WASHCOATING OF MnO_x ON FeCrALLOY MONOLITHS

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***Abstract*— Two MnO_x catalyst as powder, prepared by decomposition of two different $MnCO_3$, have been deposited on a FeCrAlloy® metallic monolith by means of washcoating using slurry concentration of 25 and 40 wt(%) (PM25, PM40 and AM25). When increase slurry concentration increase the amount of deposited material, but lower adhesion of solid retained is observed. The obtained monoliths showed excellent catalytic activity in the combustion of ethyl acetate and toluene, being the monoliths activity order: PM40 > AM25 > PM25. Nevertheless, the conversion g^{-1} and conversion m^{-2} show that PM25 is the more active monolith.**

***Keywords*— MnO_x; FeCralloy; monoliths; VOCs.**

I. INTRODUCTION

Volatile organic compounds (VOCs) are a class of contaminants produced in various industrial processes such as printing graphic, the paint and coatings industry, metallurgical industries, chemical and electronics. There are numerous methods employed to destroy these emissions, being the catalytic incineration one of the most often used for gaseous systems. To deal with large flows and avoid problems such as the pressure drop are used catalysts supported on monolithic structures, which can be metal or ceramic (Heck *et al*., 2001; Alvarez *et al*., 2002).

Metal monoliths began to be used due to the greater resistance and thermal conductivity than that the ceramic monoliths, and also presented thinner wall thicknesses, which implies lower pressure drop. The preparation of the metal monoliths is based generally on the generation of a very thin oxide film on the surface of the metal, which serves as a substrate of the catalytic coating (Avila *et al*., 2005). The manufacturing technology of steel monoliths is essentially based on the oxidation of Fe-Cr alloys at high temperature to encourage the migration of cation at the surface and its oxidation to α-Al_2O_3 (Avila *et al*., 2005).

γ-MnO_2 (nsutite) is the best-know polymorphs of MnO_2 used by the battery industry. The structure of γ-MnO_2 is considered to be a random intergrowth of 1x1 tunnels of pyrolusite and 2x1 tunnels of ramsdellite, which are constructed of MnO_6 octahedral units with edge or corner sharing. Besides, this solid is characterized by point defects such as Mn^{4+} vacancies, Mn^{3+} cations replacing Mn^{4+} and OH^- species replacing O^{2-} anions (Chabre and Pannetier, 1995). These properties make this oxide interesting from the catalytic point of view, due to their high electrical conductivity. Previous works have shown that the nsutite is very active for oxidation reactions, in particular for oxygenated VOCs as ethanol (Lamaita *et al*., 2005a; Lamaita *et al*., 2005b).

Cryptomelane and mixed Mn-Cu oxides have been successfully deposited on Fecralloy monoliths through the washcoating technique (Barbero *et al*., 2008; Frias *et al*., 2007). However, no studies of the nsutite phase supported on metallic monoliths for being used as a catalyst for VOCs removal are found in the literature.

In this study, the objective is to develop a structured catalysts prepared by deposition of manganese oxide onto Fecralloy monoliths by the washcoating method and thus obtain a catalytic systems suitable for use in VOCs abatment. As VOCs representing molecules were used compounds found primarily in the printing industry as ethyl acetate and toluene.

II. METHODS

A. Sample Preparation

Metallic monoliths made of Fecralloy (typical analysis Cr 22%, Al 4.8%, Si 0.3%, Y 0.3%, C 0.03% Fe balance) were used as support of manganese oxides. Cylindrical monoliths were prepared rolling up a corrugated and a flat 50 μm steel sheet (L=30 mm, d= 16 mm, V= 6 cm^3, cell density 55 cells cm^{-2}). Before catalysts coating, Fecralloy monoliths were heated in air at 900 ºC for 22 hs to produce a surface composition and roughness convenient to assure adherence.

γ-MnO_2 or nsutite, was synthesized through the oxidative decomposition of 100 g of $MnCO_3.xH_2O$ (Panreac PRS, S_{BET} 45 m^2g^{-1}) at 350 ºC under flowing oxygen saturated with water at RT (500 cm^3 min^{-1}) for 24 hs, and with a heat rate of 20 ºC min^{-1}. The resulting powder was dried and calcined at 400 ºC for 2 h. This oxide was named MnO_x-*P*.

In order to study the effect of two different $MnCO_3$ precursors, another MnO_x powder was synthesized by the same procedure but using an anhydrous $MnCO_3$ (Alfa Aesar, 99.9%, S_{BET} 10 m^2g^{-1}) as precursor (MnO_x-*A*).

The monoliths were washcoated with aqueous suspensions of 25 and 40 wt(%) of the prepared manganese oxide. The powders were previously grinding in a ball mill for 5 hs. The pH of the slurry was adjusted at 8 with diluted NaOH, in accord to the zeta potential study of the manganese oxide. The washcoating of the pretreated monoliths were carried out by dipping and withdrawing the monoliths in the slurry at constant speed (3 cm min^{-1}). Afterward, the monoliths were centrifuged at