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Catalytic wet air oxidation of methylamine over supported manganese dioxide catalysts

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ABSTRACT

Catalytic formulations based on manganese oxides supported on inorganic oxides were developed for the treatment of methylamine-containing aqueous effluents via catalytic wet air oxidation (CWAO). Under the applied reaction conditions (190 °C, 50 bar total pressure) in the presence of heterogeneous β-MnO_2-supported catalysts, formate and ammonium ions were detected as primary products. As the reaction proceeded, a complete mineralization of formate ions was observed while ammonium ions accumulated in the reaction media. The catalytic formulations elaborated in this work were shown to be stable under the applied reaction conditions without any significant leaching of the active phase.

1. Introduction

Pollutants in water might be eliminated via wet air oxidation (WAO) using oxygen at elevated pressure and temperature. The objective is either to make the effluent biodegradable or to achieve full mineralization of the contaminants by converting the nitrogen and carbon fractions into N_2, CO_2 and water. The implementation of a suitable catalyst is known to increase the applicability of the WAO process [1,2]. Supported noble metal catalysts were shown to be highly active and selective to N_2 and CO_2 for many different organic compounds [2,3]. However, a drastic leaching of the active phase into the aqueous phase was recently evidenced in the case of primary amine-containing effluents [4]. This phenomenon was almost unambiguously attributed to the presence of a lone-pair of electrons localized on the nitrogen atom. The acidification of the reaction medium, in order to protonate the N-atom and decrease the affinity with the metal, suppressed the leaching but also inhibited the reaction. To overcome this problem, by decreasing the affinity between the active phase and the lone pair of electrons on the nitrogen atom, transition metal oxide based catalysts have been developed. Manganese was selected since it exists with many oxidation states and it was demonstrated to have excellent redox properties. Furthermore, some formulations containing manganese have already demonstrated some potential in the WAO of model organic compounds [5,6]. In this study, MnO_2 was supported on various oxides (TiO_2, ZrO_2, $Ce_{0.7}Zr_{0.3}O_2$, and CeO_2) and evaluated in the CWAO of methylamine (CH_3-NH_2). These supports were selected since they were earlier shown to be thermally and chemically stable under the applied reaction conditions. As a simple nitrogen and carbon organic containing molecule, methylamine was chosen as a model molecule. Furthermore methylamine is widely used in the chemical industry and frequently detected as a by-product in the production of pesticides, surfactants, dyes and pharmaceuticals [7,8].

2. Experimental

2.1. Preparation of the catalysts

All catalysts have been prepared by impregnation of four different commercial supports: TiO_2 DT51, 99 $m^2\,g^{-1}$, 100% anatase (tetragonal) from Millenium; ZrO_2, 126 $m^2\,g^{-1}$, mainly monoclinic and slightly tetragonal from Melcat Chemicals; $Ce_{0.7}Zr_{0.3}O_2$, 140 $m^2\,g^{-1}$, cubic solid solution from Rhodia Electronics and Catalysis; and CeO_2 HSA5, 230 $m^2\,g^{-1}$, cubic from Rhodia Electronics and Catalysis. The commercial supports were suspended in an aqueous solution of $Mn(NO_3)_2{\cdot}4H_2O$ (Alfa-Aesar). The amount of manganese salt was calculated to achieve a 12 wt.% loading in Mn. The water was then slowly evaporated at 60 °C under stirring to obtain a powder which was dried at 100 °C overnight and finally calcined in a muffle furnace under static air at 350 °C for 4 h.

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2.2. Characterization of the catalysts

Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance A25 diffractometer using the Cu Kα radiation (λ = 1.541 Å). Diffractograms were collected in the $2\theta = 10–85°$ range with a scanning speed of $0.01° s^{-1}$. The X-ray tube was operated at 50 kV, 35 mA. The XRD crystallographic phases were identified using ICDD-JCPDS data files.

Surface area measurements were carried out with a nitrogen sorption Sorptomatic 1990 (CE Instruments) analyzer. Before measurements, samples were evacuated for 12 h at 70 °C under primary vacuum. Adsorption–desorption measurements were performed at −196 °C. The surface area was determined by the Brunauer–Emmett–Teller (BET) approach. The pore size distribution and the porous volume were calculated from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. SEM images were acquired on a S800 Hitachi operating at 15 kV. TEM images were obtained on a Topcon instrument operating at 200 kV. For the TEM observations, the samples were grinded and deposited directly on a copper grid coated with a thin carbon film.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES, Activa Horiba JOBIN YVON) was used to measure the manganese loading on the fresh catalyst (before reaction) and the concentration of manganese in the aqueous solution after reaction in order to check for leaching.

2.3. Catalytic wet air oxidation experiments

30 mmol L^{-1} aqueous solutions of methylamine (MA) were prepared by dilution in ultra-pure water of a 40 wt.% methylamine solution purchased from Sigma–Aldrich. Catalytic wet air oxidation (CWAO) experiments were performed in a 300 mL batch reactor made of Hastelloy C22 [9,10]. The reactor is equipped with a magnetically driven stirrer set at 1250 rpm to avoid any mass transfer limitations in the liquid phase. Temperature was kept constant at 190 °C with a PID electronic controller. 150 mL of a 30 mmol L^{-1} methylamine solution was introduced into the reactor with 0.3 g of catalyst. After purging with argon to remove any trace of air, a 7 bar pressure of argon was maintained in the reactor before heating, to prevent any boiling phenomenon. The reactor was heated to 190 °C in 30 min. Air was then introduced into the reactor up to 50 bar total pressure (partial pressure of O_2 = 5.4 bar) and stirring was started. This time was considered to be the zero time for the reaction. Liquid samples were periodically withdrawn from the reactor, centrifuged and filtered through 0.45 μm syringe filters. After sampling, the pressure in the reactor was carefully adjusted to keep the total pressure constant all along the experiment.

2.4. Samples analysis

Upon CWAO of methylamine over the prepared catalysts, the two major primary degradation products in the aqueous solution were the ammonium and formate ions formed upon cleavage of the C—N bond in MA. Nitrate and nitrite ions were also formed but in much smaller quantities as described in Sections 3.1 and 3.2.

These ions were analyzed using an ion chromatograph (Metrohm 881 IC Pro) equipped with both a cationic (Metrosep C4 150/4.0) and an anionic column (Metrosep A Supp 5 150/4.0). The elutants for the cations and the anions separation were HNO_3 (1.7 mmol L^{-1})/dipicolinic acid (0.7 mmol L^{-1}) and Na_2CO_3 (3.2 mmol L^{-1})/$NaHCO_3$ (1 mmol L^{-1}), respectively. Calibrations were carried out using methylamine hydrochloride, ammonium chloride, sodium nitrate, sodium nitrite and formic acid solution (Sigma–Aldrich).

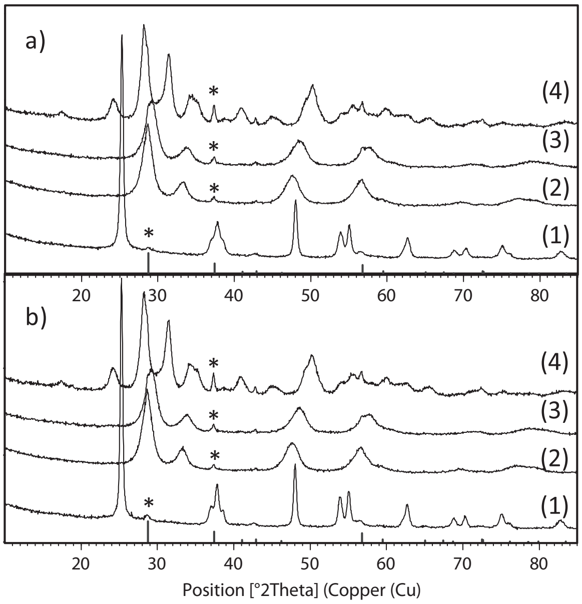

Fig. 1. XRD patterns of the catalysts (1 – MnO_2/TiO_2; 2 – MnO_2/CeO_2; 3 – $MnO_2/Ce_{0.7}Zr_{0.3}O_2$; 4 – MnO_2/ZrO_2) before reaction (a) and after reaction (b). [Vertical blue lines on the x axis correspond to the diffraction peaks of pyrolusite (JCPDS-ICDD card no. 04-007-3893); diffraction lines marked with an asterisk (*) are characteristic of the β-MnO_2 pyrolusite phase.]

The total organic carbon (TOC) and the total nitrogen (TN) were measured on a TOC-VCSH analyzer coupled with a TN unit (TNM-1) from Shimadzu.

The amount of CO_2 and N_2 produced could be estimated from the difference between the amount of C and N initially introduced in the reactor as MA and the total concentration in carbon and nitrogen containing compounds in the liquid phase at any time.

Furthermore, to check whether all intermediates and products had been properly identified and quantified, the C and N mass balances were assessed by comparison between the TOC and TN values and the ion chromatography results.

3. Results and discussion

3.1. Catalyst characterizations

Fig. 1 shows the XRD diffractograms of the different catalysts before (a) and after (b) catalytic wet air oxidation of MA. Manganese was detected in all cases as a tetragonal β-MnO_2 pyrolusite phase (JCPDS-ICDD card no. 01-072-1984). The peaks marked with an asterisk (*) could be unambiguously attributed to the β-MnO_2 phase and not to the support. However, although manganese is mainly detected as Mn(IV) both before and after reaction, one cannot conclude that Mn(IV) is the active species during the reaction. Indeed, a redox mechanism is proposed to be involved upon oxidation of methylamine and manganese would probably cycle between Mn(IV) and Mn(III) upon reaction.

The $Ce_{0.7}Zr_{0.3}O_2$ support was demonstrated to be a solid solution with the incorporation of the zirconium ions into the cubic lattice of ceria. Due to the smaller size of the zirconium ions (Zr^{4+} diameter: 0.84 Å) in comparison with the cerium ions (Ce^{4+} diameter: 0.97 Å), the incorporation of the Zr^{4+} ions involves a reduction of the lattice parameter, characterized by a shift of all of the ceria diffraction peaks toward higher angles, as observed from the comparison of patterns (2) and (3) in Fig. 1a [11–13].

The β-MnO_2 phase appeared even more crystalline after the catalytic test than before. The same trend was also observed for the TiO_2, ZrO_2, CeO_2 and $Ce_{0.7}Zr_{0.3}O_2$ supports, although