

Cerium, manganese and cerium/manganese ceramic monolithic catalysts. Study of VOCs and PM removal

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Abstract: Ceramic supported cerium, manganese and cerium-manganese catalysts were prepared by direct impregnation of aqueous precursor, and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer-Emmett-Teller method (BET), temperature programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS) acidity measurements and electrical conductivity. The catalytic activity was evaluated for volatile organic compounds (VOC) (ethanol, methyl ethyl ketone and toluene) oxidation. Additionally, catalysts were tested in particulate matter (PM) combustion. The characterization results indicated that Ce was in the form of Ce⁴⁺ and Ce³⁺, and Mn existed in the form of Mn⁴⁺ and Mn³⁺ on the surface of the Mn/AC sample and in the form of Mn⁴⁺ in the Ce/Mn/AC monolith. VOC oxidation results revealed that the Ce/Mn/AC sample showed an excellent performance compared with ceramic supported CeO₂ (Ce/AC) and MnO_x (Mn/AC) samples. The PM combustion was also higher on Ce/Mn/AC monoliths. The enhanced catalytic activity was mainly attributed to the Ce and Mn interaction which enhanced the acidity, conductivity and the reducibility of the oxides.

Keywords: monolith; VOCs; MnO_x; Ce; PM; clays; rare earths

Volatile organic compounds (VOCs) are important components in the urban environment, arising from natural and anthropogenic processes and commonly present indoors and outdoors. Fifty percent of the total VOCs and more than eighty percent of benzene emissions outdoors are due to vehicle exhaust and evaporative losses. Besides vehicular traffic, emissions from industrial sources, e.g., petroleum refineries and petrochemical plants play an important role in affecting the atmosphere quality^[1,2]. The simultaneous reduction in the emission of particulate matter (PM) and volatile organic compounds (VOCs) has been a great challenge for automobile manufacturers and researchers. In fact, in several cases, emissions of volatile organic compounds are accompanied by the emission of carbon particles. The use of catalysts in order to oxidize the carbonaceous particles is one of the promising exhaust gas after treatment systems. These catalysts also provide significant reductions in emissions of carbon monoxide (CO) and hydrocarbons (HC). For diminishing the particulate matter emissions, the catalytic filter that combines soot retention and combustion is one of the most alternatives studied. Noble metals (Pt, Pd) or transition metal based-oxides (cerium oxide) are widely used as active phases^[3–5]. Metal oxides have lower activity than noble metal catalysts but they

are cheaper and have greater resistance to some poisons. Among the transition metal oxides, manganese and cerium based materials have been considered as promising catalysts for the combustion of VOCs^[6].

Manganese oxides are widely used due to their low cost and high activity, which is attributed to the labile lattice oxygen and their capacity of storing oxygen in the crystalline structure^[6–8]. Catalysts based on cerium oxides are attracting attention as catalyst for VOCs combustion due to the oxygen vacancies and high surface reducibility produced for the Ce⁴⁺/Ce³⁺ redox pair^[9,10]. The combination of manganese and cerium could modify the redox properties of the mixed oxides, enhancing the mobility of oxygen and improving the catalytic activity for VOCs combustion^[11,12].

The properties of cerium oxides mentioned are responsible for their wide use in the combustion of soot, which is reported to involve a redox cycle where active oxygen species oxidize soot. Doping cerium based catalysts with manganese is often employed to enhance the soot combustion of cerium oxides^[10,13].

For environmental applications, high flow rates should be treated and a low-pressure drop is required. For that reason, the catalytic system most widely used for catalytic VOC oxidation is the monolithic reactor^[14].

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Being a better alternative to metallic ones, the rheological properties of clay minerals are ideal raw materials for preparing monoliths^[15,16]. Although the most common ceramic supports used is the cordierite, the abundance of natural clay and its low cost are likely to make it candidate as structured catalysts support.

Moreover, the typical method to deposit the catalysts onto the monoliths surface is preparing slurry of an existent powder. The problem of this technique is related to the adherence quality of the layer on the monolithic carrier surface. The use of clays in the formulation of monoliths could produce ceramic (macroporous) structures in which the deposition of the catalyst support can be performed directly by impregnation of aqueous precursors.

In a previous paper^[17], we studied the use of Mn, Pt and Pt/Mn supported ceramic monoliths for the combustion of ethanol and toluene. The aim of the present paper was to study the catalytic behavior of Ce and Ce/Mn supported monoliths, in the combustion of ethanol, methyl ethyl ketone (MEK) and toluene. Additionally, the combustion of soot was investigated over the prepared monoliths, in order to study if the Ce-Mn catalysts are active catalyst not only for VOCs elimination but also for particulate matter combustion.

1 Experimental

1.1 Catalyst preparation

The preparation of the ceramic monoliths (denoted as AC) used as support together with the preparation of the Mn supported monoliths (denoted as Mn/AC) were described in a previous paper^[17].

Supported Ce and Ce/Mn monoliths were prepared as follows:

Ce/AC: ceramic monoliths (AC) were immersed in an aqueous solution of 0.02 mol/L $\text{Ce}(\text{NO}_3)_3$, inside a closed vessel and put through to mechanical orbital agitation for 60 min.

Ce/Mn/AC: Mn/AC monoliths, after having been calcined at 500 °C, were impregnated with 0.02 mol/L $\text{Ce}(\text{NO}_3)_3$ in the same way as the Ce/AC monoliths. After impregnation, monoliths were washed with deionized water, dried overnight at 100 °C and finally calcined at 500 °C for 2 h.

1.2 Catalyst characterization

Textural properties of the monoliths were determined by nitrogen adsorption using a Micromeritics ASAP 2000 sorptometer. The experiments were performed over small pieces of crushed monoliths.

The sample morphology was examined with a scanning electron microscope (SEM) Philips SEM 505. The experiments were performed over small pieces of crushed monoliths.

X-ray diffraction patterns were carried out at room temperature with a Phillips PW1390 instrument by using Ni filter and Cu $K\alpha$ radiation ($\lambda=0.1540589$ nm) in the 2θ range between 5° and 70°, at 0.02(°)/min scanning speed and a counting time of 2 s per step. The samples were measured in powder form (previously ground monolith).

X-ray photoelectron spectra (XPS) of the samples were obtained (over previously ground monolith in powder form) using a multi-technique system, equipped with a hemi-spherical PHOIBOS 150 analyzer using Mg X-ray source. Binding energies (BE: ± 0.1 eV) were calculated using adventitious hydrocarbon (C 1s=284.6 eV) as the internal reference. Curve fitting was performed with the CasaXPS program (Casa Software Ltd., UK).

The temperature-programmed reduction (TPR) with hydrogen was performed using a Quantachrome equipment Quantasorb Jr. The experiments were carried out at a heating rate of 10 °C/min. The reactive gas composition was H_2 (5 vol.%) in nitrogen. The flow rate was fixed at 22 cm^3/min . Temperature was increased from ambient to 900 °C. The H_2 consumption was measured by a thermal conductivity detector, and the H_2 uptakes were quantified using CuO as a standard and taking into account that at the end of the experiments all Mn is as MnO .

Acidity of the monoliths was measured in a Metrohm 794 Basic Titrimo with interchanged unity 806 and a Metrohm electrode. A representative 0.50 g sample in powder form was suspended in 45 mL of acetonitrile solution and allowed 3 h in agitation to come to stabilization. This suspension was then titrated with 0.025 N n-butylamine solution.

The electrical conductivity of the monoliths was estimated measuring the electrical resistance in a SIEMENS ISOWID B4105 Insulation Tester, applying 500v among the monoliths. The conductivity was calculated as the inverse of the resistance.

1.3 Catalytic oxidation of VOCs

The catalytic activity of the prepared monoliths was measured for the complete oxidation of three different VOCs: ethanol, MEK and toluene. VOC oxidation was carried out in a stainless steel tubular fixed-bed reactor of 45 cm high and 2.3 cm in inner diameter, under atmospheric pressure at a space velocity of 12000 h^{-1} . The reactive flow (1000 cm^3/min) was composed of air and 1000 mgC/m^3 of gaseous VOC. Monolith was placed on the top of a carborundum bed. The reactor was surrounded by an electrical furnace equipped with three independent temperature programmers. The ignition curves were obtained over the range 100–500 °C in incremental steps (25 °C) and the reaction temperature was measured by a thermocouple placed in the middle of the monolith. The data were obtained in steady state. Monoliths were treated under 1000 cm^3/min of air at 450 °C for 1 h before reaction, and then cooled down in air to the starting

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