wet Air Oxidation

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Abstract

Oily wastewater is a difficult discarded to treat as it has high salt content, suspended solids, used oils and detergents. In this context, the heterogeneous CWAO, which involves the oxidation of these organic compounds into more biodegradable compounds or their mineralization to CO₂, is a very promising tool to purify this kind of wastewater. This study deals with the Catalytic Wet Air Oxidation (CWAO) of phenol, as representative molecule of polluting organic compounds present in bilge water contaminants, on MnCeO_x supported carbonaceous materials. The catalysts were thoroughly characterized by XRD, TPR and SEM studies. The catalytic activity of the investigated catalysts has been discussed in detail.

Keywords: Oily wastewaters, bilge water, CWAO, Activated carbon, MnCeO_x catalysts

INTRODUCTION

Oily wastewater from petroleum industry, oil refineries, chemical and petrochemical plants, metal working plants, oil terminals during washing of reserving tanks, is wastewater mixed with oil under a wide range of concentrations. The oil mixed in water can be fats, hydrocarbons, and petroleum fractions such as diesel oil, gasoline, and kerosene. Currently, many industries produce a large amount of oily wastewaters, which affect the surrounding environment, such as air pollution caused by the evaporation of oil and hydrocarbon contents to the atmosphere. Bilgewater is created by leaks of salt water, cooling water, fuel oil and lube oil, by the dewatering of sedimentation and sludge tanks, by the draining off of various cleaning processes and also by particles of soot and dirt. Before there is any question of discharging this into the sea, IMO (International Maritime Organization) regulations specify that this explosive mix has to be treated so intensively that its residual oil content is below 15 ppm. However, this minimal pollution cannot be realized cost-effectively using conventional separation techniques [1]. Among the polluting organic compounds present in bilge water, hardly biodegradable phenolic derivatives are present in large amount, therefore phenol has been selected as model molecule. The wet air oxidation (WAO) is one of the chemical oxidation methods, which could effectively convert hazardous, toxic and high concentrated organic pollutants to CO₂, H₂O at elevated temperatures and pressures using a gaseous source of oxygen (either pure oxygen or air), therefore could be considered a very promising tool to purify this kind of wastewater [2]. Elevated temperatures are required to increase the oxidation rate and

enhance the solubility of oxygen in the aqueous solution, while elevated pressures are required to keep water in the liquid state. The catalytic oxidation of organic compounds and organic-containing wastewaters over various homogeneous and heterogeneous catalysts has, therefore, received a lot of attention. Heterogeneous catalysts, with particular reference to the metal oxides are of interest because of its high reactivity not only in CWAO reactions [3-13]. Their catalytic activity had acknowledged the interest of many researchers, as evidenced by the huge amount of scientific papers published worldwide and summarized in many reviews appeared in the very recent years [14-22]. In particular, Manganese and Cerium oxides have received special consideration in the CWAO of phenol [23-25]. Therefore, this work is aimed to develop the carbonaceous supported Manganese and cerium oxides (MnCeO_x) catalysts for the CWAO of phenol. This study deals with the Catalytic Wet Air Oxidation (CWAO) of phenol on MnCeO_x supported carbonaceous materials. The Activated Carbon (AC) and Carbon Nano Tubes (CNTs) were used as carbonaceous supports. The catalysts were thoroughly characterized by XRD, TPR and SEM studies. The catalytic activities of the investigated catalysts were discussed in detail.

EXPERIMENTAL

Multi Walled Carbon Nanotubes (CNTs) were prepared by Catalytic Chemical Vapor Deposition (CCVD) of isobutane (i-C₄H₁₀) over Fe/Al₂O₃ catalyst (Fe = 17 wt %). Fe/Al₂O₃ catalyst was prepared by wet impregnation method. The purified CNTs were functionalized by 68% HNO₃ vapors then MnCeO_x supported catalysts were prepared by Incipient Wetness method reported elsewhere [5]. MnCeO_x supported catalysts were prepared by Incipient Wetness method reported elsewhere. Mixed solutions of manganese acetate and cerous nitrate were made with the molar ratios of Ce/Mn (1/1) to a total metal loading of 10wt%. The mixed solution was then added to the beaker containing support (AC/CNTs). This mixture was sonicated for 1 hr for better dispersion of the support in solution. After impregnation, the samples were dried in air at 100°C for 12 hrs, then calcined in a tubular furnace in atmospheric conditions at 300°C for 6 hrs. The catalysts were denoted as MnCeO_x/AC or CNTs-IW. The CWAO reaction was carried out in an autoclave (Parr mod. 4560) equipped with a magnetically driven stirrer, at 150°C and P_{air}=14 bar, using MnCeO_x supported catalysts (0.75 g) in an aqueous solution of phenol (1000 ppm). The reactor was loaded with an aqueous suspension (125mL) of the catalyst (0.75g) and fed with the continuous air flow. In order to give an initial concentration, 25 mL of solution containing the substrate was introduced into the

reaction vessel through the gas entrance tube after reaching the reaction temperature. Liquid samples were periodically withdrawn from the reactor and analyzed by HPLC and TOC measurements. In addition the CO₂ selectivity was determined by gravimetric analysis of the precipitated BaCO₃ formed by bubbling the outlet reactor stream into a saturated Ba(OH)₂ solution, kept stirring at room temperature.

CATALYST CHARACTERIZATION:

X-Ray diffraction (XRD) of the solids were carried out using a Ital Structures diffractometer using nickel filtered Cu K α radiation by mounting the powder samples on Plexiglas holders. The samples were scanned from 10° to 80° (2 θ) at 0.02° and 2s per step. Crystalline phases were identified by comparison with the reference data from ICDD (International Centre for Diffraction Data) files. Morphology of the samples were evaluated by means of Scanning Electron Microscope JEOL JSM-5600LV operating at 20 kV. Temperature Programmed Reduction (TPR) experiments were carried out on dried samples in a conventional apparatus, heating the sample (weight = 0.05 g) from room temperature to 900°C (heating rate = 10°C/min) under 5% H₂/He (vol%) with a constant flow rate of 30 mL/min. A molecular sieve cold trap (maintained at 193 K) was used to block water before the thermal conductivity detector (TCD).

CATALYTIC TESTING

CWAO was carried out at 150°C and P_{air} = 14bar in an autoclave (Parr mod. 4560) equipped with a magnetically driven stirrer. The pressure was maintained throughout the experiment by connecting the autoclave to an air cylinder. The reaction vessel and all the internal parts in contact with the reaction mixture were made in Teflon in order to avoid metal contamination. The reactor was loaded with an aqueous suspension (125mL) of the catalyst (0.75g) and fed with the continuous air flow. In order to give an initial concentration, 25 mL of solution containing the substrate was introduced into the reaction vessel through the gas entrance tube after reaching the reaction temperature. Liquid samples were periodically withdrawn from the reactor and analyzed by HPLC and TOC measurements. In addition the CO₂ selectivity was determined by gravimetric analysis of the precipitated BaCO₃ formed by bubbling the outlet reactor stream into a saturated Ba(OH)₂ solution, kept stirring at room temperature [3]. Used catalysts have been recovered after the reaction by filtration and dried at 80°C for 3 hrs. Reaction intermediates were identified by HPLC (Agilent 1100 series) equipped with a photo diode array detector (PAD). The reaction products were separated on a Aminex Biorad HPX87H column (300mm x 7.8mm), using mobile phase 0.005mol/L H₂SO₄ with a flow rate of 0.6mL/min. HPLC served for both identification and quantification purposes. Total Organic Compound (TOC) of the samples was measured by TOC-V_{CSH} Total Organic Carbon Analyzer- SHIMADZU instrument whose operation was based on the combustion/non dispersive infra red (NDIR) gas analysis.

RESULTS AND DISCUSSION

The support [26] and functionalized CNTs [27] were thoroughly characterized and explained in detail by our earlier studies. Whereas the Mn/Ce-Ox impregnated catalysts are characterized by the following studies. The XRD patterns of investigated samples are shown in Fig.1. The support AC (Fig.1a) shows the typical diffraction peaks at 2 θ = 26° and 43° correspond to the C (002) and C (100) reflection planes [28-29]. The characteristic peaks of MnOx and CeOx were determined from the samples 5%MnOx/AC-IW (Fig 1b) and 5%CeOx/AC-IW (Fig.1c) prepared by Incipient Wetness method. The dominant phase for MnOx was Mn₃O₄ and for CeOx was CeO₂ (2 θ = 28.5, 33.0, 47.5 and 56.3). The representative peaks of CeO₂ show weak to strong from MnCeOxAC(1:0.2)-IW (Fig. 1d) to MnCeOxAC(1:1)-IW (Fig. 1f) indicates the increase of Ce loading from 0.2 to 1. These peaks were slightly broader than that of the 5%CeOx/AC-IW (Fig. 1c); indicate that their CeO₂ crystallinity was lower than that of pure 5%CeOx/AC-IW (Fig. 1c). No characteristic peaks of MnOx were observed which demonstrate that the interaction of MnOx with the CeOx leads to the disturbance of MnOx crystal structure and diminish the volume of MnOx crystal particles [30].

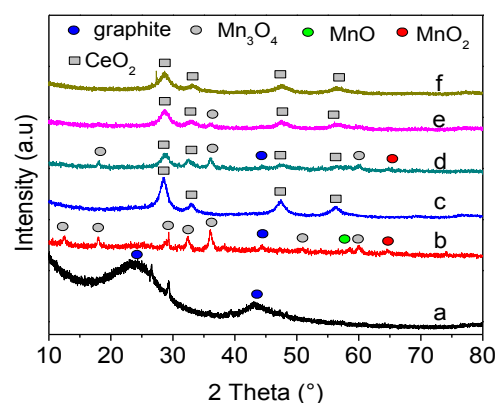


Figure 1. XRD patterns of investigated samples. AC (a); 5%Mn/AC-IW (b); 5%CeAC-IW (c); MnCeOxAC (1:0.2)-IW (d); MnCeOxAC (1:0.5)-IW (e); MnCeOxAC (1:1)-IW (g).

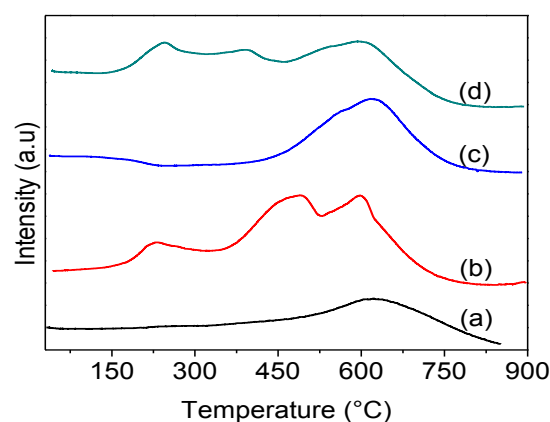


Figure 2. TPR spectra of (a) AC, (b) 5%MnOxAC-IW, (c) 5%CeOxAC-IW, (d) MnCeOxAC(1:1)-IW

The reducibility of the catalysts was investigated by H₂-TPR in Fig. 2. The support AC (Fig. 1a) displays a broad peak, centered at 630°C due to the hydrogenation of some surface carbon by H adspecies (which would lead to consumption of part of H adspecies and formation of C1–2 hydrocarbons) [31]. The characteristic reduction peaks of MnO_x and CeO_x were determined from the samples 5%MnO_xAC-IW (Fig.2b) and 5%CeO_xAC-IW (Fig.2c) prepared by Incipient Wetness method. The sample 5%MnO_xAC-IW (Fig 6b) shows a three-step reduction process of the Mn species, which could be observed at 230°C, 480°C and 595°C, respectively. The reduction process of MnO_x took place in the following order MnO₂→ Mn₂O₃→ Mn₃O₄→ MnO. The sample 5%CeO_xAC-IW (Fig. 2c) shows a reduction peak centered at 560°C belongs to Ce. The sample MnCeO_xAC(1:1)-IW (Fig. 2d) shows a peak at 245°C due to MnO₂→ Mn₂O₃, a peak at 395°C owing to Mn₂O₃→ Mn₃O₄, but a peak for Mn₃O₄→ MnO and CeO₂ overlap each other at 535°C which resembles the peak of CeO₂ at 560°C in 5%CeO_xAC-IW (Fig. 2c).

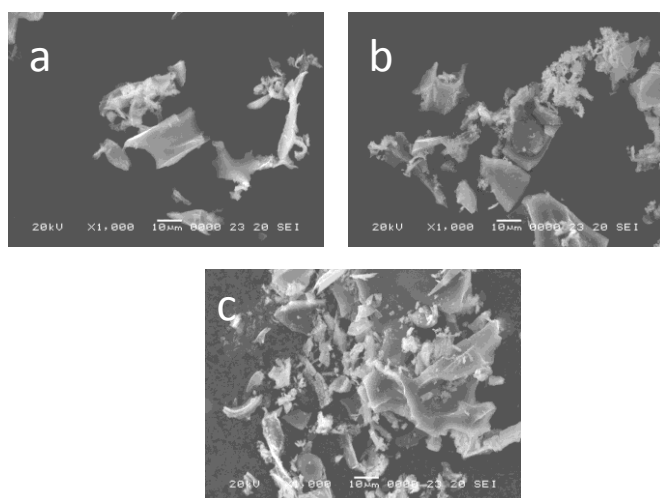


Figure 3. SEM images of the samples a) 5%MnO_x/AC-IW; b) 5%CeO_x/AC-IW; c) MnCeO_xAC(1:1)-IW

SEM images (Fig. 3) revealed that all the samples consisted of aggregates of particles. The Mn and Ce Oxides were differentiated by the SEM images of 5%MnO_xAC (Fig. 3a) and 5%CeO_xAC (Fig. 3b). It shown that the metal oxides were partly covered for the sample MnCeO_xAC(1:1)-IW prepared by Incipient Wetness method (Fig. 3c). The CWAO of phenol, at T = 150°C and P_{air}= 14 bar, leads to intermediates Hydro Quinone (HQ), Malonic Acid (Malonic-A), Acetic Acid (Ac), Oxalix Acid (Ox), Formic Acid (FA), Glyoxylic Acid (GlyA) in considerable amounts along with Maleic Acid (MA) and Catechol (CAT) in lower amounts (not shown for the briefness). Fig. 4 shows phenol removal (%) as a function of reaction time. It should be noted that in absence of catalyst (blank experiment) phenol conversion of 30% (Fig. 4a) is achieved and that it even increases up to 89% (Fig. 4b) when the reaction is carried out with un-loaded AC (Figure 4). The additional effect of Mn and Ce was found by the reaction of 5%MnO_xAC-IW (Fig. 4c) and 5%CeO_xAC-IW (Fig. 4d) respectively. The addition of Mn increases the activity towards the complete conversion whereas the addition of Ce decreases

the activity from 89% to 75%. No correlation can be drawn for the decrease in activity of the 5%CeO_xAC-IW (Fig. 4b). However the combination of Mn and Ce on the carbonaceous support leads to an almost complete phenol removal, under condition investigated (Figure 4 e,f,g) regardless the loading of the Cerium metal content.

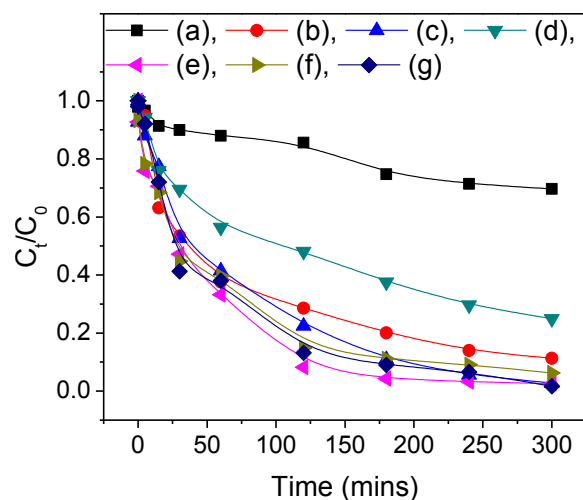


Figure 4. Catalytic activity in terms of Phenol removal Vs Contact time; (a) blank, (b) AC, (c) 5%MnO_xAC-IW, (d) 5%CeO_xAC-IW, (e) MnCeO_xAC(1:0.2)-IW, (f) MnCeO_xAC(1:0.5)-IW, (g) MnCeO_xAC(1:1)-IW

The rate of removal of phenol V_{obs} (mol g_{cat}⁻¹ min) is calculated as follow:

$$V_{obs} = \frac{phe_{ppm}(t_0) \cdot \left(1 - \frac{C_t}{C_0}\right)}{W_{cat} \cdot t}$$

where phe_{ppm}(t₀) represents the amount of the reagent (1000 ppm), C_t/C₀ represents the fraction of the reagent detected at time t, W_{cat} is the amount of catalyst and t is the reaction time (min).

The removal rate of phenol, V_{obs} (ppm.gcat⁻¹min⁻¹), calculated at 30 minutes of reaction, assumed that the carbon adsorption completes within 30 mins of the reaction; ranks in the order: blank < 5%CeO_xAC < AC < 5%MnO_xAC < MnCeO_xAC (1:0.2)-IW < MnCeO_xAC(1:0.5)-IW < MnCeO_xAC(1:1)-IW.

As expected the rate of the reaction for the blank experiment was lower. It was increased by the addition of Ce. No correlation can be drawn for the decrease in rate than the support AC by the addition of Mn. However it increases the catalytic activity gradually by the addition of increase in Ce metal content.

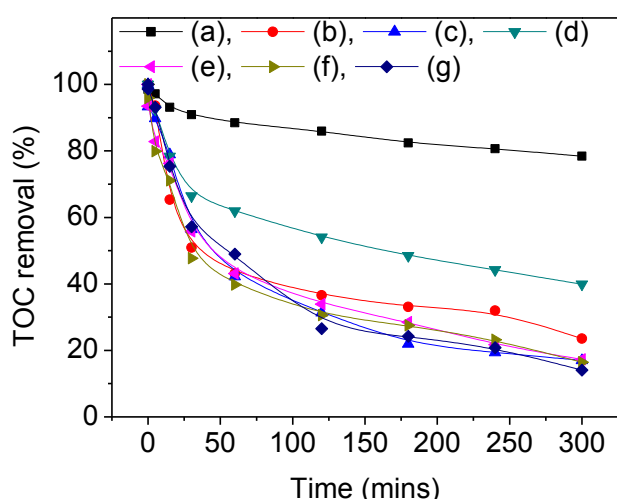


Figure 5. TOC removal (%) Vs Time; (a) blank, (b) AC, (c) 5% MnOxAC-IW, (d) 5% CeOxAC-IW, (e) MnCeOxAC(1:0.2)-IW, (f) MnCeOxAC(1:0.5)-IW, (g) MnCeOxAC(1:1)-IW

The catalysts efficiency toward the removal of the organic reagent and products, evaluated as Total Organic Compound abatement, ΔTOC (%), is calculated as:

$$\Delta\text{TOC}(\%) = \frac{\text{TOC}_{(\text{init})} - \text{TOC}_{(\text{t}=300)}}{\text{TOC}_{(\text{init})}} \cdot 100$$

$\text{TOC}_{(\text{init})}$ and $\text{TOC}_{(\text{t}=300)}$ correspond, respectively to the TOC values of the initial and the final solution.

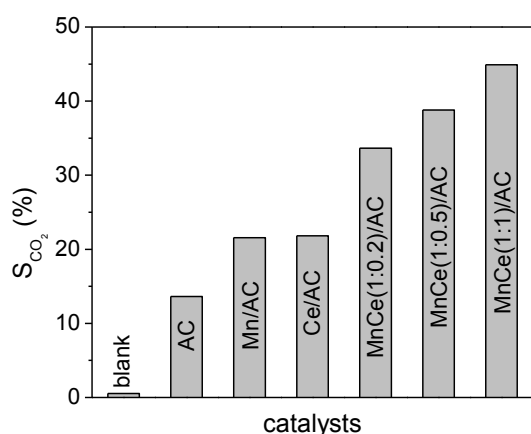


Figure 5. mineralization effectiveness towards CO_2 ($S_{\text{CO}_2}\%$)

The Fig. 5 shows around 15% of mineralization effectiveness towards CO_2 ($S_{\text{CO}_2}\%$) for the support AC, which increases to 25% by the addition of the metals Mn or Ce. However the combination of these metals leads to high mineralization effectiveness and which increases gradually by the increase in Ce metal loading. The homogeneous activity eventually arising from the presence of Ce and Mn metals were evaluated

submitting the liquid phase recovered after one catalytic cycle to a second cycle after elimination of the solid catalyst and addition of a proper amount of phenol. The phenol conversion attained after 5h is comparable with that obtained in absence of catalyst ($\approx 20\%$), indicates there is no metal leaching.

CONCLUSION

Blank reaction shows 30% of Phenol conversion and even increases up to 89% and 72% when it is carried out with un loaded AC and CNTs respectively. The addition of Mn and Ce to carbon supports leads to an enhancement of the catalytic activity towards Phenol conversion and TOC removal. Homogeneous coverage of metal oxides on the supports leads to the increase in reaction rates of the catalyst. The highest reaction rates of the samples MnCeOx/AC-Redox and MnCeOx/CNTs-IW show the complete coverage of the oxides on the support favors the catalytic reaction. No correlation has been found between $S_{\text{CO}_2}(\%)$ and reaction rate.

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